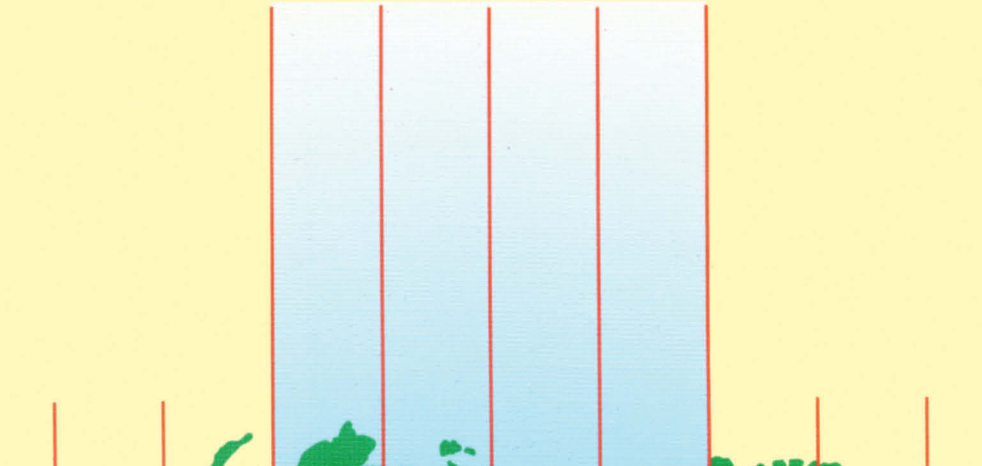
Proceedings of Regional Symposium

Brisbane, 1989

Chemistry & the Environment



Edited by

B. N. Noller and M. S. Chadha

Commonwealth Science Council

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Chemistry and the Environment

FOREWORD

On 1 and 2 September 1989, the Commonwealth Science Council, acting in cooperation with the Federation of Asian Chemical Societies, UNESCO and other regional and international agencies organised a Symposium on Chemistry and the Environment during the Chemistry International Conference in Brisbane, Australia. The Symposium sought to bring together eminent scientists to identify and discuss major environmental issues of consequence to the Asia-Pacific region having a direct association with chemistry.

Earth's atmosphere is influenced by a number of chemical reactions involving many chemical species. An understanding of the chemistry of the environment, therefore, has many-fold ramifications and implications. To an academician, chemistry of the environment could be a curiosity. To the humanity at large, this understanding is vital to preserving the environment through policy initiatives and legislative measures. The chemical dynamics of the earth's environment constitute a fascinating and scientifically exciting field of endeavour. It is one of the underlying themes in the International Geosphere-Biosphere Programme: "To describe and understand the interactive physical, chemical and biological processes that regulate the total Earth system, the unique environment that it provides for life, the changes that are occurring in this system, and the manner in which they are influenced by human actions".

Presentations and discussions in the Symposium covered a wide range and included the International Geochemical Mapping Project, fossil fuels utilisation, ozone hole, greenhouse gases and effects, specific environmental impacts of several chemicals, atmospheric and urban air modelling, major chemical accidents, and environmental monitoring aspects. Scope for regional and international cooperation was discussed in a Forum, as a result of which an Asia-Pacific regional project on Chemical Research and Environmental Needs (CREN) is being set in motion.

The Commonwealth Science Council was fortunate to secure the combined association of Dr M.S. Chadha and Dr B.N. Noller for editing the papers presented in the Brisbane Symposium. They were easily the natural choice having co-organised the Symposium itself successfully. I am profoundly grateful to both of them. It is a pleasure to acknowledge the excellent cooperation extended by the Council of Scientific and Industrial Research, India, in particular by Dr A.P. Mitra, FRS, Director-General, Dr G.P. Phondke, Director, Publications & Information Directorate and Mr. K.N. Johry, Head, International Scientific Collaboration for enabling this publication to be produced in such a short time and at a reduced cost.

The Commonwealth Science Council is pleased to make this publication available to students of the environment, scientists, policy-makers and the wider international community concerned about contemporary environmental issues.

London, UK
April 1990

G. Thyagarajan

INTRODUCTION

This Regional Symposium began as an initiative of Dr G. Thyagarajan, Secretary Commonwealth Science Council, at the 5th meeting of the Asian Coordinating Group for Chemistry (ACGC V) held at Bombay, 8-10 February 1988. Dr Thyagarajan together with Drs Mohinder Singh and J. Webb suggested an Asian initiative in a global perspective, by organising a regional workshop/symposium, dealing with chemical constituents in the environment.

This could help in the formulation of effective strategies for containing environmental problems. This could also provide required answers to the following questions:

- (i) What are the undesirable or potentially undesirable substances present in air, water, soil and food ?
- (ii) How did these originate ?
- (iii) What in quantitative terms is the effect of the undesirable constituents on living beings ? and
- (iv) What mitigative strategies are feasible?

In understanding the cause-effect relationship, identifying the problem molecules or elements and estimating their concentrations at parts-per-million/billion levels are essential. This calls for a pivotal role for chemical investigations. In particular it is necessary to develop sensitive and selective analytical chemical techniques. Analytical chemistry also has to interface with meteorology, oceanography, climatology, biology and hydrology for probing the sources of these contaminants. This requires a detailed study of the reactions and interactions of chemical species in the environment. Management and regulatory options depend upon reliable scientific inputs and a sufficiently large knowledge base. Monitoring tools have to be usable and easy to operate and maintain. Research on multi-stage techniques for chemical separations need to consider: (i) selective and scientific detection techniques (laser and chemiluminiscence based); (ii) ease of environmental sampling and analysis to minimize effect of movement and time delays; (iii) the chemical state of environmental constituents (e.g. hexavalent chromium is toxic while trivalent chromium is not); and (iv) that research on environmental problems generates massive amounts of data requiring methods and possible further studies on how to interpret and transfer information.

The Regional Symposium was therefore thought necessary to: (i) take stock of the state of the art; (ii) identify priority areas and programmes for action at national and regional levels; (iii) create increased awareness of the presence of chemical constituents in our environment and options for containing and managing them; and (iv) establish a network approach, if necessary, to mount a continuing programme of action.

The Regional Symposium was proposed to be sponsored by the Commonwealth Science Council and UNESCO and was to be an activity of ANAIC.

Dr G. Thyagarajan together with Dr T. Ramasami and Dr M.S. Chadha then prepared a background paper entitled "Chemistry and the Environment" available as a CSC Technical Publication [No. CSC (88) 156-35]. Dr M.S. Chadha was authorized by the Commonwealth Science Council to act as Co-ordinator on its behalf for the Regional Symposium. It was proposed by Dr B.N. Noller, Secretary, 3rd Asian Chemical Congress that the Regional Symposium be held at Brisbane, Australia, in conjunction with the 3rd Asian Chemical Congress during the period 28 August-2 September 1989. Drs Chadha and Noller met at ACGC VI on 30 January 1989, at Djakarta, Indonesia, and prepared a programme based on the CSC Technical Publication [No. CSC (88) 156-35] identifying possible speakers. This tentative programme was approved by ACGC VI. Nominated speakers were invited by Dr G. Thyagarajan to participate in the Regional Symposium; all invited speakers with a few exceptions accepted the invitation to attend the 2 day Regional Symposium held during 1-2 September 1989 in conjunction with the 3rd Asian Chemical Congress. Drs Chadha and Noller were asked to be the co-organizers of the Regional Symposium.

There was an overwhelming and enthusiastic response to the Regional Symposium in spite of an air strike. The Symposium was inaugurated by Dr G. Thyagarajan. Dr T. Spurling, President, Federation Asian Chemical Societies and Professor H. Thier, Director of the Chemicals Education for Public Understanding Project, University of California, Berkeley made brief remarks at the opening session. Dr D. Connell, Chairman, Environmental Chemistry Division, Royal Australian Chemical Institute welcomed the participants.

The proceedings of the Regional Symposium are based on manuscripts supplied by the authors; their adherence to the rather stiff deadlines is highly appreciated. Minor editorial modifications are made as was felt to be appropriate. Those who could not participate in person were kind enough to provide their papers for this publication.

The essential idea in publishing these proceedings is to catalyse activities in the Region which not only faces the same problems as the rest of the globe but also has to contend with high population and uncontrolled generation of pollutants. The important issues in the Region today are associated with the large population centres in Asia and the resulting pressures on the environment in Asia. The success of the Regional Symposium and publication of its proceedings would be judged by the nature of the relevant programmes which evolve in the Region. We hope that the publication of the proceedings will catalyse programmes in the region which could possibly get support from international agencies engaged in similar pursuits.

The various authors themselves have helped us greatly in the preparation of this volume. They deserve our grateful acknowledgement. We should also acknowledge the counsel and advice given by the participants at ACGC VI (Djakarta) and ACGC VII (Xiamen, China); and the overall encouragement and support given by Dr G. Thyagarajan, Commonwealth Science Council, Dr J. Kingston, UNESCO, Nay Htun, UNEP Bangkok and Dr Khairat M. Ibne-Rasa, ISESCO. Although the symposium was largely supported by the Commonwealth Science Council, the support of these other international agencies helped to bring other younger chemists to the Regional Symposium. Assistance for the preparation of abstracts and other details prior to and during the symposium was given by Dr B. Chiswell, which is gratefully acknowledged.

Permission to reproduce some of the figures and use of the published data by authors is gratefully acknowledged.

The overall guidance given by Dr G.P. Phondke, Director, Publications and Information Directorate, CSIR, New Delhi, India and painstaking efforts made by Mr S.S. Saksena and Mr K. Satyanarayana and their dedicated production and printing teams led by Ms Supriya Gupta and Mr V. Ramachandran respectively which helped to improve the present publication greatly are highly appreciated. Grateful thanks are also due to Ms Louise Carr of the CSIRO Division of Atmospheric Research, Australia and Mr Pradeep Banerjee of PID, India for providing the artwork for the front cover.

Our endeavour to bring out the proceedings within a short span of time may have resulted in some errors remaining uncorrected for which we crave the readers' indulgence. As the authors are from different countries, the use of English language including spellings has been left unchanged!

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CONTENTS

INTERACTIVE PROCESSES IN THE ATMOSPHERIC ENVIRONMENT

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Interactive chemical processes are discussed for different levels of our extended atmospheric environment for which the upper boundary has now been pushed to the far reaches of the earth-sun space. Four specific regions are involved. These are:

(i) The *tropospheric* level dominated by the chemistry of greenhouse gases of biospheric, volcanic or anthropogenic origin;

(ii) The *stratospheric* level dominated by the ozone problem and marked by an increasing role of solar radiation;

(iii) The *ionospheric* level with high power R.F. heating and injections (inadvertent or deliberate) of active gases modifying the ionosphere; and

(iv) The *plasmasphere* level allowing precipitation of trapped particles from powerline perturbations.

In this paper, the canvas will be this total environment, but the discussions will be limited to (i), (ii) and (iii).

Atmospheric chemistry for each region as we go from the troposphere through the stratosphere to the mesosphere and the ionosphere with specific identification of the natural and anthropogenic sources is described in some detail. In the first two regions the reactions are primarily neutral; in the mesosphere and ionosphere primarily ionic. There are specific boundaries where the nature of the chemistry changes.

Problems relating to quantitative estimations of budgets, identification of sources and sinks, life history of the source gases and specific benchmarks (e.g. Antarctic ozone hole, lagapedo and HAEO-C ionospheric hole experiments) are examined.

HISTORICAL BACKGROUND

Atmospheric chemistry—both neutral and ionic—has held the centre stage of atmospheric studies for more than three decades since IGY when rocket and satellite sensors discovered unexpectedly high concentrations of NO and NO^+ (both photochemical products) over a large portion of the middle and upper atmospheres and of hydrated complex positive and negative ions in the lower ionosphere. Ozone was already known as a major photochemical product. It became increasingly clear that minor constituents, existing in small abundances (a few parts per billion to a few parts per million) play a surprisingly dominant role over the entire atmospheric environment. Since the concentrations are small, these can be substantially altered through relatively small inputs, some of which, we now realize, come from industrial and agricultural practices and are, therefore, man-made.

Since these early periods of IGY and IQSY, atmospheric chemistry has moved from one region of the earth's atmosphere to another, and from the earth's atmosphere to the atmospheres of the planets with the exciting observations of Mariner IV which flew past Mars in 1964 and the discoveries of ionospheres and magnetospheres in several planets. The very intense research efforts on the terrestrial atmosphere and ionosphere in the 50's and 60's provided a backdrop for new studies of the planetary atmospheres and ionospheres as results from Venus and Mars began to come in. Reactions tried out in the earth's ionosphere were applied to the planetary atmospheres under different conditions of temperature and pressure and different neutral environment. In other words, studies of the ionospheres of the earth and the planets became complementary.

As the attention of atmospheric chemists moved to the earth's stratosphere and the troposphere with the warning on possible ozone destruction by CFM's in the early seventies and more recently on climatic roles of CO_2-NO_x-CFM-CH_4-O_3-H_2O system, the examples of runaway greenhouse effect adding about 500 K in Venus where CO_2 environment is 70,000 times larger than on earth and the cold Mars with little CO_2 in its atmosphere began to be used as benchmarks. It was apparent that the present optimum greenhouse warming of about +30K will not remain so in future. It is interesting to trace the sequence of changes in the interest of atmospheric chemists over the last three decades. This is shown in Fig.1. The very intensive interest in the anomalies of ion composition of the earth's ionosphere shifted partially to the planetary ionospheres and then in the seventies to the stratosphere and now to the troposphere as new results began to emerge on the role and effects of non-CO_2 greenhouse molecules.

SOME KEY ELEMENTS

An important element is that different levels of the earth's atmospheric environment are not isolated and that effects of human activities are not limited to the troposphere-stratosphere system but extend to ionosphere and magnetosphere. One must, therefore, consider the earth's entire environment as one entity. The upper boundary of this environment has with time been pushed upwards to the far reaches of the earth-sun space to the end of the tail swept out by the solar wind. The earth, in this context, behaves just like a comet. We are thus concerned with physical and

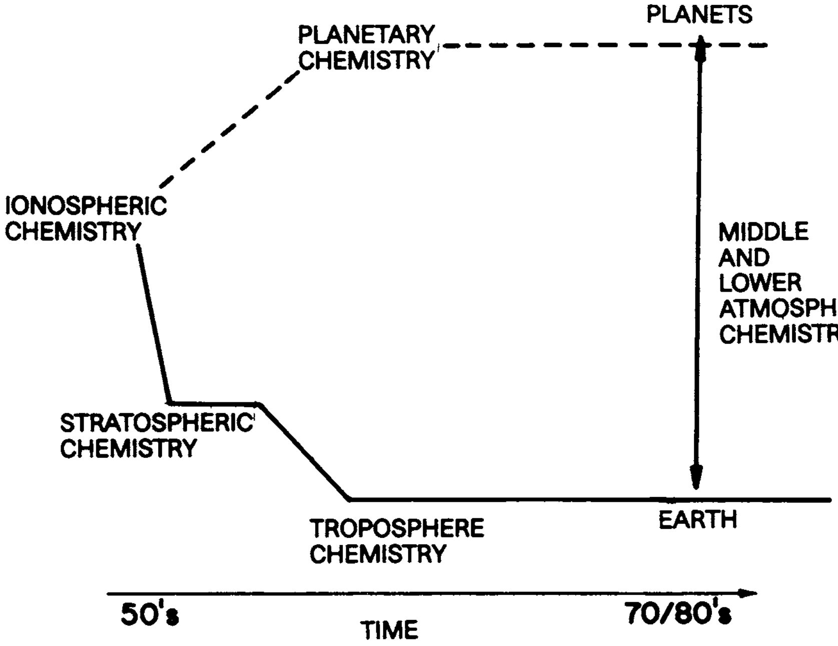


Fig. 1. A historical perspective of atmospheric chemistry research.

chemical processes of a vast region several earth radii in extent, coupled through flow of energy and matter, with chemical reactions acting as a filter.

In Fig. 2 we reproduce (from a SCOSTEP document) the linkage and interaction between the sun and this extended atmospheric environment comprising the magnetosphere, the ionosphere, the middle atmosphere and the lower atmosphere. The sun and the radiation and particles it hurls into space are at the centre of this interaction with variable radiations in the ultraviolet and X-rays and with a number of periodicities from the widely-recognized 11 and 22 years to the Milancovitch cycle.

There are several key boundaries in the atmospheric environment which demarcate regions of substantially different chemistries. These boundaries are different for chemistries involving neutral particles and for ions. But for both some basic boundaries can be identified. These are:

(i) The *tropopause* separates regions of local and global dynamics: below this level there is chemical filtering of source gases and also a "rainout" of molecules of short lifetime. It also separates the levels of ozone chemistry (stratosphere) from those of greenhouse molecules (troposphere);

(ii) The *stratopause* dividing the predominantly neutral chemistry below to a mixture of neutral and ion chemistry and the beginning of the ionosphere (~60km);

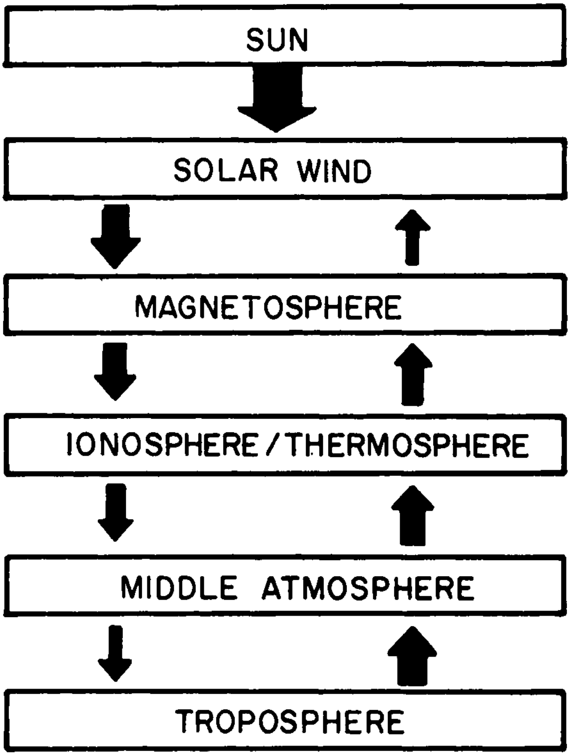


Fig. 2. Energy transfer mechanism.

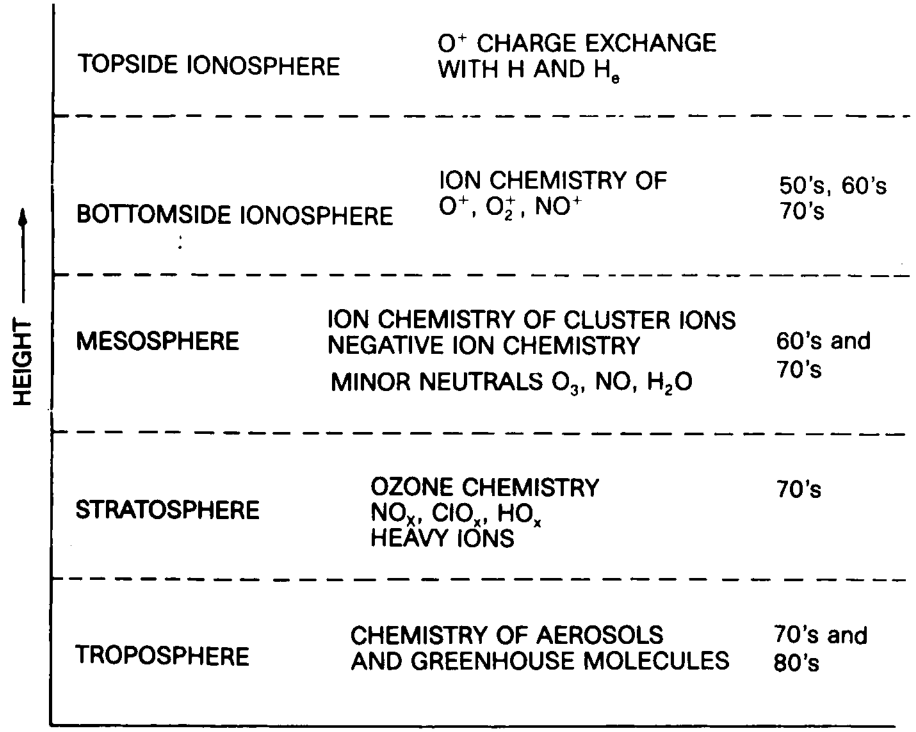
(iii) The *mesopause*, the coldest region in the atmospheric environment, at which temperature, concentration of atomic oxygen and ionic recombination show drastic changes; this is also the boundary where cluster ions change into simple molecular ions;

(iv) Levels 110-120km: above these levels diffusive separation of neutral particles begins resulting in increasing predominance of lighter particles (particularly O, H, and He) with increasing altitude; and

(v) Levels around 180km: these levels separate the region of molecular ions (below) from the region of atomic ions (above).

A simplified picture classifying these regions and the different boundaries is shown in Fig. 3.

Another important key question concerns the nature, magnitude and origin of sources and sinks of active species in all these regions. The mesopause provides a



TOPSIDE IONOSPHERE	O^+ CHARGE EXCHANGE WITH H AND H_e	
BOTTOMSIDE IONOSPHERE	ION CHEMISTRY OF O^+, O_2^+, NO^+	50's, 60's 70's
MESOSPHERE	ION CHEMISTRY OF CLUSTER IONS NEGATIVE ION CHEMISTRY MINOR NEUTRALS O_3, NO, H_2O	60's and 70's
STRATOSPHERE	OZONE CHEMISTRY NO_x, ClO_x, HO_x HEAVY IONS	70's
TROPOSPHERE	CHEMISTRY OF AEROSOLS AND GREENHOUSE MOLECULES	70's and 80's

Fig. 3. Diagrammatic representation of different chemical regions.

rough boundary below which the active species are predominantly terrestrial in origin, and above which predominantly extra-terrestrial.

The interactive chemical picture of the atmospheric environment presented in this address covers this extended canvas. For brevity only a few dominant aspects are discussed. The connecting thread is the role of human activities. At least four levels (Fig. 4) are involved where effects of human activities are discernible: for two of these the effects are approaching those from natural sources. These levels are:

(i) The *troposphere-stratosphere* system dominated by ozone chemistry and CO_2-CH_4-H_2O-N_2O-CFM greenhouse molecules;

(ii) The *ionospheric level* modified (inadvertently or deliberately) by (a) highpower high-frequency transmissions and (b) injections of active gases from rocket exhausts or as tracers; and

(iii) The *plasmasphere and magnetosphere level*, normally a reservoir of trapped solar particles, precipitating some of these particles as a result of large powerline perturbations.

In this presentation we will limit ourselves to (i) and (ii) only.

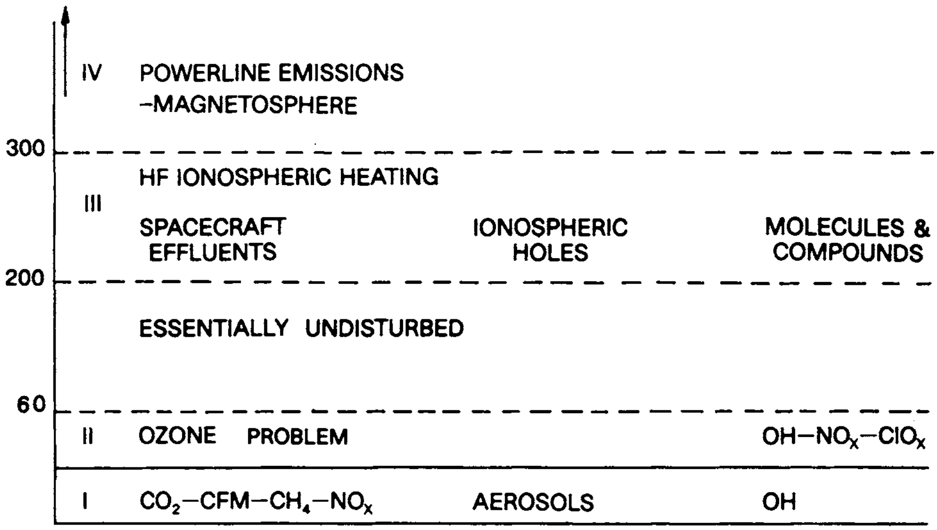


Fig. 4. Different levels of atmospheric environment subject to perturbation due to human activities.

CHEMISTRY OF THE EARTH'S ENVIRONMENT

Neutral chemistry

We first take up the problem of neutral chemistry. The dominant chemical reactions and the ways these change with altitudes and for different regions are shown in Fig. 5. The nature of the fluxes and their transports are shown in Fig. 6.

Troposphere is an oxidising region. The injections of active gases are of several types of origin: (i) biospheric; (ii) industrial; (iii) volcanic; and (iv) solar. At these levels only wavelengths longer than about 300nm can penetrate and hence direct dissociation of CFM or most of the greenhouse molecules does not occur. The only major exception is the photolysis of O_3 by radiations of ≤ 310 nm which produces $O(^1D)$. This process is crucial because $O(^1D)$ generates the catalytic radical OH from H_2O through the reaction $H_2O + O(^1D) \rightarrow 2OH$. Concentration of OH depends on the concentration of H_2O (highly variable) and also on the tropospheric concentration of O_3. Reaction with OH determines the lifetime of many important gases in the troposphere including the greenhouse molecules, and acts as a "chemical filter" for transport to the stratosphere. OH radicals are a major sink for CO and CH_4. An additional source of OH is HO_2 reaction with NO and O_3, and so reactions leading to HO_2 formation adds to OH production. Examples are:

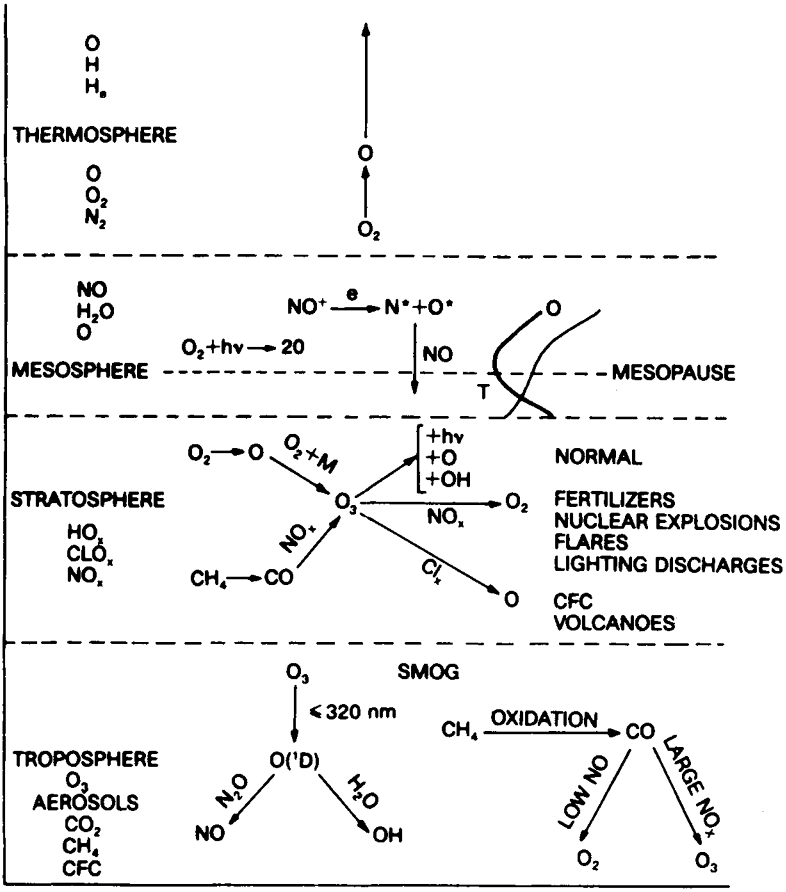


Fig. 5. Neutral chemistry.

$$HCHO + h\nu \xrightarrow{\leq 330\text{ nm}} H + HCO$$

$$HCO + O_2 \longrightarrow HO_2 + CO$$

$$H + O_2 + M \longrightarrow HO_2 + M$$

Thus oxidation of CH_4 amplifies primary OH production caused by photolysis of O_3. A simplified picture is shown as Fig. 7. Another special feature is that more than in stratosphere, heterogeneous chemical reactions are more often encountered here, such as in scavenging of trace gases by aerosols, clouds and precipitation.

The other main series of reactions involves CH_4. Oxidation of CH_4 can end up with O_2 or O_3 depending on the concentrations of NO If NO mixing ratio is less

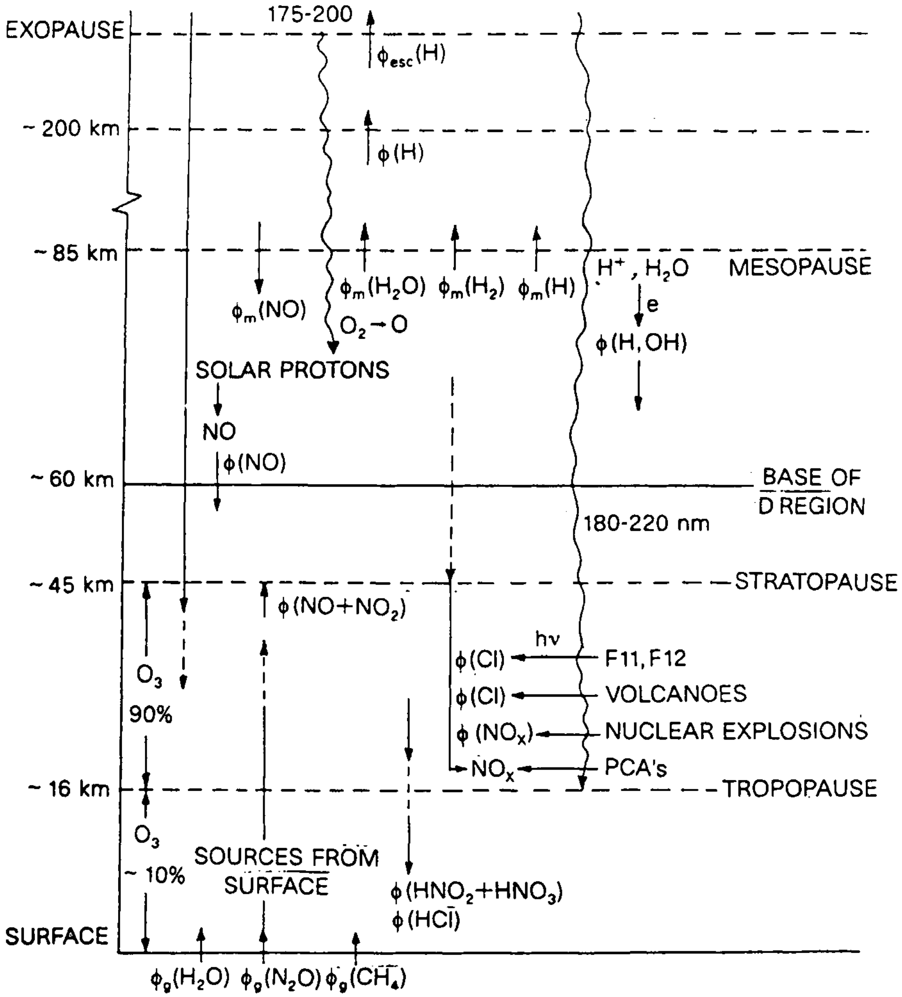


Fig. 6. Nature and sources of fluxes.

than a few pptv, then we have removal of odd oxygen (O_3) and odd hydrogen (OH, HO_2), but in polluted regions with high NO concentrations (≥ a few pptv), reactions involving CH_4, CO and NO produces ozone and odd hydrogen. Thus localised production of ozone with local climatic effect can occur.

The tropospheric ozone is either produced *in situ* through dissociation of NO_2 in the visible (Fig. 8).

$$NO_2 + h\nu \xrightarrow{< 400\ nm} O\ (^3P) + NO$$

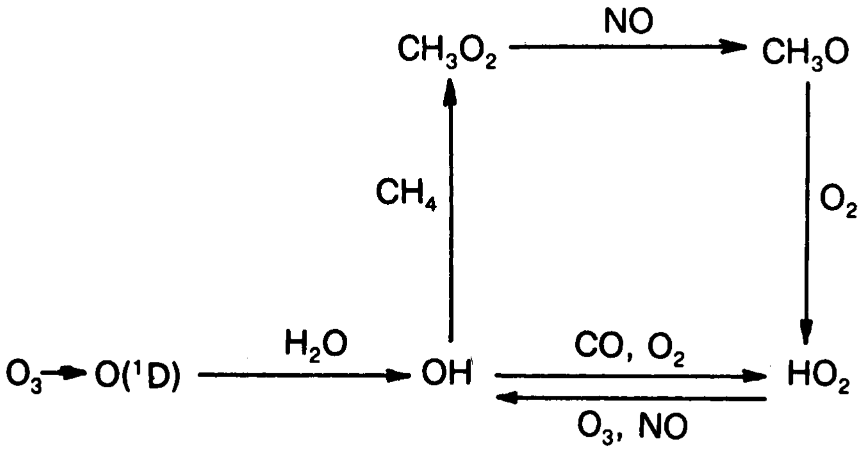


Fig. 7. Amplification of OH production.

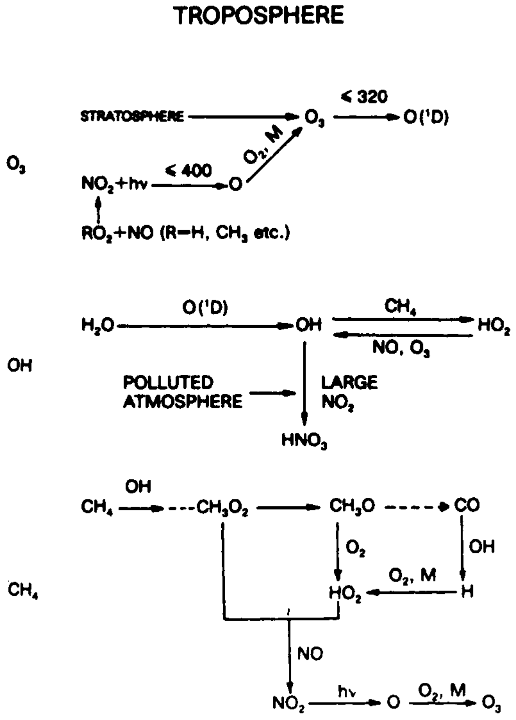


Fig. 8. Key reactions in troposphere.

followed by $O + O_2 + M \longrightarrow O_3$ reaction, or by transport from the stratosphere.

As we go into the stratosphere, several new aspects arise: firstly, solar radiations of appropriate wavelengths are now available not only for formation and destruction of ozone, but also for dissociation of CFM, CH_4, CCl_4, N_2O, H_2O and others releasing ozone-destroying active species ClO, OH and NO. The radiation involved are indicated below:

$O_2 + h\upsilon \xrightarrow[\text{Schumann-Runge bands}]{175\text{-}200\text{ nm}} O(^3D) + O(^1D)$	Mesosphere and upper stratosphere
$O_2 + h\upsilon \xrightarrow[\text{Herzberg continue}]{200\text{-}242\text{ nm}} O + O$	Stratosphere, weakly in mesosphere
$O_3 + h\upsilon \xrightarrow[\text{Hartley band}]{242\text{-}310\text{ nm}} O_2 + O(^1D)$	Stratosphere—formation of $O(^1D)$
$O_3 + h\upsilon \xrightarrow[\text{Huggins band}]{310\text{-}400\text{ nm}} O_2 + O(^3D)$	Stratosphere and troposphere—formation of $O(^1D)$
$O_3 + h\upsilon \xrightarrow{400\text{-}850\text{ nm}} O_2 + O$	Troposphere—photodissociation even at surface
$H_2O + h\upsilon \xrightarrow{135\text{-}200\text{ nm}} OH + H$	
$H_2O_2 + h\upsilon \xrightarrow{135\text{-}370\text{ nm}} OH + OH$	
$NO_2 + h\upsilon \xrightarrow{245\text{-}398\text{ nm}} NO + O$	
$\xrightarrow{135\text{-}245\text{ nm}} NO + O(^1D)$	
$ClO + h\upsilon \xrightarrow{\qquad} Cl + O$	
$ClO\ NO_2 + h\upsilon \xrightarrow{195\text{-}450\text{ nm}} \text{Products}$	

$$CCl_4 + h\nu \xrightarrow{174\text{-}238\ \text{nm}} \text{Products}$$

$$CFCl_3,\ CF_2Cl_2 + h\nu \xrightarrow{180\text{-}225\ \text{nm}} Cl_2$$

$$HCl + h\nu \xrightarrow{140\text{-}220\ \text{nm}} H + Cl$$

$$Cl_2 + h\nu \xrightarrow{240\text{-}450\ \text{nm}} 2Cl$$

$$CCl_4 + h\nu \xrightarrow{174\text{-}238\ \text{nm}} \text{Products}$$

The depth of penetration at different wavelengths (attenuation of e^{-1} for an overhead sun) is shown in Fig. 9. The variabilities of the radiations with solar activity become important in this context (see, p. 16 under **Sources and sinks**). It may be noted that the ozone-destroying processes of anthropogenic origin come mainly through NO and ClO. These have to compete with natural sources: solar proton events for NO and volcanic eruptions for ClO.

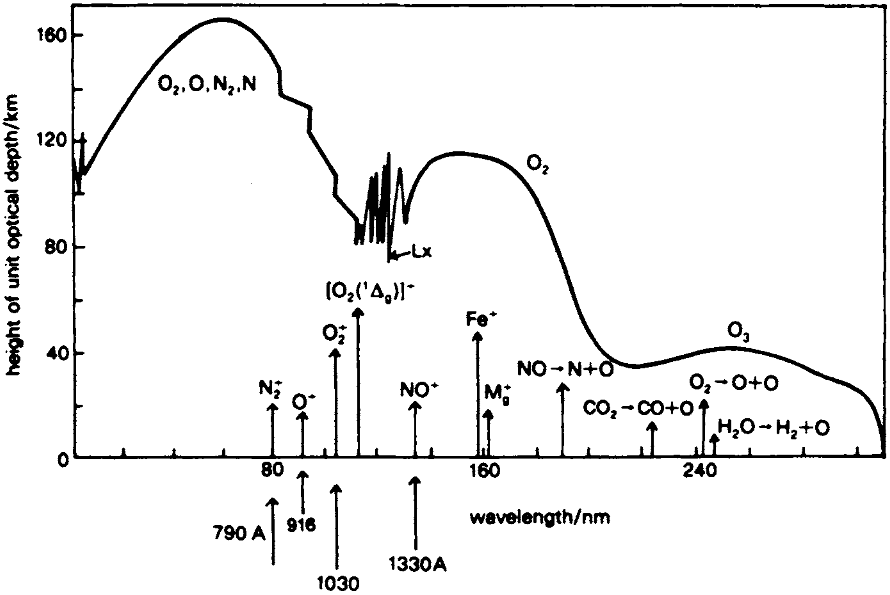


Fig. 9. Penetration of radiation to e^{-1} of intensity.

An important aspect is the oxidation of methane. The pathways of oxidation are shown in Fig. 10.

As we go to the mesosphere there is a drastic change. We are now entering the ionosphere beginning, under normal conditions, at around 60 km. Upto around 90 km where major dissociation of O_2 begins, the atmosphere remains mixed with N_2 and O_2 as major constituents. Above 90 km with dissociation of O_2 there is a rapid shifting from O_2, N_2 combination to O_2, O, N_2, N combination and at higher levels of the thermosphere to O, N combination, and then on to hydrogen and helium.

An important neutral constituent in the mesosphere, which is a minor species and a photochemical product, is NO. Its importance comes from the fact that at the lowest part of the ionosphere (60-80km) it is the main source of ionization through the process:

$$NO + h\upsilon \xrightarrow{Lx} NO^+ + e$$

Direct formation of NO through

$$N + O + M \longrightarrow NO + M$$

or $$N + O_2, O_3 \longrightarrow NO + O, O_2$$

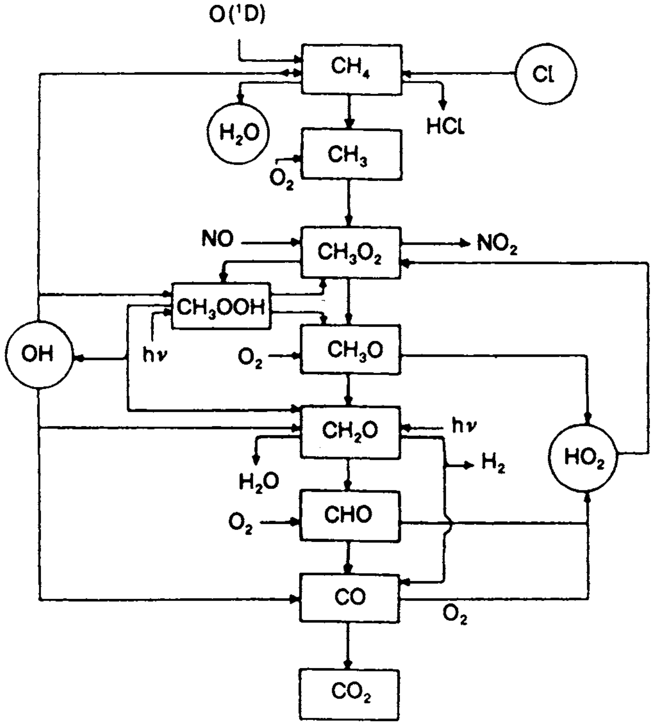


Fig. 10. Stratospheric methane chemistry (after WMO, 1985).

require the presence of atomic nitrogen but an unusual contribution comes from an ionic process:

$$NO^+ + e \longrightarrow NO + h\nu$$

which occur in the lower part of the thermosphere; NO thus produced is transported downwards. This is one of the few processes in the atmosphere we know where a sizeable contribution to the neutral constituent is coming from an ionic process.

Ion chemistry

Although the ionosphere begins only around 60 km, the so-called "non-ionized" region of the troposphere and stratosphere also contains ions, excepting that there are no free electrons. Thus over the entire atmospheric environment we are concerned with reactions of neutrals with ions, but since neutrals are more numerous (even for minor species), these have in most cases no effect on the concentrations of the neutral species.

The key boundaries are here ~35 km, 60 km, mesopause and heights around 170-180 km.

Principal ionic reactions are summarised in Fig. 11.

The boundary around 35 km separates proton hydrates (PH) from non-proton hydrates (NPH). In the region below this level, ions become increasingly complex as we go towards the surface. The troposphere is dominated by ions of the type $NH_4^+ [(NH_3)_2SO_2]_x(H_2O)_w(NH_3)_n$ where x, w and n can take different values. The ions are heavy, additional increments in mass numbers apparently go in multiples of 98. In the stratosphere below 35 km, the positive ions are of the type $H^+(X)_n(H_2O)_n$ with X believed to be CH_3CN and negative ions $R\text{-}(HR)_m(HNO_3)_n$ with HR = 98 ± 2 AMU (observed). Ion concentrations are around $10^3 cm^{-3}$ at stratospheric heights progressively increasing from low to high latitudes. This happens because the ionizing source is galactic cosmic rays whose entry into the atmosphere is modulated by the earth's magnetic field.

It is believed that PH to NPH conversion occurs through the following reaction:

$$H^+(H_2O)_n + X \xrightarrow{k} H^+X(H_2O)_{n-m} + m\,H_2O$$

One can derive threshold concentrations of X from:

$$k[PH^+][X] = X_i\,N^-[NPH^+]$$

This gives, at 35 km,

$$[X] \sim 10^5 cm^{-3}$$

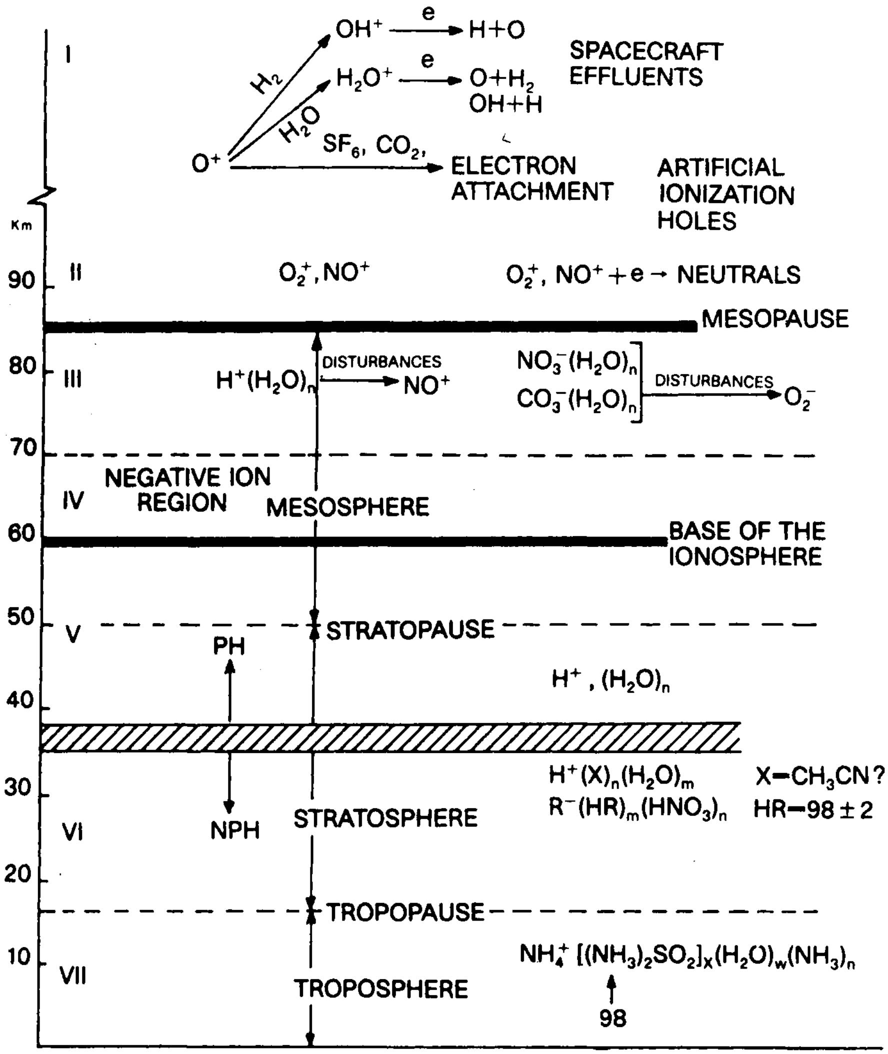


Fig. 11. Ion chemistry.

Thus, once the *nature* of X is identified, the ionic measurement provides an estimate of the participating minor species at concentration levels well below existing measurement techniques.

In the context of anthropogenic effects, the main question is whether any of the ionic processes produce active species that could interact with ozone or any of the other greenhouse molecules.

Production of H/OH can occur through dissociative reactions:

$$H_3O^+ + (H_2O)_n + e \longrightarrow (n + 1)H_2O + H$$

$$\longrightarrow H_2 + OH + nH_2O$$

$$O_2^+ \longrightarrow O_4^+ \longrightarrow H_3OH^+ \xrightarrow{H_2O} H_3O_2^+ + OH$$

Combining the two,

Ionic production of H/OH $\leq 2q$

Actual calculations show these are negligible in the stratosphere, but can be important in mesosphere during PCA (Polar Cap Absorption) events.

Can any ionic process directly contribute to the destruction of ozone? Suggestions in the past point out the following reactions,

$$NO_3^- + O_3 \longrightarrow NO_2^- + 2O_2 + 0.8 \text{ ev } (< 2 \times 10^{-12})$$

The loss rate is, however, low:

The only process, through the ionic chain, that can be of concern (especially during proton events) is given in Fig. 12.

It is important to note that a single proton event can inject NO_x into the stratosphere of a magnitude considerably larger than the GCR (Galactic Cosmic Radiation) inputs for a whole year. Thus:

	NO_x input (molecules)	
GCR	Per year	S. min 7×10^{32}
SPE (Sudden Proton Event)	August 72	32×10^{32}

From the stratosphere to the mesosphere the main change is that we are now entering the iononsphere. At heights below 75 km, negative ions are dominant. Ions below the mesopause are of the form $H^+ (H_2O)_n$ (positive ions) and $NO_3^-(H_2O)_n$ and $CO_3^- (H_2O)_n$ (negative ions). During solar disturbance events these are reduced to the simple ions O_2^-. For man-made events, these reactions can assume importance if large amount of H_2O molecules are injected (as with rocket exhausts). Above the mesopause the cluster ions disappear and the Ionosphere is dominated principally by two molecular ions O_2^+ and NO^+ upto the next key boundary of around 170-180 km. The most important reactions are:

$$O_2^+ + e \longrightarrow O^1 + O$$

$$O_2^+, N_2^+ \longrightarrow NO^+ + e \longrightarrow N + O$$

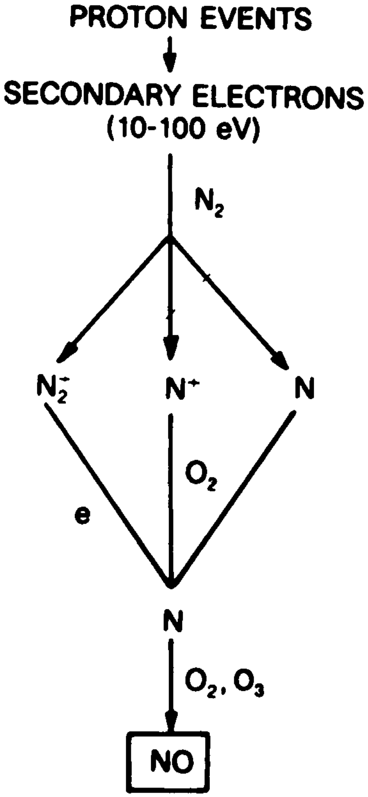


Fig. 12. NO production from solar proton events.

In this region, the predominant control is through solar radiations and no large scale effects are anticipated from man-made events.

A major difference occurs above about 170-180 km, where ions are primarily atomic: O^+. Here any injection of neutral molecules could convert O^+ ions to molecular ions with a consequent increase in recombination coefficient by as much as three orders of magnitude. This causes large scale depletion of ionization at those heights.

Sources and sinks

Solar sources — The principal sources are:

(i) Changes in solar constant;

(ii) Solar activity changes in the XUV region; and

(iii) Solar Proton Events and their occurrence frequency as a function of solar activity.

Since magnitude of variations of radiation flux with solar activity *decreases* with increase in wavelength and also since absorption coefficients of these radiations also generally decrease with increasing wavelength, sensitivity to solar activity decreases as we go down in height.

TABLE 1: Solar Flux: Wavelengths of Interest with Descending Heights

Extreme UV	10-100 nm	100-300 km	× 10	Hours to weeks to years
Lx	121.6 nm	80	× 2	Solar Cycle
UV	150		16%	Solar Cycle
	200		10%	Solar Cycle
	250		4%	Solar Cycle
	300	Surface	1%	Solar Cycle
S	$S_o = 1373 \pm 20$ Wm^{-2}			
	$\Delta S_o = 0.07 \, \Delta R_{m,\,max}$ Wm^{-2}			

Three types of changes can occur:

(i) Modulation of D-region conductivity and consequent modulation of global electrodynamics (relevant to sun-weather relationship);

(ii) Changes in ozone content and ozone profiles; and

(iii) NO production through SPEs.

For the first, we are concerned with GCR for tropospheric-stratospheric systems (*increases* with *decreasing* solar activity) and Lx (increases by 100% from sunspot minimum to maximum). For the second, at the wavelengths of interest the observed solar cycle variations are 1 to 10%. For solar proton events, NO_x injection is irregular, depending on the occurrence, magnitude and nature of the SPE. The main point to consider here is that because of the timescales involved we have to consider not just a single SPE event but the cumulative effect of such events. A rough estimate (Mitra, 1981) indicates that NO_x injection from SPEs can be roughly represented by a curve similar to that of F 10.7cm.

The solar cycle variation in the ozone profile due to such variations in the relevant radiation are comparable to those caused by increased trace gases. An example of the change from 1979 to 1986 from these two types of changes are shown in Fig. 13.

Volcanic sources

We will limit ourselves, in this discussion, to Cl_x only. An approximate way of estimating Cl_x injection from this source, is to start with Lamb's VDI/E_{max} index as a measure of the total amount of ash injected for any given eruption and then

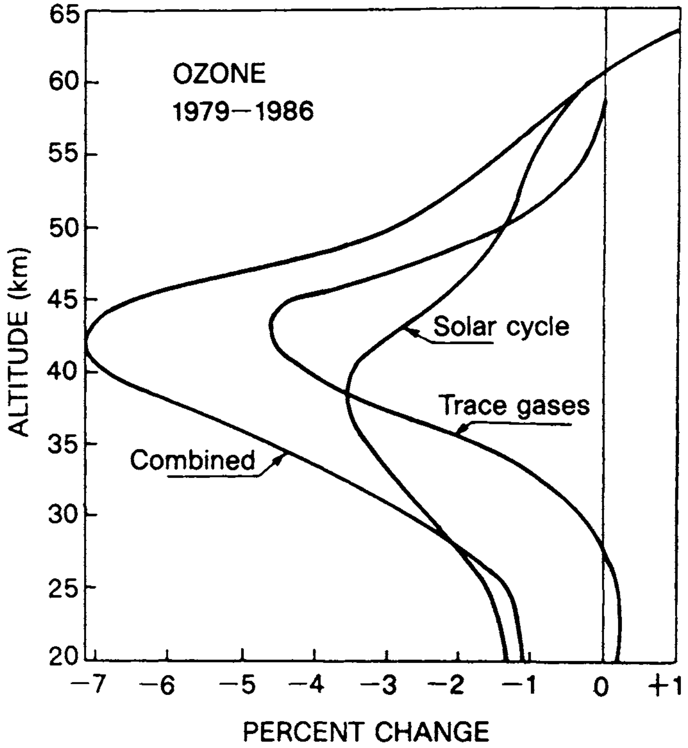


Fig. 13. Relative ozone changes between 1979 and 1986 from changes in solar radiation and those in trace species (Brasseur *et al.*, 1988).

calculate Cl_x injection by estimating $f(Cl_x) = 0.01$ f(gas). This is probably an underestimate as the observations for Mt Agung eruption of 1963 showed. An appropriate basis would be:

$$0.1\ f\ (gas) > f(Cl_x) > 0.01\ f\ (gas).$$

Representative values are shown below:

Cl_x injection for moderate volcano	~ 10^{34} molecules
Mt Agung	3×10^{32}

Volcanoes inject not only Cl_x but also a number of other species of greenhouse interest. For Mount St. Helens eruption, the reported estimates were:

CO_2 (ppmv)	< 3-19
H_2 (ppmv)	0.12-0.23
CH_4	nd-0.59
COS	nd-0.22

Biospheric and industrial sources

Carbon dioxide

Present concentration : 344 ppmv (≅ 741 × 10^{15} gC)
Seasonal oscillation due to respiration and photosynthesis within biosphere : ~ 5 ppmv (10.6 × 10^{15} gC Yr^{-1})
Fossil fuel : 5 × 10^{15} gC Yr^{-1}
Deforestation—regrowth : 2 × 10^{15}
Tropical agricultural burning : 7 × 10^{15}
Sinks: Oceans : 2.5 × 10^{15}
Atmospheric increase : 2.5 × 10^{15}

Nitrous oxide

(McElroy and Wofsy, 1985; 1984 concentration 303 ppb):

Atmospheric burden : 1500 × 10^{12} g N
Sources: Oceans : 2 ± 1 × 10^{12} g N Yr^{-1}
Combustion (Coal + Oil 4 ± 1) (biomass 0.7 ±0.2) : 4.7 ± 1.2
Fertilized agricultural fields : 0.8 + 0.4
Grasslands : < 0.1
Boreal and temperate forests : 0.1-0.5
Tropical and subtropical forests and woodlands : 7.4 ± 4
Total : 15.3 ± 6.7
Sinks: Stratospheric photolysis and reaction with $O(^1D)$ e.g. $N_2O + h\upsilon \longrightarrow N_2 + O$ $N_2O + O(^1D) \longrightarrow 2NO$ or $N_2 + O_2$: 10.5 ± 3
Accumulation (0.7 ppb/Yr^{-1}) : 3.5 ± 0.5
Total : 14.0 ± 3.5

Tropical contribution:

Biomass burning : 0.6
Soil emissions : 7.4
Total : 8.0

Special points: Soils in tropical forests emit N_2O flux 10 times larger than others:

Tropical forests : 2×10^{10} N_2O $cm^{-2}s^{-1}$
Other forests : $1\text{-}2 \times 10^{9}$
Agricultural soil : 2×10^{9}

Methane

Sources (Khalil and Rasmussen, 1983)

Enteric fermentation : $100\text{-}150 \times 10^{12}$ g CH_4 Yr^{-1}
(cattle, sheep, etc.)

Rice paddies : 100 ± 50
Wetlands : 150 ± 50
Biomass burning : 10 - 60
Others : 10 - 150

Sinks (McElroy and Wofsy, 1985; 1984 concentration 1630 ppb):

Reaction with OH : $425 \pm 125 \times 10^{12}$ g CH_4 Yr^{-1}

Uptake by dry soils : 10 ± 5

Accumulation (20 ppb Yr^{-1}) : 60 ± 15
Total : 495 ± 145

TROPOSPHERIC-STRATOSPHERIC SYSTEM

We limit ourselves to: (i) ozone problem; and (ii) greenhouse molecules.

Ozone chemistry

Ozone chemistry, since the classical work of Chapman, has gone through many complex changes, especially with the recognition of the role of catalytic radical species

HO_x, NO_x, ClO_x, all essentially brought into the stratosphere from tropospheric sources: NO_x from subsonic and supersonic aircrafts, N_2O from agricultural and combustion practices, CFCs from aerosol propellants, blowing agents and refrigerants.

The catalytic action of these radicals is similar and can be expressed as below:

$$\begin{array}{lccc} & X + O_3 & \longrightarrow & XO + O_2 \\ & XO + O & \longrightarrow & X + O_2 \\ \hline \text{Net:} & O + O_3 & \longrightarrow & 2O_2 \end{array}$$

where the catalyst X could be one or more of the following:

$$X = H, OH, NO, Cl, Br$$

Ozone scheme, from current knowledge, can be summarised as in Fig. 14.

Chapman theory (Oxygen-only atmosphere) — In this pioneering initial ozone chemistry, Chapman suggested the following sequence of reactions (see Fig. 3).

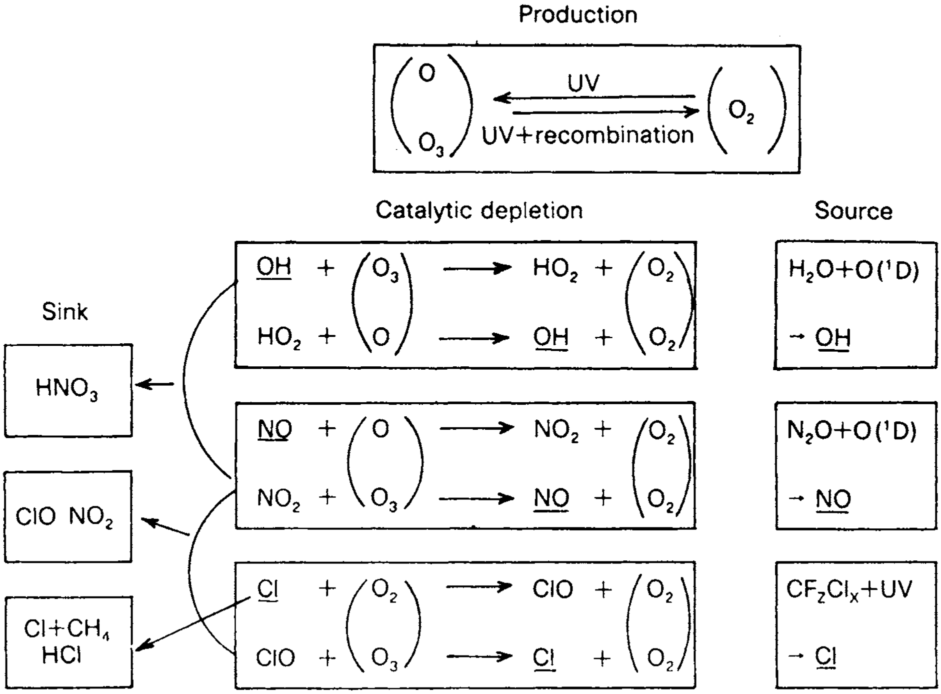


Fig. 14. Coupling between OH, NO and Cl.

$$\mathrm{O_2 + h\nu \xrightarrow{< 242\ nm} O + O}\ \text{(primarily above 20 km)} \quad \ldots (1)$$

followed by:

$$\mathrm{O + O_2 + M \longrightarrow O_3 + M} \quad \ldots (2)$$

Ozone in turn is dissociated by:

$$\mathrm{O_3 + h\nu \longrightarrow O_2 + O(^1D)} \quad \ldots (3)$$

$$\mathrm{O(^1D) + O_3 \longrightarrow 2O_2} \quad \ldots (4)$$

Hydrogen system—The OH system destroys only 10 % of O_2 but is dominant above 40 km.

$$\mathrm{H_2O + O(^1D) \longrightarrow 2\ OH}$$

Reactions particularly important *above 40 km*:

$$\begin{array}{lrcl} & \mathrm{OH + O_3} & \longrightarrow & \mathrm{HO_2 + O_2} \\ & \mathrm{HO_2 + O} & \longrightarrow & \mathrm{OH + O_2} \\ \hline \text{Net:} & \mathrm{O + O_3} & \longrightarrow & \mathrm{2O_2} \end{array}$$

OH can also be formed from oxidation of methane:

$$\mathrm{CH_4 + O(^1D) \longrightarrow CH_3 + OH}$$

with subsequent reactions as above.

H, OH, HO_2 interconvert rapidly by reactions with O, so that all three tend to be in steady state. The scavenging reaction is:

$$\mathrm{OH + HO_2 \longrightarrow H_2O + O_2}$$

resulting in formation of H_2O which drifts down out of stratosphere. Since this reaction removes odd hydrogen out of the active system, its rate is one of the most important elements in stratospheric chemistry.

Nitrogen system—Sixty percent of ozone destruction occurs through this system. The sequence is as follows:

N_2O produced by bacterial action of micro-organisms in ocean and soil (denitrification) diffuse upwards from troposphere to stratosphere, where

$$\mathrm{N_2O + O(^1D) \longrightarrow 2\ NO}$$

$$\mathrm{NO_2 + h\nu \longrightarrow NO + O}$$

and NO so formed catalyses ozone by:

$$\begin{array}{lrcl} & NO + O_3 & \longrightarrow & NO_2 + O_2 \\ & NO_2 + O & \longrightarrow & NO + O_2 \\ \hline \text{Net:} & O_3 + O & \longrightarrow & 2O_2 \end{array}$$

the reaction of NO_2 with OH:

$$OH + NO_2 + M \longrightarrow HNO_3 + M$$

produces HNO_3 which is eventually washed out of the troposphere and is the major sink.

Chlorine system—Natural chlorine contributes only very little (few percents) to O_3 destruction. CFM's (particularly $CFCl_3$ and CF_2Cl_2) are the main ozone destroyers. They are inert in the troposphere but get dissociated in the stratosphere:

$$CFCl_3, CF_2Cl_2 \xrightarrow[180\text{-}220\ \text{nm}]{h\upsilon} Cl_2$$

Then follow the following sequences:

$$\begin{array}{lrcl} & Cl + O_3 & \longrightarrow & ClO + O_2 \\ & ClO + O & \longrightarrow & Cl + O_2 \\ \hline \text{Net:} & O + O_3 & \longrightarrow & 2O_2 \end{array}$$

ClO catalytic efficiency is *reduced* in presence of NO because of the reaction:

$$ClO + NO \longrightarrow NO_2 + Cl$$

followed by:

$$NO_2 + H \longrightarrow NO + OH$$

The sink is HCl, formed through:

$$CH_4 + Cl \longrightarrow HCl + CH_3$$

$$HO_2 + Cl \longrightarrow HCl + O_2$$

Chlorine can be recycled through:

$$HCl + OH \longrightarrow H_2O + Cl$$

Balance between Cl, ClO and HCl are given by the above three reactions.

While chlorine catalysis of ozone is six times as efficient, catalysis of ozone conversion to "inert" HCl is also more efficient than conversion of HNO_3; so that the overall efficiency of the two are comparable.

Again we have a coupling reaction:

$$ClO + NO \longrightarrow ClNO_2$$

and

$$ClO + NO_2 \longrightarrow ClNO_3$$

It was thought at one time that this reaction reduces ozone depletion efficiency by other reactions from 14% to 7.5% (by a factor of 1.86). However, it seems that

$$OH + NO_2 + M \longrightarrow HNO_3 + M$$

is more efficient than

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M$$

Reaction scenario—The three principal radical species OH, NO and Cl coming primarily from H_2O, N_2O and CF_xCl_y respectively and interacting with ozone catalytically eventually end up as sink species HNO_3, $ClONO_2$ and HCl. A summary scenario is shown in Fig. 14.

Antarctic ozone hole—The homogeneous chemistry described above is inadequate for the large depletion seen in the Antarctic and now in the Arctic. Prior to the discovery of the Antarctic ozone hole, the conclusion that was emerging was of a statistically insignificant change (so far) in ozone content and of recognizable changes only at upper stratospheric levels around 40 km. Theoretical calculations, both 1-D and 2-D, also predict only a few percent of change of the total ozone content, and not the almost complete annihilation one sees over the Antarctica.

To understand the special chemistry obtaining in the Antarctic one should first understand the very special conditions under which the "hole" appears. These are:

(i) Very low T (–80° C and below);

(ii) Presence of stratospheric clouds;

(iii) ClO increase to values about 100 times larger than in mid-latitudes;

(iv) Decrease of odd nitrogen; and

(v) Chemically depleted region is dehydrated and denitrified.

The most important thing is to understand how ClO can be increased by such a large magnitude between 12 and 20 km over such a short period. The existing gas phase chemistry (Fig. 15) would suggest that in this region chlorine exists primarily in a reservoir form as HCl, $ClONO_2$.

We have two alternatives. Either conditions occur which block the diversion of ClO into reservoir species or reactions occur that release ClO from the reservoir or both. An optimum condition would involve both *increase* in ClO and *decrease* in NO_x.

The key factor, it is believed, is the occurrence of extremely low temperatures. Such low temperatures promote increased occurrences of polar stratospheric clouds (PSC's). There are two types of PSC's:

Type I	PSC	- 77°C	$HNO_3.3H_2O$
Type II	PSC	- 85°C	Ice crystals

Type I PSCs have particles of radii around 0.5-0.7 μm and occur at temperatures about 5-7 K higher than the frost point (Type II). Type I temperature is consistent with thermodynamical stability of HNO_3, 3HNO (NAT). Type II water-ice type clouds form at temperatures below the frost point, leading to large scale irreversible removal of H_2O vapour in the Antarctic.

The key heterogeneous reactions are:

$$HCl(S) + ClONO_2\,(g) \xrightarrow{0.05\text{-}0.1} Cl_2(g) + HNO_3(S) \qquad \ldots (1)$$

$$N_2O_5\,(g) + H_2O(S) \xrightarrow{0.001} 2HNO_3(S) \qquad \ldots (2)$$

$$ClONO_2\,(g) + H_2O(S) \xrightarrow{0.009} HOCl(g) + HNO_3(S) \qquad \ldots (3)$$

$$N_2O_5\,(g) + HCl(S) \xrightarrow{0.003} ClONO_2(g) + HNO_3(S) \qquad \ldots (4)$$

The sticking coefficients measured by Leu *et al.* (1988) and others show that these coefficients are appreciable.

These reactions provide pathways for removal of NO_2, thus inhibiting ClO + $NO_2 \longrightarrow ClO\ NO_2$ pathway and also releasing Cl_2 (g) as in (1) for PSC Type I and HOCl as in (3) for ice-clouds of PSC Type II. Fig. 15 indicates diagrammatically such possibilities.

Model calculations using the set of heterogeneous reactions outlined above by Salawitch *et al.* (1988), profiles of Cl_x appropriate for each year since 1960 (1.0 ppb in the upper stratosphere for 1960, 1.50 ppb for 1970, 2.4 ppb for 1978, 3.3 ppb for 1985), and with several assumptions regarding duration of PSCs and of different percentages of return of condensed HNO_3 to gas phase, showed that about 50% reductions are possible for Cl concentration above 2.4 ppb (1978 level) with

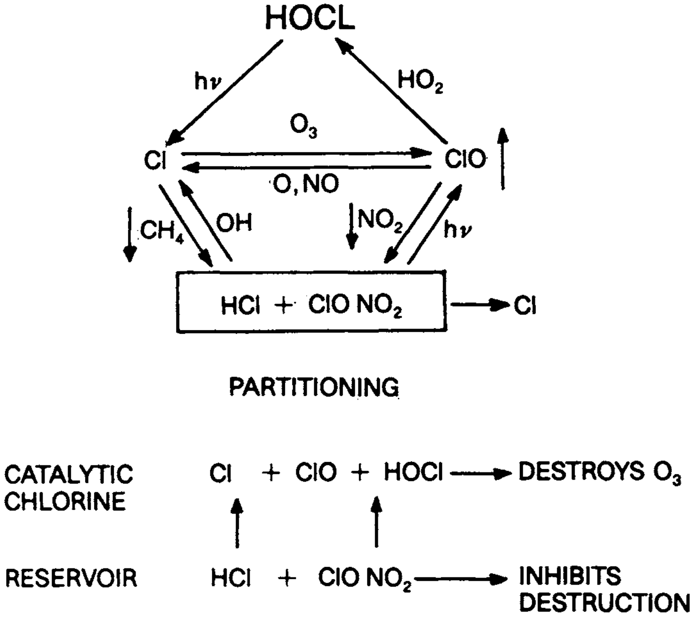


Fig. 15. Antarctic ozone chemistry.

temperatures below condensation point of water occurring for an extended period of time and with more than 80% of HNO_3 removal.

A new result of major implication is that such surface reactions are not limited to ice-clouds, but can also occur on liquid sulfuric acid aerosols. These occur at higher temperatures. Laboratory measurements have been reported on interactions of $ClONO_2$, HCl and HNO_3 on 65-75% H_2SO_4 solutions at temperatures between –63° to –43°C. These provide possibilities of ozone reduction at *lower* latitudes and provide the first evidence for possible ozone reduction at latitudes outside the Antarctic and the Arctic.

An example of ozone depletion from sulfate aerosol particles is provided by volcanic eruptions. An example was the eruption of EL Chichon in 1982 ejecting a large amount ($3\text{-}8 \times 10^{12}$g) of SO_2 in the atmosphere (Hofman and Solomon, 1989). Following this eruption O_3 concentration was depleted by about 15% between 10° and 50°N.

Greenhouse molecules

The important greenhouse molecules, in concentrations in 1979 and 1986 (solar maximum and solar minimum respectively), rate of growth calculated lifetimes are shown in Table 2:

TABLE 2: Greenhouse Molecules

Species	Mixing ratio			Recent rate of growth (%/yr)	Calculated lifetime	Ozone depletion potential[b]	HGWP[c]
	1979	1986	2050[a]				
CO_2	335.5ppm	344.0	(600)	0.5	—	—	—
CH_4	1.62ppmv	1.70	(3.3)	1	6.5	—	—
N_2O	305ppbv	310	(600)	0.25	170	—	—
F11	170pptv	220	(673)	5	70	1.0	1.0
F12	290pptv	390	(1325)	5	144	0.9	3.4
F22	50pptv	87	(631)	11.7	17	0.05	0.35

Note:

a Values for 2050 are on the basis of constant atmospheric emissions on Montreal products after 1985, using 1986, production as the atmospheric flux, for other trace gases using a linear rate of change and for CFC-22 to grow linearly by an additional 76g/year after 1985.

b Hydrocarbon Global Warming Potential relative to F11.

c Relative to F11.

The biosphere produces these gases in variety of ways. These are shown below (all in $g.Yr^{-1}$):

(i) Biomass burning

CO	$4\text{-}16 \times 10^{14}$g
CH_4	$0.3\text{-}11 \times 10^{12}$ g
NO_x	$10\text{-}14 \times 10^{12}$g N
N_2O	$1\text{-}2 \times 10^{12}$ g N
NH_3	$< 60 \times 10^{12}$ g

(ii) Rice paddy fields

CH_4	$100 \pm 50 \times 10^{12}$g CH_4

(iii) Fertilized fields, cultivations, soils

NO_x	$1\text{-}15 \times 10^{12}$ g
NH_3	$< 0.35 \times 10^{12}$ g
N_2O	0.8×10^{12} g

(iv) Enteric fermentation (cattle, sheep, etc.)

NH_3	$12\text{-}26 \times 10^{12}$ g
CH_4	$100\text{-}150 \times 10^{12}$ g

(v) Oceans and estuaries

N_2O	$2 \pm 1 \times 10^{12}$g N
NO_x $(NO + NO_2)$	0.2×10^{12}g N

The history of these gases, in their sojourn through the troposphere and stratosphere, going through a number of reactions is shown in Fig. 16 (Crutzen, modified).

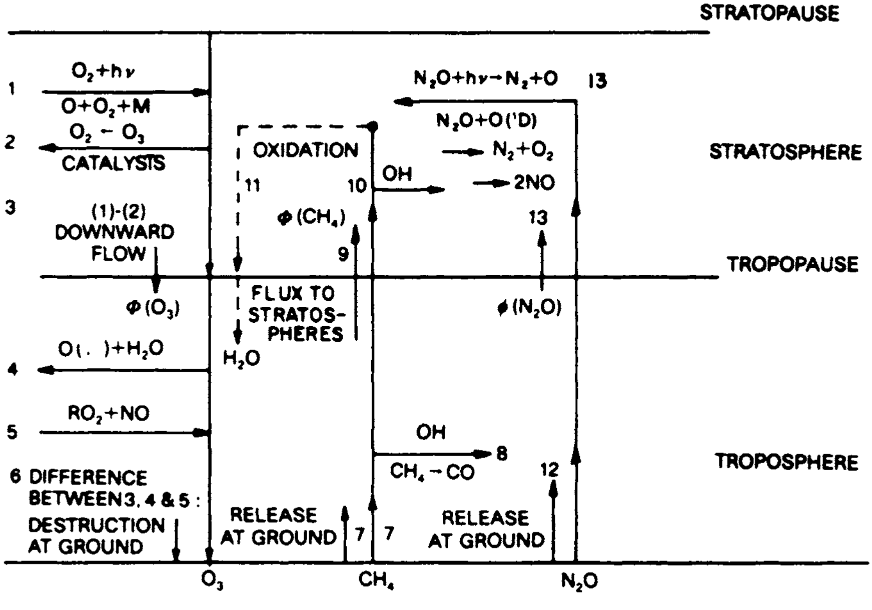


Fig. 16. Pathways of selected greenhouse molecules.

IONOSPHERIC MODIFICATIONS

As earlier mentioned, effects of human activities are not limited to the troposphere and the stratosphere—there are effects at much greater heights extending perhaps to tens of thousands of kilometers. The three major sources of perturbations in the upper stratosphere are:

(i) Spacecraft effluents;

(ii) Heating of the ionosphere by high power transmitters; and

(iii) Effects of power lines.

Of these chemical reactions are particularly dominant for spacecraft effluents. We will limit ourselves here only to this area.

Spacecraft effluents

These are of two kinds:

(i) Materials released as rocket exhausts; and

(ii) Materials released deliberately from the rocket as a tracer (the so-called "release" experiments).

Historically the first experiment of "modifying" the upper atmosphere was through "release" experiments. One of the best known experiments was the "Argus" during IGY when artificial radiation belts were produced by three nuclear test explosions 480km above the earth on August 29 and 30 and September 6, 1958 over the South Antarctic Ocean. Following the explosions a fascinating sequence of observations were observed: the brilliant initial flush of the explosion was followed by a fainter but persistent luminiscence along the magnetic lines of force through the burst point. Almost simultaneously a bright auroral cloud appeared at the conjugate point. A new radiation belt was produced.

The second well-known experiment was "West Ford"—a highly controversial experiment. In this a large number of their microwave dipoles (75 pounds) were placed in orbit around the earth as a scattering medium for radio signals in the Centimeter band.

However, those that have principal interest in the context of this address are the "Ionospheric holes" produced by rocket exhausts, because these involve chemically interactive processes. A list of these and the effects produced are summarised below:

(i) Golomb & Rosenberg	Expt. I:	150 moles of SF_6:220 km
	Expt. II:	130 moles of CO_2:220km
(ii) Project Firefly	1962	5.44 kg CO_2 at 234 km
(iii) Starfish	1962	To disturb van Allen Belts disturbences long-enduring
(iv) Skylab I	1973	H_2, H_2O from Rocket Exhausts: a total of 1.2×10^{31} molecules spread over 1800 km

(v) Lagopedo	1977	38 kg of H_2O, 16 kg of CO_2, 20 kg of N_2
(vi) HAEO-C	1979	Well planned experiment 7×10^{29} H_2O and H_2 molecules burnt from 211-501 km

In all these cases the effects were of *reduction* of ionization in the ionospheric F-region over varying areas. In the Golomb-Rosenberg experiments reduced electron densities were observed after a lapse of few minutes, lasted for 30 minutes for SF_6 release and 3 minutes for CO_2 releases. The Skylab effects, which come as a surprise, were unique in magnitude and spatial extent: a large "hole" was observed extending over an area of about 1000 km (seen through satellite TEC experiments). Lagopedo and HAEO-C experiments were planned experiments. In Lagopedo a hole extending over a radius of 30km was observed lasting for 30 minutes. In the HAEO-C experiment the hole was formed within a few seconds, was 2500 km long and 800 km wide and 300-400 km thick. There was nearly 100% depletion of electrons within 75 km of the trajectory during the maximum effect. The hole persisted until shortly after sunrise some 4 hours after launch. There were major radio effects of this depletion: VLF showed appreciable phase changes, HF signals recorded after the launch were low with increased fading.

Although there are several theories, the most reasonable (but not necessarily the only one) is that attributed to increased recombination through sudden deposition of a large quantity of H_2O and H_2 in the upper atmosphere. There are two specific levels we will consider: (i) at the level of the D-region ledge around 85 km and (ii) in the F-region. In a very simplistic way the expected concentration change = (Injection rate) × (Residence time). The residence time is given by: $(\text{Residence time})^{-1}$ = Transport removal rate + Chemical removal rate.

Normally around the ledge height the dominance of the water cluster ions disappears with NO^+ and O_2^+ being the principal ions above these levels. Recombination of these ions occur through:

$$NO^+ + e \xrightarrow{\qquad\qquad} N + O \qquad 4 \times 10^{-7}$$

$$O_2^+ + e \xrightarrow{\qquad\qquad} O + O \qquad 2 \times 10^{-7}$$

When H_2O concentrations are increased, the region 80-100 km gets changed into heavier clusters - dominated region from the predominant NO^+, O_2^+ regions. These clusters ions have 10 to 100 times larger recombination coefficients (10^{-6} to $10^{-5} cm^3 s^{-1}$), depending on the degree of clustering. Consequently a reduction of N_e occurs. If an increased H_2O ~~mixing ratio~~ of 100 ppmv is assumed, then the conversion of simple molecular ions to cluster ions is complete at 70-100 km levels. At the same time there is a reduction in UV radiation through screening by the increased water vapour concentration. An estimated reduction in daytime N_e from the combined effects is 75%. We may also note that although lifetimes of ions at these heights are short—of the order of seconds and minutes — the relevant water molecules have lifetimes of about 35 days at 85 km and 15 days at 100 km, long enough to be distributed over the globe.

The depletion is the most pronounced in the F-region. The chemistry here is as follows:

(i) Normal F_2 region dissociative recombination

$$\begin{array}{lcll} O^+ + N_2 & \longrightarrow & NO^+ + N & 1.2 \times 10^{-12} \\ NO^+ + e & \longrightarrow & N + O & 4.1 \times 10^{-7} \end{array}$$

(ii) Enhanced recombination with H_2

$$\begin{array}{lcll} H_2 + O^+ & \longrightarrow & OH^+ + H & 2 \times 10^{-9} \\ OH^+ + e & \longrightarrow & \left.\begin{array}{l} H + O(^3P) \\ H + O(^1D) \\ H + O(^1S) \end{array}\right] & 1 \times 10^{-7} \\ & & & \end{array}$$

(iii) Enhanced recombination with H_2O

$$\begin{array}{lcll} O^+ + H_2O & \longrightarrow & H_2O^+ + O & 2 \times 10^{-9} \\ H_2O^+ + e & \longrightarrow & \left.\begin{array}{l} O(^1D) + H_2 \\ O(^1D) + H_2 \\ OH + H \end{array}\right] & 1 \times 10^{-7} \end{array}$$

$O^+ + H_2$ or $O^+ + H_2O$ reactions are 10^3 times faster than $O^+ + N_2$ or $O^+ + O_2$ reactions. Furthermore, the OH radical formed through $H_2O^+ + e$ reaction can react further with O^+ through:

(i) $O^+ + OH \longrightarrow O_2^+ + H$

followed by:

(ii) $O_2^+ + e \longrightarrow O(^1D) + O$

In most cases, however, the OH radical is destroyed by reaction with O through:

$$OH + O \longrightarrow H + O_2$$

before the charge transfer reaction can occur.

If H_2O flux injected by the rocket is high in comparison with ambient ion concentrations, then a number of reactions occur that compete with the earlier reactions. These are:

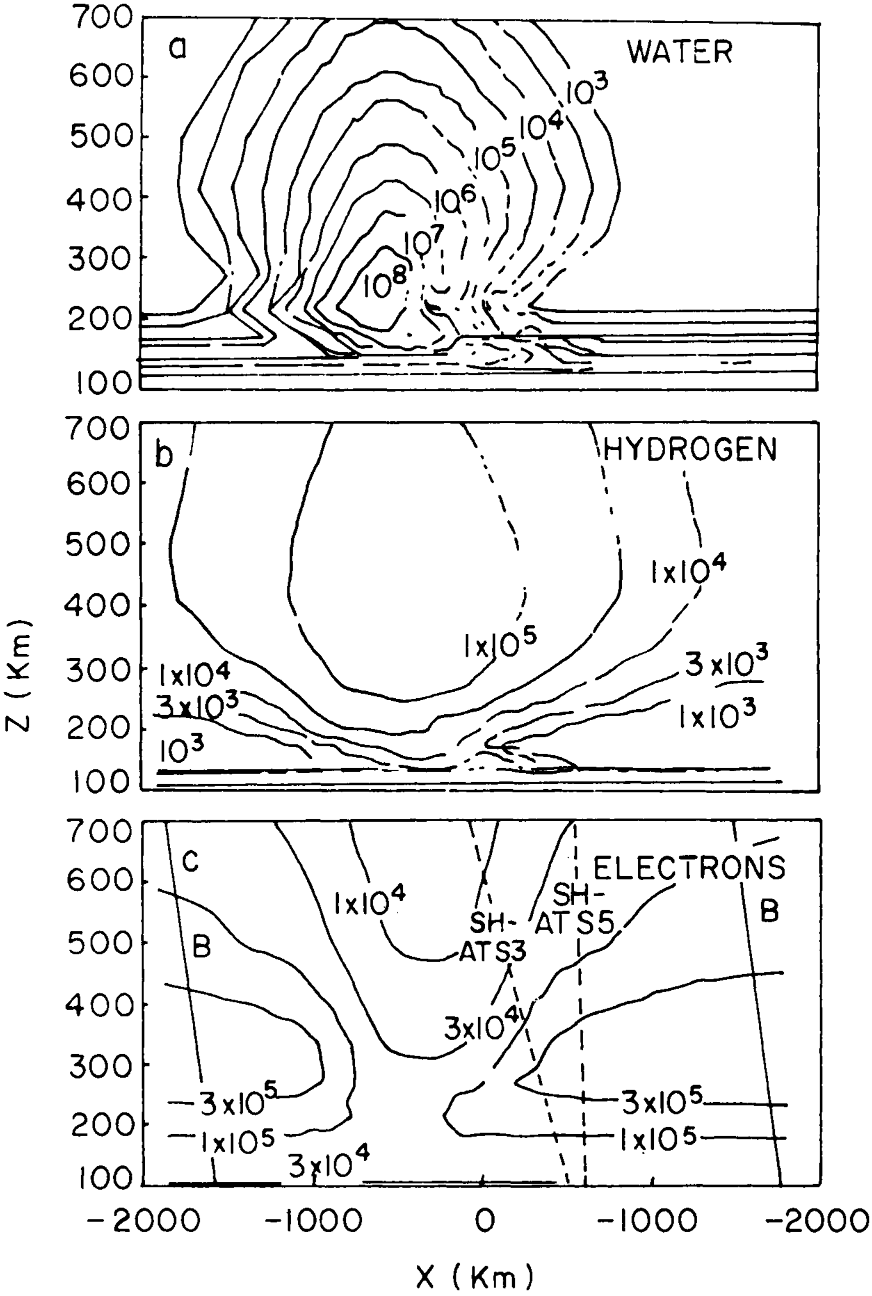


Fig. 17a. Modelling of ionospheric hole from Skylab I.

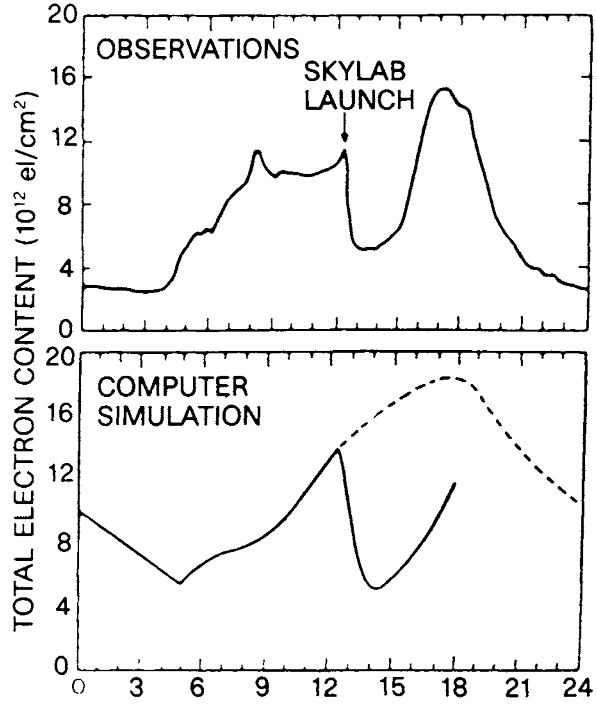


Fig. 17b. TEC (Total Electron Content) changes—observed and modelled.

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

$$OH^+ + H_2O \longrightarrow H_3O^+ + O$$
$$H_3O^+ + O(^1D)$$

followed by:

$$H_3O^+ + e \longrightarrow H + H_2O$$

The strong ion-removal effects by then exhaust particles are confined to heights above 200 km where ions are primarily atomic (O^+) and not below (dominated by molecular ions). The lifetime and the nature of the effect is determined by the residence times of the injected molecules. The time required for an H_2O molecule to fall from 400 to 200 km is about 2 hours. For hydrogen, although there is a tendency to settle, its behaviour is controlled by diffusion. H_2 cloud spreads 4 times as fast as H_2O cloud, but its setting rate is three times slower. Computer modelling of the "ionosphere hole" produced by Skylab along with the observed "hole" is shown in Fig.17 a,b

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THE INTERNATIONAL GEOCHEMICAL MAPPING PROJECT— A CONTRIBUTION TO ENVIRONMENTAL STUDIES

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There are many types of world synoptic data maps, but only within the last few years has serious attention been given to the need for a world geochemical atlas to provide an overview of relative geochemical abundance levels, regional trends and anomalous patterns. Surficial geochemical data are relevant to a wide variety of mineral resource, agricultural, forestry, environmental and health questions as well as many geological problems. Systematic maps can provide an index and a starting point for detailed studies relating to the many applications of geochemistry.

In 1988 a proposal for an International Geochemical Mapping Project was accepted by UNESCO/IUGS, to be administered through the mechanism of the International Geological Correlation Program (IGCP). The purpose of IGCP Project 259 is to create a network of scientists and organizations willing to work towards the goal of preparing systematic geochemical maps of the world's surface. The scientific, technical and financial problems are considerable. There are many data sets but not all are readily accessible. Surveys were initiated primarily but not solely for mineral exploration purposes using a variety of media and sample densities. Stream sediment sampling has been one of the most widely used techniques. Samples have been analysed for different groups of elements by a variety of analytical methods, often with uncertain quality control. Nevertheless, from a practical viewpoint these represent a large reservoir of data which, despite the imperfections, should be utilised as fully as possible. To achieve this, and to provide preliminary coverage across unsurveyed regions of the world, plans are being discussed for a new, very low-density, more uniform, sample network using the minimum number of sample types to provide control and serve as an international reference grid.

A committee structure based on scientific/technical and geographic divisions has been established. Committees have been established for North America, Western Europe, Eastern Europe, USSR, India, China, Australia and Southern Africa. Each has responsibility for making progress in its own region. Arrangements for South America are currently under discussion.

Examples of large regional geochemical surveys from a number of countries, e.g. Fenno Scandia, British Isles, Germany, Canada, USA, China, covering in total several million square kilometers, serve to illustrate both the benefits of such surveys and the problems of attempting to unite them into a systematic format.

HISTORY OF GEOCHEMICAL MAPPING

The concept of geochemical exploration dates back at least as far as Agricola in the 16th Century. The first geochemical soil studies were made for agricultural purposes by Liebig in 1840. In the 1930's Vernadski, Vinogradov and Fersman in the USSR, Goldschmidt and Vogt in Norway, Brundin in Sweden, Rankama in Finland pioneered geochemical mapping for mineral prospecting. In the 1940's, as a refugee from the Second World War, Goldschmidt, was a visiting scientist at the Macaulay Soil Research Institute in Scotland at a time when trace element studies on soils were receiving attention in order to improve agricultural productivity. After the war through the efforts of Webb, Hawkes and others in Great Britain and North America, geochemical surveys began to be introduced as a method of mineral exploration. A few progressive mining companies provided funding for research and experimental surveys. The method was being used extensively and successfully for mineral prospecting in Northern Rhodesia (Zambia) and New Brunswick, Canada, by the mid-1950's.

Government geological surveys and international development organizations began to undertake occasional geochemical surveys as a part of their operations in the late 1950's. The value of systematic geochemical surveys over large regions or whole countries had been recognised by Webb in the 1960's, and culminated in the Wolfson Geochemical Atlas of England and Wales (1978). However, the funds required for governments to place this type of work on the same routine basis as geological surveys were not made widely available until the oil-supply crisis of 1973 created a demand for uranium. Commencing in 1974 there were government programs in Canada, the USA, and elsewhere designed to assist in the discovery of uranium mineralisation. These programs provided for multi-element geochemical surveys, often in conjunction with airborne radiometric surveys, to be initiated with the intention of obtaining systematic reconnaissance coverage of large areas. It was possible to obtain acceptance of the need for multi-element surveys because geochemical anomalies can be classified on the basis of element associations. The bulk of the present North American data dates from this time.

THE VALUE OF A GLOBAL OVERVIEW

The availability of satellite imagery of the earth and planets has dispelled any doubts that may once have existed concerning the impact and importance of obtaining a global overview of key parameters. Such displays provide perspective and scale to many features and problems that cut across continents and national boundaries.

World Geological Maps have been in preparation for several decades but the first edition was only completed in 1984. It consists of 22 sheets at scales of 1:10 or 1:20 million. This work has been done under the auspices of UNESCO by the Commission for the Geological Map of the World, located in Paris. The same Commission is now coordinating the preparation of two other World map series, Tectonic and Metallogenic. These are at scales of 1/2.5 and 1/5 million. They are incomplete.

A Soil Map of the World has been completed by FAO/UNESCO. Publication commenced in 1971 and was completed in 1981. It is in 10 regional volumes, with maps at 1:500,000 scale. Geophysical and geochemical methods provide unique information about the earth that is not apparent using other techniques. They complement and refine the naked-eye observations which form the basis of geology.

Within the last two decades satellites have provided direct measurements of the global magnetic and gravity fields, allowing coarse resolution maps to be produced of these geophysical data. The same types of geophysical data are available in detail for some continents, for example North America.

Geochemical data are lacking by comparison. Systematic national geochemical surveys were not attempted until the 1960's, almost 150 years after the first national geological surveys commenced and 20 years after systematic geophysical surveys began. Another less obvious but, in the writer's opinion, equally important factor has been the omission of surficial geochemistry studies in university teaching. Consequently the geological profession as a whole has been largely unaware of their significance. The field methods, largely empirically are developed in response to the needs of the mineral industry to find new and more effective exploration methods. The weathering, solution, transportation and deposition processes which control the distribution and concentration of chemical elements and compounds in different types of natural environment are complex and still incompletely understood.

APPLICATIONS OF SURFICIAL GEOCHEMICAL MAPPING

As indicated above, surficial geochemistry was pioneered as a means of discovering otherwise non-obvious mineral deposits. In order to find such deposits, it was first necessary to ascertain geochemical background values; these have significance to broader aspects of geology, to soil science, groundwater studies, pollution studies, and every living thing that is affected by the composition of soil or water.

Mineral exploration

A mineral deposit is, by its existence, an anomalous concentration of a particular element or group of elements. The element (or elements) that are of economic value may be accompanied by others which are present only in small or trace amounts but which are nevertheless more concentrated than in a normal unmineralized environment. These may form a faint but large halo (100's of meters in diameter) in the vicinity of a deposit and are sometimes called pathfinder elements. These and/or the elements that form the deposit may (commonly) give rise to abnormal concentrations in the soil overlying and adjacent to the mineralization and in the natural drainage system downstream from it. Thus it is possible to find mineralization which is close to the surface but not exposed. Many ore bodies have been discovered in this way in the past 35 years (Govett, 1986; Mazzucchelli, 1986). The extent to which surficial geochemistry is now recognized as a sub-discipline within the earth-science community has stemmed primarily from its success in finding mineral deposits. For a more detailed description of this topic see Rose, Hawkes and Webb (1979).

Geological correlation

There is empirical evidence, recognised for many years, that certain groups of metals are congregated in certain geographic regions of the world. Rastall (1923) summarised that: "We can recognize metallogenic regions in space and metallogenic epochs in time". This predated by almost 50 years the modern concept of plate tectonics. The evidence for mobile continents, which over tens or hundreds of millions of years are subject to fragmentation and reassembly, carries with it the inference that it is possible to reconstruct, conceptually, the broken fragments of earlier continents by identifying the geochemical signatures associated with particular epochs. Thus, time and affinity-related groups of rocks may be characterized by trace element assemblages that differ from otherwise similar rock types of other ages or affinities. Certain granites are noted for their consistently high trace element levels of Sn and W. Some argillaceous rocks are noted for their distinctive metal content, for example Cu or U. Surficial geochemical studies can assist in understanding continental fragmentation. This is of considerable scientific interest as well as having the potential to assist in the mineral resource assessment of little known regions.

Biological implications

Figure 1 is a reminder of the biological activity of elements in the periodic table. Some of the elements are essential to life, some are harmful, and some are passive. Most elements are derived initially from rocks; through the process of weathering they move into soils and surface waters; from there they enter organisms. Their distribution in rocks is not uniform, with concentrations commonly varying by an order of magnitude, depending upon the rock type. In unusual situations, for example in mineralised areas, larger variations occur. Therefore, it is important to know the factors that control their part in life processes. The quantity and availability of biologically sensitive elements affects in conjunction with other factors forest growth, crop type, and crop fertility and through the food chain, animal and human health and ultimately the size and quality of life of human populations.

Known forms of life require, in addition to C, O, H and N, obtained from the atmosphere, relatively large amounts of Ca, Mg, Na, K, Fe, P, and S.

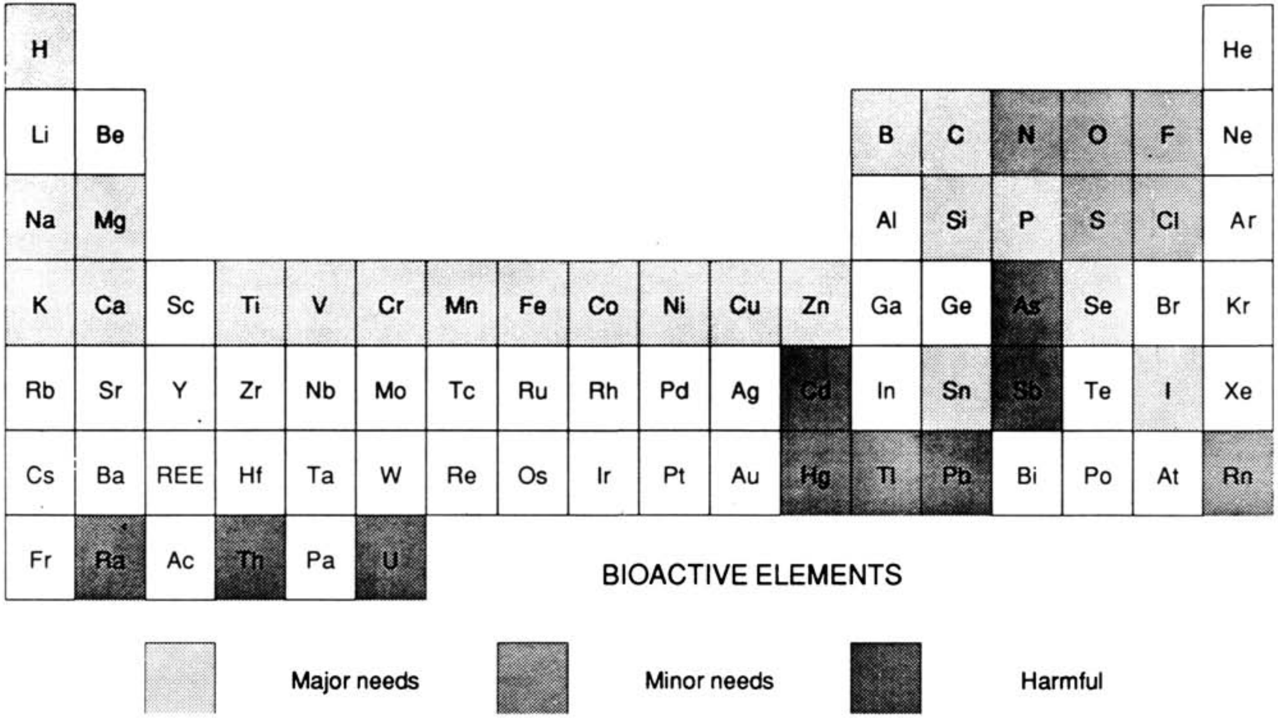

Fig. 1. Elements of periodic table which are known to be biologically active.

Trace amounts of B, Cu, Co, Se, Zn, Mn, Si, I, Cl, F, Cr, Ni, Mo, Sn and V play an equally vital, although less well understood, role. Too little or too much of any element can be harmful to organisms, with consequences manifesting themselves in many different ways. Selenium is a well documented example of a trace element which is necessary for human health, with adverse effects when the concentration in diet deviates significantly from the optimum amount (Crounse, 1986). Whilst different forms of life can have widely different tolerances, the optimal range for a given organism is often narrow.

Some elements, for example Al, although widely distributed in organisms, play an uncertain role in biological processes. Elements such as As, Sb, Be, Cd, Hg, Pb, Ra, Tl, Th and U, are generally consistently harmful to life. The consequences of their presence can be stunted growth, disease, and increased mortality amongst plants and animals.

Radioactivity is a potential hazard most commonly associated with U and Th and the decay products of these two elements, particularly Ra and Rn. However, K is in the anomalous position of being an essential constituent within most forms of life whilst possessing the harmful property of radioactivity. Potassium, U and Th are very widespread constituents in geological materials and their distribution is controlled by the same geochemical processes, and subject to the same variability, as applies to other elements.

Many factors in addition to abundance affect the availability of elements to biological processes and they may be controlling factors. These include the form in which an element occurs, the overall chemistry of a particular environment, organic as well as inorganic Hg is an example of an element where toxicity is very dependent upon form, rainfall, topography, drainage, pH, Eh, temperature, etc; many interactions, are poorly understood. The presence of unusual combinations of related elements can modify the availability of biologically active constituents, with beneficial or detrimental results. The mobility of anionic species of elements such as As, B, Se and U, is greater in alkaline and saline soils of arid regions than in acidic environments where cations such as Cd, Fe, Pb and Zn are more mobile. Anything which changes soil pH, e.g. acid rain, disturbs preexisting geochemical equilibria and so may disturb the biota. As an example, maple trees which are the commercial source of maple syrup in north-eastern North America are sensitive to the availability of K, Ca and Mg in the soil. Soils with an initially low concentration of these elements may become unsuitable for the growth of maple trees as a result of accelerated leaching of these elements by acid rain.

OBJECTIVES OF IGCP PROJECT 259

This project was conceived as a precursor to the ultimate goal of preparing a geochemical atlas of the world. In brief, the objective of the project is to facilitate, for geological and environmental applications, the production of surficial geochemical maps of the world, to complement other forms of data which describe the surface characteristics of the earth. For demonstration purposes the project will assemble available geochemical data and publish it in a standardized map form. Appendix A contains a fuller statement of the objectives.

METHODS OF GEOCHEMICAL SAMPLING

Geochemical surveys are undertaken primarily to ascertain the geographic distribution of the relative concentrations of given elements, to delineate patterns of high and low values, to obtain concentration values that will be reproducible under defined conditions and to provide explanations for the results.

Geochemical maps can be compiled from the analysis of rocks, soils and tills in glaciated regions, sediments in drainage systems, botanical samples and surface waters. All of these materials are being used, but their suitability varies considerably according to the purpose of the survey, the analytical information being sought, the region where the survey is being undertaken, the amount of detail (spatial resolution) required and the costs that can be sustained. To extend a survey into a new area, the desired sample medium or media and the sample spacing required need to be selected in advance, based on a combination of scientific, logistical and economic considerations.

Geochemical surveys of surface K, U and Th concentrations can also be carried out radiometrically from low-flying aircraft by virtue of the natural radioactivity of these elements. In this type of survey the method samples a continuous strip of whatever material happens to form the surface of the ground. Therefore the strip sampled is, most often, dominantly soil with some rock outcrop, the amount depending upon the geographic region. Although there are clearly differences in detail compared to the results obtained by conventional surface sampling the patterns obtained do not normally differ empirically by more than the differences between, for example, a stream sediment survey and a soil survey for the same area. The utility of K,U and Th surveys extends well beyond the search for radioactive mineral deposits, arising from the almost ubiquitous distribution of these elements and their distinctive behaviour in important geochemical processes. Nevertheless multi-element data are necessary for most general purposes and these can only be obtained by conventional surface sampling followed by laboratory analysis.

The advantages/limitations of the various alternative surface sample media are summarised in the following paragraphs; although these are written from the perspective of mineral exploration, the salient points apply whatever the purpose of the data. These are as follows:

(i) *Rocks* for geologically orientated investigations are the ultimate sample material, but exposures are non-existent in many places of interest and there can be no assurance that those that can be found are representative of the rocks which underlie the area; in regions where there are abundant rock exposures, because of diversity of rock types, it may be very difficult to obtain statistically representative samples except by taking a prohibitive number. For a review of the geochemical variations found in rocks in the vicinity of different types of mineralization see Govett and Nichol (1979);

(ii) *Soils* are materials derived from the weathering of rocks, admixed with living and dead organic matter; they may have developed from the *in situ* weathering of the underlying or adjacent rocks or from transported rock materials; climate and topography, age of the land surface and vegetation history control the type of soil that develops from a given rock type; soils in general thus exhibit wider chemical variability than the rocks from which they are derived, but within a given area, for similar sample sites, the relationship between parent rock type and soil composition is usually consistent within definable limits; soil sampling has been extensively used from the beginning of geochemical surveying, mainly where a closely spaced sampling pattern is required to achieve good spatial resolution of anomalous features. Useful reviews are given by Bolviken and Gleeson (1979) and Bradshaw and Thomson (1979);

(iii) *Tills*, the product of mechanical comminution of rocks by glacial action, are distributed over the extensive regions in the Northern Hemisphere which were subjected to the Quaternary glaciation; a till thus provides a composite sample of the rocks from which it has been derived; in general, in the absence of evidence to the contrary, it is assumed that the main mass of till at a given site has been derived from rocks within 2 or 3 kilometers in the direction of ice movement; till has usually been subjected to less chemical alteration than soil, which is advantageous for exploration and geological interpretation; because of the physical displacement of anomalies relative to bed-rock sources the latter can often only be located through extensive drilling. For a recent comprehensive review see Coker and Dilabio (1989);

(iv) Sediments from drainage systems are the preferred type of sample for most large area surveys; a single fine-grained sediment sample from a stream provides material which is approximately representative of the weathering products from the catchment area upstream from the point of collection; it is usual to sample streams immediately above a confluence; by selecting the size of drainage channel and if necessary sample intervals along the channel spatial resolution can be modified. In regions with large numbers of lakes and poorly defined surface drainage (such as recently glaciated areas in Canada and Finland) lake sediment sampling is an effective alternative to stream sediment sampling, with the lake catchment basin defining the limits of the source material, usually, mainly till in a glaciated region. Lake sediments have the advantage for environmental purposes of allowing, if a core is taken, a time sequence of sedimentation to be observed. For reviews on stream sediments see Plant, Hale and Ridgway, 1989 and for lake sediments see Coker, Hornbrook and Cameron (1979) and Hornbrook (1989);

(v) *Biological materials* via the analysis of particular parts of selected species of stream or swamp vegetation, or twigs, leaves or bark from certain tree species, etc., has been advocated as a method of prospecting for many years; recent work has encouraged a renewal of interest in these methods, but they have not yet been adopted for routine regional surveys; the variables which determine trace element content in vegetation are much more complex than those which apply to soils, tills or sediments and as such methods based on biological materials need to be very carefully described and controlled. For a recent concise overview see Dunn (1989);

(vi) *Surface waters* are commonly taken when sampling stream or lake sediments in order to determine pH, conductivity, U in solution and, in some surveys, F concentration. The concentrations for most elements of geochemical interest are too low in most natural waters to be determined from a small sample; there are logistical and potential contamination problems in handling large numbers of large water samples, especially where there is no convenient road access to the sampling sites. For a review see Miller (1979); and

(vii) *Radiometric* (gamma-ray spectrometric) sampling has the major advantage that sample material need not be removed and the analysis can be done in real-time from a moving vehicle, either a car or a low-flying aircraft. Adequate sensitivity is available for mapping purposes with suitable calibrated equipment. The limitation of the method is that it is restricted to radioactive elements, naturally occurring such as K,U,Th, or contaminants such as Cs-137. For a review see Darnley and Ford (1989).

Sample collection costs or flying costs in the case of an airborne survey are the largest part of the cost of undertaking a large area geochemical survey wherever there is no close-spaced road network. For conventional ground surveys orientation studies are required, prior to the main field operations, to ensure cost-effective control over site selection, sampling, labelling and handling procedures.

For regional surveys sample densities have normally ranged between 1 sample per square kilometer (in Europe) to 1 per 15 square kilometer (in N.America).

ANALYTICAL SUITES AND METHODS OF ANALYSIS

Geochemical surveys were first made for the purpose of mineral prospecting, and therefore analytical work was limited to elements which might be of immediate economic interest. Low cost and simplicity of laboratory procedures were prime considerations, especially since in the early days of this work, during the 1950's, analyses were often undertaken in field camps. Copper, Pb and Zn were the essential elements, conveniently determined by colorimetry. As mineral discoveries were made, the demand grew for information about more elements, but the theoretically desirable list was often abbreviated by the complexity and therefore cost of the analytical procedures involved. In examining the output of different institutions, the analytical suites determined by their laboratories often seem to have been influenced at least as much by the availability of equipment, methods and personnel as by the significance of certain parameters.

The steady growth in the application of geochemical surveys over the past 40 years has stemmed in large part from the progressive introduction of new and more sensitive methods of chemical analysis, amenable to tight quality control, and suitable for the mass production of data. The succession of principal methods has been emission spectroscopy, colorimetric, atomic absorption, X-ray spectroscopy, neutron activation, inductively-coupled plasma optical emission spectroscopy.

For the period since 1965, when large regional surveys commenced, analytical data have been obtained for between 10 and 40 elements, sometimes with additional parameters (pH, bicarbonate, conductivity and loss on ignition), depending upon the area and country. Recent interest in the discovery of gold has resulted in the widespread adoption of neutron activation techniques, with a much more expanded analytical suite than was hitherto available. Analytical results show that, for any given element, natural levels of geochemical abundance commonly vary by one order of magnitude and that large areas several hundreds of square kilometer or larger may have a median abundance for particular groups of elements differing from adjoining regions by two or more orders of magnitude.

Reference materials

An essential component of a systematic mapping program is the availability and use of analytical standards or reference materials. This is necessary to maintain as much consistency as possible in analytical data produced over a long period of time by different laboratories and to establish the analytical uncertainties in a quantitative manner. A survey by Abbey (1983) indicates that there were only 37 reference samples representing secondary materials out of a total of 167 reference materials of geological origin. Virtually all of these were certified for total, not partial, extraction determinations. The features which are desirable in reference materials for geochemical survey purposes include (Lynch, pers. com.): (i) the same type of sample media as will be used for routine surveys; (ii) the same type of sample preparation procedures; (iii) an appropriate range of concentration values; and (iv) determinations for both "total" extractions and specific "partial" extractions. Much time and effort is required to produce Certified Reference Materials for international distribution; and arrangements should be made by laboratories responsible for national programs to produce secondary or tertiary reference materials for routine analytical control of large sampling campaigns.

In order that airborne gamma-ray spectrometry can produce reproducible quantitative measurements of mean surface radioelement concentration, it also requires equipment calibration facilities and appropriate standards. These were first developed in the period 1968/70 and have been described in a number of subsequent publications (IAEA, 1976).

CURRENTLY AVAILABLE GEOCHEMICAL MAPS

It is one of the objectives of the IGCP project to prepare an inventory of all areas of more than 5,000 square kilometer for which geochemical maps are available and to document sample type, sample spacing, elements determined, analytical methods, etc. Lund (1987) has undertaken this task for Canada.

Plant *et al.* (1989) have listed 38 multi-element stream sediment surveys from 30 countries where areas greater than 5,000 square kilometer have been covered. The total area covered by this listing is 3.6 million square kilometer. In addition, approximately 1.2 million square kilometer of Canada have been covered by lake sediment surveys. Almost all of the conterminous USA (approximately 8 million square kilometer) has been covered by airborne gamma-ray spectrometer surveys which have enabled maps of surface K, U and Th distribution to be compiled across the full width of the North American continent (Duval, pers. com.).

Figure 2, based on Plant *et al.* (1989), shows the frequency with which there are abundance data for different elements in twelve national surveys, which each cover areas larger than 100,000 square kilometer. Sample densities vary from 1/2.5 square kilometer to 1/30 square kilometer. The number of elements for which maps have been produced varies according to country, from 15 to 39. In total 53 elements have been measured, but only 4 are common to all map-sets. These are Co, Ni, Zn and Pb. V, Cr, Mn, Cu, As, Sr, Sn and Ba are usually determined but least commonly determined are, F, Si, Cl, Ga, Br, Rb, Hf, Ta and Hg. Selenium is shown as not determined in any of the surveys examined, but it should be noted that it has been mapped in some other investigations, for example of Southern California. (McNeal, 1989, pers. com.).

Reproduction scales of published Regional Geochemical Maps vary from 1:4 million to 1:250,000 (Geochemical Atlas of Northern Fenno Scandia, 1986; Geochemischer Atlas Bundesrepublic Deutschland, 1985; Lund, 1987; National Geochemical Reconnaissance, 1981; Wolfson Geochemical Atlas of England and Wales, 1978. A wide variety of formats have been employed for displaying the results. The primary analytical data for the elements are expressed as parts per million by weight in the material analysed. These numbers may be directly reproduced on detailed maps, but at larger scales a variety of point or linear symbols, pixels or contours are employed. This is a matter where some standardization would be beneficial to non-specialist casual users. A printed map is the most direct way of showing that data are available. Obviously the prime data file is digital and there are an almost infinite number of ways of displaying and combining the data for specialist purposes.

ORGANIZATION OF THE IGCP PROJECT

A principal item of business in the first year of the project was setting up the organizational structure for the projects the aim is to encourage broad geographic participation in parallel with the establishment of specialised working groups. The latter will have to deal with technical problems on an international basis. Two groups of committees have been formed under the umbrella of a Steering Committee:

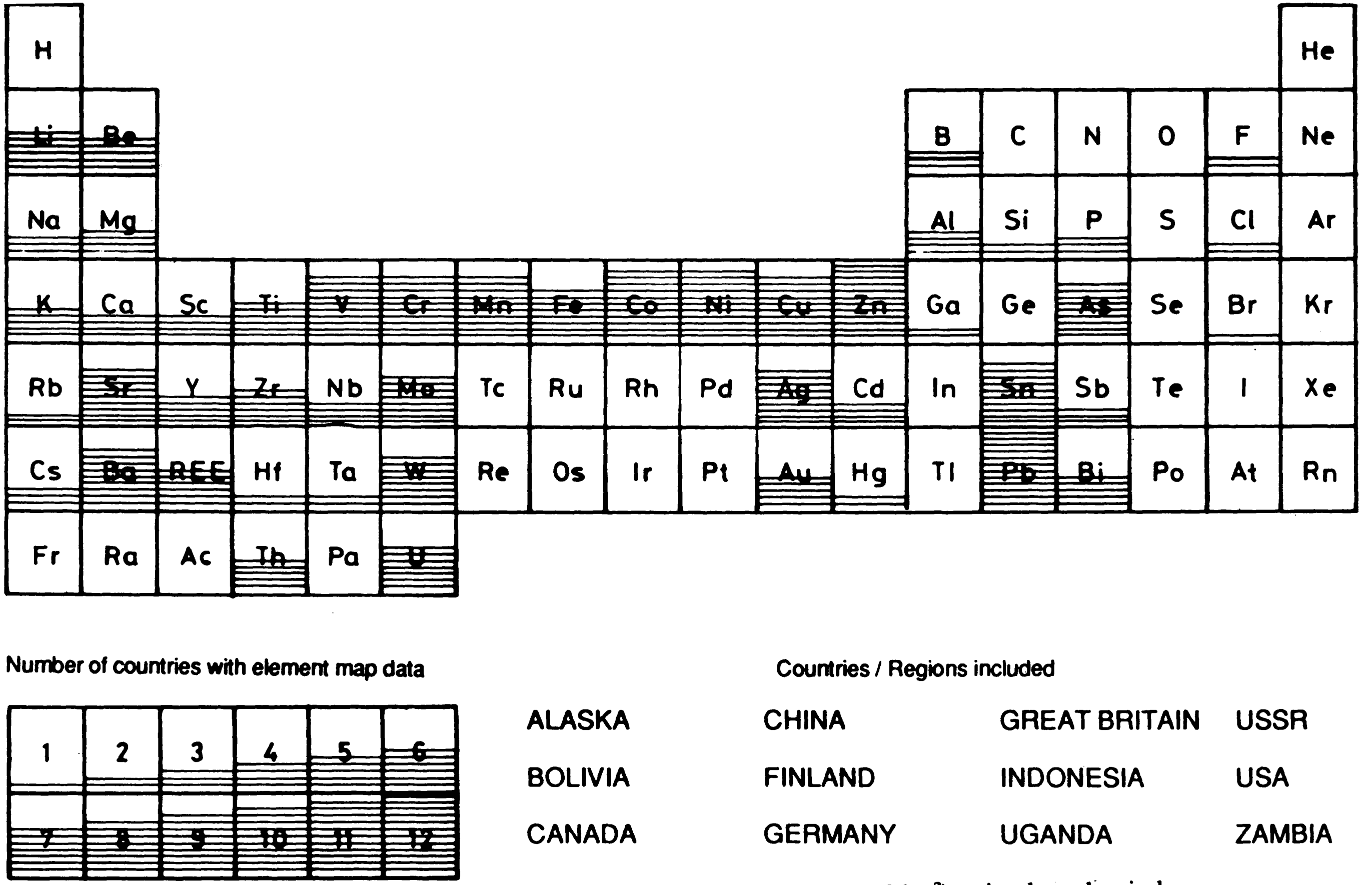

Fig. 2. Elements of the periodic table included in major (> 100,000 km²) national geochemical map compilations.

(i) Scientific and Technical; and

(ii) Geographic/Regional.

The Steering Committee, under the chairmanship of the IGCP Project Leader, is composed of the leaders of the Regional and the Technical Committees.

The Scientific and Technical Committees consist of:

(i) Field methods;

(ii) Analytical methods;

(iii) Data management; and

(iv) Radiometric methods.

The Regional Committees currently consist of:

(i) N. America;

(ii) W. Europe;

(iii) E. Europe;

(iv) USSR;

(v) India;

(vi) China;

(vii) Australasia; and

(viii) Southern Africa.

Discussions are in progress with respect to the formation of a Regional Committee for South America. In addition to the above some countries have established national committees. As of May 31, 1989, correspondents from 54 countries have expressed a desire to participate in the project (see Appendix D).

RELATION TO OTHER INTERNATIONAL PROGRAMS

More than fifty international scientific unions, associations, committees and groups are concerned with different aspects of Global Change. At the first meeting of the Scientific Advisory Council for the International Geosphere-Biosphere Program (IGBP) on Global Change in Stockholm, 24-28 October, 1988, the IGMP was accepted by the relevant Working Group (Data and Information) as a base-line component in Global Change studies. Amongst other professional groups with a special interest in geochemical mapping is the International Society for Soil Science.

An important aspect of the IGMP is its relevance to developing countries. A Working Group report on Third World Cooperation, submitted to the Scientific Advisory Council for the IGBP on Global Change in 1988, listed the features needed to make projects connected with Global Change activities of real interest to developing countries. These include the need:

(i) To create a focus for activities in as many developing countries as possible;

(ii) To place emphasis wherever possible on issues relevant to the country or region concerned;

(iii) To identify and take advantage of relevant data already collected and activities currently underway (sometimes haphazardly) in individual countries;

(iv) To strengthen the gathering and use of base-line information.

(v) To provide an integrated program (data collection, analysis and interpretation) at the national as well as the regional and global levels; and

(vi) To arrange Regional Forums to exchange information, and initiate local seminars.

It is apparent that the IGMP fits the above requirements very effectively; The products are multi-purpose, many with a potential for creating short-term economic and social benefits. The project uses skills and facilities that should be within reach of and available to every developing country.

DISCUSSION — QUESTIONS AND PROBLEMS

A variety of scientific questions will be investigated through the work of the various committees. Some are mentioned below. It is anticipated that as the project progresses the crucial issues will be discussed in workshops; it will probably be necessary to conduct some pilot studies; following these it is intended to formulate and publish recommendations in a series of technical reports.

Geochemists have long been aware of the significance of geochemical surveys to environmental studies. The practical problem is how best to convey this awareness to those that control policy. Informed members of the public, politicians and scientific policy makers in a number of countries have become aware over the past two decades of hazards posed by elements such as Rn, Cd, and As in the environment, and some recognize that "pollution" can arise from natural causes as well as from human carelessness. A few are aware of some paradoxical situations, for example potassium. The element is essential to many forms of life, but it is also weakly radioactive !

Over the past two or three years, increasing unease amongst the general public about the possibility of "Global Change" is beginning to create pressure for governments to take action to arrest these unwanted changes.

IGCP Project 259 is endeavouring to react to public concern about Global Change and the environment. As previously indicated, most existing geochemical surveys were conducted for geological/mineral exploration purposes. The Technical Committees will be considering what additional steps could be taken in order to maximize the environmental usefulness of existing or new data. For example, they are to determine to what extent environmentally significant data could be obtained from the analysis of retained sample material stored in government warehouses; also, to consider how the design of future surveys and analytical procedures could be modified.

It is particularly important to obtain a global geochemical overview as rapidly as possible in order to normalize existing survey data and fill-in gaps. To do this it is necessary to establish the most satisfactory method(s) of wide-spaced sampling, including the issue of single or composite samples. As indicated previously, stream (or river) sediments are generally considered to be the most generally available sample media but there are obviously geographic regions where alternatives must be found.

The major river systems of the world offer the possibility, by means of a few thousand samples, to achieve world-wide coverage of large areas very quickly. How would sample sites be selected? How long a sediment column should be taken? What would be the analytical requirements in order to detect significant regional differences? Could the material collected also serve for control reference purposes ?

There is a need to subdivide the world into physiographic-climatic zones within each of which geochemical methods can be optimized. It will be necessary to have overlap between the zones so that data can be normalized. Where are the most suitable areas for these overlap studies? Which institutions will take responsibility for this work ?

There are a number of important questions relating to analytical work. Should samples be totally or partially digested? For geological purposes the former is preferable; for mineral exploration applications some partial extractions are advantageous and for environmental studies more complex treatments may be required. It is easier to obtain standardized data where total extractions are used. In exploration only single element data has been reported; for environmental purposes it would be desirable to determine some complex species. Whatever procedures are adopted it will be essential to follow standardized analytical methods with routine use of intercalibrated reference materials.

There are also politically sensitive questions. A number of countries involved in the provision of technical assistance hold large files of geochemical data pertaining to developing countries. These data are potentially suitable for incorporation in world maps and it is highly desirable that they should be used, otherwise there may be delays of many years before there is information about some parts of the world. It will be necessary to obtain formal permission from the countries concerned before these data can be used for this purpose, but the initiative for seeking this permission should perhaps come from the countries that provided the technical assistance.

Lastly, but in many respects the most crucial question, concerns the need for a source of adequate funding for the work that has to be done. It is no longer possible if it ever was, to be able to find the human and material resources necessary to advance a project of these dimensions from the annual operating budgets of the national geological organizations of even the wealthiest of developed countries. The situation in developing countries is clearly much more difficult. The minimum financial provision is for funding to enable the scientists concerned with the project to meet together at regular intervals at least annually to ensure that a common project philosophy is being developed and followed, regionally and internationally, for funding to allow pilot projects to go ahead where required, and for some appropriate geochemical work to be done in each participating country. It seems probable that the necessary funding will only be found:

(i) If the project is accepted by developed countries as an integral part of national and international plans to address potential Global Change problems; and

(ii) If the project is accepted by developing countries as relevant to the solution of their economic needs.

FUTURE PROGRAM OF IGCP PROJECT 259

The preparatory work that is required in order to prepare geochemical maps of the world consists of a number of parts:

(i) Establish what data and map sets already exist;

(ii) Ascertain the level of commonality;

(iii) Establish a method for normalizing as many as possible of the existing data sets;

(iv) Prepare compilations of geochemical data, as demonstration products, for two or more adjoining countries;

(v) Ascertain what changes could be made to existing "conventional" geochemical mapping in order to enlarge its environmental usefulness;

(vi) Investigate the feasibility of devising an ultra low density sampling approach (or more than one, if necessary) for use in unmapped regions, and for normalizing data from previously mapped regions, in order to obtain reconnaissance coverage of the world as soon as possible; and

(vii) Prepare recommendations for international standards relating to sample collection and preparation, analytical standards and methods, data treatment and compilation, for future geochemical survey work.

Note that the above desiderata also apply, in principle, to geochemical data for K, U and Th, collected by gamma-ray spectrometry.

CONCLUSIONS

For environmental applications the currently available regional geochemical mapping is of somewhat limited value because the work was not undertaken with environmental significance as a prime consideration. Nevertheless, the data obtained provide the most geographically extensive and best-controlled geochemical coverage in existence and provide insight concerning the range of variables existing in the natural environment. The knowledge and experience gained in obtaining the existing data-base is an excellent foundation for expanding systematic geochemical surveys into all parts of the world. Since it is presently estimated that there are potentially useful data for not more than 10% of the world's land surface, there is some urgency to remedy this deficiency in the context of concern over "Global Change".

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APPENDICES

Appendix A—Objective of IGCP 259

The purpose of the project is to encourage and facilitate the compilation of an international series of systematic surficial geochemical maps by national and/or international organizations, based on the most appropriate types of sample material. The maps will show abundance levels, delineate regional trends and geochemical provinces, and permit the recognition of large scale anomalous features. They will complement existing international geological and geophysical map series, and will be published at scales suitable for direct comparison. To the greatest extent possible primary data will be stored in digital form to facilitate its reproduction at different scales in a variety of formats, for mineral resource, general geological and environmental studies. The data will be related to bed rock geochemistry wherever possible.

Appendix B—History of Project

This project was conceived at a workshop attended by a group of uranium explorationists in Sweden in the fall of 1984. There was concern that large quantities of exploration-related geoscientific data, with many potential applications, collected at considerable expense from most of the continents, were in danger of being lost to posterity through widespread cost-cutting economy measures instigated by industry and government. It was suggested that there should be an international effort to preserve such data. Attention quickly became focussed on radioelement surveys and geochemical data sets. Although the workshop where this was discussed was convened under the umbrella of the International Atomic Energy Agency, whose mandate is restricted to matters relating to nuclear energy, the advocates of the project recognised the need to make the data sets as comprehensive as possible.

The project was launched in April 1987 when a proposal to initiate an International Geochemical Mapping project was approved by a resolution of a joint meeting of the International Association of Geochemistry and Cosmochemistry and the Association of Exploration Geochemists in Orleans, France. Subsequently the project was formally accepted by the Scientific Advisory Committee of the IUGS International Geological Correlation Program at their annual meeting in Paris in February 1988. This recognition has brought the project to the official attention of government earth science organizations, which is an essential step in order to obtain government funds to carry out the work required and provide budgetary support for participating geochemists.

The first scientific meeting held in connection with the project took place in May 1988 at the first V.M. Goldschmidt Conference in Baltimore, USA, with a session entitled "International Geochemical Mapping".

Appendix C—Listing of Elements Analysed in Selected Surveys

Element		Region									
		ALAS	CAN	E & W	NDKT	GER	NI	SCOT	BOL	CR	PRC
1	H[a]		J			G		S			
2	He										
3	Li	A		X		G			B		
4	Be	A						S	B		P
5	B							S	B		P
6	C[b]		J							C	
7	N										
8	O										
9	F		J			G					
10	Ne										
11	Na	A			O					C	
12	Mg	A			O		N			C	
13	Al	A		X	O		N			C	
14	Si				O		N			C	
15	P				O						P
16	S										
17	Cl				O					C	
18	Ar										
19	K	A	J	X	O		N			C	
20	Ca	A		X	O		N			C	
21	Sc	A		X	O		N			C	
22	Ti	A			O					C	P
23	V	A	J	X	O	G	N	S		C	P
24	Cr	A		X	O	G	N	S	B	C	P
25	Mn	A	J	X	O		N	S	B	C	P
26	Fe	A	J	X	O		N	S	B	C	
27	Co	A	J	X	O	G	N	S	B	C	P
28	Ni	A	J	X	O	G	N	S	B	C	P
29	Cu	A	J	X	O	G	N	S	B	C	P
30	Zn	A	J	X	O	G	N	S	B	C	P
31	Ga			X			N			C	
32	Ge										
33	As	A	J	X	O		N		B	C	P
34	Se	A								C	
35	Br				O					C	
36	Kr										
37	Rb				O					C	
38	Sr	A		X	O	G	N			C	
39	Y				O				B		
40	Zr	A			O			S	B	C	
41	Nb				O				B		
42	Mo		J	X	O		N	S	B	C	P
43	Tc										
44	Ru										
45	Rh										
47	Ag	A	J		O				B	C	P
48	Cd			X		G					

Element		Region									
		ALAS	CAN	E & W	NDKT	GER	NI	SCOT	BOL	CR	PRC
49	In										
50	Sn	A	J	X	O	G			B		P
51	Sb	A	J								
52	Te	A									
53	I									C	
54	Xe										
55	Cs	A			O						
56	Ba	A		X	O	G	N		B	C	P
57	La	A			O				B	C	
58	Ce	A			O					C	
59-71	(A^+)	A^+								C	
72	Hf	A								C	
73	Ta	A								C	
74	W	A	J		O	G				C	P
75	Re										
76	Os										
77	Ir										
78	Pt										
79	Au	A	J		O					C	
80	Hg		J							C	
81	Tl										
82	Pb	A	J	X	O	G	N	S	B	C	P
83	Bi	A									
84	Po										
85	At										
86	Rn										
87	Fr										
88	Ra										
89	Ac										
90	Th	A	J		O					C	
91	Pa										
92	U	A	J		O	G		S	B	C	
TOTAL		38	22	21	37	16	20	15	21	39	18

KEY: ALAS (A) Alaska (Los Alamos National Laboratory); CAN (J) Canada (Geological Survey of Canada); E&W (X) England & Wales (Imperial College, London); NDKT (O) Northern Fenno Scandia (Nordkalott Project); GER (G) Federal Republic of Germany (BGR, Hannover); NI (N) Northern Ireland (Imperial College, London); SCOT (S) Northern Scotland (British Geological Survey); BOL (B) Bolivia (British Geological Survey); CR (C) Costa Rica (Los Alamos National Laboratory); and PRC (P) P.R. of China (Institute of Geophysics & Geochemistry).

*Note: a = pH; b = Loss on ignition.

Appendix D — Countries with Organizations Wishing to Participate in International Geochemical Mapping (IGCP 259)

[Type of institution indicated by code]

Argentina	CNEA
Australia	CSIRO, UNSW, SABM
Austria	GS, SU
Botswana	GS
Brazil	CNEN, CPRM, URJ, UB
Burkina Faso	BM
Canada	various
Chile	GS
China	MGMR
Colombia	GS
Cyprus	GS
Czechoslovakia	GS, CU
Denmark	RNL
Ecuador	GS
Egypt	NMC
Finland	GS, AA
France	BRGM, CEA
Gabon	BM
Germany (FRG)	BGR, TUB
Germany (DDR)	ZGI
Ghana	GS
Greece	IGME
Greenland	GS
Guyana	GS
India	GS, AED, UU
Indonesia	GMR
Iraq	GS
Ireland	GS, UG
Israel	GS
Ivory Coast	BM
Kenya	GS, MU
Malaysia	GS
Mexico	IMP
Mocambique	GS
Morocco	BM
Netherlands	LU
New Zealand	UA
Nigeria	GS, UPH, OSU
Norway	GS
Pakistan	GS
Poland	GS
Portugal	ENU, UA
South Africa	NDC, UW
Spain	UB
Sri Lanka	UP
Switzerland	UZ
Syria	
Tanzania	BM
Thailand	DMR
UK	BGS, UL
USA	USGS, LANL
USSR	AS, MG
Venezuela	UCV
Vietnam	GS
Yugoslavia	GS
Zambia	GS
Zimbabwe	UZ
ADB	
ESCAP	
IAEA	
UNESCO	IGBP-GC, IUGS/CGMW

Miscellaneous abbreviations:

GS = Geological survey

BM = Bureau of mines

U = University

Appendix E — Supplementary Organizational Information

The Technical Committees will each have a minimum of 5 members. Responsibilities will be as follows:

(i) *Field Methods Committee* — To include all matters concerning selection of sample media; methods of sample collection; sample spacing, including ultra-wide spacing; sample mass; particle size(s) for analysis; collection of replicate samples; use of composite samples; selection and collection of material for reference standards; in-field sample processing, etc.

It was agreed at a meeting in Helsinki in November 1988 that a sub-committee will be established to investigate various approaches to wide-spaced sampling.

(ii) *Analytical Methods Committee* — To include all matters concerning sample preparation and digestion; selection of analytical techniques; use and adoption of reference materials; provision of international inter-laboratory reference materials; expansion of analytical suites, etc.

(iii) *Data Processing and Management Committee* — To include recommendations on the organization and contents of a world index of geochemical surveys; methodology for levelling/normalizing diverse data sets; development of standard formats for trans-border data-sets and map publication; evaluation of data interpretation methods for the principal user-groups, etc.

(iv) *Radiometric Methods Committee* — To include all aspects of the collection, standardization, compilation and interpretation of geochemical data obtained by airborne gamma-ray spectrometry. A working group has already commenced work on methods for combining existing airborne radiometric data, under the auspices of the International Atomic Energy Agency, Vienna. The Convenor is Mr. A.Y. Smith of the IAEA. Note that the Radiometric Methods Committee has comprehensive responsibility for this particular technique.

The function of each of these committees is to produce technical reports, summarising recommended methods and procedures, based on a review of international information and experience. Membership of the Technical Committees is listed in Appendix C. Additional members would be welcome; names should be sent to the Project Leader. An important consideration is that in addition to having the relevant experience, in order to be active participants, committee members should be able to obtain funds to travel to meetings. Committees cannot function without periodically meeting face-to-face.

Regional Committees — these have been or are being established in the following geographic regions, where there are institutions which have indicated their support for the project; the leaders are as follows:

North America (including Greenland)	J. McNeal, USA
China	Xie Xuejing
Eastern Europe	F. Mrna, CSSR
Western Europe	B. Bolviken, Norway
USSR	P.V. Koval
Australasia	R.E. Smith
Southern Africa	N.J. Money
India	Contact not known.

Additional Regional Committees are needed to initiate and coordinate activities in other parts of the world, such as Japan, SE Asia, Middle East, Mediterranean/N. Africa, S. America. It is open to earth scientists and institutions in these areas to discuss with their neighbours how they wish to group themselves together.

The UN and related international organizations (for example the Asian Development Bank) have been, or are being informed, and their assistance requested to spread information about the existence of the project and its relevance to practical problems.

PHOTOSYNTHESIS AND THE GREENHOUSE EFFECT

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The greenhouse effect, whereby atmospheric CO_2 and water vapour prevent the Earth's surface from being totally frozen is likely to be amplified by the anthropogenic emissions of fossil fuel CO_2. The global carbon cycle links photosynthesis to the greenhouse effect on all timescales up to millions of years. Major characteristics of the Earth's atmospheric composition, notably the low CO_2 and the high oxygen concentrations were created by the evolution of plant photosynthesis. The low CO_2 concentration in the atmosphere probably came about by the substantial acceleration of rock weathering that plants, especially angiosperms, cause. Calcium released by weathering moves to the oceans where it paces the formation of calcium carbonate rocks which are a massive carbon pool that dwarfs all others combined. On a timescale of 10^5 to 10^6 years the carbon from calcium carbonate is cycled back to the atmosphere via volcanoes.

On shorter timescales of sociopolitical concern photosynthesis is involved with the current global change in atmospheric CO_2 increase. From what we know about plant photosynthetic and growth responses to increasing CO_2 concentration interacting with other limiting environmental factors, it seems very likely that the biosphere is absorbing, into standing biomass and soil organic matter, some of the CO_2 emitted from fossil fuel burning and net deforestation thereby contributing to the "missing carbon" that does not appear as an increase in atmospheric CO_2 concentration. However, the scope for accelerating this CO_2 sequestering process by planting more trees is rather limited owing to the large scale required relative to the land available and to the fact that net carbon sequestration ceases when a forest matures.

INTRODUCTION

The interplay between photosynthesis and the greenhouse effect is so complex that there is no hope of presenting a complete and balanced picture in this brief contribution, if indeed a balanced picture is known to anyone yet. One of the reasons for complexity is that the controlling phenomena determining the inter-relationship are different over different timescales. The subject considered on the timescale of years is very different from the subject considered on the timescale of billions of years. Yet to really understand each timescale other timescales must be taken into account.

The global carbon cycle links photosynthesis and the greenhouse effect. To understand the global carbon cycle fully one needs to understand other biogeochemical cycles such as the hydrologic cycle, the nitrogen cycle, the oxygen cycle, the sulphur cycle, the silicate cycle, and the convection currents in the atmosphere, in the oceans, and in the Earth's mantle — the plate tectonic cycle. A biogeochemical cycle that appears to be in a steady dynamic equilibrium when viewed on a short timescale may well be far from equilibrium when viewed on a much longer timescale. For example, we might reasonably assume that over the early decades of the ninteenth century the global live plus dead organic matter pool in the biosphere was essentially in steady state over that timescale. However, over the 10,000 year post-glacial timescale, it was a net accumulator of carbon in soil organic matter especially in the tundra peats, where carbon may still be accumulating, be it slowly.

Further hampering the discussion, is the range of meanings of both the word "photosynthesis" and the phrase "greenhouse effect". To make sense of the interaction we need to define each.

The "*greenhouse effect*" now has four meanings depending on the context.

Arrhenius is reputed to have originally coined the term in the 1890s to represent the impact of the CO_2 content of the atmosphere, then about 290 ppm, on the vertical distribution of temperature in the atmosphere, the infra-red absorbing properties correctly being seen as keeping the lower atmosphere and ground warmer and the stratosphere cooler than would otherwise pertain. And since warmer conditions lead to a higher absolute moisture content of the atmosphere, there is a water vapour greenhouse effect that amplifies the CO_2 greenhouse effect, keeping the Earth's surface from being frozen-over completely. This I term the "*original greenhouse effect*".

Second there is the "*anthropogenic CO_2 greenhouse effect*" which refers to the predicted further warming of the global surface temperature associated with the presumably man-caused increase in atmospheric CO_2 concentration since industrialization started last century. This arises not because the increase in the atmospheric content of causes increased total absorption of infra-red back radiation, but because it has the effect of concentrating such absorption into a lower portion of the atmospheric depth thereby cooling the upper portion.

Third, there is the "*augmented anthropogenic greenhouse effect*", in which the observed increase in other radiatively active atmospheric constituents like methane, chloro-fluorocarbons, nitrous oxide, and ozone are adding to the effect of increasing CO_2 concentration, because they absorb at different wavelengths than do CO_2 and H_2O vapour.

And finally, there is the "*journalists' greenhouse effect*" in which a range of phenomena more or less, or possibly, related, including the augmented anthropogenic greenhouse effect, the CO_2 fertilizing effect, the stratospheric ozone-hole over Antarctica, UV radiation at ground level, sea level change, recent warm winters and droughts in some places, and deforestation of the Amazon Basin, are all *embraced by the one phrase — the greenhouse effect* — now often truncated to just "*greenhouse*".

Photosynthesis comes into many aspects of the phenomena embraced by these different elements of the greenhouse effect.

PHOTOSYNTHESIS

At the lowest level of organizataion plant photosynthesis is a membrane-bound process in which the energy of light photons is harnessed to separate change across a membrane leading to oxidation of a reductant in abundant supply in the environment and the formation of chemical energy and reducing equivalents that are subsequently available for synthesis of organic molecules.

While, to the photosynthetic purist, such consequential synthesis may not in itself be photosynthesis, to most biologists it is acceptable to include the formation of at least the first stable product as part of the process. To whole-plant physiologists, steps subsequent to formation of the first stable organic molecule, such as sucrose and starch production, are also usefully included as part of a multi-step process of "*photosynthesis*".

For higher plants the abundant environmental reductant is water, the first stable products are ATP and NADPH, and the product to the environment is oxygen.

There is now little doubt that the world's atmosphere was virtually anaerobic until the evolution of a form of photosynthesis able to utilize water as reductant came into existence (Walker, 1984). Oxygenic photosynthesis blossomed 2 or 3 billion years ago and has raised atmospheric oxygen from virtually zero to the present 0.2 atmospheres. This has had profound effects on other geochemical cycles such as the carbon cycle and hence on global climate via the original greenhouse effect. Also since it is the interaction of UV-radiation with O_2 that produces the UV screening stratospheric ozone layer, oxygenic photosynthesis led to the low level of UV that now occurs at ground level. This permitted higher forms of life to develop.

When one stands back from the photosynthetic membrane to view the green leaf mesophyll cell as the minimal unit of photosynthesis, then the inputs become light, water, and carbon dioxide and the outputs are sucrose and oxygen. But embedded inside is an O_2/CO_2 cycle involving the interplay between photosynthesis and photorespiration. Photorespiration is a process, involving 3 subcellular organelles working together, to retrieve carbon that would otherwise be lost to atmosphere. But in the process some recently fixed CO_2 is nevertheless lost to atmosphere.

Figure 1 (from Gifford, 1988) shows how the central enzyme of the CO_2 fixation cycle — ribulose bisphosphate carboxylase or RUBISCO — also reacts with O_2. It is believed that the reaction with O_2 is inevitable and that much of photosynthetic evolution has focussed on minimizing the rate of this reaction. When O_2 reacts with ribulose bisphosphate, phosphoglycollate is produced. The photorespiration cycle serves to recover half of the carbon of phosphoglycollate at the expense of losing half of its carbon as photorespiratory CO_2. So the presence of O_2 reduces CO_2 fixation rates by three mechanisms: (1) by competitive inhibition of carboxylation, (2) by consuming some of the ATP made by the photosynthetic light reactions, and (3) by releasing some of the recently fixed CO_2 back to atmosphere.

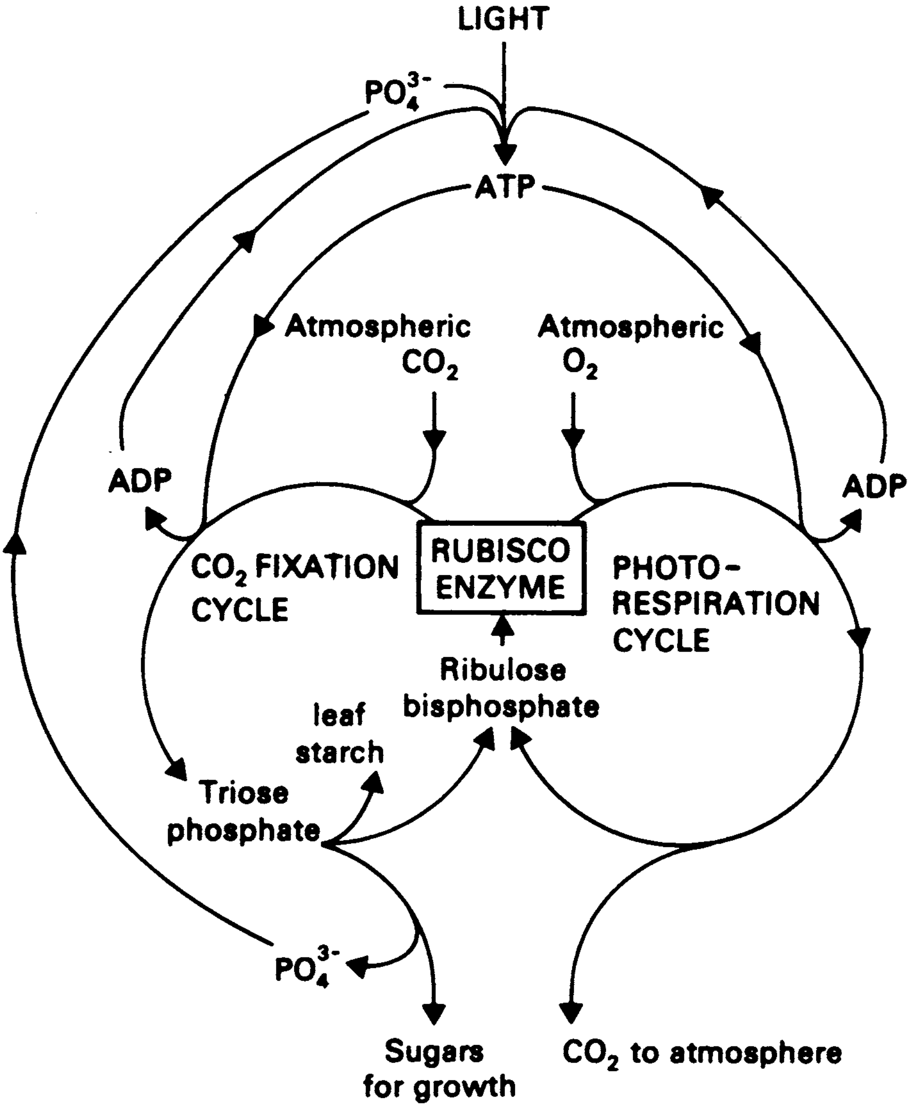


Fig. 1. Essential features of the interplay between the photosynthetic CO_2 fixation cycle and the photorespiration cycle of the mesophyll cell of C_3-species' leaves (Gifford, 1988a).

Although this internal cell cycle may appear to be inconsequential to the big picture of the global carbon cycle and the greenhouse effect, I believe that in fact it may be of considerable consequence in attenuating the current anthropogenic build up of atmospheric CO_2 in the short term.

Skipping over the individual leaf as a photosynthetic unit we can move on to the whole plant during growth. Taking the system boundary as the epidermis of the plant, and the time-frame as 24 hours, the inputs are CO_2, light and water, and the outputs are the daily increment of plant dry matter and O_2. However, the input CO_2 is net of CO_2 that is released by true (dark) respiration as well as by photorespiration.

At an ecosystem level over a whole annual cycle, the metabolism of animals and soil microorganisms is now a functional part of the photosynthesising ecosystem, and the input CO_2 is net of the CO_2 emitted by heterotrophic organisms such as decomposers. The system could not function for long without them. When annual decomposition matches annual accrual of live and dead dry matter, the net annual photosynthesis rate of the system as a whole is zero. This is what happens to a mature ecosystem integrated over a wide area. However, although one might think, as a result, that such a mature ecosystem is neutral in the dynamics of the global carbon cycle, this is *not* the case in the long term. The photosynthesis of such a system is critically involved in the biggest carbon cycle of them all — *the carbonate-silicate cycle* that determines the global atmospheric CO_2 concentration, and hence world climate, on the geological time scale of millions of years.

GLOBAL CARBON POOLS FLUXES, AND CYCLES

Some major rates and magnitudes of carbon flows and pools in the global C-cycle are helpful in understanding the carbonate-silicate cycle.

The quantity of carbon in circulation in the global carbon cycle is vast compared with the amount in the atmosphere at any one time (Table 1). The data in this table

TABLE 1: Some Global Carbon Pools Relative to the Atmospheric Pool Set at Unity (From Gifford, 1988)

Present atmosphere	1.0
Present biosphere:	
living on land	0.9
dead on land	2.8
live at sea	< 0.01
dead at sea	1.8
Dissolved in the ocean:	
surface mixed layer	1
thermocline	12
deep ocean	50
Sedimentary rocks:	
on land in reduced form	17,000
on land in oxidised form	43,000
under the sea, reduced	10,000
under the sea, oxidised	24,000

are presented relative to the amount of carbon in the present-day atmosphere. The rapidly exchanging pools of the atmosphere, the standing ('live') biomass and the well-mixed surface oceans are all of similar size [approx. 600Gt(C)]. These fast turnover pools contribute carbon to the much larger, slow turnover pools. Given that all these pools are exchanging carbon with one another, one can see that *given long enough* man-induced transfers of carbon from the reduced rock carbon (coal) to the atmosphere are likely ultimately to be re-distributed to the other pools. In the meantime we have to live with the transient perturbations that we are creating—but this transient may outlive civilization and *Homo sapiens.*

The key rates of exchange between some of these pools are indicated in Table 2. Relative to the annual increase in atmospheric CO_2 concentration, annual C turnover between net primary production (NPP) by photosynthesis on land and its decomposition back to CO_2 is large. In fact, the uncertainty in our estimate of global net primary production and of decomposition, is greater than the observed annual increase in atmospheric CO_2 of 3 Mt (carbon). So although no-one expresses any doubts that the 5.6 Gt yr^{1} of fossil fuel CO_2 release is the cause of the approximately 3 Gt yr^{1} of atmospheric CO_2 increase, it is not possible yet to state unequivocally how much of the other 2.6 Gt p.a. is sequestered into the terrestrial biosphere despite net deforestation of 0.4 to 2.4 gigaton per annum (Houghton and Woodwell, 1989).

The other possible sink is the oceans, and marine photosynthesis would play a role there. In the short term, marine photosynthesis can pump CO_2 down into deeper waters via decomposition of dead marine organisms to CO_2, as they precipitate out through the thermocline and deep ocean redissolving as they fall. Some of the dead organisms with their carbonate shells do reach the ocean floor where they ultimately form carbonaceous rocks that become subducted by plate tectonic movements into the molten magma. Reaction with molten silica causes release of

TABLE 2: Some Global Carbon Flows Between Pools in Gt(Carbon) Per Annum

1980s rate of increase in atmosphere	3
Geosphere to atmosphere transfer:	
from fossil fuel burning	5.6
natural	0.1
Atmosphere to land biosphere transfer (net primary production)	about 60
Land biosphere to atmosphere (decomposition)	about 60
Net atmosphere to land biosphere (sequestration)	0 - 3
Net land biosphere to atmosphere (deforestation)	0.4 - 2.4
Atmosphere to ocean	about 90
Ocean to atmosphere	about 90
Ocean to geosphere transfer	0.1

carbon dioxide which re-enters the atmosphere and oceans by magmatic outgassing (volcanoes, etc.), thereby completing the slowest turning carbon cycle, *the carbonate-silicate cycle.* This cycle has a carbon turnover time of about a million years.

Over that long timescale, it is the balance between carbon deposition in solid form on the ocean floor and CO_2 outgassing from the mantle into the atmosphere that determines the CO_2 concentration in the atmosphere. The smaller biological and oceanic C-cycles are of little consequence on that timescale. But surprising as it may seem, photosynthesis probably plays a critical role in the balance of this carbonate-silicate cycle and hence in long term atmospheric CO_2 concentration. This is because terrestrial photosynthesis probably sets the pace of solid carbon compound deposition on the ocean floor. It works as follows.

PHOTOSYNTHESIS AND THE CARBONATE/SILICATE CYCLE

The removal of carbon into ocean sediments is partly as dead organic matter but mostly as calcium carbonate. The organic sediments are obviously the product of photosynthesis. It is not yet settled as to the extent of biological formation of calcium carbonate shells, as distinct from its physico-chemical precipitation, in ocean floor deposition of carbonate (Wilkinson and Walker, 1989), but certainly biological shell formation is very important for accelerating carbonate precipitation and may predominate. However, whether it is biological or physico-chemical, solid carbonate cannot be formed without an input of Ca^{++} or Mg^{++} ions. Continued formation of solid carbonates therefore depends on renewal of Ca^{++} and Mg^{++} ions in the ocean which arrive via the rivers along with bicarbonate ions. These ions reach the rivers by weathering of calcium and magnesium silicate rocks and carbonate rocks on land. So the formation of marine carbonates, that remove CO_2 from the atmosphere, is paced by the rate of weathering of the rocks on land (Berner and Lasaga, 1989).

The rate of rock weathering is determined in turn by the exposed surface area of rock, the CO_2 concentration at the rock surface, other acids at the rock surface, rainfall and run off, and temperature. The reaction with CO_2 is:

$$2CO_2 + H_2O + CaSiO_3 = Ca^{++} + 2HCO_3^- + SiO_2$$

The three moieties produced, run off in the drainage water ultimately out to sea.

Photosynthesis on land sets the pace for this weathering process, enhancing it considerably over that which would otherwise pertain (Knoll and James, 1987). It can do this by several mechanisms. Photosynthesis drives the growth of plants which send roots down in search of water and mineral nutrients. Roots and associated micro-organisms accelerate the break-up rock in the process of soil formation thereby enormously increasing the surface area of rock. Roots also give off CO_2 by respiration and exude organic acids. Furthermore, microbial decomposition of dead roots also increases the CO_2 concentration in the soil where it may be one or two orders of magnitude more concentrated than in the open atmosphere.

In these ways the rate of rock weathering is greatly accelerated by the photosynthesis-decomposition cycle. The mineral ions are taken up into the plant and eventually leached from the nutrient cycle of the ecosystem and washed into the ocean.

So now we can come back to the definition of photosynthesis, this time on the scale of the terrestrial biosphere. On that scale, photosynthesis is a process the inputs to which are light, CO_2 and unweathered rock, and the outputs of which are mineral ions, especially calcium and magnesium, bicarbonate and silica into the ocean. Most of the carbon involved is just a component that is cycled between atmosphere, live plant, dead organic matter and microbes, catalysing the transfer of mineral ions from land to sea. The hydrologic cycle also helps it along.

So by this mechanism terrestrial photosynthesis paces the removal of atmospheric CO_2 into the deep ocean sediments and hence into the tectonic subduction zones. By pushing the balance between magmatic and volcanic outgassing of CO_2 and tectonic removal of CO_2 in favour of removal, terrestrial photosynthesis holds atmospheric CO_2 at a much lower value than would otherwise be.

This in turn has reduced the magnitude of the "original greenhouse effect" warming. Walker, Hays and Kasting (1981) have proposed that there is an element of negative feedback regulation over the greenhouse effect on geological timescales because weathering rate is positively temperature dependent. Introduction of vegetation photosynthesis and decomposition into the consideration, further strengthens this negative feedback, considering both the strong positive temperature dependence of primary productivity and its positive CO_2 dependence (see below).

Consider for example the implication of the increase of solar luminosity by 30% during the history of the Earth (Lovelock and Whitfield, 1982). Increasing luminosity increases surface temperature which increases rock weathering rate. It also increases both photosynthetic productivity and soil organic matter decomposition rate which would increase root-zone biological activity and hence rock weathering. Since the rate of rock weathering paces (via ocean biological productivity) the rate of carbonate deposition, atmospheric CO_2 declines leading to cooling that offsets the initial warming owing to increased luminosity. It is proposed that the progressive decrease of atmosphere CO_2 by that mechanism over Earth history, and concurrent overall cooling has occurred by this interplay of photosynthesis and the greenhouse effect, despite the continuous increase in solar intensity.

Further developing this concept of profound photosynthetic involvement in atmosphere CO_2 control over geological timescales via the carbonate-silicate cycle, Volk (1989) has proposed that the substantial displacement of gymnosperms by angiosperms 60-70 million years ago, caused a decrease in atmospheric CO_2 and a consequential reduction in global temperature of several °C. This is because angiosperms, with their deciduous photosynthetic habit, cause Ca^{++} and Mg^{++} loss to the oceans to be 3 to 4 times faster than do evergreen gymnosperms (Knoll and James, 1987).

So it is because of the evolution of photosynthesis and particularly of the deciduous habit of most angiosperm trees that global CO_2 concentration had declined to a level about as low as it can get (Lovelock and Whitfield, 1982). That is, before industralized man started cutting down the trees and burning fossil fuels, when it started to go up again around the middle of the nineteenth century A.D.

SOCIOPOLITICAL CONCERNS

This brings us back to the anthropogenic CO_2 greenhouse effect and the involvement of photosynthesis on much shorter timescales of decades (rather than millions of years)—the scale of sociopolitical significance today. Two issues of current concern are:

1. Does the photosynthetic response to CO_2 concentration observed in laboratories have any implication for understanding where anthropogenically emitted CO_2 goes?
2. Can a tree planting policy have much relevance to ameliorating atmospheric CO_2 build-up owing to fossil fuel burning?

That leaf or plant photosynthesis is CO_2-dependent in the short term has been demonstrated frequently. It is illustrated here (Fig. 2) at the whole plant level for the gymnosperm *Pinus radiata*, measured at one third full sunlight intensity of 600 μmol (photons) m^{-2} s^{-1}. This is a light intensity at which rate of photosynthesis is limited by light. In fact whole-plant photosynthesis was almost linearly dependent on light at that level. So given the concept of the law of limiting factors how can it be that photosynthesis is both light-limited and CO_2-limited concurrently?

The answer lies in *photorespiration*. As mentioned, photorespiration occurs because the active centre of the carboxylating enzyme RUBISCO also reacts with O_2 leading to a series of biochemical reactions leading to some loss of CO_2. Thus O_2 is a competitive inhibitor of carboxylation. And that is so, no matter what the level of ribulose bisphosphate (RuBP). RuBP concentration is determined by the light intensity. So even at low light intensity, higher CO_2 concentration will compete with O_2 and thereby reduce photorespiratory losses from the plant. Thus ecosystems that are light-limited such as humid tropical rainforest, or cool temperate forests also have had the opportunity to photosynthesise faster as CO_2 increased.

Elsewhere water is growth-limiting. Not only does high CO_2 increase photosynthesis it also reduces the aperture of stomata—the small pores in the surface of the leaf. This has the potential to reduce transpiration. Since water loss is the price that plants pay for opening their stomata to let CO_2 in for photosynthesis, an increase in CO_2 concentration increases the WUE of plant growth as illustrated in Figure 3 for wheat. Note the more restricted the water supply, the greater was the CO_2 effect on water use efficiency.

Another factor limiting the growth of plants is the nitrogen supply. Again, it has been observed that high CO_2 concentration increases the efficiency with which this growth-limiting nutrient is used by plants. Furthermore, at high CO_2, nitrogen

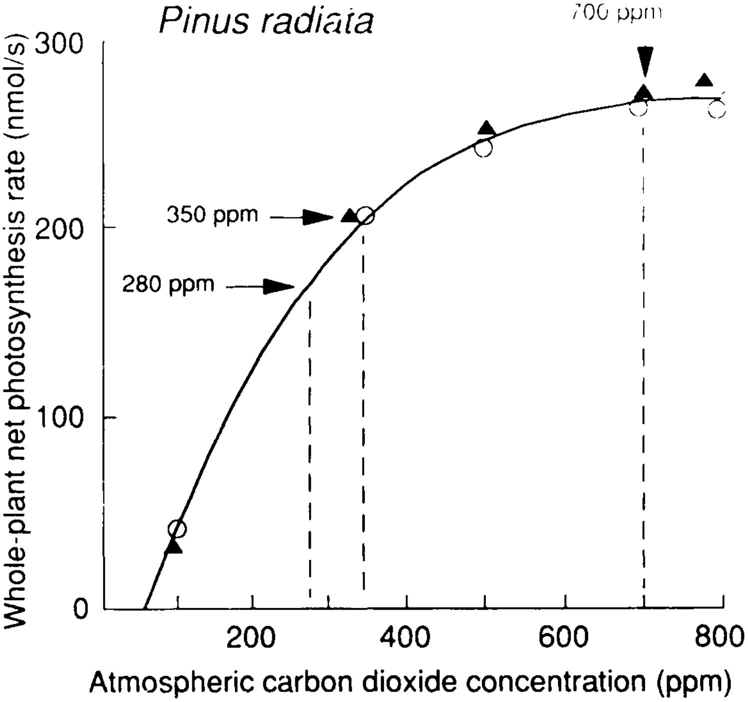


Fig. 2. Response of whole-plant photosynthesis (corrected for dark respiration) of a *Pinus radiata* (Monterey Pine) sapling, to atmospheric CO_2 concentration. Photosynthetic photon flux density was 600 μmol(photon) m^{-2} s^{-1} (Gifford, unpublished).

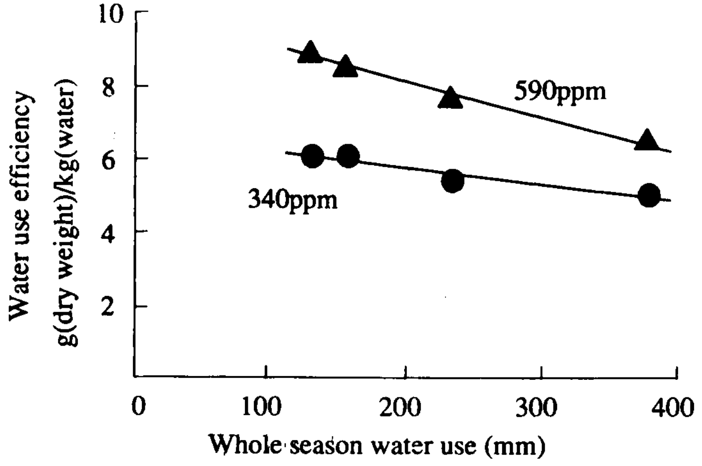
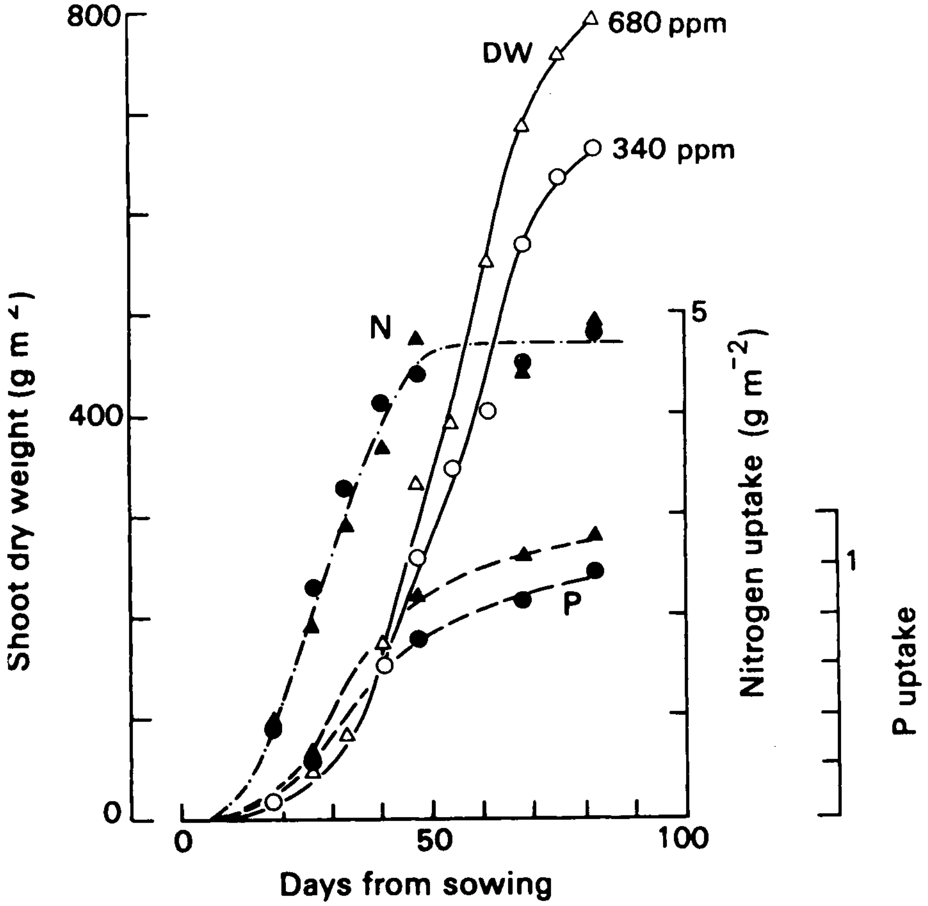


Fig. 3. Water use efficiency of water-limited seasonal wheat growth at two levels of atmospheric CO_2 concentration (Gifford, 1979).



'ig. 4. Time-course of shoot growth of wheat grown with nitrogen limitation at two levels of atmospheric CO_2 concentration. The nitrogen limitation is indicated by the failure of the CO_2 enriched crop to take any more nitrogen from the soil (▲) than the control crop (●). (Gifford and Morison, unpublished).

xing legumes fix more nitrogen. The example in Fig. 4 is for wheat canopies grown 'ith fixed and limiting nitrogen supply. They were able to accrue more dry weight espite the low amount of N available.

Similarly, what scarce evidence there is seems to indicate that even phosphate mited plants can grow faster at high CO_2. However, the evidence is more equivocal ı that interaction (Conroy and Barlow, 1987).

So, the prediction based on such results from studies in controlled environments, that vegetation in the field is likely to be growing faster as CO_2 concentration creases. This has to be tested somehow in the field, but that will be a massive task–

especially for forests. Also there is the question of whether any CO_2 stimulated incremental growth is being distributed into slow turnover pools of the ecosystem like tree trunks and soil organic matter. But there is little evidence on that.

I made a "guesstimate" of the possible magnitude of the sequestering of carbon in slow turnover pools of the global biosphere, on account of the CO_2 concentration increase since systematic monitoring began in 1958 (Gifford, 1980). I arrived at the conclusion that 1-2 Gt(C) yr^{-1} could have then been being removed from the atmosphere by that mechanism alone. When one considers the further increase in atmospheric CO_2 before and since that period together with the huge amounts of oxidised N, S and P that we are artificially putting into the global environment, it seems very likely indeed that the biosphere is sequestering something like 1-2 Gt(C) yr^{-1} extra each year (Gifford, 1988b).

POTENTIAL FOR REFORESTATION

On the question of whether we can use re-afforestation to slow down the rate of CO_2 increase, the opportunity seems to be minimal (Gifford, 1988a, 1989). Marland (1988) suggested that it would take an area of about 700×10^6 ha of fast-growing forest to absorb the annual global CO_2 emissions from fossil fuel burning. This is an area the size of Australia. Australia produces fossil fuels with a carbon content of 150 million tons yr^{-1}. About half of this is exported.

Plantation forests, on the best sites in Australia, accrue carbon into stemwood during their 30-60 year growth period at about 5t(C) ha^{-1} yr^{-1} on average. Thus to mop up 150Mt(C) yr^{-1} into stemwood Australia would need a new forest of 30 million hectares actively growing on sites which did not already bear forest i.e. on arable and pasture land (Gifford, 1989). When one considers that the area of arable and improved pasture in Australia is only 48 million hectares, and the area of remaining forest is 41 million hectares, only 1 million of which was planted, one can see what a small contribution planting special trees for mopping up atmospheric CO_2 can make on that continent given alternative land use constraints.

Furthermore, once planted such a forest must stay in place in perpetuity if the objective is to permanently keep a pool of carbon, as live and dead organic matter, out of the atmosphere. Scenarios in which, at maturity, the forest is felled for conversion to wood-products of various longevities before decomposition or burning, do provide some scope for carbon sequestration but less than if the mature forests were left undisturbed (Barson and Gifford, 1990).

SUMMARY

Photosynthesis, then, plays a critical role in many aspects of the global carbon cycle and hence in world climate and the greenhouse effect. But we cannot regard it as providing a panacea for public policy to get us out of "greenhouse" trouble over the timescale of years to decades.

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THE GREENHOUSE EFFECT: GLOBAL AND AUSTRALIAN PERSPECTIVE*

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The planet Earth has a mean surface temperature of 15°C, about 30°C above the temperature that would exist if there were no infrared-absorbing gases, greenhouse gases, in the atmosphere. These gases include water vapour, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). The global activities of Man are changing the concentrations of these naturally existing gases and adding additional greenhouse gases which are entirely Man-made. Since the middle of the last century, CO_2 concentrations have risen by 25%, CH_4 by 110% and N_2O by 8%. The Man-made chlorofluorocarbon gases were non-existant in the atmosphere prior to the 1930s.

Undoubtedly, this will change the temperature of the planetary surface. The degree of warming will depend on just how much more of these gases we release into the atmosphere, how long they stay airborne and the sensitivity of the atmosphere to each gas. This paper reviews the evidence that suggests that by the year 2030, the combined effect of all of these gases will be equivalent to a doubling of the concentration of CO_2 and that this is expected to warm the lower atmosphere by several degrees.

Because the warming is not expected to be even throughout the atmosphere, atmospheric scientists anticipate that there will be subtle, yet important changes to the way the global atmosphere mixes, leading to changes in rainfall patterns, storminess, frequency of extreme events, etc. While there is general agreement as to the nature of the global warming on average, the regional and seasonal climatic impacts are very uncertain. Some discussion is given concerning the research underway to improve the regional predictability, and the need to use climate-change scenarios to assess the sensitivity of regional hydrology and water use, agriculture, natural environment and societal responses to climate changes. The paper includes some discussion of preliminary estimates of the sensitivity of Australia to such changes. Such assessments are important in deciding to what extent considerations need to be given to planning for adaptation or avoidance of the effects.

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The global and Australian budgets of greenhouse gas emissions are presented as background to consideration of possible emission control strategies.

INTRODUCTION

There is now a strong consensus amongst atmospheric scientists that global warming during the next few decades is highly probable as a result of the accumulation of greenhouse gases in the global atmosphere (DOE, 1985 a-e; Bolin *et al.*, 1986; WMO,1986). These gases are generally long enough lived in the atmosphere that it doesn't matter where they are released, they soon become widely dispersed in the atmosphere and influence climate globally.

Without the presence of water vapour and carbon dioxide (CO_2) in the atmosphere, the earth's surface temperature would be 33°C lower than it is today. For many years the process of retaining heat in the lower atmosphere has been known as the greenhouse effect, and CO_2 as one of the key agents which causes this effect, has been known as a greenhouse gas.

Greenhouse gases such as CO_2 and water vapour bring about the greenhouse effect through the property that they absorb strongly in the infrared region of the electromagnetic spectrum. Sunlight, the source of energy for the earth-atmosphere system, is principally in the visible region, where the earth's atmosphere is almost transparent. Of the total amount of incoming radiation 31% is reflected by clouds (21%), by particles in the atmosphere (6%) and by the earth's surface (4%), while the other 69% is absorbed by ozone in the stratosphere (3%), by water vapour, clouds and aerosols in the troposphere (18%), and by the earth's surface (48%).

To maintain total energy balance, long-wave radiation, equivalent to the 69% incoming short-wave radiation which was absorbed, needs to be emitted to space. The bulk of this energy comes from the earth's surface which emits black-body radiation (at about 300 K this is infrared radiation). Greenhouse gases and clouds can intercept this radiation, and re-emit it in all directions, thus redirecting a significant amount back down to earth. As a result of these processes the earth's surface emits black-body radiation at a higher temperature until the correct amount of energy is emitted to space. This then is the greenhouse effect (Ramanathan, 1989; Dickinson and Cicerone, 1986).

GREENHOUSE GASES

Observations of, and research on the sources and sinks of CO_2 commenced in the late 1950's in Hawaii and Antarctica, and was later followed by research by scientists in Australia and elsewhere. An important consideration in this respect was that following a rapid development in the field of atmospheric chemistry, it was realised that CO_2 was not the only infrared absorbing trace constituent which was accumulating in the global atmosphere. Other substances now recognized as greenhouse gases are methane (CH_4), chlorofluorocarbons (CFCs), nitrous oxide

(N_2O), and tropospheric ozone (O_3). Present-day observations of these gases (Pearman, 1988), as well as measurements of air trapped in Antarctic ice, which allows CO_2, CH_4 and N_2O concentrations to be traced back for hundreds (Pearman *et al.*, 1986) or even tens of thousands of years (in the case of CH_4 and CO_2; Barnola *et al.*, 1987) have by now firmly established that the currently observed rising trends are a relatively recent phenomenon (within the last 200 y), closely linked to population growth, land clearing and the industrial revolution. Details are provided in Tables 1 and 2, and Figures 1 and 2.

TABLE 1: Greenhouse Gases

Greenhouse gas	Concentration		Present trend (% per y)	Possible sources of increases
	Pre-indust (1850)	Current (1989)		
CO_2	275 ppmv	350 ppmv	0.4	Fossil fuel combustion, deforestation
CH_4	750 ppbv	1700 ppbv	0.8	Rice paddies, ruminants, biomass burning, gas & coal fields, land fills, tundra
CFC-11	nil	250 pptv	4	Industrial & consumer goods
CFC-12	nil	450 pptv	4	Industrial & consumer goods
N_2O	285 ppbv	310 ppbv	0.3	Biomass burning, agriculture, fossil fuel combustion
O_3(trop.)	15-20 ppbv	20-30 ppbv	0.5a	Urban and industrial pollution

[a] Estimated to be 1% in the Northern Hemisphere, 0% in the Southern Hemisphere.

The changes from pre-industrial times have been significant, with CO_2 increasing by 25%, CH_4 by more than 100%, and the CFCs, being totally man-made, not being present in the atmosphere prior to the 1930s. From the data presented it can also be seen that the actual concentrations of different greenhouse gases vary by up to a factor 10^6 when comparing CO_2 and CFCs.

The relative warming effect of the key greenhouse gases on a global basis is shown in Table 2.

In considering the importance of emissions of each of these greenhouse gases in causing global warming it is necessary to consider:

> The effectiveness of a molecule of a greenhouse gas in trapping infrared radiation, allowing for the spectral distribution of terrestrial radiation and the overlap of absorption spectra for all radiatively important gases;

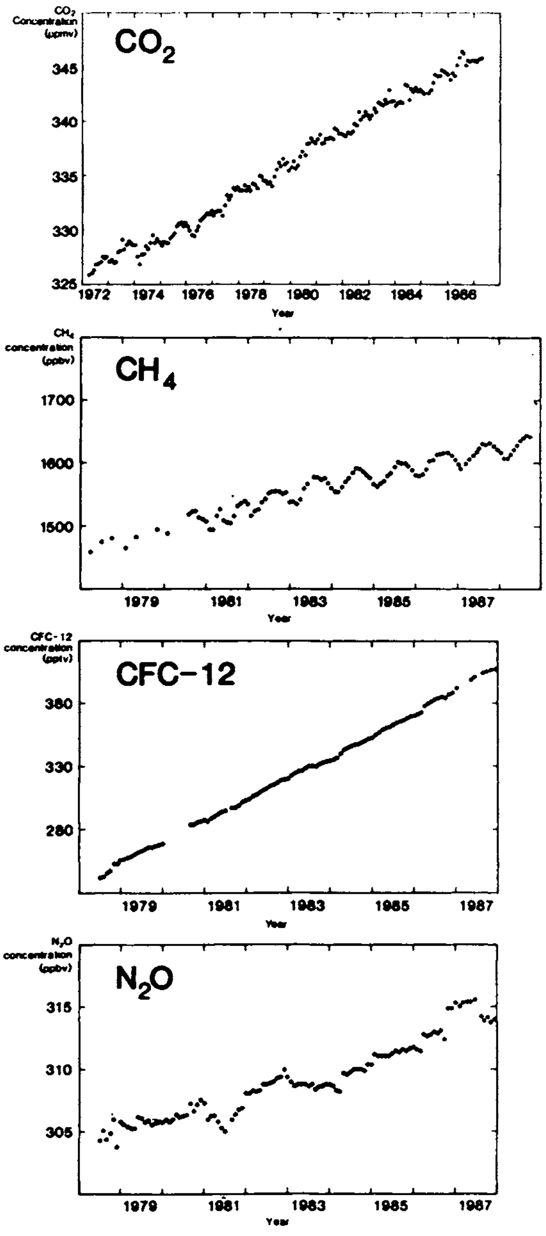

Fig. 1. Atmospheric trace gas concentrations measured over south-eastern Australia (CO_2) and at the Cape Grim Baseline Observatory, north west Tasmania (CH_4, CFC-12 and N_2O). Note that these Southern Hemisphere observations are somewhat lower than the global average, while the N_2O scale shown here is about 5ppbv too high. See Pearman (1988) for sources of data.

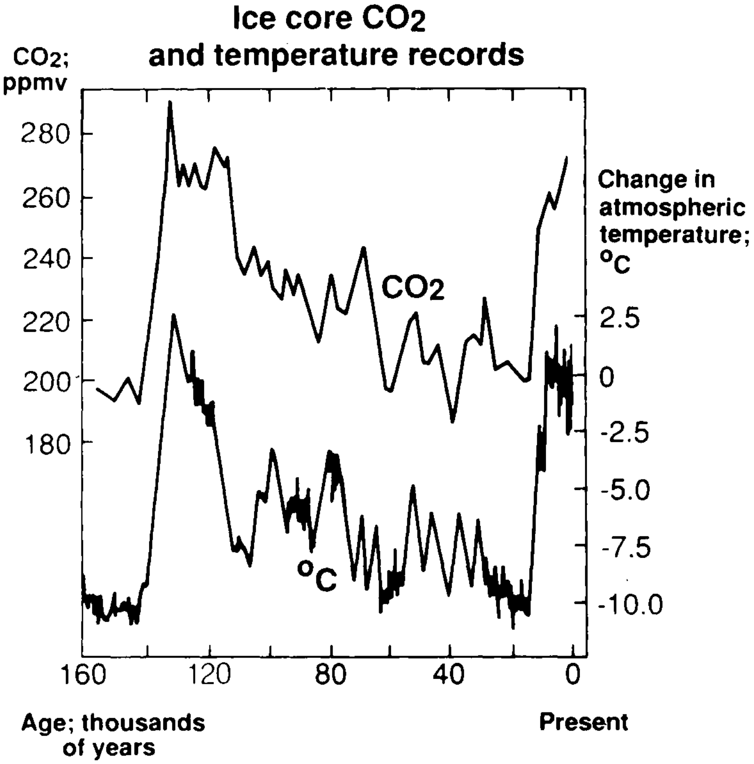

Fig. 2. Analysis of air from the Vostok ice core (Barnola *et al.*, 1987) clearly shows the strong link between atmospheric CO_2 and global temperature. It also shows that the CO_2 concentration had not been above 290 ppmv for the last 160,000 years. The current value is 350 ppmv, rising at 0.4% per year.

- The concentration of the gas; and
- The lifetime of the gas in the atmosphere. Clearly, a greenhouse gas that reacts immediately it is released into the atmosphere to become another species, is far less important than a gas that has a long residence time in the atmosphere.

Chlorofluorocarbons in particular are very effective because (i) their absorption occurs in a part of the infrared where neither H_2O nor CO_2 absorb (the so-called window), (ii) their absorption band strengths are significantly stronger than that of CO_2, and (iii) with the small amounts of CFCs in the atmosphere their impact is almost linear with concentration, while CO_2 is sufficiently abundant that it is optically thick, and its impact scales logarithmically with concentration (Ramanathan, 1988).

TABLE 2: Warming Effect of Greenhouse Gases

Greenhouse gas	Radiative forcing[a] (Wm^{-2})	Relative[b] radiative forcing per ppmv increase[a]	Atmospheric lifetime (y)	Long-term relative[b] contribution to global warming per molecule emitted	% of the total radiative forcing to date	% of the radiative forcing due to current increases
CO_2	1.3	1	60[c]	1	59	55
CH_4	0.6	36	10	6	27	20
CFC-11	0.06	14600	75	18000	3	6
CFC-12	0.12	17000	110	31000	6	12
N_2O	0.05	140	150	350	3	5
O_3(trop.)	0-0.12	430	0.2	1	2	2

[a] From Dickinson and Cicerone (1986), based on the increases in atmospheric concentrations from pre-industrial times to 1985.

[b] Relative to CO_2.

[c] The turn-over time for atmospheric CO_2 is about 6 years, but the time needed to permanently remove CO_2 to the deep ocean and the long-lived biosphere is about 60 years.

The current and past concentrations of most of the greenhouse gases are now well-known, while research into the sources and sinks of each of these gases is continuing. Although it is currently possible to make rough estimates of the sources, more accurate information is urgently needed in order to enable better estimates of future atmospheric levels to be made, and the impact of possible control strategies to be assessed (Pearman, 1988).

A benchmark increase often used in consideration of the greenhouse effect is the doubling of atmospheric CO_2 from 300 ppmv to 600 ppmv, an event which is expected by about 2075 AD. If, however, the contributions from anticipated rises in other greenhouse gases are taken into account, an effect equivalent to a doubling of CO_2 is likely to be reached by 2030 AD (Ramanathan *et al.*, 1985; Bolin *et al.*, 1986).

CLIMATE MODELLING PREDICTIONS

As explained above, the radiative forcing exerted by the increases in the various greenhouse gases can be calculated, and comes to about 4 Wm^{-2} for a doubling of CO_2. This, in turn is calculated to lead to an equilibrium surface warming of between 1.1 and 4.5 K. These calculations have been carried out using a range of mathematical models describing the global atmosphere, the most sophisticated of which are known as general circulation models (GCMs) (Tucker, 1988). The latter predict an equilibrium warming of 4 to 5 K (Ramanathan, 1988).

It is generally agreed that GCMs currently in use need a range of complex changes to increase their accuracy and their regional detail. The representation of soil hydrology, clouds, ocean/atmosphere interaction and a number of other processes needs to be improved. The spacing of the gridpoints around the globe at which key parameters are being calculated is currently too large (500-700 km) to allow detailed descriptions of regional geography and topography to be fed into the model. Nevertheless it is significant that all model calculations to date predict an increase in the global mean temperature (Bolin *et al.*, 1986; Ramanathan, 1988).

Finally, it should be pointed out that the GCM calculations are independent from the research on greenhouse gases. Research on the latter will provide us with estimates of when an effective doubling of CO_2 is to be expected. The GCM calculations will tell us what the climatic effect of such a doubling will be. It also needs to be noted that the effective doubling of CO_2 is an arbitrary target but not an end point. The increase in greenhouse gas concentrations, and therefore the resulting climatic change, is a continuing process. Lesser changes will occur prior to an effective doubling of CO_2, and greater changes after, as long as greenhouse gas concentrations are allowed to continue to increase.

CLIMATIC CHANGE

Although there are serious limitations to the detail that current GCM calculations can provide, a number of conclusions can be drawn from the results already. The most important general conclusion is that a global warming would not be uniform and would be accompanied by a change in all other parameters which make up global and regional weather and climate. Specifically, the warmer globe will be on average (but not everywhere) more humid and wetter; the warming will be least near the equator and greatest near the edges of the winter ice and snow cover; and as weather systems shift poleward, there may be a summer-drying in mid-latitudes (Ramanathan, 1988). Some of this information has recently been used to provide preliminary estimates of regional climate change (Pittock, 1988).

FEEDBACK PROCESSES

Atmospheric scientists are acutely aware that the ultimate outcome of the radiative forcing due to greenhouse gas increases is governed by the way the total climate system will respond. There are many feedback processes which can enhance or ameliorate the primary effect.

One such process is due to the extra surface warming leading to more evaporation. As water vapour is a greenhouse gas, this would result in a positive feedback which would increase the surface warming. A second feedback is linked to the observation that a surface warming will lead to reduced snow cover and less sea ice. This would reduce the amount of solar radiation reflected, and thus increase the warming at the earth's surface (to a lesser extent than the water vapour feedback, but very significant on a regional basis).

Another important feedback is that due to clouds, which play a major role in the earth's radiation balance, and which reflect a significant amount of the incoming solar radiation. Increased evaporation and increased levels of atmospheric water vapour are likely to lead to increased cloud cover. Low level clouds are known to have a net cooling effect due to their reflection of incoming sunlight, and thus can be expected to decrease any greenhouse warming. But high level cirrus clouds are known to be relatively more efficient in trapping infrared radiation, leading to an increase of the surface warming. At this stage it is not clear which of these two processes would dominate (Ramanathan *et al.*, 1989).

One other feedback process involves the oceans: given the heat-capacity of the oceans, the response of tropospheric temperatures will be governed by the response of the ocean surface to the global warming. If the radiative heating were to be sequestered to the deep ocean, the global warming would be significantly delayed.

Yet another feedback involves the role of the stratosphere and stratospheric ozone. The greenhouse warming of the lower atmosphere will be accompanied by a cooling of the stratosphere. This would under normal circumstances enhance the ozone producing processes. But the possible decline of stratospheric ozone due to the presence of CFCs will reduce the amount of incoming solar radiation trapped by the stratosphere, allow this radiation to reach the earth's surface and thus add to any tropospheric warming. The magnitude of this warming would be small compared to the warming due to increases in greenhouse gases in the lower atmosphere.

Finally, it should be noted that there may be a range of other, perhaps minor, feedback processes which at this stage are too poorly understood to be included in climate change considerations. One such process concerns the possibility of the marine production of dimethyl sulfide (DMS) (known to be involved in cloud condensation) being perturbed by climatic change. More DMS might lead to more cloud, and hence act as a negative feedback (Charlson *et al.*, 1987). Feedbacks involving changes in the vegetation cover, and thus the surface reflectivity, roughness and evaporative cooling will almost certainly be of local significance, but may be less important on a global scale, especially in the Southern Hemisphere which is dominated by the oceans.

EVIDENCE FOR CHANGE

Model calculations show that the increases of greenhouse gases to date have already committed the planet to an equilibrium surface warming of between 0.6 and 2.4° C. A large uncertainty is how much the actual warming will lag behind. The available record of the global average temperature suggests that there has been a warming of about 0.5 K over the last 100 years (Jones *et al.*, 1988), but there is no certain way as yet of establishing which of a number of possible causes is responsible for this rise, especially when one looks at the variation in the trend from decade to decade (Figure 3). It is easy to see too, that similar analyses of regional trends would have to be treated with even more caution.

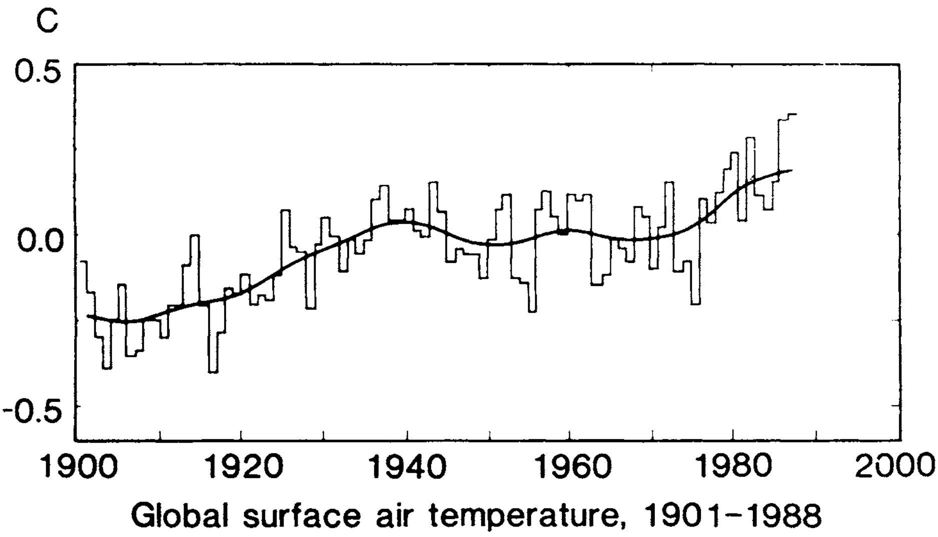

Fig. 3. The global temperature record relative to the 1950-1979 average from Jones *et al.* (1988) with 1987 and 1988 added.

While it is possible that climatic change is already in train, there will be an extended period where all the information on change in temperature, rainfall and extreme events will have to be assessed in the light of natural variability of weather and climate. In the face of this it should be remembered that the evidence of changes in the composition of the atmosphere is firm, irrefutable, and clearly linked to consequent climatic change. It is only a matter of time before it will become evident in the climatic measurements.

SECONDARY IMPACTS

A changing composition of the global atmosphere has a number of secondary impacts which need to be pointed out. Firstly, any global warming will result in some sea-level rise. This is due to two processes. One is the thermal expansion of the surface layers of the oceans which will warm along with the troposphere, the second is the increased melting of temperate ice (glaciers). For a doubling of CO_2 it is estimated that these effects would raise the global sea level by 20 to 50 cm (vander Veen, 1988). How much this sea-level rise would lag behind the surface-temperature rise is uncertain. Melting of the Antarctic ice cap is definitely not a risk for hundreds of years (Budd, 1988).

Perhaps less appreciated, but certainly important, is another consequence of atmospheric change: the fact that higher levels of atmospheric CO_2 will stimulate plant growth. Carbon dioxide is a known 'fertilizer' which in addition discriminates between different types of plants (Gifford, 1988), and this may add a very different aspect to the considerations of the impact of climatic change.

A further outcome of a changing atmosphere and global climate change which almost by definition is impossible to predict is the element of surprise. The mechanisms which govern the sources and the sinks of the atmospheric trace gases such as CO_2 and CH_4, and the mechanisms of ocean/atmosphere dynamics which determine the global climate are sufficiently complex that scientists cannot rule out the possibility of unforeseen sudden changes. Examples of such events are provided by the recent discovery of stratospheric ozone loss over Antarctica (Farman *et al.*, 1985; Fraser, 1989) and the observation from geological evidence that the global ocean circulation has in the past shown sudden and dramatic changes (Broecker,1987).

MISCONCEPTIONS

A number of misconceptions need to be laid to rest. These are:

- The greenhouse effect is only a theory.
  Incorrect. In its most fundamental form the greenhouse effect is a well established physical process, while the evidence of recent increases in the concentration of so-called greenhouse gases in the atmosphere is incontrovertible.
- The greenhouse effect is based on observed rising temperature and/or sea-level trends.
  Incorrect. The scientific debate is firmly based on the observed changes in atmospheric composition. The observed temperature and sea-level trend, although consistent with the chemical changes, only serve as circumstantial evidence which may or may not be linked to the greenhouse effect.
- The additional CO_2 would not trap any extra outgoing infrared radiation, as all of it is already being trapped.
  Incorrect. Although the absorption bands of CO_2 are almost saturated, increases will still contribute to the greenhouse effect. It is true that CH_4 and CFCs are more effective because they absorb in an otherwise clear part of the infrared spectrum—all these properties have been taken into account.
- Cloud feedback might lead to a cooling rather than a warming.
  Incorrect. As stated earlier, cloud feedback is certainly one of the aspects ill-described by current GCMs. But as it is a **feedback process,** one would still need a warming to even start this feedback, and thus in the first instance this process could slow down, but not prevent, far less reversal, a global warming.
- If weather prediction cannot get the forecast reliably beyond a few days, climate prediction would have to be a futile exercise.
  Incorrect. Although both types of effort have the physical description of the atmosphere in common, they deal with very different scientific problems. In weather prediction an instantaneous description of the atmosphere and all its properties is required. Climate modelling, by contrast, deals with statistical averages which are calculated quite differently. We can describe these average properties without necessarily having to describe in detail each individual weather event.

OPTIONS

There are two major options open in responding to climate change induced by increasing levels of greenhouse gases. These are adaption and avoidance. We can allow the concentration of the gases to continue to increase, and adapt to any changes in climate that this brings about. Alternatively, we can decide that the economic, social and environmental impacts of such changes are so large that we attempt to reduce the emissions of the gases and thus slow down the rate at which future changes will occur. Some climatic change appears to be inevitable, given the changes that have already been set in train, and the obvious difficulty of slowing down the releases at short notice. Yet, it seems that we cannot go on indefinitely allowing the planet to warm. At some time control measures will be needed. It is widely accepted that given the timescale necessary to make significant reductions to the emissions, efforts should commence now to achieve these long-term goals.

SETTING GOALS FOR EMISSION REDUCTION

During the 1988 international meeting on *The Changing Atmosphere; Implications for Global Security*, held in Toronto, the conference developed a goal for the reduction of CO_2 emissions. It was stated that attempts should be made to reduce global emissions by 20% by the year 2005. Several points should be made about this goal. First, there appeared to be little theoretical analysis made as to just what this goal would actually achieve. It was some kind of qualitative acceptance of a balance between what might be desirable and what might be achievable. Second, subsequent analysis shows that given the current state of the global carbon cycle, embarking on a global negative growth in CO_2 emissions of 1.5% y^{-1} would achieve a significant slowing down of the rate of increase of CO_2 in the atmosphere and a quasi-stabilization of CO_2 levels in the atmosphere below the 400 ppmv level about half way through the next century (Figure 4). Such a rate of reduction of emissions would lead us to a condition of about 20% reduction in emissions by the year 2005, but continuing on to a reduction of about 50% in the next 50 years. That is, it must be realized that reductions of greater than 20% will be necessary in the longer term if stabilization of the concentration is to occur, and that negative growth rates of CO_2 emissions of about 1.5% y^{-1} is what is needed.

All of this should be considered in the perspective of what has happened to emissions of CO_2 historically. Through much of the last 150 years, developing nations have experienced growth rates in energy consumption that have lead to annual growth of CO_2 emissions of about 4.5% y^{-1}. Exceptions to that have occurred during the World War periods and the last decade following the oil embargos of the mid 1970s, when growth rates, globally of about 1-2 % y^{-1} have occurred. Thus to embark on negative growth rates of CO_2 emissions will be unprecedented in industrial history. It is true, that during the last ten years the growth rate of energy usage in developed nations has been close to zero (Australia excepted), whereas for

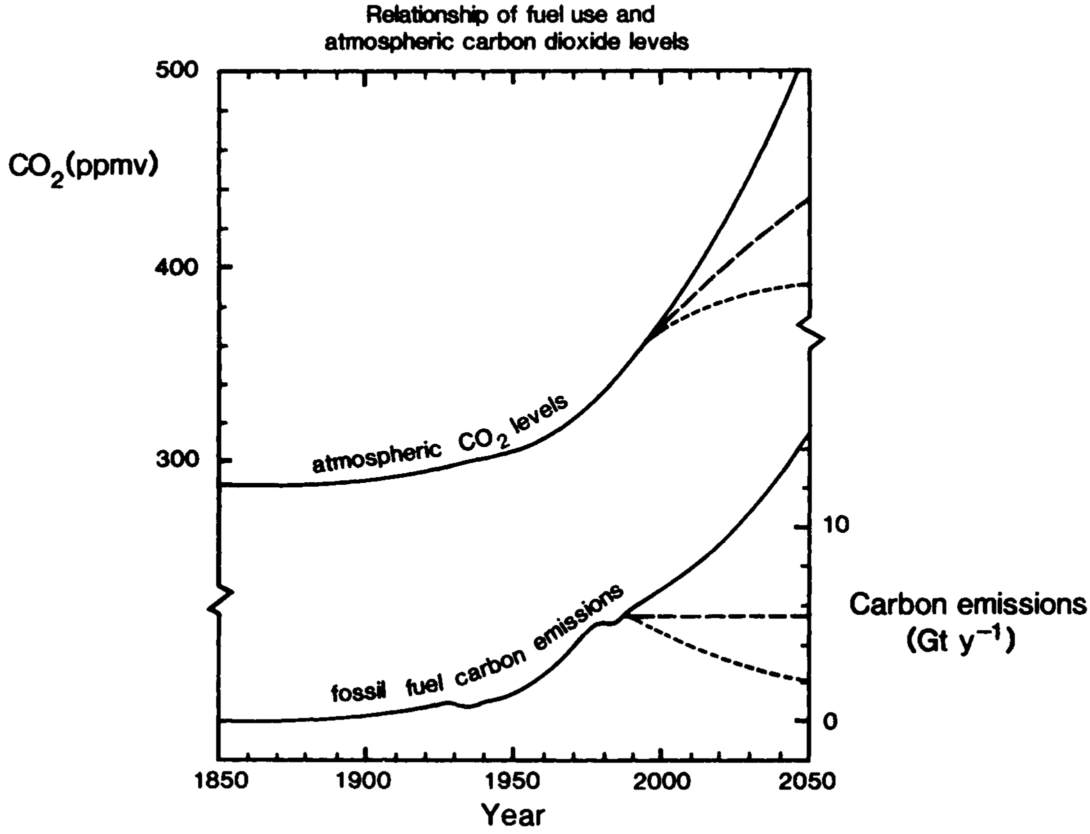

Fig. 4. The predicted relationship between global atmospheric CO_2 due to the use of fossil fuels. The diagram illustrates the economy difficulties to be encountered in bringing about substantial control of the current CO_2 increase. Calculations based on the carbon cycle model of Siegenthaler and Oeschger (1987).

the developing nations a rate of 4-5% y^{-1} has been maintained. This points to one of the difficulties in achieving global reductions of emissions, while the developed nations may be expected to increase their per capita consumption. It may be necessary for developed nations to take a disproportionate share of any attempt to reduce emissions.

AUSTRALIA'S GREENHOUSE GAS EMISSIONS

Table 3 shows the approximate relative contribution of Australia's emissions of various greenhouse gases to global warming. Such a Table gives some guide as to the emphasis that might be placed on attempts to limit emissions of one kind or the other. Of course, the practicality and costs associated with reducing one emission or the other will vary widely and also influence any emission control policy.

TABLE 3: Relative Warming Effects from Australia's Emissions of Greenhouse Gases

Gas	Source	Annual (Mt y^{-1})	Emissions (Mmoles y^{-1})	Relative greenhouse contribution per molecule emitted (From Table 2)	Relative contribution to greenhouse effect (%)
CO_2	Coal	158	3.6	1	27
	Liquids	72	1.6	1	12
	Gas	25	0.6	1	5
	Total	255	5.8	1	44
CH_4	Ruminant animals	2.2	0.14	6	6
	Other animals	0.2	0.01	6	1
	Rice	0.2	0.01	6	1
	Mining operations	0.3	0.02	6	1
	Land fill	1.5	0.09	6	4
	Natural gas grid	0.2	0.01	6	1
	Biomass burning	2.0	0.13	6	6
	Total	6.6	0.41	6	19
N_2O	Primarily agric.	0.3*	7×10^{-3}	350	19
CFCs	Refrigeration, etc.	0.012**	9×10^{-5}	25000	18
Ozone	Not significant in Southern Hemisphere				0

* Very uncertain estimate.

** Average characteristics of CFC-11 and CFC-12 used.

Research is needed to further improve the confidence associated with the numbers in Table 3. However, we believe that such research is not likely to change the major relative features of the data.

Australia's strict adherence to the Montreal Protocol for the limit of ozone destroying substances will clearly make substantial contributions to the national reduction of the growing in the greenhouse effect.

COMMENTS CONCERNING OPTIONS

Developing policy options of these kinds is not the role of atmospheric scientists. However, experience with the field in general leads us to several overall impressions that may be of value to those who have this responsibility.

Australia's responsibility

Australia's contribution to the level of greenhouse gases in the atmosphere is of the order 1-2% of the global contribution. It might be argued, therefore, that what we do to curb emissions will be globally insignificant. Even expensive and socially disruptive reductions to Australia's release of CO_2 and other greenhouse gases, would have little impact on the changing global climate unless other nations take part in such actions. Sections of the Australian community have already used this to argue their immunity.

The same argument could have been used with respect to the CFC-ozone depletion issue. Instead, Australia took a leadership role by actively participating in the development of an international protocol and then passing legislation to ensure national compliance.

Australians use 50-100 times more energy per capita than Indians and Chinese. Infact, on a per capita basis, we are amongst the worst contributors to CO_2 emissions into the atmosphere.

Thus a strong moral argument can be made that we have no right to expect one billion Chinese to control the level of their CO_2 emissions below those we use to provide our standard of living. However, if they were to develop to our level of per capita consumption, this would contribute enormously to CO_2 increase in the atmosphere. Similarly, how can we call on the current major contributors to CO_2 emissions (e.g. USA) and ask them to reduce their per capita emissions below ours?

Package approach

There is no single most important contributor to the CO_2 or CH_4 emissions into the atmosphere in Australia. For example, there is no single "fix" which can be used to substantially reduce our CO_2 emissions. What is needed is an examination of all areas of energy utilization and the identification of methods for the reduction of CO_2 emissions via the options of:

- Energy conservation;
- Improved energy-use efficiency;
- Alternative energy resources (solar, nuclear, renewable, etc.); and
- Changes to the proportions of energy generated by the various fossil fuels as some are more energy 'efficient' in terms of CO_2 emissions than others.

Policy based on such an examination would be developed with due consideration of the effectiveness of the "package" of changes implemented to reduce CO_2 emissions and the economic, sociological and environmental costs incurred in making the adjustments.

Considerations similar to those given for CO_2 will also need to be applied to gauge the extent to which reductions in CH_4 and N_2O emissions can be achieved. For CFCs this process is already in train, and can even serve as an example.

Preparedness to make policy assessments

The Australian energy community is currently ill-prepared to provide the assessments necessary for a comprehensive policy to be developed. There has been some natural reluctance to accept changes, particularly as these relate to a threat which is poorly understood by the energy community. At this point in time, most of those industry-related assessments have tended to start with the premises that growth in energy usage will continue, and that particular sectors of the energy community should be protected. Such positioned arguments, similar to the anti-nuclear stance, have not been particularly objective.

Recognizing the above, last year, CSIRO through its Institutes of Minerals, Energy and Construction and Natural Resources and Environment, commenced organizing a National Conference on Greenhouse and Energy: Australia's Options, to be held at Macquarie University, December this year. The objectives are:

- To provide a forum for the rational presentation of opportunities in Australia, in all areas of the energy sector, to reduce CO_2 emissions;
- To encourage the assessment of economic, societal and environmental costs associated with these opportunities;
- To promote research into energy systems and alternatives for reducing CO_2 emissions in Australia; and
- To publish a document based on the reviewed proceedings of the meeting which will provide policy-makers with a set of options from which choices can be made.

The Federal and State Governments will need these evaluations before substantial policy changes can be implemented. Further, it is most likely that the "mix" of options most appropriate (maximum CO_2 reductions—minimum economical and societal disruption), will be different for example, for Victoria than New South Wales, and different for Australia than for, say, Switzerland.

Acting now

It is suggested that the issue of climate change is sufficiently important that policy initiatives should not be delayed until research has examined at length all options. But it is prudent that it is recognized that we are in a state of rapidly changing information with respect to knowledge of the greenhouse effect, its impacts, and our capacity to adjust and the options for avoidance.

CONCLUSIONS

Considerations of the greenhouse effect have by now moved from the realms of academic curiosity to a position of conviction that global warming is a highly probable expectation for the future. While there are a number of loose ends to be tied up, there is now amongst atmospheric scientists a realisation that the problem has implications and interactions far beyond their restricted domain. The time lag between atmospheric change and climatic change, and between climatic change and sea-level rise, is such that what we do or do not do today has significant repercussions for generations to come. If one accepts this premise, then the need to research what those changes might be, and the need to assess how greenhouse gas emissions might be controlled becomes obvious.

The task of carrying out research aimed at providing more detailed information concerning potential climate change for the Australian region is currently being undertaken by CSIRO scientists in collaboration with scientists in the Bureau of Meteorology, and in close collaboration with the various Australian States and some colleagues in the Universities.

The task of planning reductions in the various greenhouse gases has only just commenced. CFCs are to be controlled soon, mostly because of their stratospheric ozone depleting properties. Methane and N_2O may be difficult to control. Carbon dioxide, being linked so closely to fossil fuel use is amenable to reductions, but many aspects need to be considered. One such aspect is the amount of CO_2 emitted for a given fuel source (Table 4). Fuel switching, energy conservation, and a move towards renewable energy will probably all have to be explored to offer any prospect of significant CO_2 emission reductions. It is unlikely that there exists a single solution to CO_2 emission reduction. Instead there will be a need for a'package' of changes. Determining what this package should consist of, and what is appropriate for one state or the other, or one country or the other, is a matter for urgent attention. Obviously any changes in the energy area will have economic consequences, but so too will uncontrolled climatic change and sea level rise.

TABLE 4: Carbon Emissions from Fossil Fuels[a]

Fuel	Energy content (MJ/kg)	Carbon[b] content (%)	Carbon[b] emission (kg/GJ)	CO_2 emission (ratio to natural gas)	Australian CO_2 emission by sourcec[c] (%)
Natural gas	50.0	75	15.0	1	11
Oil	42.0	84	20.0	1.3	35
Black coal	23.0	65	28.3	1.9	40
Brown coal	7.7	24	31.2	2.1	14

[a] Adapted from figures provided by the Australian Institute of Petroleum.

[b] CO_2 emissions are generally measured by their weight as carbon.

[c] Data for 1987. Total Australian CO_2 emissions are about 1.5% of the globalemission of about 5 Gt (measured as carbon).

Tree planting has recently been suggested as a method of countering the greenhouse effect. However, the sheer magnitude of the task at hand needs to be kept in mind. Ten billion trees, occupying 10 million ha, planted today, would take up enough CO_2 to reduce the world's annual CO_2 emissions from burning fossil fuels by about 1% (Marland, 1988). Thus it should be clear that, while planting trees will be good for many other reasons (to stop land degradation, maintain ecosystems, etc.), as a means of countering the build-up of atmospheric CO_2 it can have a significant effect, but only if carried out on a large enough scale.

That the atmospheric changes have already committed the earth to a global warming, and that it will be well-nigh impossible to stop any future change should be clear by now. We are left with the task of planning for the change and limiting the ultimate magnitude of the change. How exactly we will tackle these issues remains to be seen.

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THE ATMOSPHERIC IMPACT OF EXPANDED COAL UTILISATION

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The combustion of fossil fuels is the main contributor to the increase in the concentration of not only carbon dioxide in the atmosphere but also of oxides of nitrogen and sulphur dioxide. Coal now contributes about 25% to the primary energy generation in the world and its use is projected to increase substantially even as the overall contribution of fossil fuels to energy generation decreases. To mitigate the resulting adverse environmental effects of the increased use of coal, it is imperative that the development and adoption of newer environmentally acceptable technologies for coal conversion is accelerated. These emerging technologies are reviewed and relevant R & D needs identified. These are summarised below:

- Reduction of ash and sulphur in coal to yield cleaner/modified coal.
- Development of better combustion systems such as: pressurised fluidised bed; slagging combustors with sorbents like limestone to fix sulphur; and circulating fluidised bed.
- Conversion of coal into: gaseous fuel for integrated gasification combined cycle power generation; and synthesis gas for methanol production.
- Better techniques for removal of SO_2 and NO_x.
- Hot Gas Clean-up Technology.
- Retrofit possibilities of some of these technologies in existing power plants.

Reference is made to the need for more refined analytical tools and techniques for H_2S, COS, CS_2, SO_2, SO_3 and NO_x monitoring in the environment and advanced research on the chemistry of SO_2/NO_x and systems modelling but this is not discussed in detail.

INTRODUCTION

The greenhouse effect is now well understood and it is known that, during this century, CO_2 concentration in the atmosphere has increased from about 280 ppmv to about 350 ppmv. Vegetation loss and fossil fuel combustion are the main contributors to this increase. Fossil fuel combustion further contributes to the increase of oxides of nitrogen and sulphur dioxide; particulate matter in flue gases of coal combustion also releases heavy metal and metal ions in the air. These emissions deleteriously disturb the delicately balanced chemistry of the atmosphere—perhaps even in the thermosphere.

COAL AS ENERGY SOURCE

On a global basis coal supplied about 30 percent of the primary energy in 1975 and is likely to increase further. There was a time, when coal was the main source of industrial organic chemicals. Then came the "Oil age", during which time coal became the forgotten feed stock of the 1960's; and then came the phenomenal rise in crude oil prices (Table 1). Coal, largely overlooked up to the sixties, became suddenly "affordable"; of course it was always "available". Expansion in coal mining was never behind demand.

TABLE 1: Oil Prices

Year	Cost per barrel (US Dollars)
1950's	< 2
December 1978	~ 13
1979	~ 36

The OECD countries discovered that their energy consumption was outpacing energy production and energy policy decisions were taken towards coal utilisation. Developing countries like India were no better off. In fact, the rising oil prices hit them more severely. Money was neither available to pay for oil nor for converting their economies to coal by increasing coal mining or establishing coal conversion technologies.

The 1979 oil prices shock was much more severe than that of 1973-1974 and the International Energy Agency (IEA) adopted "the Principles for IEA Action on Coal" and established a Coal Industry Advisory Board (CIAB). A landmark report (Wilson, 1980), was published by the World Coal Study Group, generally referred to as the WOCOL report, Wilson (1980). Research and Development in integrated utilisation of coal was very well funded in several countries e.g. Australia, Federal Republic of Germany, German Democratic Republic, Japan, the Netherlands, the United Kingdom, the United States of America and the USSR. Environmental protection aspects were very much kept in mind. As the oil prices declined, funding for environmental protection also decreased, especially in the United States of America in the Reagan era during the 1980's. Calm in the oil market has always lulled governments and industry into a false sense of security. The proven world reserves of coal are estimated to be around 665 billion tonnes of coal equivalent and at the present rate of mining and consumption will last about 240 years. But the total resource base of coal is much larger; it is about 11,000 billion tonnes. Technological advances in mining and technologies of the future such as underground coal gasification can make these resources recoverable. The single major use of coal is for generation of steam and power by coal combustion. In the industrial fields, iron and steel and cement are the main users; the former is using coking coals. Domestic use is now confined to developing countries by and large.

The global primary energy supply projection estimates are given in Table 2 and the estimated annual rate of growth in coal use is given in Table 3.

TABLE 2: Global Primary Energy Supply Projection (Mintzer, 1987)

Year	Energy required (exajoules/year)	Percentage available from coal
1975	250	28
2000	360	—
2025	530	50
2050	750	—
2075	930	—

TABLE 3: Estimated Annual Rate of Growth in Coal Use (Mintzer, 1987)

Year	Percent annual rate of growth
25 Year intervals	
1975 - 2000	1.7
2000 - 2025	3.0
2025 - 2050	2.3
2050 - 2075	1.5
Whole period	
1975 - 2075	2.1

COAL AND POLLUTION

Coal production and combustion contribute to pollution in several ways. As much as 25 percent of coal dust and fines are produced during mining, transport, size reduction and further utilization. During these operations, not only air but also surface waters get polluted. Power generation plants burning coal emit stack gases. These are aerosols loaded with particulate matter and noxious chemicals. In addition there is primary and secondary pollution of streams with ash. The particulate matter, coal ash and unburnt coal all have elevated concentrations of heavy metals; the noxious gases in the stack contain the oxides of carbon, nitrogen and sulphur including H_2S and COS.

The emission regulations in advanced countries are strict and are rigidly enforced. This is not yet true of less developed countries, which are power hungry but do not have sufficient funds to invest in electrostatic precipitators or flue gas desulphurisation. India can be cited as an example of a country which has all the knowledge, knowhow and awareness, but has an acute resources constraint with many competing claims on limited finances. India prescribes standards for sulphur dioxide emission, on the basis of control effected only through prescribed height of the stack depending upon the size of the power plant. Particulate matter standards prescribed in India are given in Table 4.

What then will be the global environmental impact of increased consumption of coal for power generation? Large industrial boilers emit 5-8 × A kg of particulate matter per tonne of coal combusted, where A is the ash percent in coal.

The sulphur dioxide emission is approximately 19 × S kg per tonne of coal, where S is the percent sulphur in coal.

Mintzer (1987) has estimated the addition of carbon to the atmosphere by coal up to 2075 as given in Table 5.

TABLE 4: Emission Regulations for Particulate Matter in Power Plants in India

Boiler size	Emission (mg/Nm^3)		
	Pre 1979	Post 1979	Protected area
Less than 200 MWe	600	350	150
200 MWe and above	-	150	150

TABLE 5: Addition of Carbon to the Atmosphere by Coal Use

Year	Energy from coal (exajoules)	Carbon added (billion tonnes)
1975	75	-
2000	115	31
2025	243	65
2050	429	115
2075	620	167

MITIGATING COAL BASED POLLUTION

What then are the methods that can be adopted in the future to mitigate the increased environmental pollution by the projected increase in the utilisation of coal for energy generation? Electrostatic precipitation and wet flue gas desulphurisation are well established industrial technologies. The challenge is to develop newer cost effective methods of:

(i) Utilising coal fines;

(ii) Removing particulate matter and SO_x and NO_x from gaseous streams;

(iii) Minimising the formation of NO_x; and

(iv) Coal conversion that are, *per se*, less noxious to environment.

An attempt will be now made to outline the main technological approaches and the state of development. The chemistry involved is simple; much more interesting chemistry is involved in the mechanisms of formation of the gaseous pollutants and their interactions with other reactive chemical entities at various levels and will be referred to later in brief. The chemistry of formation of oxides of nitrogen and sulphur in solid and liquid fuel combustion is reviewed in a special report on Combustion Chemistry (Miller and Fisk, 1987).

UTILISING COAL FINES

Coming back to mitigating the effects of pollution from coal usage, the first pollutant to be handled is coal fines. The disposal problem is more acute with high ash coal. One promising approach is to agglomerate these with oil, if necessary, after further processing through froth flotation/oleo-flotation. A process developed by the National Research Council of Canada has been demonstrated at a scale of 30-40 tonnes per hour at Pennsylvania Coal Cleaning Facilities. It uses less than 7 percent oil as compared to 10 percent or more in earlier processes and the cost of production of the agglomerates is estimated to be between US $ 6.50-11.00 per tonne.

A 10 tph pilot plant is about to be commissioned at the Patherdih washery of Bharat Coking Coal Ltd. (India), using the process knowhow of Central Fuel Research Institute, Dhanbad of the Council of Scientific & Industrial Research, New Delhi. The oil consumption is 8-12 percent and laboratory studies on reducing it are in progress.

PARTICULATES REMOVAL

The quantity of particulate matter in stack gases depends both on the ash content of the coal and on the type of boiler. The average emission levels are as given in Table 6

TABLE 6: Particulate Emissions from Coal Fired Industrial Boilers

Ash in coal (%)	Particulates in coal (kg/tonne)
10	50-80
20	100-160
30	150-240
40	200-320

Electrostatic precipitators do remove more than 99 percent of these but at atmospheric pressure. With many pressurised fluidised bed combustion and coal gasification plants likely to be built, knocking down the particulates under pressure has become imperative. Several technologies are under various stages of development. Ideally such a technology should aim at :

(i) Working at emission gas temperature, pressure and velocity;

(ii) High particle loading;

(iii) High efficiencies, both overall and for the removal of submicron size particles;

(iv) Low pressure drops; and

(v) Higher cycle times.

Some of the technologies being developed are outlined below:

Granular shallow bed (GSB)

This is meant to be used with pressurised fluidised bed combustion (PFBC) and uses 620 μM sand as the bed medium. A six element bed was used and gave a collecting efficiency of 99.2 percent at a flowrate of 500 cfm and at 11 atmospheres and 1600°F (~870°C) (Westinghouse Electric Corporation with Ducon Inc., and Burns and Roe, Inc.).

High temperature moving bed granular bed filter

This has been evaluated with an atmospheric fluidised bed combustion and operated at a gas velocity of 1600 cfm at 1500-1600°F (~820-870°C). The overall efficiency was above 99 percent with a submicron collecting efficiency of more than 96 percent.

Electrostatic granular bed and electrocyclones

These are being developed and tested by General Electric Co.

High pressure electrostatic precipitators

These are also under development. Tests at the PFBC test facility at Curtis-Wright, New Jersey, showed a particle collecting efficiency in the range of 98-99.5 percent at 1400-1500°F and 84 psi.

Ceramic filters

These are receiving the most attention and are of several types.

POROUS CERAMIC CROSSFLOW FILTERS

These permit combustion at high gas velocities (3.35 metres/min.) and operate at 800°C and 162 psi, with a modest pressure drop of only about 0.3 psi. Particle loading up to 5000 ppm can be tolerated; the cycle time is 25 min.

HIGH TEMPERATURE HIGH PRESSURE (HTHP) CERAMIC TUBE FILTERS

These are considered the most promising for commercial application. EPRI have tested a ceramic element filter module at the PFBC pilot facility in Grimethorpe, UK. The module contains 130 cylindrical elements made of porous ceramic, each 4.5 ft. long and with an i.d. of 1.7 in. and with an inner support made of silicon carbide granules and a thin outer layer of fine alumina fibres and silicon carbide grains. Ceramic seals and a counterweight hold the elements in place in a refractory lined vessel; cleaning is by pulse jet air. Though the process leads in scale up, commercially available hardware may not be available for a few years to come.

SULPHUR COMPOUNDS, FORMATION AND RELEASE

The formation and release of S compounds (SO_2, H_2S, COS, CS_2) during coal combustion depends upon several factors including the following:

(i) *Coal type*—Bituminous coal produces more SO_2 and less H_2S, COS and CS_2 levels compared to sub-bituminous coal;

(ii) *Stoichiometric ratio*—Increase of air increases S conversion and SO_2 levels and decreases S, COS and CS_2 levels;

(iii) *Swirl of the secondary air* also affects the distribution of the sulphur species, if the stoichiometric ratio is kept constant, Zang (1989);

(iv) *Sulphur composition of the coal* (pyritic, sulphate and organic S)—The organic sulphur is released early during coal devolatilisation and the pyritic sulphur is released only later during char combustion. X-Ray studies have shown that the reaction products of pyritic combustion are $FeS_{(1+x)}$, FeS and Fe_2O_3;

(v) *Combustion temperature and combustion rate* also affect the sulphur release pattern; and

(vi) *The nature of the coal bed,* fixed or fluidised, also plays a part in this (Schouter *et al.,* 1987).

The main research and development emphasis on removal of sulphur compounds from flue gases is on the development of cost effective hot gas desulphurisation methods as an alternative to wet flue gas desulphurisation. Hot gas cleaning assumes special importance in integrated gasification combined cycle (IGCC) mode of power generation, because the sensible heat of raw gas is retained.

DESULPHURISATION TECHNOLOGIES

The different methods of removal of sulphur compounds from flue gases can be roughly grouped as follows:

(i) Addition of sorbents like limestone during combustion. The sulphur dioxide is converted into calcium sulphite and oxidized to calcium sulphate which will be distributed in the ash and flue gas particulates;

(ii) Injecting lime based dust in flue gas duct;

(iii) Conversion of sulphur dioxide to sulphites; the subsequent release of sulphur dioxide, its concentration and oxidation yields sulphuric acid; and

(iv) Use of metal oxides or mixed metal oxides such as Fe_2O_3; CuO; ZnO; CuO/ZnO; V_2O_5/V_2O_3; zinc ferrite ($ZnFe_2O_4$); zinc vanadium oxide/V_2O_5.

These methods are briefly described below:

As stated, one method of fixing sulphur in coal is the addition of sorbents like limestone. In fluidized bed combustion, the sorbent can be fed directly into the combustor. The particle size of the sorbent and its structure—crystalline or amorphous, hard or soft—and composition are important. Dolomitic limestones with over 20 percent magnesium carbonate enhance sulphur dioxide absorption at lower Ca/S molar ratios, reduce carryover and can slightly lower NO_x in the flue gas.

Addition of sorbents during combustion changes the nature of the ash and discharge mechanisms have to be carefully designed, e.g. the ash contains reactive pozzolanas of small particle size; unreacted limestone, grit from limestone and calcium sulphate from the sulphur absorption reactions are the other constituents; possible uses are soil stabilisation, structural fill and cement additives.

Sorbents also change the nature of the solids in the flue gas. For example, calcium sulphate becomes cementatious in the presence of moisture and filter bags can be blinded. ESP designs are also affected because sorbents in fluidised bed operations increase the dust loading compared to fly ash without sorbent addition. If sorbent addition equipment is to be retrofitted to an existing power plant with an electrostatic precipitator, the change in the quality and quantity of the solid emissions is a matter of some concern. Different boilers have different requirements for sorbents but, generally the Ca/S ratio varies between 2/1 and 3/1 for removal of 80-90 percent SO_2. Some Circulating Fluidised Beds (CFBs) have recorded Ca/S between 1.4/1 and 2.2/1 for 90 percent SO_2 removal from coals containing 5 percent S (Makanse, 1987).

Amongst the several Clean Coal projects under the US Department of Energy Clean Coal Technology Program, a TRW Proposal of Advanced Slagging Combustor Utility Demonstration Project is typical of the magnitude of work, the time scale and the funding involved.

Research and development started in 1975 with coal injection experiments and flow parameters; coal fired combustion tests that varied air injection techniques and pressures followed. A full sized plastic coldflow model was constructed to optimise combustor geometry through detailed aerodynamic flow visualisation tests. A computer model was developed in parallel to analyse thermochemistry, aerodynamics, combustion, heat transfer and slag flow. Feasibility test units with 34, 70 and 170 MM Btu/hr (6 atm) were then successively constructed and used for power generation on an MHD test unit.

Parallel development work on similar atmospheric pressure combustors was carried out to construct test units of 10 MM Btu/hr with sorbent injection and then of a 40 MM Btu/hr unit. In all, well over a thousand test runs on different units were carried out before the construction of the 40 MM Btu/hr unit. In this unit, 94 percent of the slag and 90 percent SO_2 could be removed and NO_x controlled at 230-450 ppm with over 99.5 percent carbon burnout. Then followed a 40 MM Btu/hr combustor built to commercial standards and installed on an industrial scale boiler. Till October 1988, over 6000 hours of operating time had been accumulated.

It has now been proposed to retrofit a 69 MWe boiler with four 160 MM Btu/hr slagging combustor operating at a high enough temperature to keep the ash molten and in an oxygen deficient mode to minimise NO_x formation which would otherwise be increased due to the high operating temperature. Combustion is completed in a secondary burner; the sorbent is injected into the combustion products as they enter the host boiler. The sorbent is removed from the flue gas along with residual ash by bag house filtration. Essentially it is a staged combustion system to prevent excessive NO_x formation, the SO_2 being removed by sorbent injection.

Further optimisation to improve process economics will be simultaneously studied at TRW's test site in Cleveland, Ohio where the 40 MM Btu/hr industrial boiler is already fitted with a slagging combustor system (SCS). It will be modified to demonstrate waste sorbent recycle to minimise fresh sorbent requirements and thus minimise Ca/S ratios. Flue gas humidification will also be studied as an approach to reduce sorbent consumption and maximise SO_2 capture. The project is estimated to cost US \$ 49,000,000 and is to be completed in three years.

Another method being developed is the direct injection of sulphur absorbing lime based chemicals in dry or slurry form into the existing duct work through which flue gases leave the coal fired boiler. Careful control of the moisture content in the flue gases leads to the production of a dry particulate solid waste instead of a sludge. This solid waste can then be easily removed along with the flyash in existing particulate removal system. Removal of sulphur dioxide is, however, claimed to be only 50-70 percent at a total cost which is only about half of the conventional wet scrubbing (Anon., 1989).

SULPHUR DIOXIDE ABSORPTION METHODS

Other methods centre around the absorption of sulphur dioxide in alkalies or sodium sulphite in aqueous solution or slurry and can be described by the following chemical reactions:

$$CaCO_3 \longrightarrow CaSO_3$$

$$MgO \longrightarrow MgSO_3$$

$$Na_2SO_3 \longrightarrow NaHSO_3$$

If limestone has been used, the resulting calcium sulphite is air oxidised to calcium sulphate and disposed off. The magnesium sulphite resulting from absorption in magnesium oxide suspension is roasted in a rotary kiln to regenerate magnesium oxide and the sulphur dioxide released is used for sulphuric acid manufacture. From the sodium bisulphite solution resulting from absorption in aqueous sodium sulphite (Wellmann-Lord Process), the sodium sulphite is regenerated by heat and concentrated in a forced circulation evaporator; the sulphur dioxide is used for sulphuric acid manufacture through the following chemical reactions:

$$CaSO_3 \longrightarrow CaSO_4$$

$$MgSO_3 \longrightarrow MgO + SO_2$$

$$2NaHSO_3 \longrightarrow Na_2SO_3 + H_2O + SO_2$$

The *DESOX process* is based on the oxidation of sulphur dioxide to sulphuric acid by bromine and electrolysis of the resulting hydrobromic acid to hydrogen and bromine. Hydrogen and sulphuric acid are sold and bromine is recycled:

$$SO_2 + Br_2 + 2H_2O \longrightarrow H_2SO_4 + 2HBr$$

$$2HBr \xrightarrow{\text{electrolysis}} H_2 + Br_2$$

The process is being currently tested in a power plant in Sardinia which produces 32000 m^3/h flue gas with 5-10g/m^3 SO_2. These are contacted with an aqueous solution containing less than 1 percent bromine and about 10-20 percent sulphuric acid. The method is claimed to be cheaper by 20 percent than other sulphuric acid generating processes for SO_2 removal. Capital costs are estimated to be of the same order as other conventional wet scrubbing processes and the operating costs lower (Anon., 1989).

The *SHELL Copper Oxide process* uses sorbent supported copper oxide. The bed is regenerated by heating to about 400°C with hydrogen and steam to release sulphur dioxide in a concentration of 4-7 percent; this is subsequently increased to about 90 percent by stripping steam. The process is operating in a 40 MWe boiler in Japan.

Other processes use a variety of sorbents such as sodium carbonate on alumina or copper impregnated alumina spheres. Fluidised bed pilot reactors are also being tried with sorbents.

ELECTRON BEAM RADIATION

Radiation with high energy electrons is quite a departure from the approaches so far outlined. Flue gas is bombarded with short and frequent pulses of electron beams in a pulsed energised electron reactor. Electrons convert sulphur dioxide to sulphur trioxide which is collected as sulphuric acid or reacted with a sorbent. These short electron beams consume less power than in the traditional electron beam approach.

NITROGEN OXIDES FORMATION

NO_x formation, during coal combustion, can be derived from nitrogen of the air (thermal NO_x) or the nitrogen present in the coal matrix (fuel NO_x). As would be expected, the aliphatic compounds of coal nitrogen are rapidly expelled on heating and the aromatic nitrogen compounds are released only after fragmentation of high boiling tars and heterocycles. In pulverised coal flame, the residence time is not sufficient for complete devolatilisation and a substantial portion of the fuel nitrogen remains in the char. However, laboratory studies have shown, if sufficient time is given, all the nitrogen initially present in the coal can be removed from the char matrix, because, unlike carbon, nitrogen does not form stable structures at combustion temperature and the process is kinetically controlled. There is no apparent direct relationship between coal nitrogen content and the NO_x formed but coals with high volatile nitrogen content, when burnt in fuel lean conditions are more likely to produce high NO_x levels.

The mechanism of formation of oxides of nitrogen is not yet fully understood, but the nitrogen species are perhaps first converted into hydrogen cyanide and ammonia. Two pathways are then available: (i) reaction with oxygen to generate nitric oxide; or (ii) combining with nitric oxide itself to produce nitrogen. Char catalysed reduction of nitric oxide by carbon monoxide also takes place (Burdett and Pye, 1987) giving the following chemical reaction:

$$\begin{tikzcd}
\text{Coal } N_2 \arrow[r, "\text{combustion}", "\text{processes}"'] & HCN \arrow[d, "\begin{matrix} NH_3 \\ \text{oxygen} \end{matrix}"] \\
& NO
\end{tikzcd}$$

The kinetics of this reduction are of interest. These have been measured in the temperature range 400-750°C, the effective diffusion coefficient was determined by fitting effectiveness factors in different particle sizes. Using these data the NO conversion by coal char under the conditions of fluidised bed combustor was estimated (Schuler *et al.*, 1987). Another study has shown that in the combustion of the residual coke, the degradation of coke and the formation of NO_x are parallel. 80-90 percent of the fuel nitrogen is converted to NO_x. A major portion of the NO_x formed during pyrolysis is, however, reduced to elemental nitrogen. Investigations of the kinetics of the reduction of nitric oxide on char, in the temperature range 300-500°C, showed that both the reaction rate and reaction order are dependent upon particle size (van Heek and Muehlen, 1985). This assumes importance in fluidised bed reactors.

Flame structure has a strong effect on NO emission; measurements of gaseous species formation in a coal combustion test furnace have shown that with proper control of secondary air mixing wlith primary fuel/air jets, NO_x exhaust gas levels could be reduced to 100 ppm; NO is produced in the oxidising flame zone which envelops the central reducing flame and is destroyed in the mixing interface between the two zones (Arashi *et al.*, 1985).

In NO_x formation, the reverse reaction is the thermodynamically favoured one, but is practically prevented by the rapid cooling of the products, as follows:

$$N_2 + xO_2 \rightleftharpoons 2NO_x$$

Staged combustion is thus a method of minimising the formation of oxides of nitrogen. A reference to staged combustion was made earlier when dealing with TRW's slagging combuster system. In laboratory test furnaces, it has been possible to achieve nitric oxide concentrations as low as 100 ppm or even less. Oxides of nitrogen are potent sinks for odd oxygen species O_3, $O(^3P)$ and O^1D), via the following chemical reactions:

$$\begin{array}{lcl}
NO + O_3 & \longrightarrow & NO_2 + O_2 \\
NO_2 + O & \longrightarrow & NO + O_2 \\
\hline
O_3 + O & \longrightarrow & 2O_2
\end{array}$$

This catalytic cycle (30-45 km altitude) destroys two odd oxygen species each time it occurs. Of course, nitric oxide also helps the production of ozone via the following reactions:

$$\begin{array}{lcl} HO_2 + NO & \longrightarrow & NO_2 + OH \\ (2x)\ NO_2 + h\nu & \longrightarrow & NO + O(^3P) \\ (2x)\ O(^3P) + O_2 + M & \longrightarrow & O_3 + M \end{array}$$

(where M is another molecule of oxygen or nitrogen that is unchanged.)

Nitrogen oxides removal

The *NOXOSO process* (Fig.1) is a promising one for the simultaneous removal of SO_x and NO_x from fuel gas. The sorbent is an alumina substrate loaded with sodium aluminate. The process works at about 250°F i.e. at normal power plant flue gas temperature. An advantage is that particulate removal upstream of the absorption is not required and a cyclone suffices to knock down the large particulate flyash to prevent its entrainment later in the fluidised bed. The spent sorbent is heated with combustion gas in a multistage bed to about 1000°F. This decomposes and releases the products of NO_x absorption as nitrogen, oxygen and nitric oxide; these automatically mix with the combustion air and are fed to the boiler. The regeneration of the sorbent is then effected by feeding the hot sorbent to a countercurrent fluid bed generator where a reducing gas like methane reduces the sulphur dioxide to a 1:2 molar mixture of sulphur dioxide and hydrogen sulphide, which is then fed to a Claus unit to make elemental sulphur. The process is completely dry and produces no sludge.

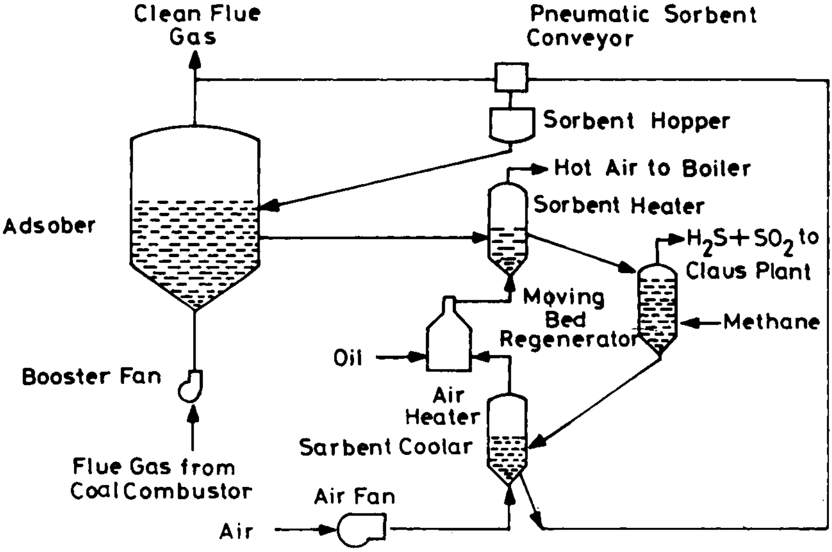

Fig. 1. Schematic diagram of the combined NO_x and SO_2 reduction (NOXOSO) process.

The process has been tested on a small scale at the Tennessee Valley Authority's Shaunee facility and at the U S. Department of Energy's Pittsburgh Energy Technology Research Centre (PETC). The test facility at PETC was equivalent to 0.75 MWe and the fluidised bed had a cross section of $1m^2$ with variable expanded heights. The sorbent used was 3-8 percent sodium aluminate coated on a gamma alumina substrate. The sulphur dioxide removal efficiency was about 95 percent and NO_x removal averaged 80 percent.

The NOXOSO process is being tried at a 5 MW coal fired unit at an Ohio Edison plant in Toronto, Ohio. A consortium of NOXOSO Corporation, M.W. Ferguson, W.R. Grace, Ohio Edison, the State of Ohio and PETC is funding the project. The 1984 estimates placed the cost of NOXOSO units at US $ 162/kw of installed capacity (Wuebbles *et al.*, 1989).

Environment friendly coal conversion technologies

There are several environmentally acceptable technologies now available for generating electricity from coal. These are:

(i) Fluidised bed combustion— atmospheric (AFBC) (bubbling bed), circulating fluidised bed (CFB); and pressurised (PFBC);

(ii) Gasification—IGCC and underground; and

(iii) Partially solvent refined coal.

Atmospheric fluidized and pressurized bed combustion

Atmospheric fluidised bed combustion is now a well established technology for steam/power generation with numerous plants in operation and several international technology vendors to choose from. The year 1987 was regarded as the watershed year for the scale up of fluidised bed boilers in the United States, with boilers as large as 900,000 lb/hr on order. The emphasis has shifted to pressurised from atmospheric fluidised bed combustion and also PFBC based combined cycle operations (Fig. 2).

Circulating fluidized bed combustion

Circulating fluidised bed (CFB) technology has also penetrated many different industries such as pulp and paper, food processing and cement. CFB is also a fluidised bed combustion technology, but in contrast to the bubbling bed it employs much higher fluidisation velocities. In a bubbling bed, the solids should not be elutriated from the bed into the convective passes, so the fluidisation velocities are kept between 5-12 feet per second. The very purpose of CFB is to promote the elutriation of the solids and, therefore, fluidisation velocities can be as high as 30 feet per second. CFB permits longer residence time, increases combustion efficiency and improves the absorption of sulphur dioxide. All fluidised bed combustions are environmentally

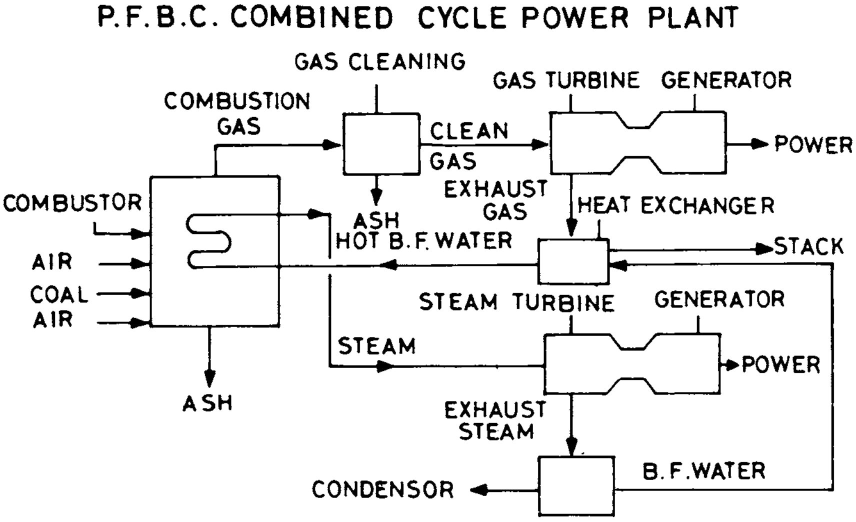

Fig. 2. PFBC Combined cycle power plant.

friendly, the oxides of sulphur being removed by adding limestone to the bed; the formation of oxides of nitrogen is minimised because of the lower temperatures of combustion and 'staged combustion', as already mentioned.

Integrated gasification combined cycle

In conventional power plants, the high pressure steam from coal combustion—pulverised coal or stoker type—is expanded through steam turbines to produce electricity. In PFBC, the hot combustion gas, after being cleaned, is expanded through a gas turbine and the hot exhaust gases from the gas turbine preheat the boiler feed water/raise steam. Steam for the steam turbine is raised by steam coils placed in the PFB combustor.

In Integrated Gasification Combined Cycle (IGCC), most of the ash is discharged from the gasifier and the gas is much easier to clean by scrubbing. In most processes, the sensible heat is recovered from the raw gas before cleaning and combusting and the chemical heat (CO, H_2, CH_4) is utilised through the gas turbine, with the exhaust gases being again used for steam generation. Additional power is thus generated through steam turbines viz. Heat Recovery Steam Generator (HRSG).

The coal gasification technology is well established commercially and processes are classified as fixed bed, fluidised bed and entrained bed. To date the largest number of gasifiers are the Lurgi fixed bed, producing more than 2000 MM Scf/day medium Btu gas. This process has been modified in collaboration with British Gas so that ash is removed in molten form and not as dry ash—British Gas Lurgi (BGL). A commercial plant is yet to be built.

Fluidised bed gasification technology is at a large PDU scale with only one commercial plant gasifying about 730 tpd of lignite at Berrenrath near Cologne, FRG, by the high temperature Winkler process (HTW). The gas is converted into methanol. At PDU scale, are the IGT Chicago and KRW Pittsburgh plants. The entrained bed processes can be of wet or dry type. The wet process was developed by Texaco and is now operative in Japan (UBE—1350 t/NH_3 per day), Federal Republic of Germany (Oberhausen-Holten) USA (Eastman Kodak 900 t/coal per day) (Cool Water 120 MWe electricity combined cycle).

Dow Chemicals have licensed this process from Texaco and have substantially modified it to gasify about 2000 tpd of lignite to generate about 165 MW power in Plaquemin, Louisiana, USA.

Plants at PDU stage using dry entrained bed are the Shell 200 tpd plant near Houston, USA. and the Prenflo 50 tpd plant at Fuerstenhausen, FRG. A 1000 tpd Prenflo plant was to be built (Krupps-Koppers Technology).

Underground Coal Gasification

This technique was first studied in the USSR at depths of up to about 400 m. Deep underground gasification (1 to 2 kms) is being intensively studied in USA, FRG, France, Denmark and also in India. Two boreholes are drilled and connected underground by horizontal drilling. Air/oxygen and steam are introduced through one borehole; gasification takes place *in situ*, and the gas flows out through the other borehole.

Partial solvent refining of coal

This technique is being studied in Japan, Peoples Republic of China and India. In the Indian programme (Central Fuel Research Institute), finely powdered coal in a suspension of anthracene oil is hydrogenated at about 400°C and 80 kg/cm^2; weak linkages are broken and the coal is solubilised. After filtration from sedimented ash, the solvent is distilled off for reuse and the pasty reconstituted coal can be blended with coal for steel making.

CONCLUSIONS

To sum up, increased use of coal need not lead to increased pollution. The unanswered question is whether poorer countries having adequate coal reserves and needing more electricity for their development can afford the expense (or luxury ?) of antipollution technologies when even a beginning has not been made to monitor the environment, much less to prevent/minimise pollution.

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OZONE PUZZLES—WILL A HOLE OCCUR OUTSIDE POLAR REGIONS ?

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The importance of the ozone layer in the stratosphere has long been known and is only briefly explained here. During the 1970s theories were developed which implicated man-made organic chlorine chemicals in the progressive destruction of the ozone layer. However, until the last few years these theories were in some difficulty because there were no real measurements of ozone being depleted, let alone any depletion being attributable to anthropogenic chlorine. The recent Ozone Trends Panel report has gone a long way towards clarifying the relationship between chlorine and ozone destruction.

The recognition of the Antarctic ozone hole in 1985 was a surprise. The hole develops very rapidly each spring, and was soon shown to be a lower stratosphere phenomenon. This did not fit the established theories for ozone destruction by chlorine which involve catalytic chlorine action in the upper stratosphere.

Intensive experimental work in and under the ozone holes of 1986 and 1987 established the direct involvement of chlorine and also some new heterogeneous chemistry for ozone destruction depending on the seasonal formation of polar stratospheric clouds.

The question then arises: Could these rapid heterogeneous reactions ever lead to major ozone depletion away from the polar regions? Recent theoretical and experimental work by Hofmann and Solomon indicates that while high concentrations of chlorine remain in the stratosphere, we are vulnerable to severe ozone depletion in the aftermath of a major volcanic eruption, by way of heterogeneous reactions involving sulphuric acid droplets.

Can international treaties such as the Montreal Protocol prevent a catastrophy of this sort? Much broader international acceptance of the Protocol is required and the cutbacks of ozone depleting substances must be much greater than those presently in the agreement, before there can be long term stability for the ozone layer.

THE NATURAL OZONE LAYER

Solar ultraviolet radiation, which is harmful to most animal and plant life, is largely filtered out by the atmosphere. The main ultraviolet absorber is ozone.

Although ozone is found throughout the atmosphere, about 90% resides in the lower part of the stratosphere, a distinct layer of the atmosphere between 15 and 50 kilometres up.

The existence of the ozone layer is the result of a balance between the amounts created and destroyed. Both these processes occur naturally in the upper atmosphere. In the upper stratosphere, at altitudes of about 50 km, oxygen molecules, O_2, are destroyed by high energy ultraviolet radiation and can reform as ozone, O_3. This ozone has an appreciable lifetime in the atmosphere, until it too succumbs to ultraviolet radiation, usually in the lower stratosphere, and reforms the common oxygen gas. The amount of ozone over any one place depends not only on this photochemical balance, but also on the stratospheric climate, the winds that disperse the ozone. These processes cause quite large weekly and seasonal variations. For example there is about 50% more ozone over New Zealand in spring than in autumn. The global distribution is shown in Figure 1, which clearly shows the lower natural ozone concentrations in the tropics and higher values towards the poles.

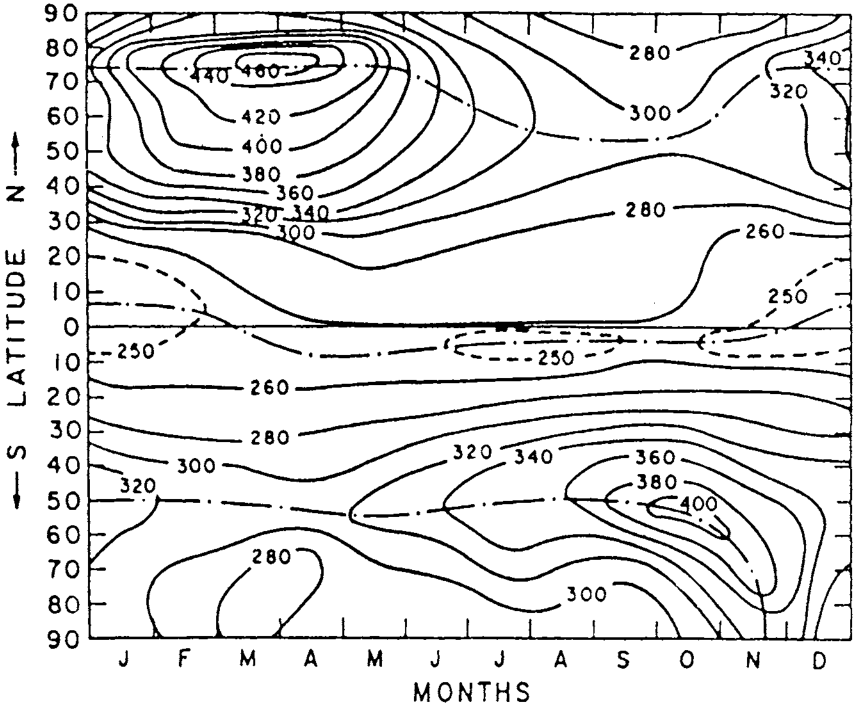

Fig. 1. Latitude-season characteristics for total ozone, 1958-1977 (London, 1980).

The stratosphere itself is dependent on ozone for its existence. The energy absorbed by the ozone in the course of the creation and destruction of its layer warms the surrounding atmosphere, so that as one passes upwards through it the temperature actually increases, it is a temperature inversion. This inverted layer, which is the stratosphere, is very resistant to vertical movements of air, and so acts as a cap on the turbulent weather processes in the troposphere below. Thus the balance established by these natural stratospheric chemistry processes is of critical importance to our climate at the surface.

OZONE DESTRUCTION BY CHLOROFLUOROCARBONS

It was not appreciated until the 1970s that the ozone layer might be vulnerable to anthropogenic emissions of gases, even from the surface. A particular gas emitted may be chemically very inert in the troposphere, but any molecule can be decomposed by solar ultraviolet radiation if it survives long enough to be transported high enough into the stratosphere to encounter ultraviolet radiation of sufficiently short wavelength. Molecular fragments resulting can take part in reaction chains involving ozone, so interfering with the natural processes of ozone creation and destruction.

Many of these reaction sequences are now well known (e.g. WMO, 1986) and one of the most important is that from the breakdown of stable organic chlorine compounds, mainly chlorofluorocarbons (CFCs), where an active chlorine atom can catalytically destroy ozone:

$$\begin{array}{lrcl} & Cl + O_3 & \longrightarrow & ClO + O_2 \\ & ClO + O & \longrightarrow & Cl + O_2 \\ \hline \text{net :} & O_3 + O & \longrightarrow & O_2 + O_2 \end{array}$$

Figure 2 shows this interference with the natural ozone cycle in a simplified format. First we have the natural ozone cycle converting oxygen between its two forms(I). When a CFC molecule encounters the high energy ultraviolet radiation in the upper stratosphere, a chlorine atom is split off (II). The chlorine interacts with ozone to form chlorine monoxide (III) which subsequently reacts with an oxygen atom to regenerate the free chlorine atom (IV). The net effect of this reaction sequence is the loss of ozone. The chlorine atom is then available to initiate ozone destruction once more.

Laboratory work indicates that one chlorine atom can destroy about 100,000 ozone molecules by this process before it is itself destroyed, usually by encountering a molecule such as methane with which it reacts. We also note that this chlorine catalysed destruction of ozone is dependent on the presence of sufficient single oxygen atoms. This limits this reaction to occurring in the upper stratosphere.

In spite of this theory being well established in the chemical literature since 1974, there has always been doubt about it, as there remain possibilities of interfering reactions or feedbacks which are not yet appreciated. Thus the report of the Ozone Trends Panel (WMO, 1989) is of particular significance. This is the first broadly-based scientific consensus to identify a depletion of ozone over much of the globe that is beyond what is attributable to the natural variations such as the solar cycle,

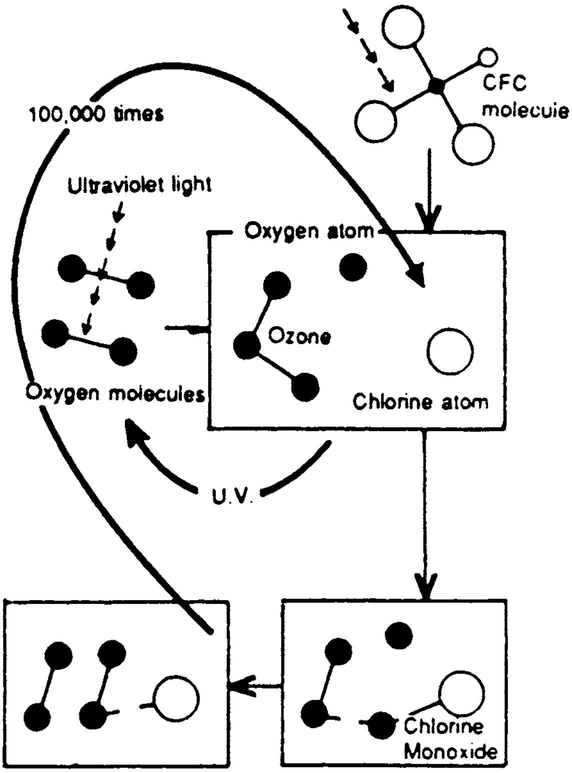

Fig. 2. A simplified representation of the interference of chlorine in the natural reactions of stratospheric ozone.

TABLE 1: Percent Total Ozone Change for 1969-1986, from the International Dobson Instrument Network [Ozone Trends Panel, WMO (1989)]

	Latitude band		
	53-64 deg N	40-52 deg N	30-39 deg N
Winter average	−6.2±1.5	−4.7±1.5	−2.3±1.3
Summer average	+0.4±0.8	−2.1±0.7	−1.9±0.8
Annual average	−2.3±0.7	−3.0±0.8	−1.7±0.7
(Uncertainties represent one standard error)			

the quasi-biennial oscillation, and volcanic activity. The depletions identified for the period 1969-1986 by the Panel are summarised in Table 1.

The Ozone Trends Panel has reported only for latitudes between 30 and 64 degrees North, on account of the lack of confidence in data for other regions. The

Panel noted that it appeared that Southern Hemisphere depletion was at least as great through the same period, and that the depletions determined for high latitudes and in winter were generally greater than predicted by the best regarded theoretical models.

THE OZONE HOLE

The first reports of severe depletion of ozone from the Antarctic (Farman *et al.*, 1985) took the scientific community by surprise. The knowledge of stratospheric catalytic cycles at that time did not allow for the rapid disappearance of ozone in spring over such a wide region, and for a time it seemed that there may have been other mechanisms for this "hole" formation, not involving chlorine chemistry in a major way.

However, the first season of intensive study on this phenomenon, in the austral spring of 1986, revealed that although only about a third of the total ozone column was vanishing from over the Antarctic continent, in a layer between 12 and 20 km up (the very lowest parts of the stratosphere), virtually all ozone was being destroyed during September (Hofmann, 1987). This could not possibly have been by the established mechanisms for ozone destruction by chlorine, as outlined above which are known to require upper stratospheric conditions of short wavelength solar ultraviolet radiation and relatively high concentrations of unattached oxygen atoms. This mechanism does not destroy ozone very rapidly, particularly because there are important interferences from other species, e.g. NO_x, which constrain it.

The ozone hole is now a well established annual phenomenon (e.g. UNEP/WMO, 1989), and many of its characteristics are understood as the result of the intense efforts to study it, especially with the Airborne Antarctic Expedition of spring 1987. The 1987 work coincided with the deepest hole so far, with virtually all ozone between 12 and 20 km up disappearing from mid-September until well into November.

HETEROGENEOUS CHEMISTRY

In order to understand the processes that lead to gas phase chlorine compounds destroying gas phase ozone over Antarctica in spring, we must introduce some heterogeneous chemistry, with solid or liquid particles involved. The airborne experiments in Antarctica in spring 1987 established the importance of some very unusual chemistry.

In the polar stratosphere, the important solid surface is provided by ice crystals, in the form of "polar stratospheric clouds". Such clouds will only condense in an exceptionally cold stratosphere, colder than –80 degrees C. This condition is reached only within the polar stratospheric vortex, an Antarctic circulation feature which confines Antarctic stratospheric air to high latitudes right through winter and spring, where the air can cool in the polar night without mixing back to warmer regions.

Throughout the stratosphere, much of the chlorine is in the form of HCl and $ClONO_2$, relatively inactive compounds, which are referred to as "reservoir" species.

In order for a reaction to occur, the chlorine must be released to take up a more reactive form, and active nitrogen oxides must be suppressed to reduce the occurrence of

$$Cl + NO_2 \longrightarrow ClO + NO$$

which does not involve ozone depletion. The presence of an ice surface on which HCl is absorbed allows:

$$ClONO_2(g) + HCl(s) \longrightarrow Cl_2(g) + HNO_3(s)$$

which can serve the dual purpose of releasing the chlorine in an active form, and tying up active nitrogen oxides as the reservoir species HNO_3.

Experiments in 1987, and recent laboratory work (e.g. Molina *et al.*, 1987) have confirmed the enhanced activity of HCl when absorbed on ice crystals, and also the existence of nitric acid trihydrate as part of polar stratospheric clouds.

Thus in the Antarctic spring, in the presence of polar stratospheric clouds and the returning sunlight, active chlorine is available to take part in chemical and photochemical reaction chains. The catalytic cycle outlined above for lower latitudes cannot account for the huge ozone loss in the lower stratosphere and several other cycles seem to be implicated. For example

$$\begin{aligned} Cl + O_3 &\longrightarrow ClO + O_2 \\ ClO + ClO &\longrightarrow Cl_2O_2 \\ Cl_2O_2 + uv &\longrightarrow Cl + ClOO \\ ClOO + M &\longrightarrow Cl + O_2 + M \end{aligned}$$

There are other similar cycles which also appear to be active, some of which involve bromine, but the idea is the same. Chlorine destroys ozone catalytically, ClO is an intermediate, and single oxygen atoms are not required.

The 1987 airborne work in Antarctica confirmed a very strong anticorrelation between ozone and ClO amounts, and also confirmed the exceptionally low concentrations of active nitrogen. Chlorine chemistry is definitely the leading contributor to the formation of the annual Antarctic ozone hole.

Thus as a result of the Ozone Trends Panel and our understanding of the ozone hole mechanisms, we can see that stratospheric chlorine is the main culprit, and we know that most of this comes from anthropogenic emissions of CFCs.

A recent evaluation of the 1987 ozone hole experimental studies seems to indicate that there may yet be other mechanisms involved to account for observations of some rapid ozone destruction outside the ozone hole and also earlier in the season (Proffitt *et al.*, 1989).

Figure 3 shows how chlorine has been building up over the past few decades. From a pre-industrial level of about 0.6 ppb (parts per billion) we have steadily increased the concentration to over 3 ppb, with a continuing increase of about 5% per year.

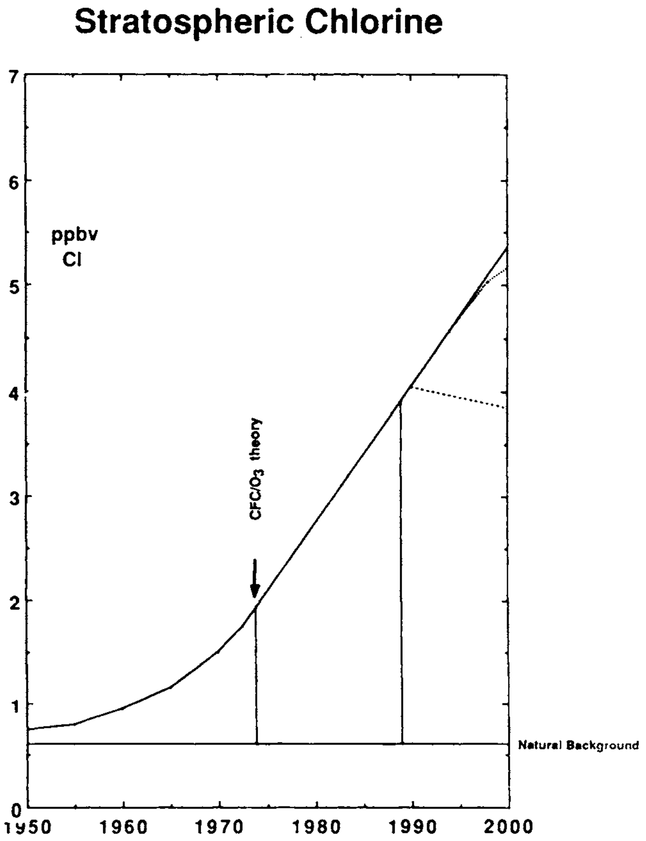

Fig. 3. The solid line shows estimated stratospheric chlorine concentration with no controls over CFC emissions, with the dotted line showing the projected influence of the present Montreal Protocol. The dashed line is an approximation of the effect of an immediate halt to all chlorine emissions.

OZONE HOLES ELSEWHERE ?

In the paragraphs above we have seen that there are two distinct sets of mechanisms for destruction of ozone by CFCs.

First there is the "standard" mechanism, outlined first, occurring mainly in the upper stratosphere, destroying ozone quite slowly, and giving rise to the trends reported on by the Ozone Trends Panel. Then there is the "ozone hole" mechanism, occurring low in the stratosphere, requiring polar statospheric clouds and acting very fast.

Under what conditions could the rapid "ozone hole" reaction occur away from poles? The main requirement appears to be a suitable reaction surface in the lower stratosphere to tie up the active forms of nitrogen and to release chlorine from its inactive reservoirs.

As a result of the work on the Antarctic ozone hole, it is now widely accepted that reactions on the surfaces of particles can have a major influence on stratospheric trace gas composition. In particular heterogeneous reactions can affect the partitioning of chlorine and nitrogen species between active and less active species. As explained above, this can happen in the extreme cold of the polar winter and spring stratosphere where the formation of water or nitric acid clouds can occur.

Although sufficiently cold temperatures can occur in the equatorial stratosphere, it appears that insufficient active chlorine can become available there because the air resides there for too short a time. In mid-latitudes, however, there is another possibility. Throughout the lower stratosphere there is an aerosol layer, the "Junge" layer, composed mainly of sulphuric acid droplets that have arisen from tropospheric SO_2 and COS rising into the stratosphere, oxidising and hydrating. This aerosol layer may be vastly increased in concentration after a large volcano injecting sulphur gases into the lower stratosphere. The droplets added through volcanic action are postulated to provide the reaction surface to enable the release of active chlorine, the suppression of nitrogen dioxide and the consequent rapid destruction of ozone, that is, an ozone hole phenomenon at mid-latitudes. The interactions between these particles have been modelled and supporting laboratory studies have recently been put forward by Hofmann and Solomon (1989).

Since the build-up of chlorine in the stratosphere there have been no very large volcanic eruptions. The largest eruption of the past decade, El Chichon in 1982, was not large enough to cause a major drop in ozone levels globally. However, there was a significant reduction in total ozone in mid-latitudes of both hemispheres during the year following El Chichon which is consistent with the Hofmann and Solomon models and which has not been explained by any other mechanism. Larger volcanoes, such as Krakatoa (1883) and Tamboura (1815) put much more material into the stratosphere and we could expect a volcano of such a size perhaps about once a century. A Krakatoa-sized volcano could possibly lead to the destruction of much of the ozone layer over the mid-latitudes, for months or even years.

If the Hofmann and Solomon scenario is reinforced by further laboratory and field experiments, it appears that while sufficient chlorine remains in the stratosphere for an "ozone hole" type of reaction to occur we are vulnerable to catastrophic ozone destruction in mid-latitudes by a large volcano. Whatever we do, stratospheric chlorine is unlikely to sink below 2ppb in the next century, and will probably last longer because of continuing use of CFCs. A stronger Montreal Protocol may be all that can save us.

CAN THE MONTREAL PROTOCOL SAVE US ?

The Montreal Protocol on Substances which Deplete the Ozone Layer had been ratified by about 50 countries up to the end of 1989.

This agreement coordinated by the United Nations Environment Programme requires the Parties to progressively phase down their use of five CFCs (11, 12, 113, 114 and 115) to half the 1986 use, by 1999. Three halon compounds are also required to be controlled to their 1986 consumption levels by 1992. These are all widely used industrial and consumer chemicals with high ozone depletion potentials (ODP). The ODP of CFC-12 is defined as 1.00. Low ODP compounds such as the hydrochlorofluorocarbons e.g. HCFC-22 (ODP = 0.05), are not controlled and may be suitable alternatives to the controlled substances.

As chlorine is at present accumulating in the stratosphere at about 5% per year, the best the Protocol can hope to do is slow this rate of growth, perhaps to 2% per year. That is, the Protocol still allows a build-up of chlorine to continue into next century. Even a slowing of this build-up can only happen if use of other ozone depleting compounds is not markedly increased, and if there is a high rate of compliance with the requirements of the 1987 Protocol.

Recent scientific opinion (UNEP/WMO, 1989) is that the existing ozone layer is not sustainable while chlorine levels remain above 2 ppb and the hole in the Antarctic ozone layer will be an annual phenomenon also while chlorine levels remain above 2 ppb.

Since the Protocol was drafted in 1987, scientific evidence on ozone depletion has strengthened. As a result of the airborne work of 1987 mentioned above, the role of chlorine has been established far more confidently. The report of the Ozone Trends Panel of 1988 has determined how much global ozone loss appears to be attributable to human chemical influences. The ozone holes of 1987 and 1989 were striking in their completeness of ozone loss through the lower stratosphere of Antarctica and their persistence right to the end of November. The hole of 1989 was notable for the rapidity and completeness of its development during September, in spite of a possible moderation of the effect by the coincidence of the 11-year solar maximum in late 1989.

Thus there is strong scientific justification for a substantial strengthening of the Protocol. A major review is scheduled for 1990, and by late 1989 a series of comprehensive international assessments had been completed and subjected to preliminary negotiations directed towards a stronger Protocol. These assessments take into account the scientific, environmental, technological and economic issues.

At the time of writing, January 1990, all the assessment groups have acknowledged the inadequacy of the present Protocol for protecting the ozone layer. However, the Protocol is recognised as an established framework for taking stronger action.

The present Protocol is most strongly directed towards the elimination of the most widely used CFC compounds, CFC-11 and CFC-12. However, these compounds contribute only about 60% of the anthropogenic chlorine presently burdening the stratosphere. Other major contributions are about 15% from methyl chloroform (also known as 1,1,1-trichloroethane) and about 15% from carbon tetrachloride. Methyl chloroform is manufactured in large amounts as a cleaning solvent, and in spite of its relatively short atmospheric lifetime, the large emission rate and the large chlorine content (three atoms per molecule) enhance its effect. Because the atmospheric lifetime of methyl chloroform is only about seven years, compared to times of about a century for the principal CFCs, a phasing out of methyl chloroform will have a much greater benefit in the short term when compared to a similar action for the CFCs.

Because the longer lived CFCs already produced will continue to contribute active chlorine to the stratosphere through the next century, action taken in controlling them will have little benefit until several decades have passed. The elimination of methyl chloroform thus becomes important for near-term protection of the ozone layer.

Within the constraint of no-one wishing to upset the economic and technological infrastructures associated with present CFC use, it appears that much stronger measures are possible. Some of the options now being considered by the Parties as control measures are shown in Figure 4. Continuing with the existing Protocol would lead to the highest chlorine option with a trebling of the atmospheric burden during the next century. Even a 100% phaseout of the presently controlled substances (including halons) would leave the atmosphere with more than double its present amount of chlorine. The only prospects for stabilising the chlorine at levels not much above present levels require stringent controls on methyl chloroform. The only option in Figure 4 for which the chlorine loading of the stratosphere is actually reduced during the next century requires not only phaseouts of CFCs, halons, methyl chloroform and carbon tetrachloride, but also strict controls on the use of HCFC substitutes, such that not more than 20% of the phased out uses of existing CFCs, etc.,

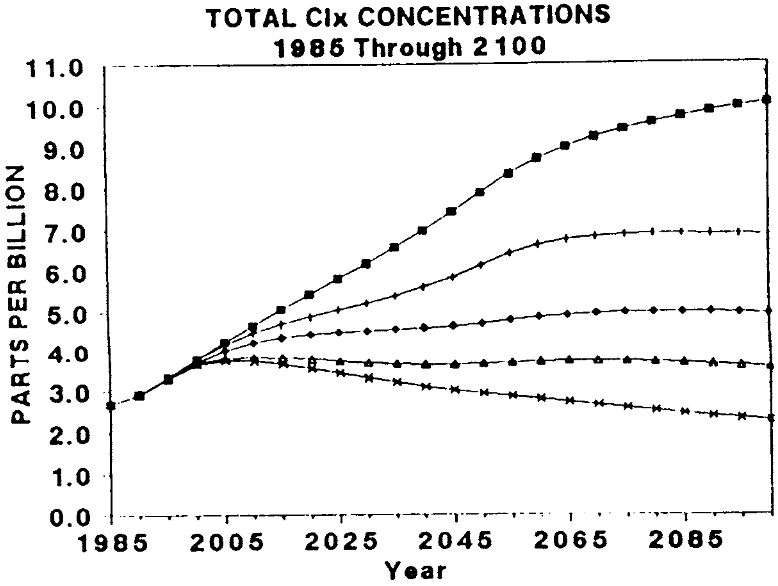

Fig. 4. Five possible futures for the Montreal Protocol and their effects on global stratospheric chlorine (being discussed by the Protocol nations, 1989-1990): 1. Existing Montreal Protocol; 2. CFC phaseout; 3. Methyl chloroform freeze; 4. Carbon tetrachloride and methyl chloroform phaseout; and 5. Maximum of 20% HCFC (av. 0.02 ODP) substitution for CFCs.

are replaced by HCFCs, and even then only an average ODP value of 0.02 is allowed. This in effect cuts out the use of HCFC-22 which has an ODP value of 0.05 and has so far been seen as a part of the technological solution in the short term, to reduce dependence on CFCs 11 and 12.

These predictions of chlorine increase still have a certain amount of optimism associated with them, because they assume 100% global participation in an improved Protocol. So far some of the world's most populous developing countries have not signed or ratified the Protocol and their compliance will be essential if the ozone layer is to be protected. The major problems are of a political or economic type, because of the association of the use of CFCs with advanced industrial development. There is a well-founded perception by the low consuming countries that the problem has been caused by the developed nations, who have already reaped the benefits and so it is appropriate for the developed nations to make the major contribution to a solution.

What the nations of the world must decide is what level of chlorine in the stratosphere is acceptable—should we be allowing indefinite springtime occurrences of the Antarctic ozone hole and continuing our vulnerability to a large volcano as discussed above. The final sentence of the paper by Hofmann and Solomon (1989) should make us think. "A larger eruption than El Chichon occurring in the next half-century or so would therefore provide an important test .... and perhaps determine whether contemporary biological systems may also go the way of the dinosaurs."

The existing Montreal Protocol is inadequate on scientific and environmental grounds for protecting stratospheric ozone, and the technological and economic information now available indicates that a stronger Protocol is both necessary and feasible, and offers the possibility of maintaining the ozone layer as a sustainable resource for mankind and the biosphere.

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TROPICAL ATMOSPHERIC ACIDITY : WHAT NOW AND WHERE TO?

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Our current understanding of acidification in tropical countries is briefly reviewed, and set within the context given by the growing recognition that the tropics are of great importance for the atmosphere globally as a major source of reactive atmospheric chemicals. Key issues are identified, and specific scientific goals for study of tropical atmospheric acidity are outlined, with special reference to relevant parts of the International Global Atmospheric Chemistry (IGAC) program.

INTRODUCTION

Acidification of the atmosphere and acidic deposition to the earth's surface are well known phenomena in Europe and North America, as are the range of adverse environmental consequences thought to result (Goreham, 1989; Cowling, 1989; Falkengren-Grerup, 1989; Likens, 1989; Tamm, 1989). Much effort has been expended in these two major, industrialised regions over the last two decades in order to define the extent, causes and consequences of this atmospheric acidification and resultant deposition : it is now very clear that activities such as generation of electricity from fossil-fuels, use of liquid fuels for transportation, and smelting/refinement of metals are major sources of the atmospheric oxides of nitrogen and sulfur that are involved (Mohnen, 1988; Galloway, 1989; Schwartz, 1989). The emission of these gases on a large scale is a natural consequence of the energy-intensive styles of living enjoyed by many of the industrialised nations. The occurrence of acidification as a very serious environmental problem is now seen to be an equally predictable consequence (Mohnen, 1988; Galloway, 1989; Rodhe, 1989; Schwartz, 1989). Table 1 gives an insight into the extent which human activities have perturbed the global sulfur and nitrogen cycles.

The question of the extent of acidification in other parts of the globe naturally follows (Rodhe and Herrera, 1988; Galloway, 1989; Rodhe, 1989). However, regions outside Europe and North America have received little scientific attention until recently, so answers have been unsatisfactory or unavailable. For this reason the SCOPE project, Acidification in Tropical Countries, was initiated in 1984, culminating

TABLE 1: Estimated Source Strengths for the Global Atmospheric Sulfur and Nitrogen Cycles [Summarised from Moller (1983) and Liu and Cicerone (1984)] [The figures shown are uncertain, and must be considered to be indicative only; units are Tg/yr]

Source	S	N
Anthropogenic	75	25
Natural	72	30

in a workshop in Caracas in 1986. The outcome of the project was publication of the book SCOPE 36 (Rodhe and Herrera, 1988), containing a range of papers summarising what was known about acidification in several tropical countries. It was clear that the question of acidification was very relevant to the tropics—some areas of acidification were identified (for example southwestern China) as were some areas for which the soil/water system was assessed as highly susceptible to acidification. However, a common feature of all the areas investigated was a profound lack of relevant data outside the industrialised countries of Europe and North America.

The purpose here is to continue the focus on acidification in tropical countries initiated by the SCOPE project. The tropical region contains a large population and is the area of the globe where changes in population, energy usage, industrial capacity and agricultural practices are currently most rapid. Table 2 gives an indication of the importance of the tropical region as an area of human habitation, and underscores

TABLE 2: List of Cities between 30°N and 30°S with Population Exceeding 4 Million

Country	City	Population (millions)	Date
Mexico	Mexico	18.0	1986
China	Chongqing	13.9	1983
	Guangzhao	6.8	1983
	Nanjing	4.6	1983
UAR	Cairo	12.0	1984
India	Calcutta	9.2	1981
	Bombay	8.2	1981
	Delhi	5.7	1981
	Madras	4.3	1981
Brazil	Sao Paolo	7.0	1980
	Rio de Janiero	5.1	1980
Indonesia	Jakarta	6.5	1980
Pakistan	Karachi	5.1	1981
Hong Kong	Hong Kong	5.0	1981
Colombia	Bogota	4.3	1982
Peru	Lima	4.2	1981
Nigeria	Lagos	4.0	1980

the expectation that rapid industrialisation and development of tropical regions must lead to large increases in anthropogenic atmospheric emissions of all types. It is essential that the present levels and future likelihood of acidification be assessed so that tropical countries may avoid the acidification problems now so evident at the northern mid-latitudes. What follows is a brief review of the current understanding about acidification in tropical countries, leading on to discussion of areas where further work is required.

INITIAL PERSPECTIVES

The region under consideration encompasses a considerable range of environments, ranging from the borders of the continental, mid-latitude temperate regions, to sub-tropical and tropical deserts, to humid, equatorial-continental, and maritime (island) regions. Thus overall the tropics cannot be considered to be in any sense homogeneous, and we must expect to confront atmospheric chemical questions differently in differing environments within the region. Furthermore, given the peculiarities of the region scientific understanding gained already in the well-studied mid- to high-latitude areas of the northern hemisphere cannot be assumed a priority to be directly transportable to tropical regions.

The need for a broad perspective when considering the tropics can be illustrated by highlighting just a few features peculiar to particular parts of the region. First, we can note examples of particular geographical features, one being that active vulcanism can be found for example in the Indonesian archipelago, which clearly may have local atmospheric significance. Another geographical feature is that acid-sulfate soils occur naturally in the tropics (for example 40% of the world's acid-sulfate soils occur in the Asian region), so that acidification phenomena such as aluminium toxicity leading to fish kills are already experienced in fish farms where pond walls leach high levels of acidity, sulfate and aluminium when subject to heavy rain (Singh, 1982).

Meteorologically, in addition to temperate climates at the mid-latitude extremes the region also includes areas of the wet-dry tropics and humid tropics, plus the ITCZ (Inter-Tropical Convergence Zone). Clearly atmospheric composition may well differ according to whether air masses originate in the northern or southern sides of the ITCZ, or whether rain falls on practically every day, or does not occur at all for months at a time. At some times of the year in some locations the winds have remarkable persistence in direction (e.g. the various trade wind regimes) which may profoundly influence such things as source-receptor relationships.

Given large populations in many countries, the anthropogenic contribution to air chemistry in the tropics must be expected to be very significant, particularly in certain regions, for exmple southwestern China where acidic deposition has been well documented (Rodhe and Herrera, 1988; Zhao *et al.*, 1988; see Table 3). About half the global population resides in the Asian region, for example, and anthropogenic pressure on atmospheric composition and chemistry is likely to increase rapidly with time in regions such as this as population growth rate overall is 3 times that of the US/Europe/Western-OECD countries.

TABLE 3: Precipitation pH Data (Monthly Means) from Four Locations in Guizhou Province, China, in 1984 [Data from Zhao and Xiong, 1988]

Month	Guiyang (urban)	Luizhang (rural)	Keyang (rural)	Shisun (rural)
Jan.	3.9	4.3	4.3	5.9
Feb.	4.0	4.4	4.1	4.3
March	3.8	4.4	4.2	3.9
April	4.1	4.2	4.6	4.7
May	4.0	4.5	4.6	4.3
June	4.5	4.9	5.4	5.1
July	4.5	4.9	5.1	4.7
Aug.	4.1	4.6	4.5	4.5
Sep.	3.7	4.8	4.5	4.4
Oct.	3.8	4.3	4.6	4.5
Nov.	3.7	5.4	4.5	4.7
Dec.	3.4	5.4	4.3	4.7

Compounding increased pressure on the atmospheric environment from population growth, we can expect additional increased pressure from changes in lifestyle, as less developed tropical countries seek economic development and increased standards of living (see Hameed and Dignon, 1988; Dignon and Hameed, 1989, for perspectives on increasing energy use and emissions from the tropics in comparison with other regions). For example tropical Australia as an example of a developed country has per capita atmospheric emission of reactive nitrogen in the form of NO_x from controlled combustion sources (largely power generation and transport) of 14.5 kg/y. For three representative countries of southeast Asia (Thailand, Malaysia and Vietnam) the figure is an order of magnitude less at an average of 1.4 kg/y, similar to India at 1.1 kg/y (Galbally and Gillett, 1988).

Finally, pressure on the environment may be compounded yet again if fertilizer usage in Asia generally increases towards that of developed countries. Again in per capita terms, fertilizer usage as N stands at 59 kg/y for tropical Australia, an order of magnitude above the figures of 4.4 and 5.7 kg/y respectively for the three southeast Asian countries and for India (Galbally and Gillett, 1988).

ATMOSPHERIC COMPOSITION : WHAT WE KNOW

Consider first the local scale/acute-level of pollution, in other words the major urban/industrial centres and their immediate vicinities. The tropical region can probably be considered to have at least some of these localities moderately well-served by observation networks, data bases and quantitative or semi-quantitative understanding of local atmospheric chemical processes : urban smog is a well known phenomenon in a number of places in the region. Bangkok would be an example of such a site. Much of the data gathered by the Environmental Protection authorities or equivalent bodies in such places does not find its way quickly into the international scientific literature, but with appropriate personal contacts can be accessed and perhaps could provide a useful perspective on photochemical pollution in cities across the whole region. It is important that this information be accessed, as photochemical conversion of the acid precursors NO_x and SO_2 is likely to be an important acid production pathway in the tropical atmosphere. As well, however, there also must be many centres with little or no information yet available on even the local scale atmospheric composition.

At the other extreme, that is from the mesoscale up to the scale of the whole region, not very much is known at a quantitative level. However, we can make some general observations.

Tropical regions are characterised by agricultural activities and practices such as rice farming and biomass burning, which provide sources of CH_4, NMHC, CO, NO_x and N_2O to the atmosphere [see 24 papers in *J. Geophys.* (D), Feb. 1988; Clairac *et al.*, 1988; Suman, 1988; Talbot *et al.*, 1988]. In some regions, such as parts of China (see Table 4), large quantities of fuel are also burned in numerous, widely distributed, low level sources giving consequently large area source strengths for SO_2 (Rodhe and Herrera, 1988; Zhao *et al.*, 1988). If the source strengths for all these activities are large enough, then the lower troposphere in such locations may be an important source region for greenhouse gases and acid precursors, as well as exhibiting a high potential for photochemical reactions involving ozone, NO_x and NMHC.

TABLE 4: Energy Produced from Coal in China [from Zhao and Xiong, 1988] [Total energy in tonnes-coal-equivalent]

Year	Total energy	% from coal
1953	54	94.3
1962	165	89.2
1970	293	80.9
1975	454	71.8
1982	619	73.9

In a number of areas the tropics include extensive regions of tropical rainforests where active exchange of gases and aerosols between the atmosphere and the biosphere takes place as a natural process (Ayers and Gillett, 1988a; Zimmerman *et al.*, 1988; Clairac *et al.*, 1988). Further poleward the desert areas, central Asia for example, are a source of soil dust particles, which are transported by prevailing westerlies at certain times to places far afield such as the northwest Pacific region. These soil dust particles also participate in rainwater chemistry along the way, and are thought to be major contributors to the alkaline rainfall that has been observed in parts of India, Bangladesh and perhaps Thailand (Huebert *et al.*, 1988; Khemani *et al.*, 1989 a, b; Mahadevan *et al.*, 1989; Varma, 1989), as may be inferred from Table 5.

TABLE 5: Data from Ten BAPMoN Precipitation Composition Stations in India and one in Thailand; Monthly Volume-weighted Means [Source: World Meteorological Organisation]

BAPMoN site	Mean pH	Length of record
Allahabad	6.82	10/06/77 - 27/12/85
Jodhpur	7.25	01/05/74 - 08/10/85
Kodaikanal	6.02	04/02/77 - 01/12/85
Minicoy	6.50	01/09/77 - 03/12/85
Mohanbari	6.11	01/10/74 - 19/12/85
Nagpur	6.12	05/06/77 - 16/12/85
Pune (weekly)	6.60	12/02/84 - 10/11/85
Port Blair	6.12	27/02/75 - 01/11/85
Srinagar	7.06	05/01/77 - 08/12/85
Visakhapatnam	6.42	03/05/77 - 19/11/85
Kosichang	6.54	15/11/83 - 31/07/85

There are also some highlights from a few individual studies. Examples are the fact that routine measurements of greenhouse gases are now underway at several sites in the tropics, and at least at one tropical site in northern Australia the strong seasonal influence of biomass burning on CO appears in the data record. Other data are available to show that at least in specific instances tropical fires are also strong sources of C_2-C_5 hydrocarbons (Ayers and Gillett, 1988a and refs therein), while tropical vegetation is a strong source of the very reactive hydrocarbon isoprene (Ayers and Gillett, 1988a; Zimmerman *et al.*, 1988; Jacob and Wofsey, 1988).

There are many examples of rainwater studies from the Indian sub-continent (Khemani *et al.*, 1989a,b; Mahadevan *et al.*, 1989; Varma, 1989) consistently showing rainfall to have relatively alkaline pH values of 6 or above are common), while at the other extreme independent studies in northern Australia yield acidic rain, with pH values at the start of the wet season near or below 4 (Galloway *et al.*, 1982; Ayers and Gillett, 1988b). However, in these cases sulfate and nitrate concentrations are each only a few μ equivalents/L, with simple organic acids contributing most of the acidity. The sources of these organic acids remain uncertain (see also Sanhueza *et al.*, 1989).

There have also been a number of studies in southeast Asia looking at the cycling of N through fertilised and unfertilised rice paddies. These have demonstrated clearly the emission of reactive gases from these systems, including large losses of ammonia in Chinese experiments where ammonium bicarbonate is used as fertilizer.

Finally we can note again from Chinese studies that the widespread combustion of coal in low level sources leads to very high atmospheric levels of SO_2, sulfate and ammonium. In the southwest of the country where alkaline substances are not so prevalent in the atmosphere, rainfall acidity is very high, and corrosion, vegetation damage and soil acidification have all been documented (Rodhe and Herrera, 1988; Zhao *et al.*, 1988; Huebert *et al.*, 1989).

KEY ISSUES

Since data on the spatial distributions and temporal variations of trace gases and aerosols are so limited in the tropics a wide variety of key issues may be identified. The emphasis here is on atmospheric acidity, however all the key atmospheric chemistry issues are inter-related, so discussions such as that here need to explicitly acknowledge this fact by at least mentioning all the issues. Indeed the justification for choosing particular issues above others, or for addressing them at all, must be discussed so that priorities may be arrived at and clearly articulated. We simply begin the discussion here by suggesting that the possible influence of atmospheric chemistry in the tropical regions on (a) climate (via effects on radiative transfer); and (b) biological productivity (via direct effects on vegetation of atmospheric oxidants, etc. or via acidic deposition) underpin the following suggested list of key issues.

Thus we suggest that in the tropics there is a lack of quantitative knowledge or understanding as to:

(i) Urban/industrial source strengths of SO_2, NO_x and NMHC;

(ii) Biomass burning source strengths of SO_2, NO_x and NMHC, as well as a range of other gases (e.g. NH_3, CO, aldehydes and acids, etc.) and aerosols (e.g. elemental carbon, etc.);

(iii) Natural emissions of S, N, C and hydrocarbon species;

(iv) The effect on atmospheric composition of agricultural practices (and changes in these practices), including wetland farming, fertiliser use and deforestation;

(v) Regional scale atmospheric photochemistry in the light of (i)-(iv);

(vi) Influence on climate (greenhouse gases, etc.) in the light of (i)-(iv);

(vii) Meteorological control on atmospheric chemistry (note that tropical meteorology itself remains an understudied subject), including such things as consequences of seasonality in persistence of wind flow, and occurrence of precipitation; the role played by strong vertical transport associated with strong convective activity in and outside clouds in parts of the region;

(viii) The role played by tropical oceans as sources and recipients of atmospheric constituents (for example: Is there any connection between the enormous biological productivity of the region's extensive, tropical coral reefs and the atmosphere?); and

(ix) Acidic deposition and the current state of environmental acidification throughout the different parts of the region.

FUTURE DIRECTIONS

Having set the scene and put the question of tropical atmospheric acidity within the wider context of tropical atmospheric chemistry in general, the focus is now returned specifically to the question of what can be done immediately to further our knowledge of current levels of tropical atmospheric acidity and their causes. Four specific directions are proposed as follows:

(i) Development of a comprehensive anthropogenic emissions inventory for NO_x, SO_2 and NMHC covering all countries in the region, just has been carried out for CO_2 on the global scale by Marland *et al.* (1985);

(ii) Detailed experiments leading to a comprehensive understanding of the role played by biomass burning as a source of reactive trace gases and aerosol;

(iii) Observational and modelling studies of photochemical processes and reactivity in tropical air; and

(iv) observational studies (a comprehensive, tropical precipitation chemistry network) leading to a regional workshop on acidification, perhaps modelled on the framework provided by the global SCOPE Acidification in Tropical Countries Project.

The implementation of these suggestions will be best carried out by international co-operation between scientists from the countries in tropical regions, in partnership with experts from the industrialised countries. An example of a concrete framework for achieving such co-operation is given by the International Global Atmospheric Chemistry Program, although other avenues (e.g. via SCOPE or other such sources of international support, or via bilateral/multilateral scientific agreements) should also be pursued.

A summary of the appropriate parts of the IGAC Program is particularly illustrative as that Program is right now at the initiation stage. The relevant parts of IGAC are the two major foci : Natural Variability and Anthropogenic Perturbations of the Marine Atmosphere, and Natural Variability and Anthropogenic Perturbations of Tropical Atmospheric Chemistry.

The first of these foci has as its third project the East Asian/North Pacific Regional Study (APARE) for which the goals are: to assess the transport and chemical transformation of air pollutants over the East Asian region both over land and over the north-western Pacific Ocean; and to determine the deposition of primary and secondary pollutants (sulfate, nitrate and organics) in the East Asian region. While much of this project would be concerned with the northern mid-latitudes, its coverage of southern China and Taiwan ensures that it also has relevance to the question of tropical atmospheric acidity.

The second of these major foci, Natural Variability and Anthropogenic Perturbations of Tropical Atmospheric Chemistry, more obviously deals with issues related to tropical acidity. All four projects under this heading are relevant to the acidification question, particularly the second. The projects and goals are:

Project 1 : Biosphere-Atmosphere Trace Gas Exchange in the Tropics (BATGE)

Goals

- To determine the fluxes of chemicals between representative tropical biological environments (biomes) and the troposphere.
- To determine the factors that control these fluxes.
- To develop the ability to predict the impact on these fluxes of both climatic and land use changes.

Project 2 : Deposition of Biogeochemically Important Trace Species (DEBITS)

Goals

- To determine the rates of deposition from the atmosphere of a range of biogeochemically important chemical species.
- To identify the factors which regulate these deposition fluxes.

Project 3 : Impact of Tropical Biomass Burning on the World Atmosphere

Goals

- Characterise the fluxes of chemically and radiatively important species (especially carbon monoxide, nitrogen oxides, methane and other hydrocarbons, sulfur compounds, and cloud condensation nuclei) from biomass burning into the global atmosphere.
- Assess the consequences of biomass burning emissions on chemical and physical climate. Particular emphasis will be placed on the photochemical formation of tropospheric ozone in the tropics and on other perturbations of the oxidative characteristics of the atmosphere.

Project 4 : Chemical Transformation in Tropical Atmospheres and their Interaction with the Biosphere

Goal

- To understand the photochemistry of the tropical atmosphere and how this is affected by changing gaseous emissions from changing industrial and agricultural developments.

Project 2 has as its initial activity an experiment on the Composition and Acidity of South-East Asian Precipitation (CAAP). This experiment will be based on a precipitation chemistry network in the SE Asian region, from India through China, to south of Australia and the Pacific islands.

The goals of CAAP are:

- To quantify the wet deposition component of the atmospheric cycles of nutrient/reactive species (S, N, C, P and sea-salt species).
- To assess the current state of rainwater acidity across the region and identify the acid/base species involved.

The first year of CAAP will involve identification of appropriate scientists and sites in the Asian region. Emphasis will be placed on sharing or otherwise co-operating with existing facilities in many countries, in particular sites already part of the World Meteorological Organization BAPMoN network, and other sites run by local institutions for nutrient accession studies. Other avenues for support will also be explored; however a strong commitment to utilising existing local resources is intended.

Clearly CAAP or other studies like it, along with additional work of the types outlined in the IGAC projects, is essential if the current extent and future possibility of significant acidification in the tropics is to be assessed.

CONCLUSIONS

Tropical acidification has been identified, especially by the SCOPE project Acidification in Tropical Countries, as a potentially serious consequence of changing patterns of industrialisation and land use in tropical regions. However, the information necessary to assess the current levels of environmental acidification across the whole of the tropics is lacking, although some specific regions have been the subject of intense work in the last few years.

As the importance of tropical emissions and tropical atmospheric chemistry for global atmospheric chemistry has been realised in recent times, it has become clear that considerable effort is needed to provide an understanding of factors affecting the chemistry of the tropical atmosphere at the quantitative level now available for the atmosphere at mid-latitudes. Studies of tropical atmospheric acidity and environmental acidification sit properly within this perspective. Concrete proposals for action in this area are needed now, and possibilities have been illustrated here with reference to appropriate parts of the International Global Atmospheric Chemistry Program, which is currently being implemented.

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THE ROLE OF TRACE ELEMENTS AND FREE RADICALS IN THE PREVENTION OF DISEASE

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Evidence is accumulating that most of the diseases that afflict humanity have their origin in deleterious free radical reactions. These diseases include cardiovascular problems, cancer, inflammatory joint disease, senile dementias, and degenerative eye complaints. The basic process of biological aging is also the result of accumulated free radical damage to the organism. The utilization of oxygen in living organisms produces superoxide ($O_2^{\cdot-}$) and hydroxyl OH: radicals, and the activated oxygen species, singlet oxygen ($^1O_2$) and hydrogen peroxide (H_2O_2). Metabolism of various organic compounds also yields a range of carbon-centered free radicals. These electrophilic species can damage genetic material and oxidize unsaturated fatty acids in cell membranes. Our natural protection against free radicals and activated oxygen compounds involves a sophisticated multi-layered defence screen of enzymes such as catalase and superoxide dismutase, and molecular antioxidants including ascorbic acid (vitamin C) and α-tocopherol (vitamin E). The antioxidant enzymes have, at their active centres, elements such as copper, zinc, iron, manganese and selenium. These, and other trace elements, play a vital role in maintaining our health. Australians in general are depleted in the essential element selenium. Selenium is in the active centre of the enzyme glutathione peroxidase, the function of which is to catalyze the reduction of lipid peroxides and thus maintain the integrity of cell membranes. For all trace essential elements there is a fairly narrow range between essentiality and toxicity. Too high an intake can be just as damaging as too low. Copper, for example, appears to lead to an increased risk of heart disease if the dietary intake is too low, but a fairly small excess may increase the risk of cancer. Research into the role of trace elements in health and disease is in its infancy, and many important questions remain to be answered.

THE NATURE OF FREE RADICALS

A free radical is any atom or molecule that contains one or more unpaired electrons; an unpaired electron being one that occupies an atomic or molecular orbital on its own. Figure 1 shows that π^* 2p (outer) orbitals of some oxygen species (Halliwell and Gutteridge, 1984). Even ground state molecular oxygen (the type we breathe) is a free radical, which explains its high reactivity(oxidation) with many compounds (Halliwell and Gutteridge, 1985). However, oxygen cannot normally accept a pair of electrons from a non-radical molecule during oxidation because spin reversal would need to occur before the vacant spaces in the π^* orbital could be filled. Thus oxygen must accept electrons one at a time, which makes the kinetics of many of its reactions slow, unless it gains two single electrons from another free radical (Halliwell and Gutteridge, 1984; Proctor and Reynolds, 1984). By contrast, singlet oxygen ($^1\Delta_gO_2$) can readily accept a pair of electrons, and its reactions with other molecules are very fast. Note that the peroxide ion is not a radical.

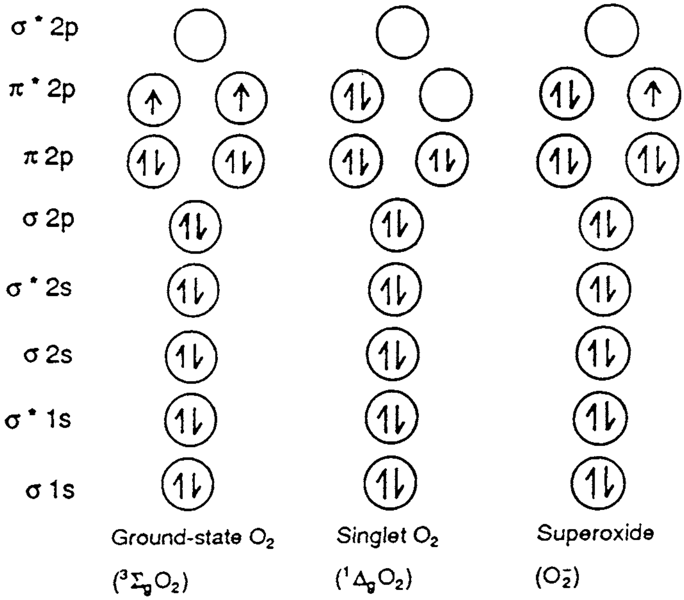

Fig. 1.

Most transition metals are free radicals (Halliwell and Gutteridge, 1985; Gutteridge *et al.*, 1986) (zinc is an exception). Many transition metals can engage in one-electron valency state changes, which makes them excellent redox catalysts, e.g., Fe (II)-(III), Cu (I)-(II), and Mn(II)-(III). Some oxidases use these transition metals as catalysts at their active centres to overcome the sluggish reactions of molecular oxygen (Halliwell and Gutteridge, 1985).

Table 1 lists some free radicals and activated oxygen species that have been implicated in biological processes, plus their approximate half-lives in a biological system (Harman and Pryor, 1984). Some free radicals and activated oxygen species, e.g., hydrogen peroxide, lipid peroxide and the semiquinone free radical, are sufficiently stable to diffuse some distance in cells, whereas others, such as the hydroxyl radical ($OH^{\cdot}$), will react with the first organic molecule they encounter (Pryor, 1986).

Other biologically important free radicals, not listed in Table 1, are nitrogen dioxide and several carbon-centered free radicals. Ozone (O_3), even though it is not a free radical, is a more powerful oxidizing agent than ground state oxygen.

TABLE 1: Approximate Half-lives of Some Biological Free Radicals and Activated Oxygen Species

Species	Symbol	Half-life(s) at 37°C[a]
Molecular oxygen	O_2	$>10^2$
Hydroxyl radical	$OH^{\cdot}$	1×10^{-9}
Superoxide radical	$O_2^{\cdot -}$	1×10^{-6}
Singlet oxygen	$^1O_2$	1×10^{-6}
Hydrogen peroxide	H_2O_2	10[b]
Lipid peroxide	ROOH	$>10^2$
Alkoxyl radical	$RO^{\cdot}$	1×10^{-6}
Peroxyl radical	$ROO^{\cdot}$	1×10^{-2}
Semiquinone radical	$Q^{\cdot -}$	$>10^2$

[a] In biological system.

[b] Short lifetime in presence of catalase or glutathione peroxidase.

However, like many highly reactive non-radical species, most of the reactions of ozone with organic compounds involve free radical production (Pryor, 1986; 1986a).

Photochemical smog contains ozone and NO_x ($NO + NO_2$). Both NO and NO_2 are stable free radicals that react rapidly with biological compounds such as thiols and hemoglobin. Whereas smog usually contains less than 1ppm of NO_x, undiluted cigarette smoke has several hundred ppm; in fact gas-phase tobacco smoke contains 10^{17} reactive oxyradicals per puff (Cross, 1987; Hoffmann, 1987)!

Carbon-centered free radicals are also common in biological systems. Here the odd electron is located on a carbon, rather than an oxygen, atom. Similarly, nitrogen (e.g., amines) and sulfur (e.g., thiols) centered free radicals are commonly encountered.

Lipid peroxidation

Lipid peroxidation is one of the most important free radical-mediated biological processes, and involves both oxygen- and carbon-centered free radicals (Gutteridge *et al.*, 1986; Halliwell, 1987; Halliwell and Gutteridge, 1985). Lipid peroxidation involves attack on a polyunsaturated fatty acid molecule (e.g., linoleic acid) in a biological membrane, leading to decreased membrane fluidity, increased non-specific membrane permeability ("leaky" membranes) and inactivation of some membrane-bound enzymes. Accelerated lipid peroxidation can result from lack of free radical scavengers in the membrane (e.g., vitamin E) or increased oxidative stress as a result of the intake of xenobiotic drugs (e.g., antimalarial drugs) or breathing air with a higher than normal concentration of oxygen (DiGuiseppi and Fridovich, 1984; Fridovich, 1984; Emanual, 1985). The aging process almost certainly involves accelerated lipid peroxidation, and lipid peroxides have been called the "ultimate" toxin because of their long biological lifetime and their highly damaging nature (DiGuiseppi and Fridovich 1984; Emanuel, 1985; Slater *et al.*, 1984).

Lipid peroxidation is a chain reaction. A hydoxyl radical initiates the process by abstracting a hydrogen atom from a polyunsaturated fatty acid (PUFA) side chain (LH) to form water and a carbon-centered free radical ($L^{\cdot}$). This carbon radical then undergoes an internal rearrangement to yield a conjugated diene, which then reacts with molecular oxygen to give a peroxy radical ($LOO^{\cdot}$). The peroxy radical then abstracts a hydrogen atom from a second PUFA side chain to yield another $L^{\cdot}$ and continue the chain reaction, forming a lipid peroxide (LOOH) in the process [DiGuiseppi and Fridovich (1984) and Emanuel (1986)]. A single hydroxyl radical can thus cause a calamitous cascade of membrane oxidation. The antioxidant vitamin E (α-tocopherol, EH) terminates this chain reaction by donating a hydrogen atom and trapping peroxy radicals (Wefers and Sies, 1988; Willson, 1983).

$$LOO^{\cdot} + EH \longrightarrow LOOH + E^{\cdot} \qquad \ldots (1)$$

$$LOO^{\cdot} + E^{\cdot} \longrightarrow \text{non-reactive product} \qquad \ldots (2)$$

Vitamin E is the most efficient known terminator of lipid peroxidation; one molecule of α-tocopherol can protect 1,000 lipid molecules (Pauling, 1986).

Source of biological free radicals

Free radicals in biological systems can originate from a variety of sources. Molecular oxygen can react with a range of small organic molecules, including thiols, hydroquinones, flavins and catecholamines, to yield superoxide radical (Byczkowski and Gessner 1988).

$$O_2 + e^- \longrightarrow O_2^{\cdot -} \qquad \ldots (3)$$

Hydrogen peroxide is a product of $O_2^{\cdot -}$ dismutation:

$$O_2^{\cdot -} + O_2^{\cdot -} + 2H^+ \longrightarrow H_2O_2 + O_2 \qquad \ldots (4)$$

Superoxide dismutase catalyses this rather slow reaction, making it about 10^4 times faster (Halliwell and Gutteridge 1984).

Numerous enzymes generate superoxide radical during their catalytic cycling (Halliwell and Gutteridge, 1984; Byczkowski and Gessner, 1988). These include xanthine oxidase, aldehyde oxidase, and dihydroorate dehydrogenase (Byczkowski and Gessner, 1988). Peroxisome enzymes such as urate oxidase and D-amino-acid oxidase are potent, direct sources of cellular H_2O_2, and the cytochrome P-450 (mixed function oxidase) system, responsible for the metabolism of foreign hydrophobic chemicals, produces both $O_2^{\cdot}$. and H_2O_2 (Freeman and Crapo, 1982; Naqui and Chance, 1986). Microsomal and plasma membrane-associated enzymes such as lipoxygenase and cyclooxygenase are utilized in arachidonic acid metabolism, a reaction that involves carbon-centered free radicals and a heme-bound hydroxyl radical (Freeman and Crapo, 1982; Naqui and Chance, 1986).

The mitochondrial electron transport chain reduction of oxygen proceeds via oxygen free radicals and H_2O_2:

$$O_2 + e^- \longrightarrow O_2^{\cdot} \qquad \text{... (5)}$$

$$O_2^{\cdot} + e^- + 2H^+ \longrightarrow H_2O_2 \qquad \text{... (6)}$$

$$H_2O_2 + e^- + H^+ \longrightarrow H_2O + OH^{\cdot} \qquad \text{... (7)}$$

$$OH^{\cdot} + e^- + H^+ \longrightarrow H_2O \qquad \text{... (8)}$$

Net:

$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O \qquad \text{... (9)}$$

This reaction is catalyzed by the heme-copper enzyme cytochrome oxidase but, despite the high efficiency of this enzyme, some $O_2^{\cdot-}$ and H_2O_2 escape into the mitochondrion and the cytosol (Greenwood and Hill, 1982).

Hydroxyl radical can be produced directly as the result of the reaction between H_2O_2 and a suitable reductant such as glutathione or NADH (Florence, 1984; Florence, 1986):

$$NADH + 2H_2O_2 + H^+ \longrightarrow NAD^+ + 2H_2O + 2OH^{\cdot} \qquad \text{... (10)}$$

In addition, the iron- or copper-catalyzed Haber-Weiss reaction can also produce $O_2^{\cdot-}$ and H_2O_2:

$$Fe\ (III) + O_2^{\cdot-} \longrightarrow Fe\ (II) + O_2 \qquad \text{... (11)}$$

$$Fe\ (II) + H_2O_2 \longrightarrow Fe\ (III) + OH^- + OH^{\cdot} \qquad \text{... (12)}$$

Suitable catalysts for this fairly slow reaction are iron-EDTA and copper-1,10-phenanthroline (Florence, 1984). Vanadium, titanium and cobalt redox couples can also act as catalysts (Halliwell and Gutteridge, 1985). It is debatable, however, if effective iron and copper catalysts exist *in vivo* except in unusual diseases, since the presence of "free" (non-protein bound) iron or copper in biological fluids has never been proven (Cross, 1987; Florence, 1984). Ferritin has been suggested (Halliwell and Gutteridge, 1985; 1986) as a source of free iron, but iron may only dissociate from aged or degraded protein (Florence, 1984). However, by administering salicylate to volunteers, and measuring hydroxylated salicylate derivatives in urine, Halliwell *et al.*, (1985) provided some evidence that hydroxyl radical is produced *in vivo*. A hydroxyl radical bound to iron in a heme molecule ("crypto" hydroxyl radical) may be involved in biological oxidations by cytochrome C and heme oxidases (Florence, 1985; Halliwell and Gutteridge, 1985; Youngman, 1984). An intriguing theory to explain the high rate of cardiovascular diseases in developed countries is based on the much higher iron status of people in affluent societies (Weinberg, 1984).

Singlet oxygen ($^1O_2$) is a potent oxidizer of lipid membranes (Halliwell and Gutteridge 1985; Naqui and Chance, 1986). It can arise in biological systems from photochemical reactions involving prophyrins, flavins, and chlorophylls. It is also formed when hypochlorite reacts with H_2O_2 (Halliwell and Gutteridge, 1986).

$$OCl^- + H_2O_2 \longrightarrow Cl^- + H_2O + {}^1O_2 \qquad \ldots (13)$$

Since hypochlorite is formed during phagocytosis with the enzyme myeloperoxidase, reaction (13) may be relevant *in vivo* (Cross 1987; Halliwell and Gutteridge, 1985).

Hydroxyl radical and singlet oxygen are the most reactive of the activated oxygen species. Their very reactivity, however, may limit the damage they can produce, since they can be scavenged so easily (Cross, 1987; Florence, 1983). For example, intracellularly-produced $OH^·$ was extremely toxic to the marine diatom *Nitzschia closterium* whereas extracellularly-produced $OOH^·$ was completely innocuous (Florence and Stauber, 1986). Apparently, organic molecules in the growth medium or on the exterior of the cell membrane scavenged the hydroxyl radical before any damage could be done. The less reactive, but much more stable, H_2O_2 molecule, on the other hand, can cross cell membranes as readily as water, and could diffuse unimpeded to a vulnerable part of the cell where it could react with a suitable reductant to produce $OH^·$ (reaction 10), leading to damage of, for example, genetic material. Lipid peroxides are similarly very dangerous because of their relative stability and selective reactivity (DiGuiseppi and Fridovich, 1984; Emanuel, 1985).

It should be pointed out that oxygen free radicals, despite being so dangerous if generated in the wrong place or at too high a concentration, do perform several life-sustaining tasks in living organisms (Halliwell and Gutteridge, 1985; Florence, 1983). They are essential to respiration (reactions 5-9) and they are the lethal agents in phagocytosis, where a circulating leucocyte engulfs a pathogenic microorganism and destroys it with a burst (the "respiratory burst") of $O_2^{\cdot -}$, H_2O_2, OCl^- and, possibly $OH^·$ (Halliwell and Gutteridge, 1985). Prostaglandin synthesis and the metabolism of alcohol also involve free radicals, and free radical modification of DNA may be necessary for heritable change (Tomlasoff *et al.*, 1980).

FREE RADICAL SCAVENGERS

Utilization of oxygen

All aerobic organisms have an impressive array of free radical scavengers. Many of these scavengers are designed specifically to protect the organism from oxygen-derived free radicals and other activated oxygen species. Man has the longest maximum lifespan potential of all mammals because he has superb free radical defenses (Tomlasoff *et al.*, 1980; Cutler, 1984; Ono and Okada,1985).

Life apparently arose spontaneously 3.5 billion years ago from basic chemicals produced from the primitive oxygen-free atmosphere by free radical reactions initiated by ionizing radiation from the sun (Harman, 1981). About one billion years later, blue-green algae appeared, and some 1.3 billion years ago the concentration of atmospheric oxygen, produced by the photosynthesizing algae, had reached 1% of the present value, the toxic level for the fermentative anaerobes (Greenwood and Hill, 1982). The anaerobic procaryotes disappeared, except for a few in oxygen-deficient areas, and the sturdier, more complex, and more energy efficient eucaryotes became the dominant cells. Up to 18 times more energy in the form of ATP can be extracted from glucose by oxidizing it to CO_2, compared with anaerobic glycolysis (Greenwood and Hill, 1982).

The utilization of oxygen is, however, not without its problems. The *in vivo* reduction of oxygen produces $O_2^{\cdot-}$, $OH^{\cdot}$ and H_2O_2 (reactions 5-9) which are highly damaging to the cell, and this toxicity increases rapidly if the oxygen concentration becomes much higher than the ambient 20% of the atmosphere. Our margin of safety is narrow. We possess defenses against oxygen toxicity which are sufficient to meet ordinary demands, but which can be easily overwhelmed (Halliwell and Gutteridge, 1984).

Enzymatic defenses

Superoxide dismutase (SOD) removes $O_2^{\cdot-}$ via catalysis of reaction (6) (Ansher *et al.*, 1986). There are three forms of SOD; copper-zinc, manganese and iron (Cutler, 1984; Oberley *et al.*, 1980; Totter, 1980). Copper-zinc and manganese SOD are found in eucaryotic cells (including human), while iron-SOD occurs in bacteria (Tomlasoff *et al.*, 1980; Ono and Okada, 1985).

Copper-zinc SOD consists of two identical sub-units, each having a single intramolecular S-S bond (Florence, 1980). These bonds are essential to the stability of the protein, and are unusually resistant to radiation and chemical attack, a property doubtlessly essential to the efficient functioning of SOD as a free radical scavenger (Florence, 1980).

Two enzymes, glutathione peroxidase and catalase, are used to catalyze the decomposition of H_2O_2. Glutathione peroxidase has four atoms of selenium/mole, and uses glutathione as substrate to reduce H_2O_2 and lipid peroxides (Shamberger, 1984). Catalase is a hemoprotein, and has the advantage that it does not require an auxiliary reductant to destroy H_2O_2. These two enzymes, together with SOD, work in a synergistic fashion to protect lipid membranes and protein sulfhydryl groups, especially in the mitochondrion, from attack by O_2^- and H_2O_2 (Griffin, 1979). Glutathione peroxidase also removes lipid peroxides, and thus inhibits the chain reaction of lipid peroxidation.

Non-enzymatic defenses

The free radical dissociating enzyme defense system is backed up by an array of non-enzymatic defenses (a "strategic reserve"), consisting of small nucleophilic molecules that constitute a multi-layered defense array against activated oxygen species, and which also scavenge carbon-centered free radicals (Halliwell and Gutteridge, 1986; Slater, 1984; Wayner *et al.*, 1987). Some of these antioxidants, with approximate average concentrations in human blood plasma (mgL^{-1}) are: ascorbic acid (vitamin C), 10; reduced glutathione, 400 (whole blood); α-tocopherol (vitamin E), 10; uric acid, 50; β-carotene, 2; and ceruloplasmin, 340 (Ames, 1983; Oliver *et al.*, 1984). Albumin and glucose also have free radical scavenging properties (Halliwell and Gutteridge, 1986).

Vitamin E, like β-carotene, is lipid soluble and occurs where it is most needed, in the cell membrane, where it performs the critical task of terminating the potentially calamitous chain reaction of lipid peroxidation. Ascorbic acid is not lipid soluble, but is a versatile reductant, and reacts synergistically with vitamin E and reduced glutathione (GSH) to produce a powerful antioxidant system (Wefers and Sies, 1988; Florence, 1983; Lathia *et al.*, 1988).

Selenium

Selenium may be the most important antioxidant element in the human body (Shamberger, 1984; Clark and Combs, 1986; Dreosti, 1986). In addition to being essential to the functioning of glutathione peroxidase, it appears to have other more subtle roles, such as enhancing DNA repair mechanisms while delaying cell mitosis (Ip, 1985). This role may allow initiated cancer cells to repair themselves before division, so that the progeny are not malignant. An international study of the selenium content of the diet showed an excellent inverse correlation with cancer incidence (Clark, 1985), as did blood selenium and cancer incidence in Provinces across China (Yu *et al.*, 1985). China is an ideal country to study the epidemiology of cancer and selenium, because the soil (and hence crops) in some areas of China are so low in selenium that a specific type of cardiomyopathy (Keshan Disease) occurs (Shamberger, 1984; Yu *et al.*, 1985), while soil selenium is so high in other Provinces that chronic seleniosis sometimes occurs (Yu *et al.*, 1985).

New Zealanders are particularly low in selenium, and suffer high rates of cancer, cardiovascular disease, asthma, and sudden infant death syndrome (SIDS). Low dietary selenium has also been linked (Robinson, 1988) with inflammatory diseases such as rheumatism, arthritis, and repetitive strain injury, a not unlikely situation considering the free radical scavenging properties of selenium. A study has been initiated in Christchurch Hospital on the relationship between dietary selenium and SIDS (C.C. Winterbourn, private communication).

Selenium yeast is a cheap and convenient dietary selenium supplement for those who are not yeast sensitive.

PROTECTION AGAINST CANCER AND AGING BY DIETARY CONTROL OF FREE RADICAL FORMATION

The possibility that cancer can be minimized and, the rate of aging reduced by the intake of antioxidants (free radical scavengers) has intrigued nutritionists for the past 20 years (Florence, 1983; Gey *et al*,, 1987; Young, 1983). If cancer and aging are indeed caused by oxidizing free radicals, an increase in the concentration of antioxidant in tissues and the circulatory system may offer some protection. Certainly, many serum antioxidants show a decline with age (Young, 1984), and an increase in dietary antioxidants usually brings about an increase in mean lifetime (but not maximum lifespan) in experimental animals (Harman, 1984). Prospective human studies have shown that lower rates of cardiovascular disease and cancer are associated with a high status of serum vitamins A and E, β-carotene and selenium. Several epidemiological studies have indicated that the cruciferous vegetables, cabbage, broccoli, brussel sprouts and cauliflower, protect against cancer (Florence, 1983; Ansher *et al.*, 1986). The active compound in these vegetables is believed to be a dithiolthione (Ansher *et al.*, 1986).

Based on the ascorbic acid content of a primitive vegetarian diet, Pauling (1970) estimated that modern man needs a diet with an average of 2.3g of vitamin C per day. The degree of supplementation required will, of course, depend on individual diet and lifestyle, but 2.3g of vitamin C per day will lead to an ascorbic acid serum concentration about three times the unsupplemented level (Pauling, 1970). Tobacco smoking lowers serum vitamin C (each cigarette destroys about 25mg of ascorbic acid), and some smokers suffer from chronic, sub-clinical scurvy (Pauling, 1986).

Nitrosamines, formed from dietary amines and nitrite (present in preserved food or produced naturally from nitrate), are perhaps the most universal and potent class of carcinogen (Hoffmann, 1987; Lathia *et al.*, 1988; Shamberger, 1984). We are exposed to them continuously, and they are probably the specific cause of gastric (stomach) cancer (Shamberger, 1984). Their formation is catalyzed by dietary compounds such as thiocyanate, iodide and polyphenols, and several nitrosamines are present in tobacco and tobacco smoke (Hoffmann, 1987). Ascorbic acid destroys nitrosamines rapidly and completely, and a combination of vitamins C and E is even more effective (Lathia *et al.*, 1987). A high concentration of free vitamin C in the stomach, intestines, bladder and tissues would seem to be desirable for protection against nitrosamines.

The argument is often put forward that intakes of vitamin C greater than about 150 mg per day are unnecessary because, when more than this is taken, vitamin C often appears in the urine. However, despite its appearance in the urine, much more than 150 mg per day is usually needed to ensure tissue saturation of the vitamin (Pauling, 1986). There are no known ill effects of vitamin C when taken at the rate of 1 to 3 grams per day (Pauling, 1986). The frequently-raised connection between oxalate renal stones and vitamin C is false, and arose from inadequate analytical methods, where urinary vitamin C interfered in the determination of oxalate (Pauling, 1986; Cathcart, 1985).

Australia is one of the few countries in the world where the over-the-counter sale of dietary supplements containing selenium is prohibited. In excess, selenium, like many freely available drugs such as aspirin, is toxic (Shamberger, 1984). But this is not sufficient reason for making it unavailable to the public. The Chinese cancer study (Yu *et al.*, 1985) suggests that the optimum serum concentration of selenium is 250-300 mg/L. In most countries, supplementation, e.g., by low-cost selenium yeast tablets, would be necessary to achieve this serum concentration. If the tablets were prepared to contain, say, 50 μg selenium per tablet, a huge excess over the recommended dosage would be needed to cause even low-grade chronic selenium toxicity (Shamberger, 1984).

FUTURE RESEARCH

The association between disease, especially age-related diseases such as cancer, senile dementias, cardiovascular diseases and arthritis, and free radical formation is rapidly achieving more credence (Cross, 1987; Marx, 1987). Dietary antioxidants may offer protection against these free radical diseases, but research in this area is hindered by lack of funding and by skepticism from parts of the medical profession. With the escalating costs of medical treatment and of caring for an aging population, any simple preventive scheme such as dietary supplementation would have tremendous economic benefits. However, since deterioration from these age related diseases can take place over 30-50 years, supplementation should, ideally, be carried out for the whole of the adult life.

Ideally, all the vitamins and minerals needed for maximum protection from disease would be obtained from food alone. In a modern society, however, this is unlikely to occur because of variations in the nutrient content of food (e.g., soils) are becoming deficient in selenium (Frost, 1983), and because of the increasing addiction of most of the population to "fast" and packaged foods.

Research is urgently needed into the *in vivo* formation and detection of free radicals in humans (Ip, 1985), the existence in biological systems of factors such as free iron and copper that can catalyze the formation of hydroxyl radical, and the role of natural free radical scavengers. Previously unsuspected protective factors such as germanium which is present in garlic and onions (Kidd, 1987), and the dithiolthiones in cruciferous vegetables (Ansher *et al.*, 1986) may be important. There may be many potent, naturally-occurring free radical scavengers that could profitably be used as dietary supplements. Large-scale prospective epidemiological studies on disease and antioxidants should be initiated to establish the role of dietary free radical scavengers, and to determine their optimum intakes for protection against the degenerative diseases.

Preventive medicine, sadly neglected in Western countries, must be taken much more seriously.

TRACE ELEMENTS IN HEALTH AND DISEASE

The first half of this century saw the rapid development of an understanding of the role of vitamins in human health. The second half of the century belongs to trace elements.

There are now 15 trace elements known to be essential to human health and development — arsenic, chromium, cobalt, copper, fluorine, iodine, iron, manganese, molybdenum, nickel, selenium, silicon, tin, vanadium and zinc — and four others —cadmium, lead, lithium and tungsten — may be essential. Because life developed in the presence of *all* the elements, it is likely that more will, eventually, be found to be essential.

While a deficiency of these elements will cause ill health and even death, an excess may be just as dangerous. For every element there is a window of safe intake, between essentiality and toxicity. For some major elements, e.g., calcium, this window is wide but, for most trace elements, e.g. selenium, it is quite narrow. In this respect, trace elements are different to vitamins, especially the water-soluble vitamins, where a large excess over the RDA is usually harmless. Antagonistic effects between trace elements are also common; an excess of one element may severely inhibit the uptake of another. For these reasons, the random use of trace elements as dietary supplements should be viewed with caution, and any dosage well in excess of the RDA should be prescribed only by a professional qualified in this area.

Although research into the role of trace elements in health and disease is expanding rapidly, we are still profoundly ignorant about this vital and fascinating area of biology. Some recent developments are now described.

Iron—In a typical Western diet of meat and vegetables, over 80 percent of the iron absorbed by the body comes from meat. Whereas the bioavailability of iron from grains and vegetables is very low, typically 1-5 percent, heme iron in meat is nearly 40 percent available (Monsen *et al.*, 1978). In addition, heme promotes the absorption of non-heme iron. For this reason, with the exception of some pre-menopausal women and vegetarians, aenemia is rare in Western countries. In third world countries, however, where meat intake is low, aenemia is so prevalent that it is probably the world's most common disease.

Cardiovascular disease is the most common cause of death in Western society, and the rate is very much higher than in the underdeveloped countries. This is usually explained by our higher intake of fat and lack of exercise. Blood cholesterol certainly correlates with the incidence of cardiovascular disease, but it has been apparent for some time that there must be another important contributor to heart disease that has not yet been discovered (Buist, 1989).

Sullivan (1981; 1989) proposed that iron overload is a significant factor in ischemic heart disease, and that the high iron status of Westerners (high ferritin, low unsaturated iron binding capacity) is the cause of their excess rate of heart disease compared with people in underdeveloped countries. This theory would also explain why pre-menopausal women have a much lower rate of heart disease than men, and why the rate after menopause approaches that of men. Iron loss by menstruation or blood donation may be protective against heart disease. This hypothesis would be readily checked by a retrospective epidemiological study of cardiovascular disease in long-term blood donors.

The iron overload theory is consistent with the well known ability of free iron to catalyze biological free radical reactions. Takkunen *et al.*, 1989 however, have criticized the suggestions that high iron status leads to heart disease and cancer (Weinberg, 1984) and claimed instead that high body iron stores may actually *decrease* morbidity and mortality.

Zinc—Zinc is one of the most important trace elements, being involved in the functioning of over 50 enzymes in the human body. Yet it is extremely difficult to find a measurable index of zinc deficiency; the zinc "taste test" is probably as good as any (Stevens *et al.*, 1988).

Some severe cases of anorexia nervosa respond dramatically to zinc supplementation (Stevens *et al.*, 1988; Jones, Bryce-Smith and Simpson, 1984; Dinsmore *et al.*, 1984). Originally it was believed that zinc deficiency in these patients was a result of fasting, but it now appears that low zinc intake may actually contribute to the onset of anorexia (Schauss and Bryce-Smith, 1987).

Copper—Although several studies have set the RDA of copper at 2 mg/day, the role of this trace element in human health is a complete enigma. While some studies have shown unequivocally that a deficiency of copper can lead to high serum cholesterol and an increased risk of cardiovascular disease (Reiser *et al.*, 1987) other work suggests that excess copper causes neurological complaints, hypertension, liver and kidney disfunctions, cancer, and accelerated aging (Pfeiffer and Mailloux, 1987). Certainly, copper is a potent catalyst of lipid peroxidation and free radical reactions. It has been claimed that a typical Western diet does not provide sufficient copper (Klevay *et al.*, 1980) but tapwater from a copper pipe water service typically contains 0.5-1.0 mg copper/litre, so most people would obtain much of the RDA from drinking water alone.

Vitamin C and zinc significantly reduce the bioavailability of copper (Finley and Corklewski, 1983).

Selenium—Selenium has emerged as a vital trace element for protection against cancer, heart disease, and inflammatory joint disease. A large epidemiological study in China, where soil (and hence crop) selenium concentrations vary widely, showed an excellent inverse correlation between serum selenium and cancer rate (Yu *et al.*, 1985). This study suggests that in Australia we could lower cancer rates by as much as 40% if we increased our serum selenium from the present 0.09 mg/litre to 0.25 mg/litre, a value typical of Japan and some South American countries where the rates of colorectal, breast and lung cancer are very low. Recent research indicates that RSI, cot death, and arthritis may also be responsive to selenium supplementation.

Manganese—Although manganese is an essential trace element, an excess can cause a neurological complaint similar to Parkinson's disease (Bell, 1988). Aborigines living on Groote Eylandt, Northern Australia, where the soils are high in manganese, suffer from a Parkinson-like disease (Bell, 1988). Aborigines have a "close-to-the-earth" lifestyle and, on Groote Eylandt, are exposed to high levels of manganese. Manganese appears to exert its neurotoxic effect by catalyzing the oxidation of the neurotransmitter, dopamine (Florence and Stauber, 1988).

Lead—It has always been assumed that only organolead compounds (e.g., tetraethyl lead) can be adsorbed through the skin. Recent work in our laboratories has shown, however, that all lead compounds, such as lead oxide, lead metal powder and lead nitrate, will dissolve in sweat and be transported rapidly through the skin and into the circulatory system (Florence *et al.*, 1988; Beckmann, 1989). Skin adsorption therefore represents another potential hazard when working with this, and possibly other, heavy metals.

Aluminium—The neurotoxic effects of aluminium are now well known. What is not so well known, however, is that some drugs and dietary substances greatly enhance the bioavailability of aluminium. Citrate, for example, increases aluminium absorption nearly 10-fold (Alfrey, 1987). Some deaths have occurred in the USA when patients being treated with large amounts of citrate for kidney stones, have taken aluminium hydroxide gel preparations for indigestion or as an anti-diarrhoeic (Alfrey, 1987). Since citrate is common in many foods, it is important that aluminium intake should be kept to a minimum.

Dietary trace elements play a vital role in human health, yet there is obviously a great deal of confusion about the optimum intake and the safe range of each element. Much research remains to be done, and new essential elements will certainly emerge. For example, in our laboratories we have recently found that human blood contains 1-2 micrograms/litre of platinum. This is an extraordinarily high concentration of such a rare metal. Does it have a biological function? In many chemical reactions, platinum is an excellent catalyst, so perhaps Nature has made use of it in living organisms. These and other unanswered questions ensure that biological trace element research will continue to expand.

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N-OXIDES AND NITROSAMINES: THEIR ENVIRONMENTAL IMPLICATIONS

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The concentration of N_2O has risen steadily. There are many sources for its formation. It gives rise to NO, NO_2 and eventually to HNO_3. NO_2 along with NO is a common pollutant. The two together can give dinitrogen trioxide (N_2O_3) and NO_2 on dimerisation gives dinitrogen tetraoxide (N_2O_4). Pathways for the nitrosation of primary, secondary and tertiary amines are fairly well understood. Kinetics of nitrosation of many secondary amines have been worked out.

Nitrosation of food constituents has attracted considerable attention. This has led to changes in curing of bacon and modifying processing of barley malt for beer production, resulting in reduction in N-nitrosodimethylamine (NDMA) levels. Many nitrosamines have been identified from tobacco. Efforts have been made in recent years to correlate risk to human cancer from exposure to N-nitroso compounds. Also, some understanding of metabolism and mode of action of N-nitroso compounds has been obtained.

Though sensitive and reliable methods of analysis for nonvolatile nitrosamines have been developed, yet the situation regarding the analysis of volatile nitroso compounds is far from satisfactory.

INTRODUCTION

In addition to the possible long term and secondary effects of the oxides of nitrogen on the ecosystem, compounds like nitrates, nitrites, amines and nitrosamines have profound effects on the living systems.

Nitrosamines arise generally from the interaction of nitrous acid with secondary or tertiary amines. Both amines and nitrosating agents are widely distributed in the environment. Many bacteria are capable of reducing nitrate to nitrite. Many types of nitrosatable amines including amino acids are present in the environment. Nitrosation can take place in the human stomach and compounds like thiocyanate can enhance the nitrosation reaction by a few orders of magnitude.

Nitrosamines have been known since nineteenth century but have come into sharp focus eversince Magee and Barnes (1956) showed that nitrosodimethylamine is a potent carcinogen. Besides the occurrence of nitrosatable amines in some food items, tobacco has been found to be a serious source of nitrosamines. Today there is vigorous effort related to the occurrence, formation, analysis, chemistry, metabolism, mode of action and biological activity of N-nitiuso compounds. A resume of these efforts is presented.

N-OXIDES

The concentration of N_2O has been rising steadily and was estimated at 303 ppb in 1984 providing with an atmospheric burden of 1500 × 10^{12}gN. The sources include oceans, combustion of fossil fuels, fertilized agricultural fields, tropical and subtropical forests and woodlands. The principle sinks are photolysis and reaction with $O(^1D)$ as follows:

$$N_2O + h\upsilon \longrightarrow N_2 + O$$

$$N_2O + O(^1D) \longrightarrow 2NO$$

N_2O diffuses upwards from troposphere to stratosphere to give NO as shown above. NO so formed reacts with ozone as below :

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O \longrightarrow NO + O_2$$

$$\overline{\hspace{6cm}}$$

$$O_3 + O \longrightarrow 2O_2$$

The reaction of NO_2 with OH is as follows :

$$OH + NO_2 + M \longrightarrow HNO_3 + M$$

HNO_3 is washed out of the troposphere. A major portion of O_3 destruction takes place through this system. Oxides of nitrogen are also involved in the following reactions:

$$ClO + NO_2 \longrightarrow ClONO_2$$

$$ClONO_2 + h\upsilon \longrightarrow NO_3 + Cl$$

$$NO_3 + h\upsilon \longrightarrow NO + O_2$$

Nitrogen dioxide (NO_2) is a common pollutant along with nitric oxide (NO) by combination process. The two together on combination can give dinitrogen trioxide (N_2O_3).

$$NO + NO_2 \rightleftharpoons N_2O_3$$

Nitrogen dioxide can also undergo dimerisation to dinitrogen tetraoxide:

$$2NO_2 \rightleftharpoons N_2O_4$$

These reactions are more favoured in solution than in the gaseous phase. Thus N_2O_3 and N_2O_4 could accumulate on particulate matter and in polluted atmosphere.

At high concentrations N_2O_3 ($\rightleftharpoons NO + NO_2$) react with amino compounds in solution to produce N-nitrosamines (Challis and Kyrtopoulos, 1978, 1979) :

$$R_2NH + N_2O_3 \xrightarrow{HO^-} R_2NNO + NO_2^- + H_2O$$

where N_2O_4 ($\rightleftharpoons 2\ NO_2$) gives a mixture of N-nitrosamines and N-nitramines.

$$R_2NH + N_2O_4 \xrightarrow{HO^-} \begin{array}{l} R_2NNO + NO_3^- + H_2O \\ \\ R_2NNO_2 + NO_2^- + H_2O \end{array}$$

It has been shown that N-nitrosamine formation from nitrogen oxides has considerable free radical character. Challis *et al.* (1982) reacted N-methylanaline with gaseous NO_2 and observed the formation of a number of products resulting from nitrosation and nitration as given in Fig. 1.

Significant amounts of N-nitrosamines are obtained even when dilute gaseous NO_2 (5 ppm) reacts with heterocyclic amines (such as morpholine, pyrrolidine, etc.). Since the dimerization of NO_2 to $ON\text{-}ONO_2$ in aqueous solution is a facile reaction even at low concentration of NO_2, the existence of lower limit below which N-nitrosamine formation can be ignored therefore seems unlikely according to Challis *et al.* (1982).

N-NITROSATION

N-Nitroso compounds are produced by the acid-catalysed reaction of nitrite with certain nitrogen compounds. N-Nitroso compounds are divided into N-nitrosamines derived from dialkyl, alkylaryl, diaryl or cyclic secondary amines and the nitrosamides derived from N-alkylureas, N-alkylcarbamates and simple N-alkylamides. N-Nitroso derivatives can also be made from cyanamides, guanidines, amidines, hydroxylamines, hydrazines and hydrazides.

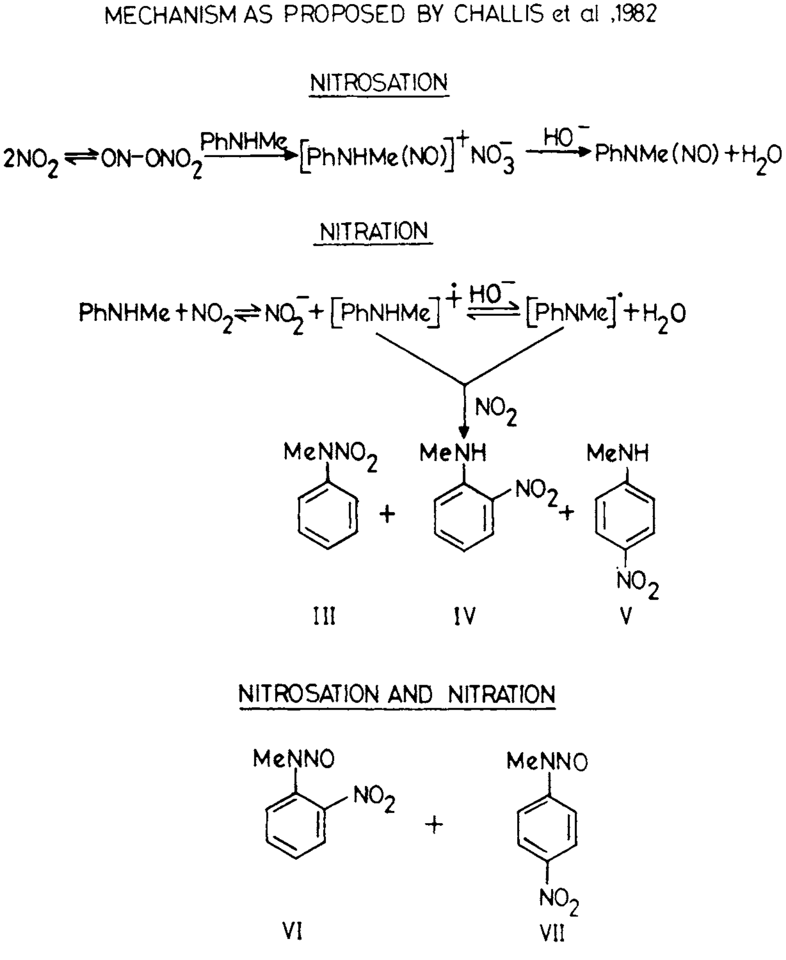


Fig. 1. Two different reagents responsible for nitrosation and nitration.

Possible pathways for the formation of nitrosamines from secondary, tertiary and primary amines are given in Fig. 2. Nitrosation of the secondary amines is of importance due to their occurrence in food, especially after fermentation and cooking. Fish contains relatively large amounts of dimethylamine. Some secondary amines are also used as drugs and pesticides.

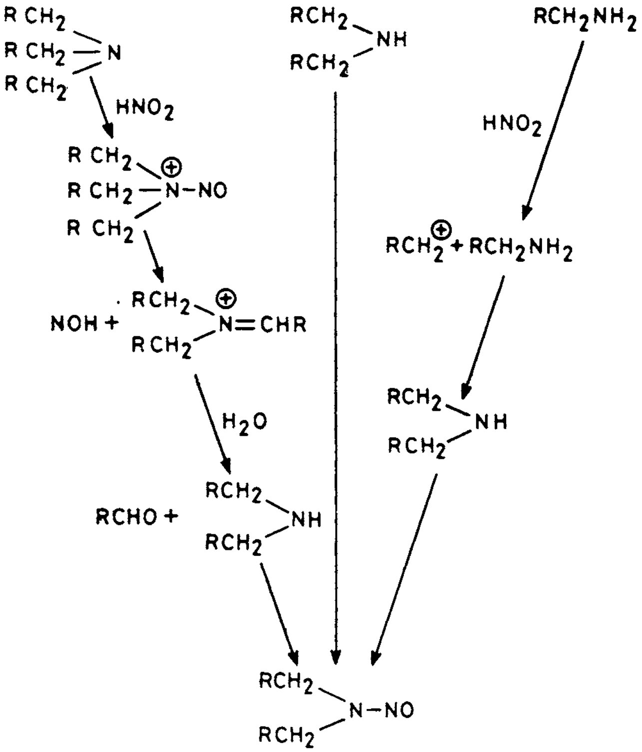


Fig. 2. Proposed pathways for the formation of a nitrosamine from a secondary, tertiary and primary amine (Scanlan, 1975).

Most secondary amines are nitrosated according to the following equations:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

$$R_2NH + N_2O_3 \longrightarrow R_2N.NO + HNO_2$$

$$\text{rate} = k_1\ [R_2NH]\ [HNO_2]^2 \qquad \ldots [A]$$

$$\text{rate} = k_2\ [\text{ amine}]\ [\text{nitrite}]^2 \qquad \ldots [B]$$

Nitrosating agent N_2O_3 is produced from two molecules of HNO_2, the rate of nitrosation is proportional to [amine] and $[N_2O_3]$ i.e. $[HNO_2]^2$

In [A] [nonionized R_2NH] and free $[HNO_2]$ are used and k_1 should be independent of pH, but $[R_2NH]$ and $[HNO_2]$ have to be calculated for each pH. The equation [B] is more appropriate where rate constant k_2 varies with pH although the total concentration of amine and nitrite are used irrespective of species involved. The reaction rate k_1 and k_2 show maximum value at pH 3.4 (pka of HNO_2).

Mirvish (1975) has given the rate constants k_1 and k_2 of a large number of secondary amines. As k_1, values varied only times 34, showing that the nonionized species of the amines had somewhat similar reactivities towards N_2O_3. Therefore if k_1 were constant, k_2 would be a function of pka of the amine and from [A] and [B] above the following expression would emerge:

$$k_2 = \frac{k_1\,[R_2NH]\,[HNO_2]^2}{[\text{amine}]\,[\text{nitrite}]^2}$$

Thiocyanate, bromide and chloride increase the rate of nitrosation. The order of activity is $NCS^- \gg Br^- > Cl^-$. In presence of thiocyanate, the rate of nitrosation of morpholine, N-methylamine, aminopyrine and sarcosine were found to increase.

Tertiary amines may be nitrosated under mild acidic conditions in low yields and also give corresponding aldehydes and ketones. Singer (1980) used tri-n-butylamine (TnBA) for his studies and determined the products using GC-MS as given in Fig. 3.

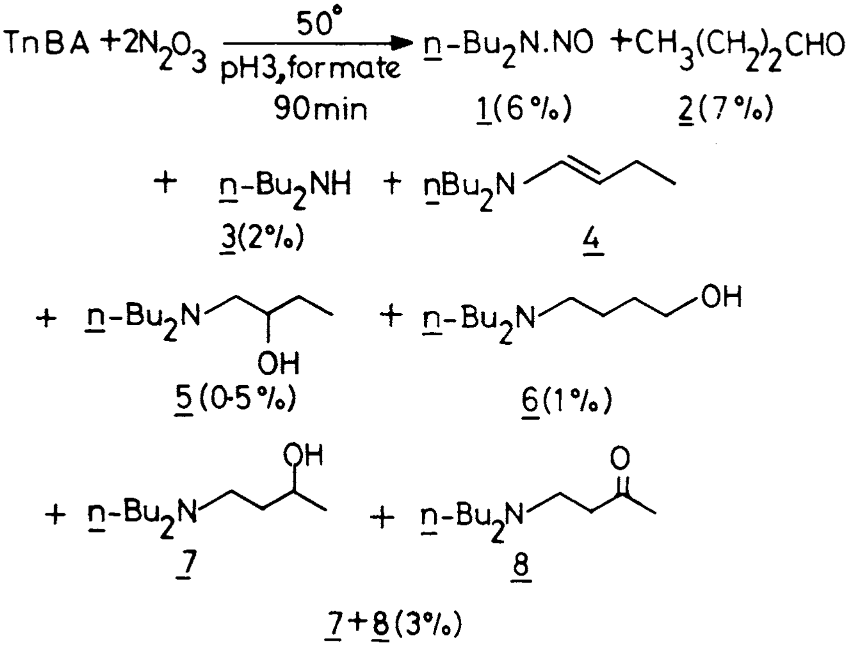
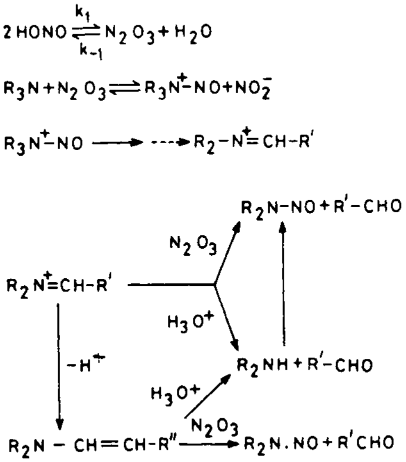


Fig. 3. Products of nitrosation of tri-n-butylamine (Singer, 1980).

A summary of the possible reaction in which N-nitroso ammonium ion is the likely intermediate is given below :



The occurrence and distribution of alcohols and the ketone (5-8) (Fig. 3) have been rationalised by "ω-1" radical cation mechanism by Singer (1980) as shown in Fig. 4.

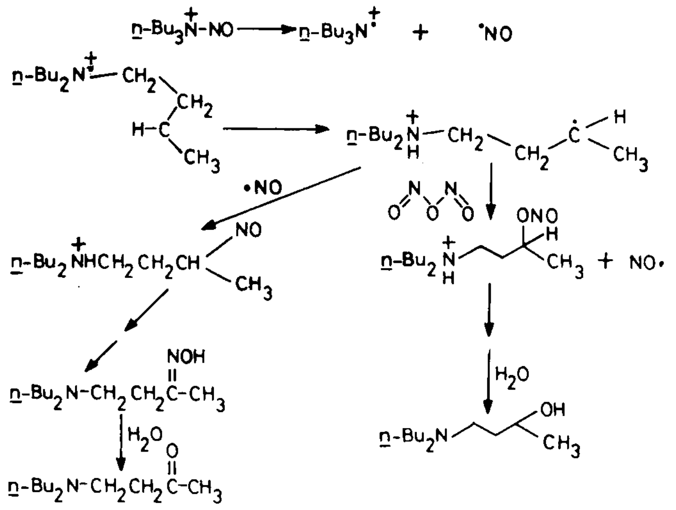


Fig. 4. Possible mechanism of formation of oxygenated products via "ω-1" radical-cation pathway.

FORMATION OF NITROSAMINES IN ORGANIC SOLVENTS

The formation of nitrosamines in aqueous solution has been well established. Iitsuka *et al.* (1985) have studied the formation of nitrosamines in organic solvents as organic solvents are frequently used in food processing, cosmetics and drugs. The organic solvents used by them were chloroform, benzene, ethyl acetate, n-hexane, acetonitrile, acetone and ethyl alcohol.

Their results indicated that the level of nitrous acid in aqueous systems containing organic solvents was higher than that in the control at pH 2-5. Acceleration of the formation of the nitrosamines in the aqueous system containing organic solvents may be due to the increase in available nitrous acid level in the pH range. It was concluded that most organic solvents suppress ionization of nitrous acid and accelerate the nitrosation of secondary amines. The secondary amines also dissolved readily in organic solvents as the unprotonated forms which are the reactive forms for nitrosation. Suppression of protonation of the amines in non-aqueous solvent systems or aqueous systems containing organic solvents may also have contributed to the accelerated formation of the nitrosamines.

FORMATION AND OCCURRENCE OF NITROSAMINES IN FOOD

In foods, the nitrosation of food constituents usually takes place through nitrous anhydride, which is formed from nitrite in acidic, aqueous solution. In some cases nitrosodimethylamine formation takes place as a result of direct fire drying process. In this case, oxides of nitrogen in the drying air nitrosates amines in the food being dried.

Nitrosodimethylamine (NDMA) is the most commonly occurring volatile nitrosamine while nitrosopyrrolidine (NPY) occurs to lesser extent. Cured meats, cooked bacon, beer, some cheeses, nonfat dry milk and fish have been shown to contain nitrosamines. The volatile nitrosamines generally occur in the µg/kg range. There are possibly several hitherto undetected volatile nitrosamines present in food materials and large amounts of nonvolatile nitrosoamines.

Of the various N-nitroso compounds, N-nitrosamines have been studied most extensively in foods and reviewed by Scanlan (1983). In 1956, Magee and Barnes described the induction of liver tumor in rats by feeding NDMA. During the last 33 years a large number of nitrosamines have been tested for their biological effects and found to be carcinogens. This has been a cause for continuous concern.

As has been discussed before the rate of nitrosation is pH dependent and is dependent on the total amounts of nitrite and amine as shown below:

$$\text{Rate} = k_1 \,[\text{amine}]\,[\text{nitrite}]^2$$

Since the unprotonated amine reacts with the nitrosating agent the rate of nitrosation for a secondary amine is inversely proportional to amine basicity. Morpholine (pka 8.7) forms nitrosamine considerably faster than does diethylamine (pka 10.7) at the same pH. The pH optimum for most secondary amines for nitrosation is between 2.5-3.5. The range is sufficiently close to the acidity of the human stomach to allow nitrosation to proceed there.

The chemistry of food is complex as the composition of food constituents is very complicated. Nitrosation of food constituents is affected by the concentration and nature of nitrosatable substances, the concentration and type of accelerators and inhibitors and factors such as time, temperature, pH, etc.

The picture is further obscured as adequate analytical methodology exists only for volatile nitrosamines but not for nonvolatile ones. Although methods are available for the determination of a few nonvolatile nitrosamines, but generally analytical methodology for nonvolatile nitrosamines and other N-nitroso compounds is still in early stage of development.

Some data as compiled by Scanlan (1983) on some food materials will be summarized in the following:

Cured meats

Since sodium nitrite is used for curing meats and sometimes sodium nitrate is also added, this category of food has received much attention and also cooked bacon has been subject of much investigation. In cooked bacon NPYR, and usually NDMA and N-nitrosohydroxypyrrolidine (NHPYR) are the most consistently occurring nitrosamines. Some of these levels have been compiled by Gray (1981). Much of the volatile nitrosamines (60-95% of total NPYR and 95-100% of NDMA) are lost in the fumes when bacon is fried (Gough *et al.*, 1976). With restriction on the levels of nitrite and increased amounts of ascorbate in bacon curing in the United States, the NPYR levels have decreased from 1971 onwards. Cured meats other than bacon contain NPYR, NDMA, N-nitrosodiethylamine (NDEA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR) and N-nitrosoproline (NPRO). Though the levels of these nitrosamines are less than 1 μg/kg when present.

Dairy products

A number of cheeses and dried dairy products have been shown to contain low levels of NDMA. It is, however, intriguing why some cheese samples contain NDMA and others not.

Fish

As many species of salt fish contain considerable amounts of dimethyl and trimethylamines, fish has been a subject of much examination for volatile nitrosamines. Gough *et al.* (1978) reported NDMA levels of 1-10 μg/kg in over 1/3rd of nearly 60 samples of uncooked fish examined by them. Some of the samples of cooked fish did not contain NDMA perhaps due to the volatility of the compounds. Nevertheless, the mode of cooking can influence the NDMA content (Matsui *et al.*

1980). In their studies Matsui *et al.* showed that NDMA content in fact increased during broiling by a factor of 2-3, possibly due to the interaction with oxides of nitrogen produced from the gas range.

Beer and Malt

The presence of NDMA in beer has been reported by various workers. Mangino *et al.* (1981) have summarized NDMA levels found by workers in different parts of the world. The source of NDMA in beer is barley malt, wherein it is produced from reaction of oxides of nitrogen and barley malt alkaloids during the direct- or fire-drying of malt. By modifying the firing kilns to indirect ones and by the use of sulphur dioxide during drying, considerable reduction in the NDMA levels has been achieved. The nitrosatable amines which occur in barley malt have been studied by Mangino *et al.* (1981) and Mangino and Scanlan (1982). Both hordenine and gramine are biosynthesised in green malt during fermentation. Possible mechanism for the formation of NDMA from these two alkaloids during direct firing process are given in Fig. 5 (Scanlan, 1983).

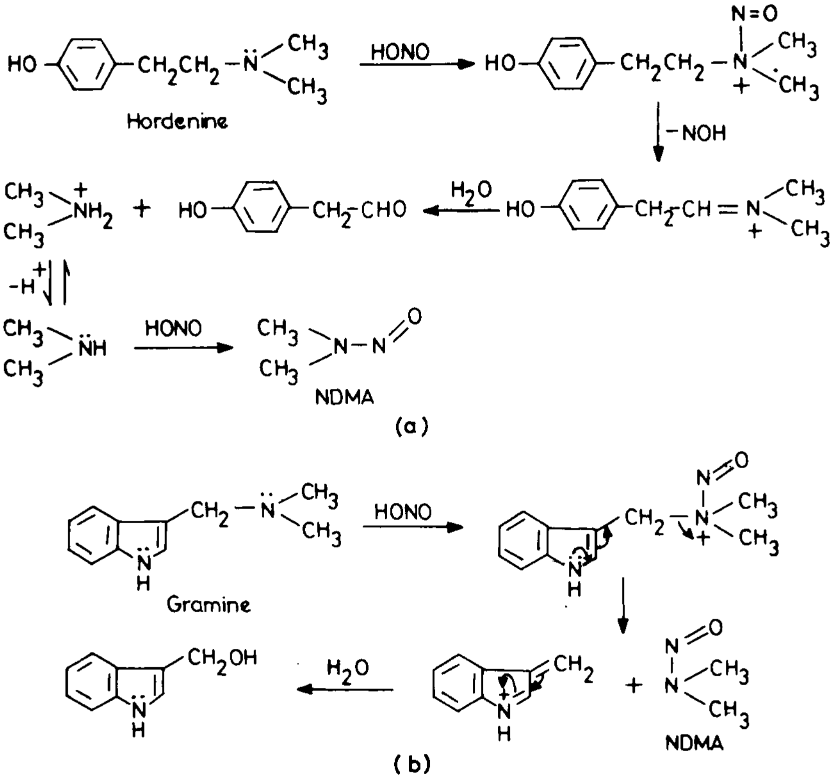


Fig. 5. (a) NDMA Formation from hordenine via nitrosative dealkylation and (b) Possible mechanism for NDMA formation from gramine (Scanlan, 1983).

Baby bottle rubber nipples

In the recent examinations of baby bottle rubber nipples and pacifiers (Preussmann *et al.*, 1981), the presence of several nitrosamines like NDMA, NDEA, N-nitrosodibutylamine (NDBA), NPIP and 1-nitrosomethyl phenylamine (NMPHA) was observed. The concentrations ranged from 1-230 µg/kg. The source could be vulcanizing retardants and nitrosamines in contaminated air.

From a recent compilation of estimated exposures of humans to nitrosamines in the United States by the National Academy of Sciences in 1981, Scanlan (1983) has adapted the data (Table 1). From Table 1 it is clear that besides food there is a large exposure to a variety of nitrosamines from cigarette smoking.

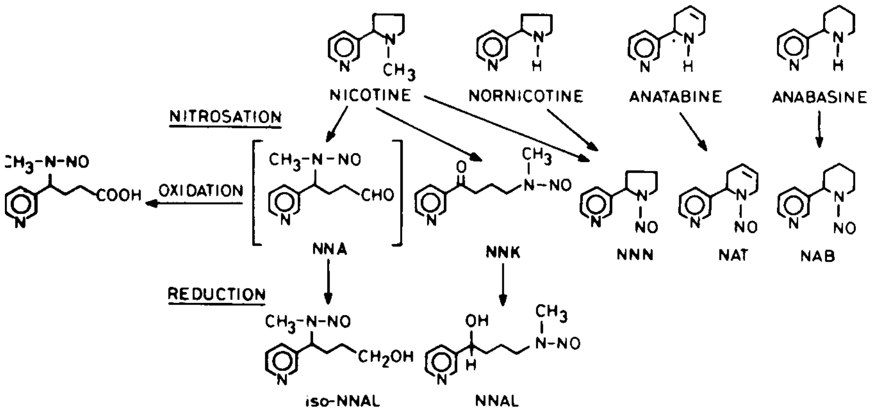
TABLE 1: Estimated Relative Exposure of U.S. Residents to Volatile N-Nitroso Compounds (Scanlan, 1983)

Nitrosamine*	Source	Route	Daily exposure (µg/person/day)
SEVERAL	Cigarette smoking	Inhalation	17
NDMA	Beer	Ingestion	0.3 – 0.97
NDMA, NMOR, NDEA	Automobile interiors	Inhalation	0.2 – 0.5
NDELA	Cosmetics	Dermal	0.41
NPYR	Cooked bacon	Ingestion	0.17
NDMA	Scotch whiskey	Ingestion	0.03

* NDMA = N-nitrosodimethylamine;
NMOR = N-nitrosomorpholine;
NDEA = N-nitrosodiethylamine;
NDELA = N-nitrosodiethanolamine;
NPYR = N-nitrosopyrrolidine.

Tobacco specific nitrosamines

In recent years there has been much activity in identifying N- nitrosamines from tobacco. Nicotine and minor nicotine alkaloids are considered to be the major habituating agents in tobacco products. They also give rise to carcinogenic, tobacco specific N-nitrosamines (TSNA). Some of these nitrosamines have been characterised in tobacco and/or tobacco smoke (Fig. 6). The most potent carcinogens amongst these are N-nitrosonornicotine (NNN) and 4-(methylnitrosamino)-1-(3-pyridyl)butanone (NNK). N-Nitrosamines were detected, characterised and quantified in the commonly used chewing tobacco in India (Bhide *et al.*, 1985) and in the saliva of the users (Sipahimalani *et al.*, 1984). According to Hoffmann *et al.* (1989) the levels of NNN and NNK in chewing tobacco amount to 0.67-8.2 ppm and 0.1-0.4 ppm; those in Snuff range between 0.01-135 ppm and 0.1-13.6 ppm respectively.



NNA	4 - (METHYLNITROSAMINO)-4-(3-PYRIDYL) BUTANAL
NNK	4 - (METHYLNITROSAMINO)-1-(3-PYRIDYL)-1-BUTANONE
NNN	N'- NITROSONORNICOTINE
NAT	N'- NITROSOANATABINE
NAB	N'- NITROSOANABASINE
iso-NNAL	4 - (METHYLNITROSAMINO)-4-(3-PYRIDYL) BUTANOL
NNAL	4 - (METHYLNITROSAMINO)-1-(3-PYRIDYL)-1-BUTANOL

Fig. 6. Nitrosation of nicotine.

These amounts exceed by at least 2 orders of magnitude the levels of carcinogenic N-nitrosamines in other consumer products.

In beetle quid with tobacco, both TSNA and Areca-derived nitrosamines are formed. The chemical nature of nitrosamines from arecoline are given in Fig. 7. These are nitrosoguvacoline (NG) N-nitrosoguvacine (NGC), 3-(methylnitrosamine) propionaldehyde (MNPA) and the powerful carcinogen 3-(methylnitrosamino) propionitrile (MNPN). Their concentration in saliva of beetle quid chewers is reported to contain 1.2-38 ppb (NNN), 1.0-2.3 ppb (NNK), 2.2-350 ppb (NG), 0.0-30.4 ppb (NGC) and 0.5-11.4 ppb MNPN (Hoffmann *et al.*, 1989).

In studies carried out on Indian tobacco (Tricker *et al.*, 1989) for N-nitroso compounds, a number of volatile nitrosamines viz NDMA, NMEA, NDEA, NDPA, NDBA, NPIP, NPYR, NMOR, nonvolatile nitrosamines and tobacco-specific nitrosamines viz. NAB, NAT, NNN, NNK and iso-NNAL have been determined in a variety of tobacco products including chewing tobacco, *zarda*, *kiwam*, *masheri*, *bidi*, chutta and pipe tobacco. The estimated consumption figures on daily usage basis of some tobacco products are given in Table 2.

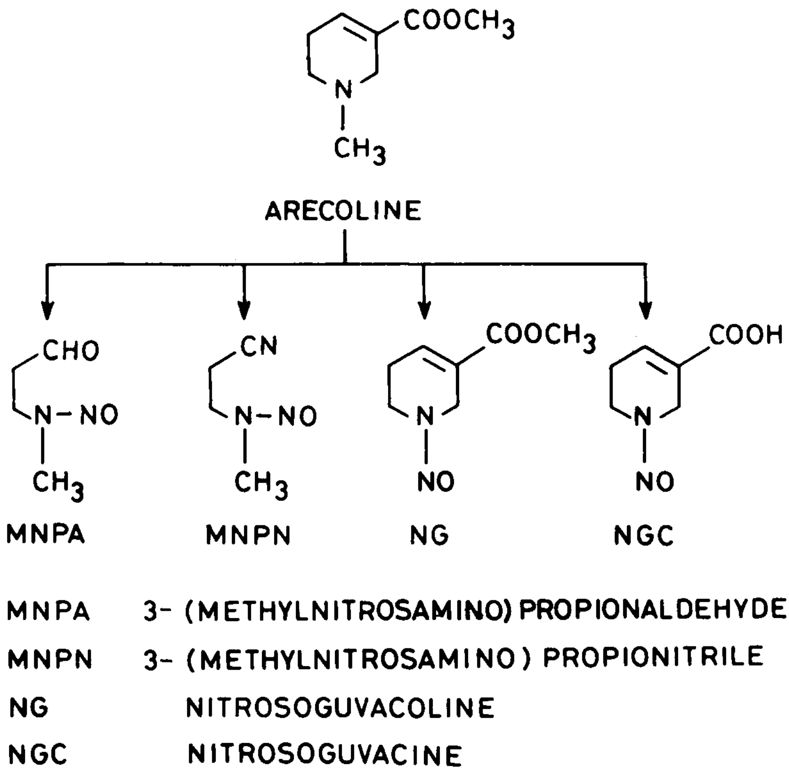


Fig. 7. Areca derived nitrosamines.

TABLE 2: N-nitroso Compounds in Some Indian Tobacco Products (Tricker *et al.*, 1989)

Tobacco type	Average usage (g/day)	Mean daily exposure (μg/day) Total NA	NNN & NNK
Zarda	10	405.3	174.5
Kiwam	3	36.0	14.6
Masheri	2	15.0	3.9

NA = Nitrosamines;

NNN = Nitrosonornicotine;

NNK = 4-(methylnitrosamino)-1-(3-pyridyl)’butanone.

RISK OF HUMAN CANCER

Surveys have been carried out in some countries to estimate the average per capita exposure to N-nitroso compounds (Forman, 1987). In Table 3 estimates from a few countries are given. The present intake is likely to be sufficiently lower as many changes in manufacture of bacon and beer have taken place lately. Nevertheless, it is now apparent that many food items contain unidentified N-nitroso compounds. This is due to the fact that improved methods are now being developed to determine the total concentration of nitroso compounds in foods, including both volatile and nonvolatile compounds. Some of the hitherto unidentified compounds are likely to be nonvolatile nitrosamides which are often extremely unstable and likely to be broken down during cooking. Until constituent compounds can be isolated, chemically characterised, and biologically tested it will not be known whether or not these are carcinogenic. However, some correlations have been made from the available evidence. Association between consumption of beer and oesophageal, colorectal and renal cancers has been established. Human epidemiological studies have concentrated largely on the role of N-nitroso compounds in relation to oesophageal and gastric cancers. There is some evidence for an increased risk of stomach cancer associated with consumption of nitrite cured meat. There is also some evidence for the risk factor when salt pickled vegetables and salted fish are consumed by Chinese and Japanese populations. Specific mutagenic N-nitroso compounds, especially non-volatile nitrosoamides have been isolated from items like pickled Chinese cabbage.

TABLE 3: Estimate of Daily Intake (μg) of Volatile N-nitrosamines in Different Countries (Forman, 1987)

Country	Estimate	Major sources	Reference
UK	0.53*	Cured meats (81%)	Gough *et al.* (1978)
Japan	2.26	Dried fish (72%)	Maki *et al.* (1980)
Germany (FRG)	1.23	Beer (57%) Cured meats (17%)	Spiegelhalder *et al.* (1980)
Holland	1.0	Beer (90%)	Stephany and Schuller (1980)

* Beer not included.

The risk from endogenous formation of N-nitroso compounds can be of equal importance to that from the exogenous N-nitroso compounds. The two main precursors, nitrosating agents and nitrosatable amino substrates are both likely to be found in abundance in the diet. Nitrite occurs in certain cereal products, root vegetables, non-volatile beverages and as a curing agent in meats and some cheeses. Nitrite occurs principally in vegetables like lettuce, beetroot and spinach, in contaminated drinking water and from its use as curing agent. Nitrate acts as a nitrosating agent after its reduction to nitrite by bacterial microorganism found normally in the saliva and in ingested gastric juice. It is estimated that nearly 5 percent of ingested nitrate is converted into nitrite in this way. In many countries, during past few decades the nitrate concentration of certain vegetable crops as well as nitrite levels of drinking water supplies have been on the increase. This has resulted due to the extensive use of inorganic fertilizers from which the nitrate can be leached and run off into surface and ground water and also absorbed by crops.

As is known, there is a wide variety of food items containing amino compounds and of these secondary amines and alkyl amides are the most likely substrates for nitrosation. Many types of fish are rich in these substances as also are pork-based products, coffee, tea, beer, wine, evaporated milk and certain spices. There is, however, no *a priori* reason to expect that simple cause and effect relationship between the presence of a precursor and induction of cancer exists. It is known for instance that diets with a high level of nitrate like vegetables may also contain protective and anticarcinogenic agents. Vitamin C can act as a protective agent as it acts as a competitive substrate for nitrite. Other inhibiting agents can be tocopherol, indoles, tannins and other polyphenolic compounds. Shephard *et al.* (1987) have reviewed the assessment of the risk of formation of carcinogenic N-nitroso compounds from dietary precursors in the stomach and have concluded that ureas and aromatic amines present potentially important risk factors in gastric cancer. The risk contribution of amines (including the proteins), guanidines, primary amino acids is uncertain. The risk factor due to alkylamines (primary and secondary), secondary amino acids is most probably negligible. They have recommended that for future investigation, the sources and levels of arylamines and ureas in the diet should be studied comprehensively and the carcinogenic potencies of key nitrosated products should be determined more precisely. Shephard *et al.*, (1987) have given estimates of relative risk posed by various nitrosatable precursors as shown in Fig. 8.

METABOLISM AND MECHANISM OF ACTION OF N-NITROSO COMPOUNDS

It is well established that N-nitroso compounds are not active as such, but require *in vivo* activation. The formation of an alkylating electrophile to interact with nucleophiles in DNA (and other biopolymers) to form stable adducts such as alkylated purines and pyrimidine bases appears to be a requirement. The alkylation of genetic material is probably the initiating event in carcinogenesis. The important role of α-hydroxy-N-nitrosoamines as proximate carcinogens (Fig. 9) has been confirmed by chemical and biological investigations.

A summary of present knowledge of human exposure to environmental N-nitroso compounds has been attempted by Preussmann (1984), and is given in Fig. 10. Although a qualitative picture does emerge, yet quantitation of endogenous exposure for risk estimation has not been possible so far. However, some recent developments may serve as a breakthrough in this area.

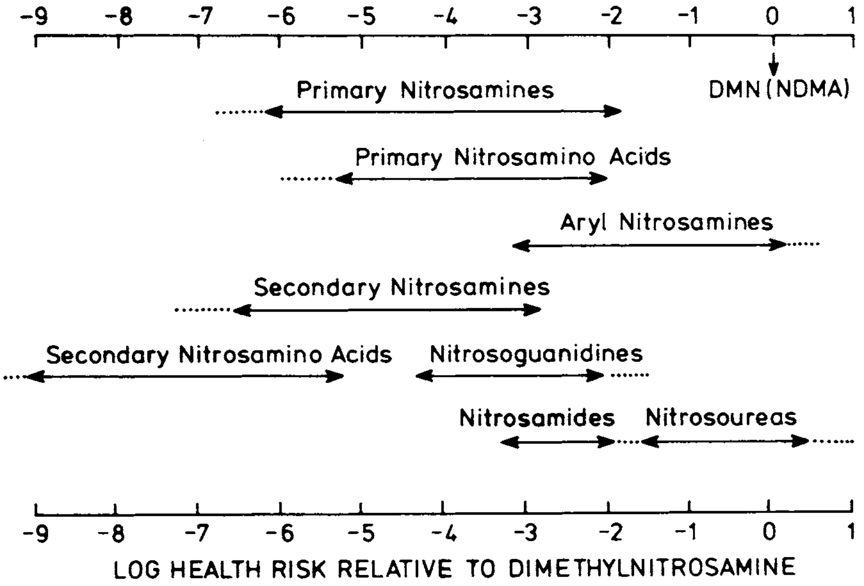


Fig. 8. Relative risk posed by dietary intake of nitrosatable precursors as compared to risk from dietary intake of dimethylnitrosamine (→Shows high nitrite concentration; ←shows low nitrite concentration; and . . . shows low pH) (Shephard *et al.*, 1987).

ANALYTICAL PROCEDURES

Sen and Kubuacki (1987) have recently reviewed the methods that are available for the determination of total N-nitroso compounds, N-nitrosamides, N-nitrosamino acids and a variety of other nonvolatile N-nitroso compounds in foods and beverages. They have divided the methodologies into two broad categories: (a) methods for volatile N-nitrosoamines (VNA) and (b) methods for nonvolatile N-nitroso compounds (NVNC). Though the methodologies for VNAs have been well developed, but the situation with respect to NVNCs is not very satisfactory.

Hotchkiss (1981) has reviewed the analytical status with respect to the volatile N-nitrosamines. The VNAs can be extracted or distilled from the sample and after

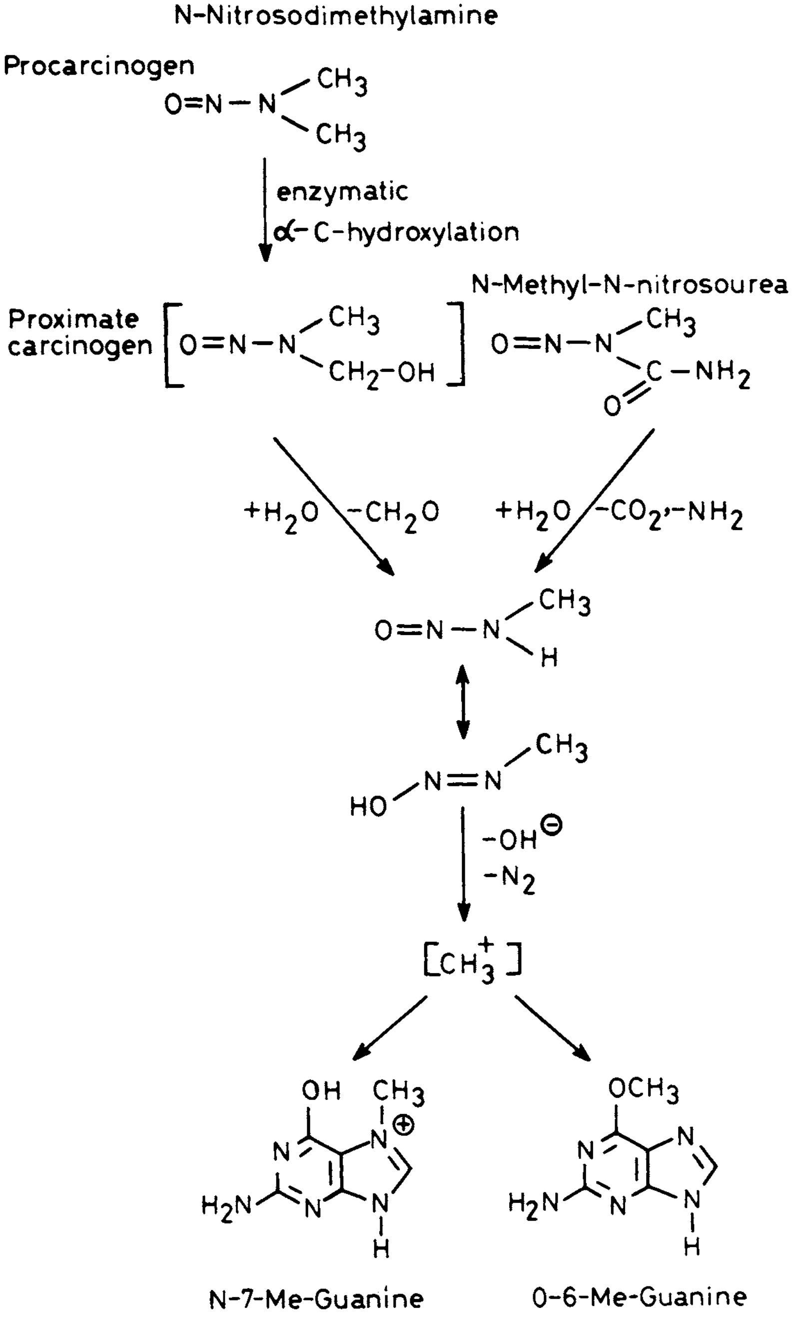


Fig. 9. Metabolism of N-nitroso compounds.

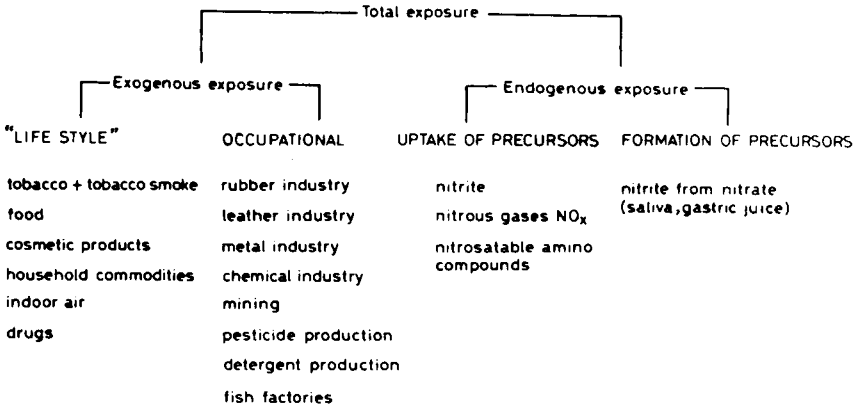


Fig. 10. Environmental N-nitroso compounds and human exposure.

suitable cleanup and concentration can be submitted to separation techniques. Chromatography has been used for quantitative and qualitative estimation and identification on VNAs. Use of TLC has been made for separation and densitometry of the fluorescent derivatives of VNAs in cooked bacon described for quantitative estimation. Gas chromatography is the method of choice for the separation of volatile NAs. In addition to packed columns, open tubular columns have been used most often in conjunction with mass spectrometry. The use of fluorescent derivatives of the amine produced by nitroso group cleavage has been made to detect and quantitate NAs in foods. Derivatisation has also been used to yield nonvolatile NAs amenable to gas chromatography.

The flame ionisation detector has found limited use in the determination of NAs in food because of lack of specificity. Alkali flame ionisation detector (AFID) or Coulson electrolytic conductivity detector (CECD) have also been used as a selective detector for volatile NAs in foods. NAs themselves are not amenable to electron capture detection but can be derivatised to electron-capturing species. Commercially available thermal energy analyser (TEA) is highly selective for N-nitroso compounds. TEA can be used as a detector for both gas chromatography (GC-TEA) or liquid chromatography (HPLC-TEA).

For TEA, N-nitroso compounds after exiting from chromatographic column, enter a flash heater and a catalytic pyrolysis chamber where the relatively weak N-N bond is ruptured. The nitric oxide produced is swept through a cold trap (–150°C) where organic compounds are frozen out. The emerging nitric oxide is made to react with O_3 in a small chamber to produce an energy emission in the near infrared. This emission is detected by a photomultiplier tube, amplified and recorded. The response is proportional to N- nitroso group concentration in the original sample. The

GC-TEA system has been compared with GC-CECD, TLC and GC-MS for determination of volatile NAs in fishmeal and fried bacon by Fine *et al.* (1976). GC-TEA was found to be atleast 50 times more sensitive and warranted less cleanup of the sample while GC-TEA give excellent analytical data, yet mass spectrometry (MS) has been considered the most reliable procedure for confirming the presence and identity of NAs. The maximum sensitivities reported for MS confirmation of NAs in food range over 4 orders of magnitudes.

The analytical methodologies for VNA have been well developed as discussed above but the situation with respect to methodologies on NVNCs is not quite as satisfactory.

In principle any nonvolatile compound in food with an NH group can be nitrosated to give NVNC. The concentration of most of these may be of no consequence. However, the most important NVNCs in foods appear to be N-nitrosamino acids—mainly N-nitrosoproline (NPRO), N-nitrosothiazolidine-4-carboxylic acid (NTCA) and N- nitrososarcosine (NSAR). The methods reported for the determination of total N-nitroso compounds of foods fall in two categories. In the first category, use is made of the UV photolysis of the compounds to nitrous acid (HNO_2) and calorimetric determination of the liberated nitrite. In the second category, the N-nitroso compounds are cleaved chemically by treatment with HBr and the liberated nitrosyl bromide of nitric oxide (NO) is then measured colorimetrically or by using a chemiluminescence detector.

The most abundant of all the NVNCs are the N-nitrosoamino acids of which NPRO is the most common. Also NPRO is believed to be one of the precursors of NPYR in fried bacon. Most of the methods for the determination of N- nitrosoamino acids in foods are based on GLC-TEA analysis of suitably volatilised derivatives and a few use HPLC-TEA technique. The separation of N-nitrosamino acid anions can be achieved by ion-exchange or reverse phase HPLC. The GLC-TEA technique offers some advantages.

Of all the NVNCs, the nitrosamides have proven to be the most difficult to determine in foods. Since most N-nitrosamides are nonvolatile and thermally unstable they cannot be analysed by GLC and MS. Some recent modifications in TEA instrument have given encouraging results and allowed sensitive detection of some of the N-nitrosamides by GLC-TEA. There is, however, great deal of scope for developing sensitive methodologies for determination of N-nitrosamides which are direct acting carcinogens. Determination of N-nitrosopeptides is still in exploratory stages. Possible contaminants of food e.g. N-nitroso derivatives of some pesticides and a few indole compounds have been investigated. The formation of N-nitrosoharman and N-nitrosonorharman during cooking of tryptophan-rich foods has been postulated but suitable analytical methods for their determination in foods are not yet available.

As in the case of VNAs the final confirmation of the structure of the NVNCs rests with mass spectrometric techniques. Alternatively NVNCs can be directly analysed by HPLC-MS which would eliminate the need for derivatisation. This technique will be especially useful for confirmation of NVNCs that are not amenable to derivatisation and are thermolabile and for determination of compounds of unknown structures.

CONCLUSION

Since the levels and nature of N-nitroso compounds in the environment and their effect on human health are intimately linked, it is important that data from different countries and regions are collected and compared. Analysis of air and water samples, edibles and tobacco from various regions needs to be carried out for nitrosamines and their precursors. Further refinement of methods for qualitative and quantitative analysis of volatile nitrosamines and concerted effort to develop analytical techniques for nonvolatile nitroso compounds is imperative. Systematic work on relative risk posed to human and animal health by dietary intake of nitrosatable precursors needs to be intensified.

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PESTICIDES — HANDLING AND FATE

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Pesticides are used in all areas of agricultural and animal production to control the various pests that reduce yields and impair the quality of the product. Application methods range from wide-spread treatment of large areas of plant production or large numbers of animals, through specific treatments of isolated commercial crops or handling facilities, to small scale home garden use or individual dosing of animals. All of these uses contribute to the environmental burden of pesticides.

Following application, residues of the pesticides persist in or on the produce at concentrations and for times that are dependent not only on the amount applied but also on the chemical characteristics of the pesticide and on the conditions that exist in that environment. In addition, residues of pesticides may persist in other parts of the environment such as in soils or on the surfaces of structures.

The impact of such residues will be illustrated by considering the persistence of organochlorine and organophosphorus pesticides in the environment, the ways in which these compounds enter animal products and their rate of disappearance from animal tissues. In addition, some consideration will be given to the many toxic compounds which occur naturally in food.

Control of residues of agricultural chemicals in food is maintained through a system including establishment of legal limits, Maximum Residue Limits, for residues in food and policing observance of these limits by analysing samples of foodstuffs. The setting of limits and the requirements for laboratories involved in analysis are discussed.

INTRODUCTION

Agricultural chemicals are used in many ways to help provide us with ample supplies of good quality food at reasonable prices. They enter many different parts of our environment either by intentional application, by accident, or by misuse. Examination of those parts of our environment associated with food and food production provides insight into some of the ways pesticides enter the food supply. The major part of the discussion will consider pesticides which have had an impact on the animal industry in Australia in recent years. This impact resulted in increased investigations of residues in meat products. The way in which meat was surveyed for organochlorine pesticide residues will be considered and the extensive escalation of laboratory facilities involved in that task will be illustrated. Some consideration will also be given to the significance of such residues in comparison with poisons which occur naturally in foods.

APPLICATION OF AGRICULTURAL CHEMICALS

Chemicals may be applied directly to animals to control external parasites or they may be incorporated in feed either as intentional additives or as residues remaining in the feed from a use during growth or storage. Plants may be treated at any stage of growth from planting to harvest and again for storage or transport. In addition, soil may be treated pre-planting and during plant growth for control of weeds and various pests which live in soil.

Methods of application are many and varied. Animals may be sprayed, dipped or jetted, chemicals may be applied as spot or line treatments on the skin, deposited subcutaneously in slow release form, injected subcutaneously, intramuscularly or intravenously, infused into the mammary gland or into the eye, administered orally as slow release boluses or continuous release devices, or mixed in feed or water. The rate of absorption into the animal can be influenced by changes in the formulation of the active ingredient and this consequently influences the concentration of residue which results in the edible products, such as meat, milk and eggs, from those animals. For example, antibiotics are used to treat mastitis in dairy cows. Various formulations are used and have differing impacts on residues in milk. When the formulation includes aluminium monostearate, residues of the antibiotic usually persist in milk for extended times, so this product is usually applied to dry cows. When glyceryl monostearate is incorporated, the antibiotic levels decline much more rapidly, and this formulation, with appropriate withholding periods, can be used in milking cows (Schultze, 1975).

Although the range of application methods for plants and soils appears less extensive, there are many ways of delivering agricultural chemicals to the target. Concentration and formulation are varied to suit the mode of application and the target plant surface (Corty, 1983). Application may be as a spot application, general spray, fog or dust, and for large areas spraying or dusting may be performed from aircraft. Some products are applied to soil as pellets which slowly release the active component. Of course, part of the pesticide aimed at plants also arrives on the soil, and residues left on the plant break down with time (Willis and McDowell, 1987).

Addition of pesticides to the local farm environment also occurs when farm buildings are treated for pest control. Termites are a continuous threat to wooden structures and persistent pesticides such as aldrin are used during construction for protection. On occasion, existing fencing has been treated for termite control. Spiders may present a problem in some animal handling facilities. Inappropriate treatment may lead to residual contamination of that environment. In addition, use which was legitimate in years gone by may have left residues of chemicals that are no longer acceptable. For example, organochlorine pesticide use on sugarcane or cotton was allowed for many years, and pesticide can still be present in the soil. If animals graze on or near such land, they may accumulate residues above the Maximum Residue Limit (MRL).

MAXIMUM RESIDUE LIMITS

The MRLs are legal limits which show the maximum concentration of a chemical residue which may be present in a food at market following correct use of the chemical concerned. In Australia (Anon., 1989a; Hamilton, 1988), they are incorporated in State legislation on recommendations provided by the Pesticides and Agricultural Chemicals Committee of the National Health and Medical Research Council (NHMRC). The MRLs are developed after detailed study of extensive toxicology data provides a No Effect Level (NEL), No Observable Effect Level (NOEL) or No Observable Adverse Effect Level (NOAEL). Although these terms have slightly different meanings, they are usually used interchangeably. The NEL is then reduced by a large factor to give the Acceptable Daily Intake (ADI). This ADI is the intake which, on present knowledge, could be consumed every day for a life time without ill effect. Residue data are examined to determine what is actually present following correct use and the MRL is established at that level, provided the ADI would not be exceeded, considering all foods which may contain the chemical. Note that the MRL is set on residue data generated on products on farm and relates in general to food products before processing. For many products with inedible peel, such as bananas and pineapples, the MRL is still set on the whole product. If the residue is mainly on the skin, the edible portion of treated produce may contain very much smaller concentrations than are specified as an MRL. Occasionally, processing concentrates the chemical in a product and a separate MRL is set. For example, if wheat is treated near harvest or in storage, residues of the chemical may all be on the surface of the wheat grains. When the wheat is milled most of the chemical remains with portions such as bran and the concentration in the bran may be higher than for the whole wheat.

The best way to ensure that MRLs are not exceeded is to analyse samples of all food products at regular intervals. Unfortunately, that is an impracticably expensive operation. Nevertheless, appropriate analytical data must be generated to give a reasonable assessment of the residue status of food. To do this effectively, the system must include laboratories which are adequately staffed and equipped to handle the necessary tasks. This aspect will be discussed later.

BEEF TRADE CRISIS

Over the past few years there have been a few instances of disturbance about pesticide residues in food. Perhaps the most spectacular was the crisis in the USA-Australia beef trade beginning in May, 1987, when the US authorities detected DDT in three samples of Australian beef (Anon., 1989a). Actual levels were 104, 28 and 6.7 mg/kg compared with the US tolerance of 5 mg/kg and the Australian MRL which was then 7 mg/kg and was later reduced to 5 mg/kg. Consequently, additional testing was conducted and several other situations were detected where excessive residues appeared to be present. This precipitated a trade crisis with the USA threatening to close down Australia's export beef trade, valued at about $1 billion. The response by the Australian Commonwealth and State Governments was an Integrated Action Plan which included a range of measures to reduce or remove availability of the chemicals of concern, to detect and correct problems and to educate primary producers about residue problems and their prevention.

Within Australia, residue testing had been in progress in several laboratories since the early 70's. In addition, the Australian Quarantine Inspection Service (AQIS) had testing for organochlorine pesticides in place as part of the National Residue Survey (Anon., 1988) and the export certification process. Thus, an important part of the Integrated Action Plan was to escalate the level of testing of meat at export abattoirs. The initial plan was to increase sampling to one animal in every 100 for beef cattle and this programme was subsequently extended to one animal in every lot presented for slaughter. Samples were also taken of pig and sheep meats, but at lower sampling rates. In due course the sampling programme was extended to include domestic abattoirs.

Another factor which increased the analytical demand was the need to "trace-back" those animals in which excessive residues were detected. Detection alone was not enough to correct the problem. Since the origin of both pigs (through tattoos) and cattle (through tail-tags) could be determined, it was possible to investigate the property of origin of animals with residues. Once the source of the chemical involved was found, measures to clean up the problem could be commenced. Finding the source often involved analysis of many diverse samples—soil, dust from feed bins, scrapings from rails and posts, feed materials, as well as other environmental samples.

ANALYTICAL ESCALATION

The initial escalation of testing requested by AQIS was handled by the relatively few laboratories actively involved in pesticide residue analysis in meat products. Additional laboratories became involved over the following months either by diverting effort from other areas or by developing new laboratories for the purpose. One laboratory which was involved from the early stages was the Biochemistry Branch of the Queensland Department of Primary Industries, located at the Animal Research Institute at Yeerongpilly. The Pesticide section of the Branch had, over the preceding 20 years, analysed approximately 45,000 samples of beef, pig and poultry fat, as part of research, method development and Departmental surveys, so staff were well experienced in this area of analysis. Analyses were continuing during 1986/87 at 80 samples/week. When AQIS requested analytical support in late May, numbers were immediately increased. By 9 June, 1987, capacity was 100-120 abattoir fat samples/day and a turn-around time of 48 hours was promised. Industry quickly intimated that was not adequate, because it was essential that results were available for each day's slaughter by 6 a.m. on the next working day, to allow boning out to commence. The turn-around time was therefore reduced and results of samples received by 4.00 p.m. were forwarded by facsimile from 6.00 a.m. the following day.

Further escalation was in place by 6 July, 1987—to 300 samples/day; and by 1 September, 1987—to 500 samples/day plus 100 samples/day from traceback investigations. On 1 October samples from domestic abattoirs were included and this sampling plan was extended from 1 February, 1988.

In the period from 9 June, 1987 to 11 March, 1988, this group analysed:

Slaughter fat samples, export	52,500
Slaughter fat samples, domestic	6,000
Traceback—Biopsy fat samples	3,900
Environment samples	2,900
Cartoned meat samples	1,000
TOTAL	66,300

To appreciate the extent of this work we must consider briefly what is involved in analysis of each sample of fat. Note also that environmental samples generally require a higher work input per sample than the fat samples because each sample must be assessed to decide the appropriate extraction method and samples frequently require individual attention. Each fat sample is received individually wrapped and labelled. It is then unwrapped and detail recorded. The analytical procedure is:

(i) Chop and melt fat;

(ii) Inject fat into clean-up column;

(iii) Elute pesticide from trap;

(iv) Inject into Gas Chromatograph;

(v) Confirm positives; and

(vi) Over MRL—confirm by GC-MS.

To ensure reliability of results it was essential to include standard spiked fat samples in every run—each run was 8 samples plus 2 standards. Results from each standard had to show adequate recovery, correct retention times and absence of contamination.

MECHANISM OF ESCALATION

This vast increase in throughput was achieved mainly by reorganising the logistics of the analytical process. No significant changes were made to the analytical methodology. Obviously there was a considerable increase in the numbers of units of equipment available, and additional staff, initially untrained, were employed.

Before June, 1987, individual analysts received samples and then handled the whole analytical procedure and reported the results. To handle large numbers it was necessary to set up the procedure on an assembly line basis. Groups, each under the supervision of an experienced person, were set up to handle each step of the procedure. Duties were:

(i) Receive and identify samples with a code which was carried through the whole process;

(ii) Macerate the fatty tissue, melt, recover fat;

(iii) Inject the fat into codistillation units and elute traps to recover pesticides;

(iv) Analyse by gas chromatography (GC);

(v) Check identification and quantitate in a second GC when pesticides are detected. Confirm, when appropriate, by GC-MS;

(vi) Report results by facsimile. Enter results into data base; and

(vii) Administrative group—ordering of equipment and reagents; Preparation of invoices.

The overall supervisor maintained an overview of the whole operation and ensured maintenance and repair of equipment and organised staff training. Particular care was taken to ensure that the identity of each sample was maintained throughout the process, because any error in identification could create major problems in the abattoirs and in field investigations.

Working hours were reorganised, with the first staff arriving at 5.30 a.m. and increasing numbers starting as the samples began to arrive at the laboratory. Work continued until all samples were processed and placed in the sample trays of the automatic GCs, usually from 8.30 p.m. to 11 p.m., but sometimes later. During the peak demand months, considerable overtime was worked.

The extra labour needed was obtained initially by stopping all other work relating to pesticides and allocating the staff to this programme and coopting, from the rest of the Branch, all staff with any relevant experience. Then additional staff were employed, first as casuals and subsequently as temporary staff. Many of these had little or no previous laboratory experience but were enthusiastic and diligent in their duties and were rapidly trained to do specific tasks.

EQUIPMENT NEEDS

Laboratory space was obtained by reallocating laboratories used for other purposes. Additional GCs were purchased, and codistillation and fat-melting units were constructed in the workshop. Necessary glassware construction was provided by the Agricultural Chemistry Laboratory's workshop. Thus, achievement of this enormous analytical task was the result of tremendous cooperation among very diverse groups, but it must be recognized that it could not have been accomplished without the expertise and dedication of the laboratory staff involved and the cooperation of the Departmental Administration and the Minister in providing finance and the mechanisms to obtain quickly the needed staff and equipment.

When such a laboratory is needed for pesticide residue analysis, the whole situation must be considered: the location of sample collection; collection of samples without contamination; integrity of labelling; transport to the laboratory; analysis methodology and procedures; reporting of results; turn-around time from sampling to reporting; and follow up action when residues of concern (not just over MRL but also near MRL) are detected. The following comments relate only to the section from receipt of samples at the laboratory to reporting of results.

We will look very briefly at each step from arrival of the samples at the laboratory to reporting, examining three of these steps in more detail. Remember, of course, that the logistics of collecting samples, accurately labelling them and getting them to the laboratory are an extremely important part of short turn-around times.

Samples arrive chilled in insulated containers and are unpacked and details recorded. This step needs adequate space so that unpacked samples can be spread out for sorting. Then the fatty tissue is chopped up and heated. Rendered fat is collected and rewarmed in preparation for clean-up by sweep codistillation.

As an example, consider the equipment needed for the next steps to analyse 96 samples per day, simplifying the real world (described previously) by assuming that we are allowed a standard eight-hour day, all the samples arrive promptly at starting time and results can be reported at the start of the next working day.

CLEAN-UP

In the clean-up step, each unit has 10 tubes. This means we must handle 12 batches, each of 8 samples and two standards, and make some allowance for faulty runs requiring repeat analysis. So in these steps of Clean-up, Gas Chromatography and Confirmation of identity and quantitation, we will calculate the number of units of equipment needed at each point and make some estimates of allowances needed for maintenance and repair.

The clean-up process requires first an injection into each tube mounted in a heated block. The fat spreads over the interior packing and the pesticides are carried in the gas stream to the trap where they are absorbed on florosil. Traps are eluted with hexane-ether. Each batch takes about one hour, and if everything goes perfectly, each unit could process eight batches in the 8-hour day, but seven is a more realistic assessment. Hence we need two units which could be operated by one skilled operator, with support staff to clean columns, pack the traps, prepare elution solvents and carry samples to the next step. These two units would have some spare capacity—one batch each per day—to cope with any repeat analysis requirements. There is no allowance for breakdown and essentially no time for maintenance. I would want a spare unit. Also needed would be two spare sets of traps for each unit.

GAS CHROMATOGRAPHY

First samples for GC analysis arrive about 1.5-2 hours into the day. Some calibration with standard solutions has already been done. Each scan takes about 15 minutes. Hence four injections can be completed per column hour. Twelve batches require 120 injections but there will be some repeats and additional calibrations—possibly a total of 140 injections. These require 35 column hours. Assume GC units are automatic, dual-column and so can run overnight to provide results by starting time next morning. There are 22 hours available, so one dual-column unit can handle this task, but there has been no checking of identity of any detected peaks and no check of quantitation. We need at least one extra unit for checking purposes and another as reserve for breakdowns and to allow for maintenance. Note that under these conditions the report after 24 hours is only "Sample clear" or "Sample suspect". One skilled operator could handle the first GC screen and do the checking of quantitation.

CONFIRMATION

Samples with residues above MRL must have the identity of residue confirmed, if possible by GC/MS. An alternative is accurate checking of retention times on at least three different columns. Calculations of needs in this area depend on the incidence of residues above MRL. At the Australian incidence of 0.2 - 0.4% for organochlorines we might have one or two samples per week. Of course sampling is not likely to be random and will be targeted at sources where residues are more likely to be detected. This will provide additional samples for confirmation, but will not be sufficient to keep a GC/MS fully occupied. The versatility of the equipment is sufficient that this should not be a problem in any working laboratory.

Recording and reporting of results are essential tasks. The reports must be checked by an experienced officer before being sent out. When time is important, results are sent by facsimile. Recording on micro-computer offers many advantages.

This sketch of an approach to planning laboratory development is a brief introduction aimed at stimulating thought on the subject. Many operational problems have not been addressed—for example, 500 samples of about 200 g each of fatty tissue received each day—how long do you keep the remaining sample to allow later checking of the result? How do you dispose of the remains (100 kg/day)?

LABORATORY ACCREDITATION

In all laboratory work it is important that analytical results be reliable. Thus, it was necessary to have external as well as internal checks on the quality of the work done. The laboratory performed extremely well in tests organised through AQIS.

There were about 50 different laboratories providing results for the monitoring programme. AQIS required new laboratories entering the programme to be accredited by the National Association of Testing Authorities (NATA) and all laboratories to participate in a Check Sample Analytical Programme. Fat samples with added pesticide were prepared by Australian Government Analytical Laboratories and distributed to participating laboratories. Analyses had to be completed and results returned within a fairly short time slot. Results were assessed to determine which laboratories needed to improve performance. All results were distributed to all laboratories, but each participant was identified only by a code letter. These requirements were good first steps towards attaining consistent performance across laboratories. To ensure continuing high quality results from all laboratories, it would be necessary to introduce regular audits of performance by an independent authority and insertion of secret check samples into each laboratories work load. Such checks would be extremely expensive, and difficult to organise.

ORGANOCHLORINE RESIDUES—ACCUMULATION

The major pesticides of concern during 1987-88 were the group including BHC, chlordane, DDT, dieldrin and heptachlor and commonly known as organochlorines. Problems were also experienced with some organophosphates but these were more easily corrected because organophosphate persistence in animals and in the environment was much less than for the organochlorines.

The nature of the organochlorine pesticides is that they accumulate in animals exposed to them. Being fat-soluble, within the animal they distribute throughout the fat deposits. Metabolism and excretion is generally very slow, but absorption is fairly efficient. In the short term, it is a reasonable approximation to assume that all organochlorine compounds ingested by a ruminant are absorbed and excretion is negligible. So an estimate of the impact of environmental contamination on a food producing animal can be assessed by making a few calculations. Consider a 300 kg bullock. This animal has about 20% of its body weight as fat, about 60 kg. Now suppose some posts in that animal's environment have been treated with aldrin to prevent termite attack, and soil around the base of the posts has been soaked during application. The bullock occasionally licks the posts and ingests some soil. Over the course of a week or so, it ingests 12 mg of aldrin. This is absorbed, converted to dieldrin and approximately 12 mg of dieldrin is distributed in the animal's fat—12 mg/60 kg or 0.2 mg/kg, equal to the Australian MRL for dieldrin. If the soil had 120 mg/kg of aldrin, ingestion of 100 g (about 4 ounces) of soil would provide the 12 mg.

Similar calculations are made for other species. A review of the literature (Noble, 1989) provides data summarised in Table 1, indicating that the factors of accumulation from the levels in feed are high, but vary considerably depending on species and the compound involved. Detailed analysis of fatty tissues of five steers which had been accidentally exposed to dieldrin (H. Mawhinney, Biochemistry Branch, Queensland Department of Primary Industries, Personal Communication) showed levels were consistent in all clean dry fat from the various tissues of each animal. Actual fat concentrations ranged from 0.15 to 2.0 mg/kg in the five animals.

These ratios come from a wide range of experimental situations and the table conveys a sense of precision which is not really valid, because conditions influence the numbers considerably. Even when conditions are seemingly uniform, individual variations occur between animals. Groups of cattle have been examined for pesticides (H. Mawhinney, Biochemistry Branch, Queensland Department of Primary Industries, Personal Communication). Levels found are illustrated in Table 2. The figures in Groups 2 and 3 are representative of those groups and include the highest and lowest results obtained. It was believed that each group these animals had received consistent

TABLE 1: Accumulation Ratios

Pesticide	Milk fat	Body fat				Eggs
		Dairy	Beef	Layer	Broiler	
Aldrin	3.3	3.0	—	14	13	1.3
Dieldrin	5.9	1.3	—	14	13	1.3
α-BHC	2.0	—	11.4	1.8	3	1.3
β-BHC	7.5	2.9	9.8	19	14	1.9
γ-BHC	0.9	—	—	2	2.3	0.2
DDT	1.8	—	—	12	11	1.1
Heptachlor	5.7	—	4.0	11.5	18	1.0

TABLE 2: Residue Variations in Groups

Group 1 9 Cattle Dieldrin	Group 2 40 Cattle Dieldrin	BE	Group 3 120 Cattle DBBE	Ethion
0.09	0.32	0.51	0.39	0.78
0.09	0.37	<0.1	<0.1	0.34
0.11	0.21	0.39	0.39	0.48
0.12	0.28	0.74	0.52	1.10
0.12	0.38	1.63	2.99	0.39
0.16	0.44	0.85	1.18	0.78
0.07	0.35	0.62	0.58	0.60
0.13	0.32	1.38	2.04	0.85
0.27	0.37	0.85	1.18	0.78

BE = Bromophos-ethyl
DBBE = Desbromo-bromophos-ethyl

treatment in the same environment. Bromophos-ethyl and ethion are organophosphorus pesticides used in dipping vats in Queensland to treat cattle for control of cattle tick. Desbromo-bromophos-ethyl is formed in some cattle dips by replacement of a bromine atom by hydrogen. It was apparent that some animals in Group 3 had escaped being dipped in bromophos-ethyl, but this would not be unusual on a large property. The figures in Table 2 indicate that residues might be expected to vary by a factor of two across a group of apparently uniform animals. I suspect this could be an underestimate.

ORGANOCHLORINE RESIDUES—PERSISTENCE

The organochlorine pesticides also persist for long times in the environment and in animals. A wide range of factors influence what happens, so it is not possible to be precise about half-lives. In fact, it seems likely that different mechanisms control what is going on at different concentrations in animal tissues, so depletion does not necessarily follow expected trends. In soils it is likely that the breakdown depends on the specific microorganisms present and on the conditions which influence the activity of those microorganisms, although movement of pesticides in soil appears to be governed by physico-chemical properties (Jury *et al.*, 1987; Suntio *et al.*, 1988). The figures in Table 3 are assembled from a wide range of references (e.g. Anon., 1980; Bull, 1972; Connell, 1988; Edwards, 1966; Knipling and Westlake, 1966; Stickley, 1972) and experience of Biochemistry Branch, Qld. Department of Primary Industries staff participating in more than two hundred investigations of contaminated properties. These figures give a rough idea of how long the chemicals may stay in the environment, but we can hope that workers attempting to develop methods to accelerate the breakdown process will soon be successful.

A recent paper (Petterson *et al.*, 1988) describes the long slow process of elimination of heptachlor epoxide (HCE) and oxychlordane (OCD) from cattle which initially had 1.2-67 mg HCE/kg and 0.3-18 mg OCD/kg in their fat following accidental exposure to commercial heptachlor. Commercial heptachlor can contain

TABLE 3: Persistence of Pesticides

	Half-life in fat (Live animals)	Half-life in soil
DDT	4-12 weeks	3-10 years
Dieldrin	6-12 weeks	1-7 years
BHC	3-6 weeks	2-3 years
Heptachlor	6-12 weeks	7-12 years
Ethion	*c.* 5 days	—
Bromophos-ethyl	*c.* 4 days	—
Chlorpyriphos	*c.* 2 days	—

up to 30% chlordane and within the animal these compounds are converted to heptachlor epoxide and oxychlordane. After 488 days residues were 0.01-0.26 mg HCE/kg and 0.01-0.43 mg OCD/kg, so even after this interval some of the animals still had residues above the MRLs (heptachlor 0.2 mg/kg; chlordane now 0.2 mg/kg then 0.05 mg/kg).

OTHER RESIDUES IN FOOD

Another residue situation which has had some publicity in recent months is the use of daminozide (Alar) on apples. The compound is a plant growth regulator which makes fresh fruit firmer, controls induction of flowering, prevents premature fruit drop and enhances storability and colour. It is used on apples, pears and peaches in Australia while in the USA there is also use on cherries. During processing, daminozide degrades to UDMH (Unsymmetrical dimethyl hydrazine) which is a potential carcinogen. The Australian MRLs for daminozide are 30 mg/kg for peaches and pome fruit. It is interesting to compare these figures with the results of a recent small US survey (Saxton *et al.*, 1989). The levels found are listed in Table 4.

TABLE 4: Daminoxide Residues

Daminozide	(Canned)	Apples	0.6 mg/kg
		Cherries	5.9 mg/kg
		Apple Juice	1.1 mg/l
UDMH	(Canned)	Cherries	0.6 mg/kg
		Apple Sauce	0.06 mg/kg

Although the product has been on the market since 1963, it is only in recent years that concern has been expressed about possible hazards from residues, particularly in processed apple products. The very extensive debate about this use illustrates how difficult assessment of the situation is. Two recent letters present different attitudes. One (Groth, 1989) from the Consumers Union of the US argues about interpretations of what is safe but the most important comment relates to the public perception of risk: "However big a risk may be, whether it is acceptable or not is a value judgement and is heavily influenced by the MORAL dimensions of the risk". The letter goes on to state that risk management must balance values and ethical choices and is inevitably a political process, and that public reaction to risk is related to perception of the ethical aspect of the risk and bears little relation to the magnitude of the risk. The next letter (Ames and Gold, 1989) emphasises the need to compare the risks from pesticide residues with those from natural components of foods. The authors provide some risk calculations to show that common foods such as one daily mushroom, or 100 g daily servings of celery, cabbage or Brussels sprouts provide much higher risks than are likely from residues of UDMH in a daily glass of apple juice. Information is also given about natural carcinogens in food and the significance of risk assessment.

DOSE-RESPONSE

Public concern over pesticide residues in foods is stirred up from time to time and is often fuelled by rather exaggerated statements about the adverse effects such pesticides might have. The dose-response relationship is ignored and effects at high dose are emphasised with the tacit assumption that the same response occurs following consumption of the trace amounts present in food. There is also an assumption that pesticides are somehow worse than the naturally occurring, but often extremely toxic chemicals in foods.

Dose response is readily apparent to us in many aspects of daily life although we often overlook it. Medications such as antibiotics are prescribed at specific doses to obtain the effect of destroying a microorganism with minimal effects on the person. Doses for children are smaller than for adults because of lower body weight and sometimes greater susceptibility. Ethyl alcohol is a chemical with well-known dose related effects. Many people in our society consume ethyl alcohol in a wide range of alcoholic drinks and experience a dose related response. Most are aware of the immediate dose response and adjust intake accordingly. Legally the dose response is taken into account by relating blood alcohol levels to capability to drive motor vehicles. When the dose is sufficiently high, acute toxic effects are observed—staggering, slowing down of reaction time and other symptoms of alcoholic intoxication. Repeated high dosage over an extended period of time produces other dose responses such as cirrhosis of the liver.

Generally the dose-response relationship is that the higher the dose the greater is the biological effect. This concept of "*The Dose Makes The Poison*" cannot be too strongly emphasised.

TOXIC COMPOUNDS IN FOODS

Natural foods contain a whole pharmacopoeia of hazardous chemicals (Fenwick, 1986; Hoskins, 1978; Kaplan, 1983; Liener, 1980; Wogan, 1969). For example: *cyanide* occurs widely in foods such as sweet potato, maize, peas, beans (especially haricot, navy and lima), in the kernel of almonds, cherries, apricots, prunes, plums, and in seeds of apples and pears; *saponins* occur in spinach, beetroot, asparagus, soybeans and tea; *estrogens* occur in wheat, oats, rice, barley, potatoes, apples, cherries, plums, rice, carrots and in some vegetable oils; *enzyme inhibitors*, such as anti-trypsins, occur in soybeans, potato, sweet potato, in most varieties of beans, in peas, peanuts, all grains and more than 50 common plant foods; *goitre-inducing thioglycosides* occur commonly in all *Brassica* such as cabbage, cauliflower and kale, and in mustard, horse radish, turnips and onions; *oxalate* is present in high concentrations in rhubarb; and in addition there are numerous allergens, anti-vitamins, organic acids, tannins and alkaloids intrinsic in common foods. In the course of cooking we pyrolize complex carbohydrates and proteins to yield, among other toxic chemicals, 3,4-benzpyrene—a potent cancer-producing agent.

Other foods such as milk and honey can accumulate highly toxic natural chemicals and many other foods such as bananas, chick peas and condiments contain active compounds which would be harmful in larger doses. Consequently, it is not appropriate to exaggerate possible hazards of traces of pesticide residues in foods.

INTAKE OF PESTICIDES

Following treatment, residues may be on a food product or in the product. MRLs normally apply to the whole product, so additional safety margins are in place when portions of the product containing residue are discarded.

When most of the residue is on the surface of a vegetable or fruit product, amounts in the food consumed are reduced, sometimes eliminated, by washing or peeling. However, when the chemical has been absorbed systemically and is present in the product, its distribution and the way residues are bound in the product structure are controlled by the chemistry of that compound.

Although data are not very extensive as yet, more investigations are being directed at determining the effect processing has on the amount of residues actually consumed. In addition to concentration changes reflecting changes in moisture content during cooking, residues may be removed by boiling, baking or roasting. For example, studies of dieldrin in pig meat have shown approximately 50% reductions in concentration following cooking in several ways — pan-frying, baking, microwave and braising, although there is a trend through this sequence of reduced losses (Maul *et al.*, 1971).

In some circumstances the apparent possible intake of a chemical present in a food is much greater than the actual intake. If, for example, we have a 500 g steak, nominally containing 1 ppm (1 mg/kg) DDT, we naturally expect 0.5 mg DDT to be present. However, since DDT is a fat soluble pesticide, the analytical result is expressed as a concentration in fat, so the 1 mg/kg is actually 1 mg in every kg of fat in the meat. Now if the 500 g steak is moderately fatty it will have about 20% fat—100 g, so at 1 ppm the raw steak actually contains 0.1 mg DDT. When the steak is grilled about 50% of the fat is lost and the DDT it contains goes with it. So actual intake of DDT by consuming that steak is 0.05 mg not 0.5 mg.

Considerable international attention has been directed at estimating dietary intake of pesticide residues. "Guidelines for Predicting Dietary Intake of Pesticide Residues" (Anon., 1989b) has been developed over many years through cooperation between World Health Organisation, the United Nations Environment Programme, the Food and Agriculture Organisation and the Codex Committee on Pesticide Residues. It is recognized that sufficient food intake data to make accurate calculations is rarely available and is expensive to generate. Consequently, effort is directed at assessing whether or not possible residues could be a cause for concern, so that resources can be used to generate data in appropriate areas.

Since food consumption patterns differ markedly from country to country, and even within a country, it is not possible to generate a single standard diet from which to assess pesticide intake. Thus, it is appropriate for each country to do its own calculations.

When assessing intake, the simplest and crudest calculation is the TMDI—Theoretical Maximum Daily Intake—which uses the MRL and the average daily per capita consumption of each food for which an MRL has been established:

Quantity of food (kg) × MRL (mg/kg), the sum all foods.

This gives mg/person/day. Assume body weight is 60 kg and so convert the amount to mg/kg/day and compare with the ADI. The TMDI is a gross overestimate of intake but if the result is less than the ADI, no further examination is necessary. If the TMDI is larger than the ADI, then calculations must be refined to provide a more realistic intake figure.

The next step is to calculate the EMDI (Estimated Maximum Daily Intake). The EMDI uses data on residue concentration in the edible portion of the foods involved, rather than the MRL, and applies correction factors for changes in residues during processing and cooking. These factors do not necessarily reduce the estimate. This still provides a considerable overestimate of intake but is closer to reality than the TMDI. Again, if the EMDI is less than the ADI, no further examination is necessary, but if it is greater than the ADI, the next step in assessment is to calculate the EDI (Estimated Daily Intake). In addition to food intake the following data is needed:

(i) Known uses of the pesticide;

(ii) Known residue levels;

(iii) Proportion of the crop treated;

(iv) Ratio of home-grown to imported in the market place; and

(v) Changes during storage, processing and cooking.

If the EDI is greater than the ADI, use of the compound may need to be restricted. It is important to understand that the TMDI and EMDI are exaggerated figures —gross overestimates of actual intake. They are steps in a process designed to identify those situations where more careful examination of possible intake is warranted. They do not, of themselves, indicate cause for concern.

SOURCES OF PESTICIDES

As mentioned earlier, pesticides are absorbed into animals from their environment. During investigations of excessive residues detected in 1987-88, it was found that in Queensland, the organochlorine pesticides most frequently detected were dieldrin (*c.* 70%), heptachlor and BHC (*c.* 10% each), and DDT (*c.* 7%).

The most important sources of organochlorines in the environment of food animals were:

(i) From termite and spider control, in animal handling yards; on posts where animals have access; in buildings where animals are housed or their feed materials are stored; and in silos particularly where feed grains are stored;

(ii) Land used for sugarcane or cotton growing when the organochlorine compounds were permitted. In addition, adjacent areas may also be a source of residue because of soil movement as washings or dust, or possibly from spray drift during application; and

(iii) From use for animal feed of small crops, especially root crops, grown in land previously treated with organochlorine compounds.

Another possible source is vegetable waste from canneries. Although this does not appear to be a significant source, the waste is used as animal feed and care must be exercised to prevent accumulation in animals. Any residues present in produce are likely to be predominantly in the discarded portions which go for animal feed. Accumulation as described above could lead to unacceptable residues in the animals or their produce.

The sources of dieldrin detected following 131 successful field investigations by officers of the Queensland Department of Primary Industries have been summarised (McEwan and Stocks, 1988). Animal handling yards and poles treated for termite control accounted for 42 sources while yards around dipping facilities provided another eight. Treated sheds and silos caused contamination of hay in 20 cases and of grain in another 13 cases, while contaminated grain transported to feed lots caused five cases. Pasture grown on land previously used for small crops (14 cases) and cane growing (17 cases) was an important source. The remaining 12 were miscellaneous sources.

CONCLUSION

It is important therefore to realise that all different parts of the environment interact. This discussion illustrates some aspects of the way residues appear in food and how animal industries can be affected by chemical use in other areas. We must therefore be aware that in all areas, unexpected interactions are possible, even likely, and be alert to detect these and prevent adverse side effects.

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ENVIRONMENTAL MONITORING

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The increasing population, galloping technology and economic development have created awareness of environmental crisis and the need for achieving a balance with nature. In the world today, higher production and consumption of profit oriented commodities are the yardstick of progress. Very often, these pursuits have resulted in the use of air, water and land as free dumping grounds. The experience of the last few decades, has, however, brought into sharp focus the fact that man must start to think of living in harmony with nature. The old concept of progress which has prevailed for the last 200 years must also take into account the means to safeguard air, water and land which sustain man. The cost of environmental protection *must* be included in the cost of basic production activities. Development of new technologies must balance benefits thus acquired against the existing benefits bestowed by nature which are required to be sacrificed. The basic recognition of ecoscience made a beginning in the sixties. A review of activities of International Council of Scientific Unions (ICSU), other major international (MAB, UNEP) and national bodies i.e. CES, NASA, NOAA, of USA reveals that substantial thrust in Earth System Sciences is being devoted to research and global measurements of changes in Geosphere and Biosphere. Apart from Satellite observation of atmosphere, oceans and biosphere, study of atmospheric chemistry, which basically affects earths environment, is receiving high priority (Anon., 1989a). The Greenhouse effect causing global warming and transport of air and water pollutants across the national boundaries has given the problem a global dimension (Hileman, 1989). The International effort is in addition to vigorous national level efforts for protection of the environment from human activities.

As a basic step towards study and management of pollution, introduction of man-made pollutants and their interference with the natural processes (and the resultant imbalance/risk) are sought to be determined. Considerable progress has been made in recent years in respect of monitoring of chemical pollutants in air, water and land as well as their complex inter-relationships. The complexity of this gigantic task requires sustained efforts and commitments. Determination of diverse chemical pollutants before and after the remedial measures is a major part of environmental monitoring. This helps in evaluating the risks involved and success achieved. This data is also necessary as basic input for policy decisions and statutory laws for environmental protection.

AIR MONITORING

Monitoring of troposphere during early period was limited to the study of smoke and sulphur dioxide. However, with population increase, industrialisation and better standards of living, emission gases like carbon monoxide, methane, nitrogen oxides and sulphur dioxide started extensively fouling the limited resources. The effect of each of these gases cannot be read in isolation but is inter-related in a complex manner. To them, was added chlorofluorocarbons (CFC's) which inspite of their low concentration, contributed to global warming and proved to be prime culprits in the destruction of ozone protective shield around the Earth (Hileman, 1989; Zurer, 1989). Increasing release of NO_x, as pollutant emissions, causes rapid destruction of ozone while unfavourable ratios of hydrocarbon with NO_x also retard ozone formation. Both dry and wet oxidation of sulphur dioxide and nitrogen oxides by hydroxyl radical and photochemically generated oxidants like hydrogen peroxide and ozone respectively, are also leading to deposition of sulphuric acid and nitric acid, broadly termed as Acid Rain (Lee,1988). However, air-monitoring programmes for ambient air, air pollution from mobile and stationary sources broadly cover the following :

(i) Suspended particulate matter (SPM) : its magnitude, particle size, distribution and elemental composition;

(ii) Analysis of SO_2, CO, NO_x, O_3, CH_4, CO_2, chlorine monoxide, etc.; and

(iii) Determination of benzo-(a)-pyrenes, aldehydes, ethylene, chlorofluorocarbons(CFC's) and other pollutants from specific sources.

The need for more sensitive and selective analytical techniques gradually came into focus as very low concentrations of pollutants were required to be accurately monitored. The present need for unattended continuous chemical monitoring is an important requirement when larger multi-pollutant surveys in far flung areas are to be conducted over extended periods. Consequently, the traditional wet chemical analysis techniques have been gradually replaced with compact instrumental methods with automatic recording. Some significant examples of such improved basic techniques are given in Table 1 (Lee, 1988; Liptak, 1974; Mishra, 1985).

Sophisticated instruments for analysis are expensive to buy and more difficult to maintain in developing countries. Recourse to older monitoring methods is still taking place, though a gradual change is also visible. Increasing use is also being made of mobile environment monitoring laboratories (housed in a large van) which have speeded up generation of requisite data at site, covering air pollution, meteorological and other data (such as water pollution, etc.) (Liptak,1974; Ayers, 1987). Specific statutory limits and test methodologies are stipulated at national levels in case of emissions from various industries, chemical plants and now the incinerators for high temperature burning of solid toxic wastes (Liptak, 1974; Anon., 1989a). Threshold limit values and Occupational Safety and Health Administration Standards, USA in various chemical and allied industries involving toxic emissions, ensure

TABLE 1: Current Analytical Techniques for Chemical Species

Chemical species	Analytical technique
Carbon monoxide	Thermister based on heat of reaction, Infrared analyser
Sulphur dioxide	Sulphation rate by spectrophotometry, UV pulsed fluorescence coulometry, Flame photometry
Chlorine monoxide	Resonance fluorescence (High altitude)
Nitrogen oxides	Chemiluminescence
Carbon dioxide	I.R. analyser
Methane	I.R. analyser/Gas chromatography
Ozone	Chemiluminescence
Suspended	Continuous analysis based on particles (SPM) Beta absorption using C^{14} or Cr^{85}
Elemental	Atomic absorption spectro composition of SPM photometry, X-ray spectrometry, Energy dispersive X-ray fluorescence, ICP—Atomic emission spectrometry, Neutron activation, analysis
Benzo-(a)-pyrenes	TLC with fluorescence spectrophotometry
F, Cl, NO_3, NH_3, etc.	Ion selective electrodes

occupational safety and are also the basis of monitoring (Wadden and Scheff, 1989). Monitoring at high altitudes using special planes involves automatically operated systems to measure ozone, chlorine monoxide, nitrogen species, water, aerosol particles and other atmospheric constituents. These efforts are primarily meant to determine changes in ozone concentration and movement of long lived tracers in air (Gunderson, 1988).

MONITORING OF QUALITY OF WATER AND WASTE WATER

The quality of water available to man has received the earliest attention and over the years comprehensive national and international standards have been laid down for drinking water, water used in agriculture and industry as well as liquid effluents from sewage, industrial and other sources. The present list of contaminants generally monitored, covers nearly 25 items both organic (alkyl-benzene sulphates, phenolic compounds, alcohols, chloroform extracts, etc.) and inorganic radicals. Added to this would be additional contaminants such as entire range of pesticides, organic compounds of mercury and specific toxic chemicals depending upon the nature of chemical discharge (Liptak, 1974).

Ground water represents 97% of total fresh water reserves excluding polar ice-caps. Nearly 50 to 70% of domestic water supply is from ground water. Pollution of this resource occurs due to mine drainage, industrial waste, land fills, radioactive waste and agriculture pollution due to fertilizers (nitrates) and pesticides (ethylene dibromide), chlorinated hydrocarbons, etc. Ground water monitoring for inorganic salts (chloride, nitrate) as well as organic contaminants is hence an important requirement, especially when an impact of larger use of agro-chemicals and adverse effects of leaching and drainage from toxic wastes is being increasingly discovered (Ritter, 1986).

Although initially great emphasis was placed on monitoring of water quality as per statutory standards, their intrinsic enforcement remained unsatisfactory. The emphasis has therefore rightly shifted to the control of effluents and the composition of waste water finally discharged. Consequently all the advanced and developing countries are today prescribing adequate standards for effluents from various industrial and civic sources thereby assuring minimum pollutions of water including the sea (Lee, 1988; Sharma and Agarwal, 1980).

Monitoring of water pollution is not confined to organic and inorganic constituents, but thermal pollution arising out of hot water discharge, is equally being restricted. Similarly natural radionuclides in sea water and disposal of radioactive effluents has also come under constant surveillance. A wide variety of chemical and biological tests are prescribed separately while modern water quality data collection systems, record several (8 or more) parameters simultaneously and continuously, making it possible to generate reliable and comprehensive data even at remote places. Today typical data generation on effluents both before and after treatment (decontamination), would cover pH, colour, temperature, suspended solids, dissolved oxygen, BOD, COD, oil, grease, chloride, phosphate, phenols, cyanides, sulphides, sulphates, fluoride, arsenic, bromine, sodium, cadmium, lead, chromium, mercury, nickel, selenium, silver, zinc, pesticide residues, coliform, etc. Even these estimations are often inadequate to confirm the harmlessness of the discharged effluents. Bioassay techniques based upon fish additionally help to determine the extent of effluent discharged into the natural water system which would ensure only permitted level of adverse effect to the aquatic life. Toxicants in aquatic system are often biomagnified through the food chain and hence mere low level of certain chemicals (lead, mercury, cadmium, DDT, HCH, PCB's) is not a guarantee of safety. Biological sampling and chemical analysis of fish, clams, shelfish, crayfish, leaches, blood worms, etc. for mercury, lead, pesticides (especially chlorinated hydrocarbon type) etc. has become essential requirement (Sharma and Agarwal, 1980).

FOOD CONTAMINATION STATUS

Contaminated food could be a major health risk and this fact has been a basis of regulatory monitoring of food and feed for a long time. However, over the years, growing industrial pollution, increased use of agrochemicals, and emergence of processed/packed foods has aggravated the food contamination situation. Comprehensive monitoring and regulatory efforts in advanced countries have lead to a near satisfactory situation but this cannot be said for the developing countries at present. Considering the serious implications of contaminated food for human consumption, a Joint UNEP/FAO/WHO Food Contamination Monitoring Programme

(GEMS/Food) was initiated in 1976. At present nearly 35 countries are involved and about 20 specially selected contaminants are being monitored. This Programme basically attempts a global presentation, synthesis and evaluation of major contaminants in food (Anon., 1988b). FAO and WHO have also several programmes (Codex Alimentarius Commission) concerning establishment of contaminant residue limits (pesticides, heavy metals, etc.) in agriculture produce and other foods as well as limits of Average Daily Intake (ADI) of contaminants, through diet. However, within limitations of international and national standards and the available monitoring data, it has been possible to determine the extent of contamination and effectiveness of the regulatory measures instituted. An overview of some of the major contaminants in food is presented in Tables 2 and 3 (Anon., 1988b; Ware, 1989; Mehrotra, 1985).

Heavy metals (lead, cadmium, nickel, mercury, etc., Table 2) and industrial organic contaminants like polychlorinated biphenyls (PCB's), dioxins, acrylamide, vinyl chloride, etc. (Table 3) are derived from diverse sources and hence their reduction is dependent on industrial management and introduction of major strategies for utilisation of substitutes or altering the production/use pattern. For instance, elimination of lead as contaminant from petrol car exhausts would require alternate lead-free fuels and modified automobile engines. Similarly, regulated use and substitutes for PCB's are slow in introduction, more so, in developing countries.

Persistent organochloro group of pesticides (DDT, HCH, Lindane, Aldrin, Dieldrin, Chlordane, Endrin, Toxaphene, Heptachlor, etc.) have been gradually replaced with less persistent and easily degradable molecules such as organophosphorus compounds, carbamates and synthetic pyrethroid group of pesticides. Since the seventies a progressive decrease in the environmental presence of organochloro group of pesticides to acceptable levels has been ensured in the advanced countries. But this is not the case in several of the other developing countries, which continue to use DDT, HCH, Lindane, etc. due to their low cost and requirement for poor farmers and the public health programmes for control of malaria and other insect borne diseases (Anon., 1988b; Mehrotra, 1985; Bami, 1987). Recently a comprehensive survey in USA involving monitoring of nearly 15,000 samples of food (both local and imported) confirmed that less than 1% of the samples contained residues that exceeded permitted tolerances for the entire range of pesticides (Yess, 1988). Total dietary studies in USA in respect of pesticides, heavy metals and PCB's have also clearly indicated a low level of contamination well below the international and national statutory limits (Gundenson, 1988; Anon., 1988b). It is therefore clear that choice of pesticides coupled with good agricultural practices have offered the desired protection from this source. However, if for economic or other reasons, use of persistent pesticides is being continued, the problem of contamination and resultant hazards are inevitable. The society will have to bear the cost of change over.

MONITORING OF GENERAL INDUSTRIAL POLLUTION

Nearly 70,000 chemicals are at present in general use and 500-1000 are being added yearly with no limit in sight. In fact quadrupling of global economic activity

TABLE 2: Chemical Contaminants in Food

Sl. No.	Contaminants	Sources	Toxicological properties/ Health effects	Tolerance limits and analytical methodology	Present status
1	Barium (as sulphate and chloride)	Drilling mud, pigments, X-ray contrast medium, barium salts in water and food	Drinking water with up to 10 mg/L of barium provided cardiovascular risk. No data on carcinogenicity.	Maximum contamination level 1 to 4 mg/L. *Method*: A.A. Spectrometry	Less than 200 μg/L generally concentrations over 1 mg/L also encountered in drinking water. Low levels in food.
2	Cadmium (chloride and oxide)	Rock phosphate, alloys, batteries, pigments, plastics, electroplating and even in cigarettes, municipal wastes, potteries, etc.	No known carcinogenic effect. Chronic high exposure leads to renal toxicity and other adverse symptoms. Bioaccumulation even in fish and meat.	Provisional tolerable weekly intake 7mg/kg b.w. Limit in food around 10 to 100 mg/kg. Maximum WHO limit for water 5μg/L *Method*: A.A. spectroscopy	Low levels in food
3	Mercury (mercuric salts and methyl mercury)	Electrolytical processes, catalysts, dental amalgam, paper and pesticide manufacture.	Acute poison. No evidence of carcinogenicity, etc., chronic mercury poisoning through sea-food by bioaccumulation. Methyl mercury most toxic.	WHO drinking water limit 1 μg/L. Provisional tolerance weekly intake 3.3 μg/kg b.w. Limit in food/-fish 0.5 mg/kg generally. *Method*: A.A. spectroscopy (cold vapour technique)	Dietary intake high due to contaminated fish mainly
4	Nickel (nickel chloride and oxide)	Nickel salts in geological materials, plumbing and from industries	No clinical or epidemiological studies on oral exposure. Dermititis and respiratory tract cancer due to occupational exposure.	Acceptable intake 1.46 mg/kg b.w./day. Ambient water 632 μg/L. *Method*: A.A. Spectrometry	Contamination levels generally low. Hazard only through inhalation (nickel carbonyl)

(contd.)

(Table 2 Contd.)

Sl. No.	Contaminants	Sources	Toxicological properties/ Health effects	Tolerance limits and analytical methodology	Present status
5	Lead (as salts)	Batteries, solder, ammunition, pigments, galvanising, plating and fuels (as tetraethyl lead), lead pipes, and lead soldered containers.	Accumulative poison affecting haematopoietic and nervous systems, kidney. Exposure by inhalation, food and water.	Provisional tolerable weekly intakes 25 μg/kg b.w. Maximum level in fruit juices, etc. 300 μg/kg. *Method*: A.A. spectrometry	Variable residues in food, human milk and infant foods. Dietary intake higher in industrial and high traffic areas.
6	Nitrate and nitrite	Inorganic fetilizers, explosives, glass, heat storage systems, cured meat, printing. Also part of nitrogen cycle.	Toxicity of nitrate due to its reduction to nitrite which interferes with transport of oxygen. Formation of nitroso compounds with secondary and other amines.	Nitrate, nitrogen limit in water 10 mg/L while for nitrite only 1 mg/L. *Method*: Nitrate is reduced and combined nitrites estimated	High dietary intake by water only due to fertilizers and wastes.

TABLE 3: Organic Contaminants in Foods

Sl. No.	Contaminants	Sources	Toxicological properties/ Health effects	Tolerance limits and analytical methodology	Present status
1	Acrylamide-(2-propenamide or ethylene carboxamide)	Used as ground and soil stabilizer. As polydacrylamide in water treatment, adhesive, food packing, photography, oil recovery, metal coating, etc.	Cumulative poison, damages central and peripheral nervous system. A probable human carcinogen.	Polyacrylamide products should not have more than 0.5 μg/L of monomer. No safety limit prescribed due to cancer risk. *Method*: HPLC	Low levels in food and water in USA and UK
2	Vinyl chloride (monochloroethylene).	Vinylchloride and PVC are used in plastic, rubber, paper, glass, automotive industries, insulation, pipes, equipments, packing and building materials.	Clinical symptoms on inhalation exposure only. Risk of carcinogenicity but rapidly degraded with no bio-accumulation	Limit in water 2 μg/L. Tolerance in food not required due to easy metabolism. *Method*: GC	Contamination if present is low

(Contd.)

(Table 3. Contd.)

Sl. No.	Contaminats	Sources	Toxicological properties/ Health effects	Tolerance limits and analytical methodology	Present status
3	TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) (Dioxin)	By-product in several chlorinated phenolic compounds. Present in flyash, flue gases	Results in chloracne, liver damage, etc. Evidence of carcinogenicity in animals.	Limit in man 0.1 µg/kg b.w./day. Fish with more than 50 ppm unfit for eating. *Method*: GC/MS	Bioaccumulation in fish and mammals. Low level in food including meat.
4	Polychlorinated biphenyls (PCB's)	Dielectric, heat transfer and hydraulic fluids, lubricants, plasticisers, adhesives, plastics, copying paper, etc.	A possible carcinogenic risk to humans. Contamination of edible oils leads to intoxication	No FOD/WHO ADI but USA prescribes limits of 1 µg/kg b.w./day *Method*: GC/MS	Often high values in human milk and fish in Developed countries. Decreasing trend due to use restriction/ replacement.
5	Organochloropesticides (a) DDT	Since 1940 used as insecticide extensively in agriculture and public health. At present mainly used in developing countries.	Storage of DDT in body tissues but no ill effect even in infants taking high DDT content human milk. Bioamplification through food chain.	ADI for DDT 20 µg/kg b.w./day. Maximum residue limits 50 to 1000 µg/kg in different foods. *Method*: GC	Contamination low where DDT use discontinued. Otherwise persistent presence in environment and human milk.
	(b) HCH (and gamma isomer- LINDANE)	Technical HCH (BHC) a mixture of alpha, beta, gamma and delta. Being banned/restricted for many years but Lindane still used.	Storage of HCH isomers (beta persistent) in body tissues and human milk. Bioamplification through food chain. Suspected potential carcinogen only.	ADI for gamma HCH 10 µg/kg b.w./day while proposed for alpha isomer 5 µg/kg b.w./day, beta isomer 1 µg/kg b.w. Variable MRL's for lindane in foods. *Method*: GC.	Contamination and dietary intake low where use of HCH discontinued. Otherwise high values in food feed and human milk.
6	Aflatoxins (*Aspergillus flavus* and other mould products)	Four major aflatoxins in plants and foods under specific temperature, humidity and soil conditions. Contaminated feed leads to Aflatoxin M1 in cow's milk.	Potential human carcinogens. Reves syndrome, kwashiorkor impaired immune functions and other adverse effects.	Limits of aflatoxins in food (5-20 µg/kg) and feed (10-50 µg/kg). Limit in milk 0.05 to 0.5 µg/kg. *Method*: HPLC, TLC, RIA, ELISA.	Variable food contamination due to temperature, humidity and post harvest handling. Residues generally low.

since 1950 has lead to increasing chemical wastes, not to mention the application of fertilizers, pesticides, detergents, food additives, etc. The chemical monitoring of heavy metals had commenced early but a big alarm was sounded by Rachel Carson (1962)on the ill-effects of DDT in the environment. Since then, there has been no looking back. Chemical and toxicological monitoring of contaminants belonging to diverse chemical groups has become integral part of extensive national and international programmes to safeguard man and his environment. Monitoring of hazardous wastes deposited on land (sanitary land fills) and their disposal by incineration, are other areas which have received intensive attention during the last two decades. The problem is acute in the case of industrialised nations but the third world countries are also catching up with increase in their population and industrial development.

It would be pertinent to note that with respect to 70,000 chemicals in general use, majority of them have not been evaluated with respect to their toxicity. Such data generation may need US $ 500,000 per chemical and several years of effort. Experimental data also cannot be directly correlated to human risk (say carcinogenicity) and even epidemiological studies fail to give clear answers as man is exposed to a host of chemicals at the same time. However, major incidences such as at Minamata, Japan, 1959 (mercury). Bhopal, India, 1984 (methyl isocyanate) and Chernobyl, USSR, 1986 (radioactive fall out), have further brought into focus specific pollutants and triggered the need for intensive surveillance and adequate preventive measures. Some specific areas of topical interest are briefly cited below.

TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) is highly toxic member of a family of 75 isomers of polychlorinateddibenzo-*p*-dioxins while TCDF (2,3,7,8-tetrachlorodibenzo-furan) is also a highly toxic major member of a group of 135 isomers of this class. These dioxins as a class, are present in the environment from sources like production of chlorinated phenol group of pesticides, PCB's, car exhausts and burning/incineration of wood, coal, municipal wastes, etc. The presence of this group of highly toxic contaminants has to be regularly monitored at different stages to ensure safety. In fact by 1985, USA had spent $150 million on research in this area. The problem of dioxins is however more serious in industrially advanced countries due to high production of chlorinated phenols and extensive municipal refuse incineration (Eduljee, 1988).

Automobile exhaust as well as fuel volatility on handling, especially in industrialised countries and urban areas, are sources of serious environmental pollution due to emission of lead (from tetraethyl lead), CO, hydrocarbons, acrolein and crotonaldehyde, etc. Continuous monitoring in this regard has been introduced concurrent with steps to reduce/replace lead in fuels and improvement in engine performance. Similarly, asbestos (hydrated silicate material crystallised as bundles of fibrils) is in use for 100 years. Till lately it was regarded only as an occupational hazard, but it is now considered as an indoors air pollutant. Monitoring air for millimicron size asbestos samples involves phase contrast microscopy, SEM and transmission electron microscopy. Although there is little evidence of serious health hazard so far, there are moves to restrict asbestos use (Zurer, 1985).

Monitoring and disposal of "Radioactive Waste" on land and sea has become a matter of major importance. Extensive use of radioactive materials in power generation, hospitals, industry and defence has lead to this concern. Wastes with both medium and long lived radio-nuclides are required to be transformed into solid form and then suitably packed and buried in deep geologically stable sites. Disposal technologies are being so perfected that risk is no greater than one chance in a million a year of any adverse health effect leading to premature death (Saunders and Wilkins, 1987). Recently radioactive noble gas radon (natural decay product of radium-226) has been considered as an indoor pollutant with cancer hazard, requiring monitoring and statutory control on its concentration.

Soil was considered a safe waste repository earlier with the belief that organic chemicals will be degraded, adsorbed, immobilized and volatilised to render them harmless. Use of agrochemicals and waste disposal thus continued with little monitoring of soil, atmosphere and ground water resulting in damage to the environment. In the absence of complete understanding of fate and transport of organic chemicals in soil system, recourse to actual monitoring has been indispensible (Jury *et al.*, 1987). Chemical monitoring has now been directed towards pollution created by industrial processes as well as subsequent waste disposal by land fills. Monitoring of North Sea Oil producing installation has revealed that the deleterious effect of the discharge of oil-based mud is confined to 1000 meter zone. While high concentration of organic pollutants and heavy metals in production water are rapidly diluted with little environmental significance (Gillman and Gibson, 1986). Disposal of non-degradable waste through ocean dumping is prohibited since 1972, while land fill as an alternative (though cheaper than preferred high temperature incineration) has resulted in leaching of pollutants into ground water. If this alternative is used for industrial waste disposal, regular monitoring including use of monitoring wells around the site is also considered essential (Ayers, 1987; Sharma and Agarwal, 1980).

Monitoring and control measures for excessive and continuous noise have been instituted as a part of environmental protection. Noise pollution mainly arising out of mechanical industrial operations, aircrafts, traffic, etc. causes harm to health and impairs working ability. The acoustic noise is measured in decibels (dBL) using portable Sound-level Meters and also other electro-acoustic transducers coupled with recorders and microprocessors. Regulatory standards for noise pollution are prescribed for occupational health as well as general pollution control.

Apart from direct monitoring of pollutants and studies on hazard to man, selection of a biotic community other than human has also been used as an indicator of environmental damage. Observations on wildlife are often more rewarding because these are unbiased and both presence as well as accumulation of contaminants is natural. The biotic communities best selected for monitoring covered insect, flesh and fish eating birds as well as fishes (Mehrotra, 1985; Hileman, 1988; Narayan and Verma, 1980). These studies have been extended to include reptiles, lizards, turtles specially in respect of residues of organochloro pesticides (Hall, 1980). A random monitoring study with wild dolphins and whales revealed high levels of Pb, Hg and Cd as well as PCB's and DDT in particular. These findings are significant proof of bioaccumulation and point to possible harm arising out of industrial and related pollution of the environment (Muiz *et al.*, 1988).

MONITORING AS STATUTORY REQUIREMENT AND FACILITIES

Regulatory control of toxic chemicals like lead and mercury started in the second half of the 19th century. By the middle of this century, however, all industrialized countries had some regulatory laws covering this field. Nevertheless, environmental accidents involving mercury, cadmium, PCB's, organochloro pesticides, etc. highlighted the environmental risk from anthropogenic chemicals and the need for stricter regulatory controls in more recent years. Realising that a major cause of environmental pollution arises out of industrial effluent discharge, solid wastes and air emission, these aspects formed the basis of legal provisions in sixties and seventies, at national level in respect of specific pollutants to the environment. These legal provisions and the stipulated limits of pollution are being reviewed and upgraded from time to time. However, compliance to the statutory safety standards involves in-house monitoring of original and treated wastes as well as surveillance of the final waste products released to air, water or on land. Monitoring at all these levels must be comprehensive to ensure effective help in control of environmental damage eventually. The laws are effective for achieving environmental safety only if these are implemented comprehensively, especially with respect to monitoring. This in turn needs large sophisticated testing and measuring facilities for which adequate support is most essential.

Under the Federal Insecticides, Fungicide and Rodenticide Act, USA 1972, as amended over the years, and the Environmental Protection Agency, comprehensive guidelines are provided for data generation to ensure safety with respect to environmental pollution. Similar legislations are also adopted by other industrially advanced countries with procedural differences and emphasis as per specific needs. In most of the developing countries, the last two decades, have witnessed considerable progress in establishing statutory monitoring and control measures for the industrial emissions, effluents, waste disposal as well as regulation of pesticides, food additives etc. The work of environmental pollution control is thus being upgraded and the government agencies, as well as industry are increasingly committed to make adequate investment in reduction of pollution due to solid, liquid and gaseous wastes. The task in India in this respect is entrusted to Central and State Pollution Control Boards under a recent comprehensive Environment (Protection) Act, 1986, as well as the Air (Prevention and Control of Pollution) Act, 1981 & 1987 and the Water (Prevention and Control of Pollution) Act, 1974 & 1977 (Anon., 1989b).

There has been significant regulatory effort at the international level by organisations like FAO, WHO, UNIPCS, OECD, EEC, UNESCO, etc. to harmonize environmental protection at apex level (Sheehan *et al.*,1985). For instance, United National Economic Commission for Europe has got a protocol agreed by large number of members for reduction of air pollutants after a convention on "Long Range Transboundary Air Pollution" in 1983. Recently under Montreal Protocol, a major effort is underway to phase out CFC's and replace them with safer substitutes on high priority (Anon., 1989a). WHO/FAO Food Contaminant Monitoring Programme since 1976, covering a wide variety of chemicals coupled with action under comprehensive national legislations on food, fertilizers, pesticides, etc. has also helped to significantly reduce the environmental damage (Anon., 1988b).

A survey of analytical methodologies currently in use clearly indicated diverse legal procedures and variable testing standards and facilities. This is expected for a growing scientific field. However, manual operations involving basic wet chemical analysis will have to remain acceptable till sophisticated automatic recording instruments are universally inducted. Development of compact and reliable self-recording analytical instruments, simultaneous recording of several parameters and development of mobile outfits has further streamlined the difficult analytical tasks (Mishra, 1985). For individual trace metals, analysis by graphite furnace A.A. Spectrometry is most widely accepted technique due to high sensitivity and selectivity. ICP-atomic emission spectrometry does offer a multi-element analysis capability but the sensitivity is low. For microestimation of organic contaminants a wide range of sophisticated, sensitive and accurate methods such as GC, HPLC, GC/MS, FT-IR, visible and UV spectrophotometry, etc. have been adopted. As the concentrations encountered are usually very low (microgram, nanogram levels), adoption of specific analytical technique often requires preliminary concentration or removal of interfering materials. For example, monitoring of microgram per litre concentration of trace metals in sea water required special extraction of metals as chelates followed by graphite furnace. A.A. Spectrometry in preference to other techniques like Anodic-stripping voltametry and ICP- atomic absorption spectrometry (Aston and Chan, 1987). As accuracy and reliability of monitoring data is a fundamental prerequisite for technical and regulatory actions, constant endeavour for improvement in this area is vital. Uniformity in sampling, sample preparation and selection of analytical methods specific to the concentration of chemical species in environment are major areas of research and development. Quality control/quality assurance procedures would further improve capabilities to interpret and compare trends in contamination (Delia *et al.*, 1989).

CONCLUSIONS

Conventional monitoring of chemical contaminants within soil, water and atmosphere is now being supplemented by specific screening model studies on major pathways for organic chemical transport and transformation within soil and atmosphere. Several experimental models have been tried with specific reference to toxic organic chemicals in soil-air-water ecosystems (Jury *et al.*, 1987). The data generated and predictions made fall short of complete understanding. The goal still remains to develop a unified transport and fate model, which could describe comprehensively chemical, physical and biological transformation processes occurring in case of organic chemicals in nature. At present development of such computational models is limited by paucity of detailed and accurate experimental data on the transport and fate of more complex industrial and agricultural chemicals available in the ecosystem. Major interdisciplinary programmes both in the field and laboratory will thus be needed to understand all the important parameters on which determination of total fate of the chemicals can be rationally based. However, any such attempt would still require comparison with results obtained by actual monitoring of the chemicals in the environment.

Extensive chemical monitoring of industrial wastes and their potential for harm have lead to specific technologies to reduce hazards from such sources. Efficient treatment systems, scientific land fills and high temperature incineration of wastes are providing a good measure of protection. Recycling and reusing of the industrial wastes is another fruitful area in which Japan has taken a lead (50% wastes recycled in 1983). Major emphasis is also directed towards rational use of pesticides, fertilizers, food additives, etc. and phasing out/substituting hazardous chemicals like lead, PCB's, CFC's persistent pesticides, carcinogenic chemical, etc. (Anon., 1988b, Anon., 1989a). Cleaner technologies and efficient waste management systems are thus being vigorously enforced as intrinsic measures to contain environmental pollution. Monitoring, both before and after such measures, to determine the success achieved and as an input for further regulatory and technological improvements, remains the key requirement.

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ENVIRONMENTAL IMPACT OF MAJOR CHEMICAL ACCIDENTS

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The direct and indirect effects of major chemical accidents are amongst the greatest concerns facing the industry, governments, environmentalists and the public in almost every country in the world today. With chemical industrial growth coming to be regarded as barometer of a country's development, and a 1000 or so new chemicals getting added to some 70,000 already in every day use around the world, there is genuine cause for concern in the matter of safety in the design, operation and handling of chemicals and chemical installations.

Major industrial disasters are occurring at more frequent intervals than the rate at which humanity and the environment can recover from one. Effects of chemical accidents on the environment range from a temporary change of manageable proportion through serious, acute, temporary actions of high magnitude to drastic, long term environmental impairment.

According to a 1974 UNIDO classification, a country qualified to be designated as industrialised when manufacturing industries account for more than 30% of Gross Domestic Product. Even at that time 38 countries of the Third World could be ranked as industrialised. As more and more nations expand their development activities, the chemical and allied industries naturally register rapid growth providing products for civilian and defense needs. A good number of the chemicals involved in such industries are hazardous and highly toxic to humans, animals and the environment.

Although the chemical industry has itself pioneered the invention of hazard assessment procedures and techniques and has been, in general, responding positively to demands for greater safety and controls, several recent disasters question the ability of even experienced industrial giants to face a crisis. The 'Schweizerhalle' fire caused the release of at least 30 metric tons of toxic chemicals including 150 kg of mercury into the Rhine river, in addition to roughly 10,000 m^3 of the fire extinguishing water. Severe ecological damage occurred over a length of 250 km killing river fauna and flora and the company's safety systems could not contain the damage. A more recent case has raised serious doubts whether the much advertised ability of the petroleum industry to prevent and effectively clean up oil spills is more in theory than practice. The oil leak from VALDEZ and its disastrous consequences to Alaska's ecology and environment has once again revived international debate on our ability to manage major emergencies and contain environmental upsets.

The paper will discuss four different chemical disasters as examples of varying degrees of environmental impact and highlight the following:

- Strategies for reducing threats from chemical accidents;
- Risk assessment and engineering for intrinsic safety;
- Role of information in the prevention of and response to future accidents;
- Analytical tools and techniques; and
- Areas for research and international cooperation.

INTRODUCTION

It is now well recognised that an important indicator of industrial development of a nation is the production and rate of growth of the chemical and allied products industry which caters to basic societal needs, industrial diversification, trade and national security. As more and more nations join the mainstream of this development innumerable new manufacturing units are getting established, often in locations unacceptable from public safety considerations. Chemicals are produced, stored and transported in large volumes. Chemical Abstracts lists over six million chemical species made in the laboratory. An estimated 70,000 different types of chemicals are now in use world over. World production of chemicals of all types is now several hundred million tonnes every year with demands continually increasing by 10 to 15 percent.

The manufacture of chemicals involves a complex set of unit operations and processes involving transfer of mass and heat in varying degrees and reaction conditions ranging from very low to very high temperatures and pressures requiring or releasing varying levels of energy. Chemical substances used in manufacturing operations tend to be reactive and it is this very property that forms the basis of chemical operations. A large number of them are also toxic and therefore potentially hazardous to human health and the environment. A major chemical accident can arise from uncontrolled developments in the course of an industrial or a rare natural activity involving one or more hazardous substances, with serious consequences to people and the environment. Typical examples of conditions which can cause major accidents are:

(i) Thermal radiations exceeding 5 kw/m^2 intensity for several seconds;

(ii) Release of a dangerous substance beyond the specified limits;

(iii) Vapour or gas explosions with blast over-pressures exceeding 0.5 kg/cm^2; and

(iv) Explosion of a reactive substance.

SCHWEIZERHALLE INCIDENT (Switzerland)

On 1 November 1986, in the centenary year of Sandoz, the chemical giant became the focus of international attention for having caused an ecological and environmental catastrophe from its Schweizerhalle works in a suburb of Basle, Switzerland. At nineteen minutes past midnight on that morning, a fire originated in Warehouse 956 and spread with extreme rapidity releasing noxious smoke over Basle and the French countryside further down the Rhine river. No deaths were reported but the environmental damage the disaster caused was much more serious, and shattered public faith in an industry that contributes half of Basle's earnings and the image of Switzerland as a clean and environmentally model country.

Warehouse 956 was purposely built and approved for storage of agricultural chemicals with a flash point of over 21°C. Even four days before the accident it had been inspected and cleared for fire safety. The fire produced a heavy smoke of phosphoric esters and mercaptans. Ten fire brigades with 160 men could only manage to prevent it spreading to the neighbouring warehouses and manufacturing operations. The emergency task force of the city sounded the C- (chemical) alarm warning the communities in the area and the city of Basle to stay indoors and await the 'clear' signal which was given after seven hours. For the people a threat to their lives was eliminated but for the Rhine river and the countries along its course the consequences were beginning to unfold.

In chemical terms the river received in a matter of hours roughly 66,000 pounds of highly toxic chemicals, among which were the pesticides atrazine, disulfotan, fenitrothion and parathion, phosphoric acid esters and mercaptans used as intermediates in the pesticide synthesis and an estimated 150 kilograms of mercury in aqueous concentrates. Since the fire could not be fought with foam alone, large amounts of water were used and nearly 10,000 cubic metres of this effluent also drained into the Rhine river. Atrazine, one of the toxic chemicals involved in this disaster, has a high water solubility and limited tendency to absorption to soil, and is therefore capable of persisting in ground water and deep soil layers (Pocchiari *et al.*, 1987a).

Most appalling was the action of several other major chemical companies along the Rhine who took advantage of the disaster and discharged a lot of their highly toxic wastes into the river contaminating the water further and complicating the efforts of Sandoz and the River authorities to repair the damage and restore life to the dead river. Companies reportedly (Layman, 1987) involved in compounding the tragedy were Ciba-Geigy (400L of atrazine, herbicide spill), BASF (1089 kg of 2, 4-D acid, ethylene glycol), Lonza (2.7 t of PVC), Bayer (methyl alcohol) and Hoechst (chlorinated hydrocarbons).

By the Company's own admission the consequences of "Schweizerhalle" were more ecological and psychological than on human health.

Human health

Complaints such as headache, nausea burning sensation in the eyes and respiratory discomforts were reported (Salzmann, 1987). No long term health hazard is expected although this would need to be confirmed by monitoring those who were exposed to the effects of the toxic fumes.

Ecological damage

Severe ecological damage was observed over a length of 250 km of the Rhine with the fish population, especially eels, completely wiped out. EAWAG (Swiss Federal Institute for Water Resources and Water Pollution Control) had been involved in the assessment of effects and the study reported that while the river's bacteriological regenerative capacity was not affected, the invertebrate microorganisms would be restored gradually allowing conditions for restocking with fish.

However, the psychological damage created by this disaster would take a very long time to heal especially in the other countries down course.

Schweizerhalle works subsequently implemented several measures such as cutting down insecticide production by 60%, a one-third cut in stocking of agrochemicals, discontinuation of phosgene storage and phosgene-based manufactures, along with a review of the entire manufacturing programme involving hazardous chemicals and intermediates. In retrospect it would appear that the disaster could have been avoided, had these measures been taken in the normal course of review.

BHOPAL INCIDENT (India)

"Worker panic in the plant, a sleeping community outside as the gas begins to spread. Bodies roused, coughing, crying out, eyes burning and watering. Thousands running, staggering through the dusty streets and alleys, many clutching their babies, not knowing where to run to escape.

Unconsciousness, injury and death by the thousands. Pandemonium in the hospitals. By day break, the scene of silence around those left behind; fathers, mothers, children, cows, bulls, goats, dogs, all in final repose. A peace in its eeriness never more heart wrenching. The bodies disposed of by cremation and mass burials."

The above is the chilling description by Lepkowski (1985) of the early hours of 3 December 1984, the day of the worst industrial disaster in the history of the world chemical industry. The leakage of poisonous methyl isocyanate (MIC) gas from the chemical plant of Union Carbide at Bhopal left in its wake over 2,500 dead and over one hundred thousand injured, with irreparable damage to a high percentage of them. The calamity rocked the consciousness of the chemical industry and sowed the seeds for a continuing vastness to the subject of industrial safety.

Union Carbide was producing carbaryl (Sevin) and other pesticide formulations in a large manufacturing facility in Bhopal in Central India (Fig. 1). For the synthesis of carbaryl the company employed the route (Fig. 2) involving the key intermediate MIC, one of the most poisonous and reactive chemicals known. For three years, before starting actual production at the Bhopal plant in 1980, MIC was imported in stainless steel drums from Union Carbide's MIC plant in USA. Local production of MIC in Bhopal involved production of carbon monoxide and phosgene and the process as well as basic engineering designs were provided by the parent company as for the synthesis of Sevin itself.

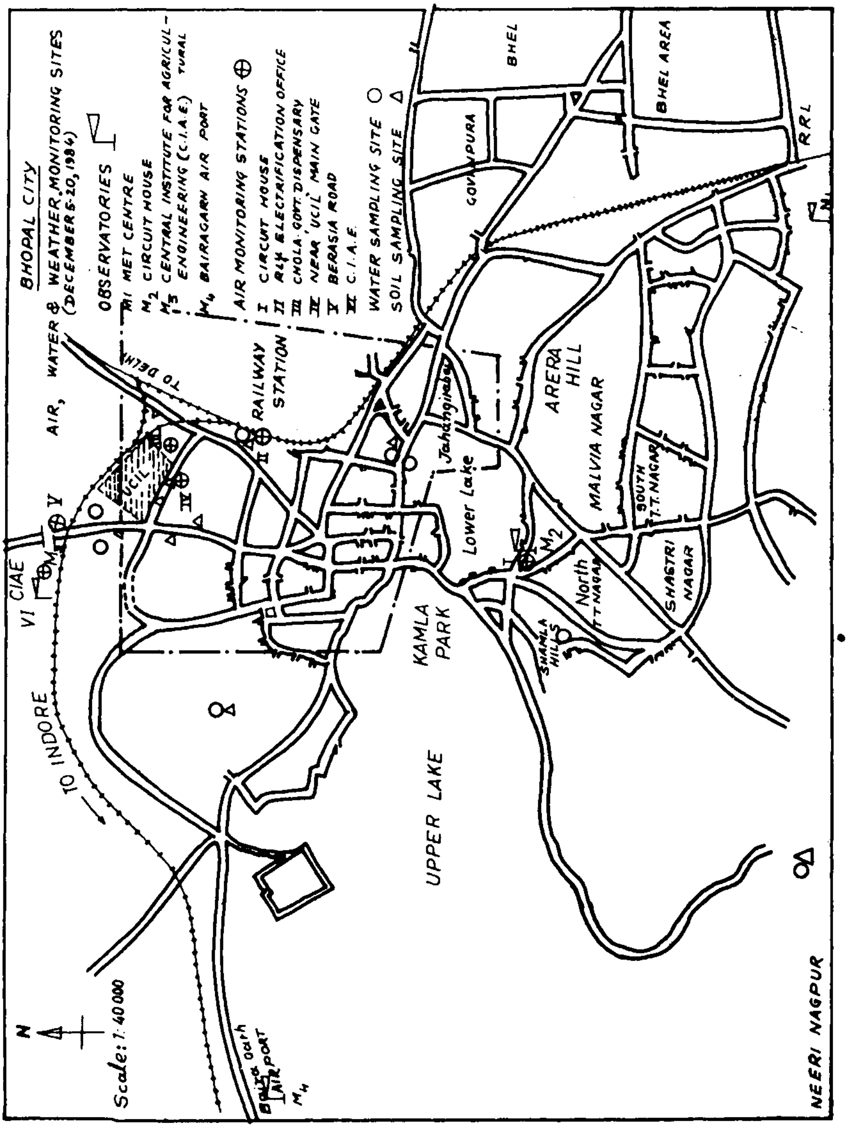

Fig. 1. Bhopal city map.

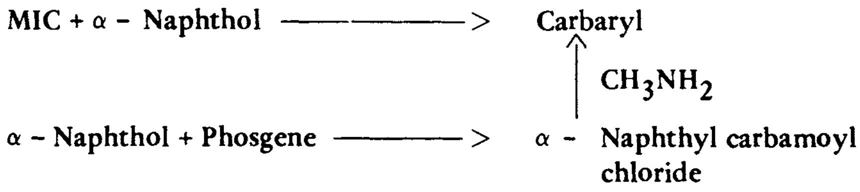

Fig 2. Carbaryl synthesis with and without MIC.

The chemical reactions involved in the synthesis of MIC are shown in Fig. 3. Phosgene and MMA were reacted in vapour phase to give MCC which upon quenching in chloroform and subsequent pyrolysis decomposed to give MIC and HCl. The pyrolyser condenser fed the MIC Refining Still (MRS) and the MIC, freed from chloroform, was led directly into the storage system which consisted of three horizontal, mounted 15,000 gallon (57 m^3) tanks designated E 610, E 611 and E 619 (Fig. 4). Normally two of the three tanks were used to store, under high priority nitrogen pressure, product of acceptable quality while the third was used to store off-specification MIC which was then reprocessed. The two tanks together would hold 90 t of MIC, a 30 days inventory for Sevin production. All three tanks were interconnected by a maze of pipelines and common headers linking the Process Vent Header (PVH), Safety Relief Valves (SRV), and Relief Valve Vent Header (RVVH) and Vent Gas Scrubber (VGS). The VGS was meant to neutralise toxic gases from the MIC production plant and from the storage system, by scrubbing them with counter current flow of 10% caustic solution, the strength of which was maintained by pumping in a 20% make up solution. Finally, a flare tower was responsible for burning vent gases, coming from VGS, MIC storage tanks, as well as from the production range.

$$2C + O_2 \longrightarrow 2CO$$

$$CO + Cl_2 \longrightarrow COCl_2$$

$$COCl_2 + CH_3NH_2 \longrightarrow CH_3NHCOCl + HCl$$

$$CH_3NHCOCl \longrightarrow CH_3NCO + HCl$$

Fig 3. MIC Synthesis.

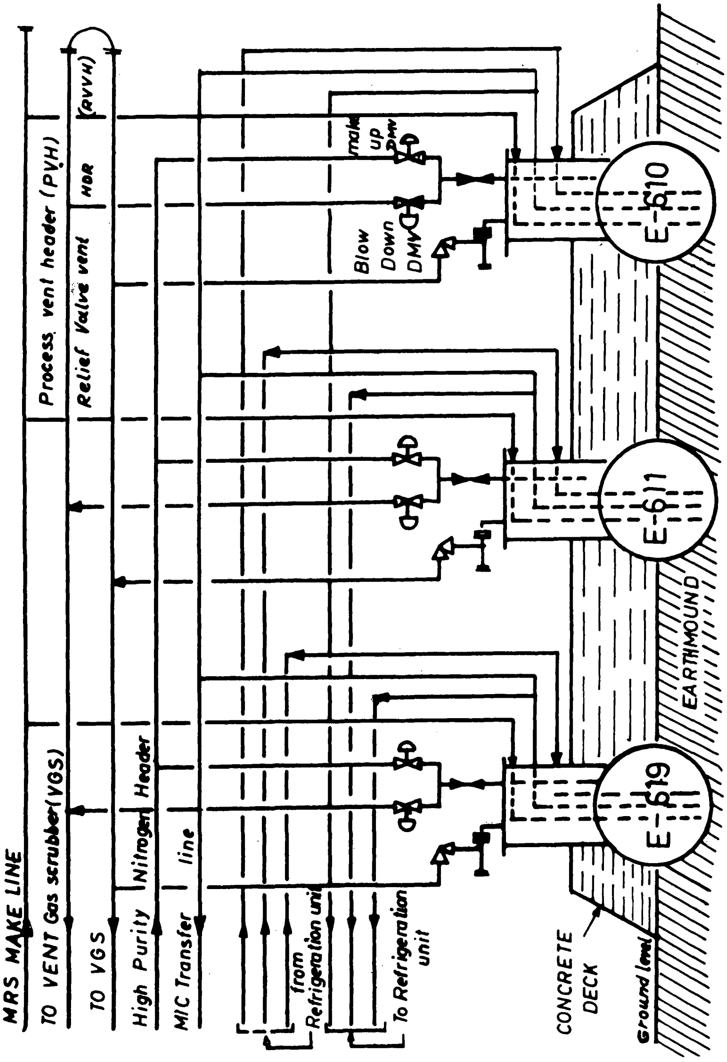

Fig. 4. Schematic layout of common headers of MIC storage tanks.

MIC (bp 30°C) itself is a highly toxic, volatile and inflammable chemical, always to be stored and handled in stainless steel 304 and 316 equipment since metallic impurities such as iron, aluminium, zinc, galvanised iron, copper or their alloys would cause violently explosive polymerisation. Purified MIC will react with itself under the influence of a catalyst (e.g. strong bases, certain metallic chlorides) to form a cyclic trimer or a high molecular weight polymer. Highly purified MIC spontaneously polymerises exothermically. With these sensitive properties MIC qualifies as an explosive besides being a highly toxic chemical.

The event

MIC produced between 7 and 22 October was stored in E 610 mixed with old material (6.4 t) already contained in it. After a transfer of 23 t to E 611, further production was fed into E 610 which at the time of the runaway reaction contained approximately 42 t of MIC. About the same quantity was present in E 611 as well.

As per operating practice MIC in the storage tank was normally maintained under nitrogen pressure of 1 kg/cm^{2}g. On 22 October E 610 registered an abnormal drop in pressure to 0.25 kg/cm^{2}g and continued so. When Sevin production was commenced MIC was drawn from E 611 but it developed a pressurisation problem on 30 November. Attempts to pressurise E 610—to draw out MIC—did not succeed. Meantime an alternative system for pressurising E 611 succeeded and MIC was drawn from this tank—a further attempt once on 1 December on E 610 proved negative.

Rapid developments occurred from 2330 hours on 2 December. MIC leakage was noticed in the MIC production area near the VGS, along with dirty water. At 0015 hours the Control Room operator observed E 610's pressure shooting up and in the range of 25-30 psig which rose to over 55 psig by 0030 hrs, along with a loud hissing noise. Efforts to start VGS failed, and the flare was not on.

The gases surged past and into the atmosphere, got condensed with cold air and aided by atmospheric inversion settled down slowly on the ground starting the tragedy.

Scientific investigations on the causes of the catastrophe have now established that the factors which led to the toxic gas leakage and its heavy toll existed in the unique properties of MIC's high reactivity, volatility and inhalation toxicity. It was foolish to store this chemical in large quantities for indefinitely long periods with no arrangement to check its quality or condition. Serious defects in design, in choice of materials of construction, in instrumentation and warning systems coupled with inadequate controls on stored MIC and underdesigned refrigeration and scrubber systems all provided a combination of conditions for such a tragedy to happen (Varadarajan, 1985).

Assessing the effects of MIC leakage in the aquatic environment involved examination of end-products of degradation of MIC in water and fish in the Upper and Lower Lakes of Bhopal. While the far-away Upper Lake recovered from MIC effects except for excessive amounts of free ammonia, the Lower Lake, nearer to the factory, was completely eutrophicated and remained dead for all practical purposes even after 140 days (of the disaster).

Air, soil and water were monitored and the environment at Bhopal was cleared as safe on the evening of 5 December.

SEVESO INCIDENT (Italy)

2, 3, 7, 8 - Tetrachlorodibenzo-p-dioxin, also called Dioxin or TCDD is 70,000 times as deadly as cyanide, and has the nickname 'Super poison'. It is invariably a contaminant in trichlorophenol (TCP) which is a key intermediate in the preparation of 2, 4, 5 - trichlorophenoxyacetic acid (2, 4, 5-T) a defoliant ill-reputed as Agent Orange. TCP itself is produced by reaction of 1, 2, 4, 5-tetrachlorobenzene (TCB) with caustic alkali.

The company involved was Givaudan belonging to the Swiss chemical giant —Hoffmann la Roche. On Friday, 9 July 1976 operators charged the reaction kettle with 2 tonnes of TCB, 27 sacks of NaOH flakes, xylene and glycol. The initiated reaction was interrupted and the plant shutdown for the weekend.

Almost 24 hours later, at 12.37 pm on Saturday, the reactor exploded rupturing the safety disk of the kettle and toxic contents spilled into the air—valve commanded a pipe located over the roof—carrying an estimated 2 kg of the deadly dioxin. Consequences, observed and feared, caused schools to be closed, whole areas were evacuated. The medical and environmental emergencies led to the opening of a

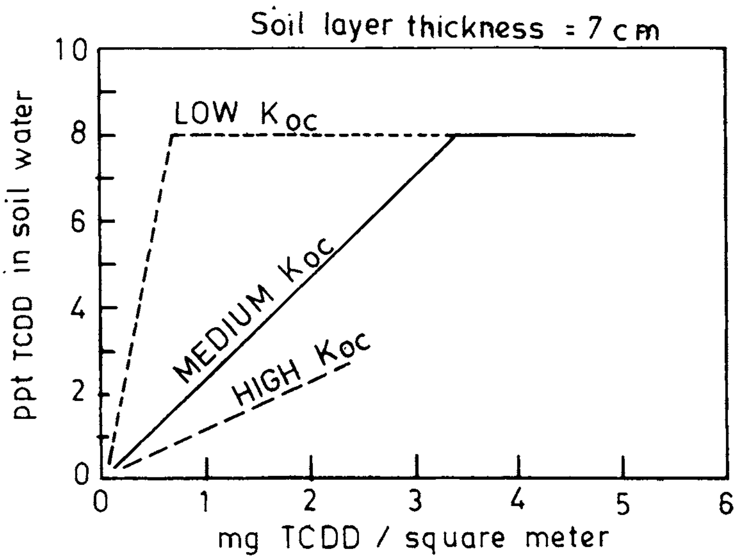

Fig. 5. TCDD saturation trend in soil.

Special Office at Seveso (SOS) in June 1977 with authority from over 11 towns with an aggregate population of 2,20,000.

Reclamation work alone lasted up to 1982 and involved scraping or washing buildings with solvents, removal of contaminated top soil to a depth of 20 cm or elimination of objects that could not be treated (Strigini, 1983). Some 8,200 m^3 of vegetation was removed. The contaminated materials thus removed had to be isolated and for this purpose two basins with a combined capacity of 2,30,000 m^3 were constructed near the site. TCDD represents a class of organic compounds with a strong tendency to be absorbed into soil as was the case after the Seveso release. Figure 5 shows that TCDD vertical distribution scarcely changed after an initial permeation—a relatively stable and long term contamination scenario (Pocchiari, 1987b). The prevention of initial permeation therefore becomes a matter for immediate attention in any rehabilitation and reclamation activity arising out of accidentally released chemicals. In the Seveso case the problem was further compounded by lack of information on its physico-chemical fate in nature. Dioxin's well documented data on carcinogenicity and embryo toxicity was equally threatening.

Immediate effects of the toxic release were:

(i) Animal deaths (over 100,000);

(ii) Chloracne—a persistent and disfiguring skin disease, with loss of muscular strength and psychological disturbances especially in children;

(iii) Spontaneous abortion in pregnant women; and

(iv) Contamination of over 1,800 ha of soil and vegetation.

Of greater concern were the 'unknown dimensions' such as:

(v) Determining who had been or had not been exposed to dioxin;

(vi) Mapping contamination areas accurately;

(vii) Area reliability before resuming agricultural activities;

(viii) Epidemiology of dioxin (carcinogenicity, embryotoxicity);

(ix) Risk of cancer and genetic defects which takes years to manifest; and

(x) Disposal of toxic waste.

Apart from individual out-of-country settlements, worker compensation and payments to affected farms, the towns affected by the accident demanded and got compensation all totalling over $100 million.

The disposal of the piled up toxic waste created another story. The 41 containers filled with an estimated 150 g of dioxin were quietly buried by a contract company in the background of a French village for nearly 8 months until it was traced and exposed. The Swiss firm took charge and destroyed the dioxin by high temperature incineration (Strigini, 1983).

The Seveso disaster is attributable to bad process practice and negligence, particularly since there had been four previous instances of TCP runaway reaction in USA (1949), West Germany (1953), Holland (1963) and UK (1968) affecting between 50 and 200 workers in each case.

LAKE NYOS INCIDENT (Cameroon)

Lake Nyos is situated in a valley in the North-West Province of Cameroon, an area with a history of extensive volcanic activity in the geologically recent past. The lake has a surface area of 1.48 km and is probably only a little over 200 m deep suggesting that it was possibly formed by the eruption of a volcano.

On 21 August 1986, late in the evening a large volume of toxic gas erupted from beneath and within the lake and the aerosol mix of this toxic cloud descended on the valleys to the north of the Lake leaving a trail of 1,700 dead people, young and old and over 4,000 dead and dying livestock.

While international relief efforts were quickly mounted to help the survivors and monitor environmental clean-up this disaster prompted several scientific investigations to understand the phenomenon and its suddenness. These studies and the scientific conferences which discussed the geological, geochemical, physical-chemical and toxicological dimensions of the disaster have produced voluminous data from which the following conclusions are summarised:

(i) The Lake lost 200,000 t of water or an equivalent volume, based on an observed recharge rate of 50,000 t of water per day. The Lake got saturated with CO_2 of volcanic origin just days prior to the event,and on the fateful day a pulse of volcanic gas—mostly CO_2 but also H_2S—caused the CO_2-charged bottom waters to surge up which, upon reaching the surface, transformed into a fine aerosol and sent a wall of water crashing across the lake, and down the valleys. About 6,000 t of gas equivalent to 3 million m^3 at atmospheric temperatures and pressures must have been released (Freeth and Kay, 1987);

(ii) In physico-chemical terms the following reaction equilibria would appear to account for the principal gases observed in a volcanic environment (Hassan El-Etr, 1987);

$$H_2 + CO_2 \longrightarrow CO + H_2O$$

$$4H_2 + 2SO_2 \longrightarrow S_2 + 4H_2O$$

$$N_2 + 3H_2 \longrightarrow 2\,NH_3$$

$$2H_2 + S_2 \longrightarrow 2\,H_2S$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

Since these involve the breaking down and re-arrangement of gas molecules, some or all of them may be slow, even at the high volcanic environment temperatures such that equilibrium is not always reached;

(iii) The dead suffered burns indicating sulphuric acid presence. Death in most cases must have resulted from asphyxia (Tanya *et al.*, 1987);

(iv) All species of living things which came into contact with the gases succumbed. No reptiles, birds, arthropods or flies were visible even one week after the disaster (Tanya *et al.*, 1987);

(v) Apart from trees and vegetation uprooted and thrown by the powerful surge of water, pastures did not suffer any lasting damage. There was no significant chemical damage to the vegetation (Freeth and Kay, 1987; Tanya *et al.*, 1987);

(vi) The seismicity of the region is on the increase with forebodings of more events in the area. The gas emanations are also indicative of future volcanic activity (Hassan El-Etr, 1987); and

(vii) Hazard evaluation and mitigation should receive high priority (Oskarson, 1987).

ACCIDENT RECORD OF THE CHEMICAL INDUSTRY

Table 1 is a partial listing of major chemical accidents around the world during the period of 1974-1988. An analysis highlights the following general causes or causative factors:

(i) Runaway reactions, explosions or fire in the plant;

(ii) Design faults leading to accidental mixing of chemicals;

(iii) Storage of unacceptably large quantities of hazardous and vulnerable chemicals;

(iv) Accidents during transportation by rail, road or sea;

(v) Inventory control failure;

(vi) Improper waste disposal practices; and

(vii) Human failure.

Specifically, major accident contributing factors are equipment or process-related. In an analysis (Sastri, 1987) of 110 losses of over US $ one quarter million each in chemical plants in the USA during 1974, 75 and 76 accidents were caused by equipment design (41%), chemical operator error (31%), maintenance (12%), process design (10%), and material hazard (6%). An analysis of 463 accidents in petroleum refineries and petrochemical complexes in Japan revealed three main causes: (i) equipment construction or engineering; (ii) management; and (iii) operator-related (Nishikawa, 1983). In the UK chemical industry 2100 accidents during a three year period 1982-85 analysed as: (i) process-related (65%) and maintenance-related (30%); (ii) over 50% of the cases involved release of harmful substances; and (iii) over 25% of the accidents occurred while maintenance work was being carried out. It was possible to assign full or partial responsibility to the site management for 75% of the cases (Robinson, 1987).

Strategies for reducing threats from chemical accidents

In industry, resources both financial and technical, are never enough to totally remove all hazards. A practical way is to be devised to minimise the hazards on a cost effective basis. Hazard analysis is a practical loss prevention tool that can be tailored to the specific need of an industrial management to restrict its preventive costs only to those hazards whose severity and probability of occurrence are high enough to warrant expenditure. To achieve this objective, an industrial manager has to evolve meaningful quantitative data from the accepted norms and with his own engineering judgement.

Conventional approaches to hazard assessment were based on empirical codes and standards and were primarily intended to check for errors and omissions in design. No attempts were made to examine a chemical project as a dynamic running unit or to involve and integrate the skills of multidisciplinary teams. These are inadequate for the new process technologies and their complexities (Raghavan and Thyagarajan, 1988).

Modern Hazard Assessment techniques involve identification and analysis. Six principal methods available today are:

(i) Failure Mode and Effect Analysis (FMEA);

(ii) Hazard Analysis (HAZAN);

(iii) Hazard and Operability Study (HAZOP);

(iv) Fault Tree Analysis (FTA);

(v) Consequential Analysis (CA); and

(vi) Risk Rating (RR).

The modern philosophy is to make Hazard Analysis a continuous process throughout the life of a chemical process facility. The optimum times to conduct such studies are: (i) conceptual design phase; (ii) design freeze stage; (iii) prestart up period; and (iv) normal and modified operations. The usefulness of hazard analysis in each phase differs in its quality. During the conceptual design phase, the analysis will assist in the site selection and plant layout. Many potential hazards due to fire, explosion and toxicity can be spotted and significant changes made at minimal cost. Hazard analysis during design freeze phase is extremely useful in making risk assessment of a new facility. Changes in the plant can still be made rather easily since most equipments, though already specified, will not have been ordered. Hazard analysis during prestart up phase should be a final check rather than an initial assessment. Of main concern would be the status of the recommended changes from the previous hazards/risks are unearthed during this phase, it is unlikely that they can be eliminated without significant cost or start up delays.

The later the hazard analysis is done, the more difficult it is to incorporate safety revisions without significant cost or time delays.

Failure mode and effect analysis

FMEA technique can be conveniently employed to a specific equipment or a particularly hazardous portion of a large process. The primary objective is to evaluate the frequency and the consequences of component failure on the process (US Dept of Navy, 1977). No attempt is, however, made to examine the component failures due to errors/deviations in operating procedures or those made by operators. This method becomes cumbersome when applied to a complex chemical process. Its utility is therefore limited.

Hazard analysis

HAZAN provides a systematic approach for the identification of risks. It may be undertaken at the preliminary stage for determining a plant location, basic design principles and process parameters to establish adequacy of basic safety of design, operation and environmental control. The major subcomponents of the study are:

(i) Identification of flow path of all the fluids/solids in the process;

(ii) Identification of likely sources of leakage;

(iii) Size and duration of hazardous gas releases;

(iv) Determination of sources of ignition; and

(v) Collection of site specific data.

Based on the HAZAN study and the identification of major hazards associated with the various engineering systems, a HAZOP study can be carried out.

Hazard and operability study

HAZOP studies are undertaken at an advanced stage of project implementation when the design criteria for a chemical plant are well established. The studies are applicable to both new and operational plants and are based on the concept of a systematic and comprehensive sectionwise examination of an installation on the basis of piping and instrumentation diagrams (Lawley, 1974). A HAZOP study supplemented by site inspection exercises enables all potentially dangerous situations likely to result from the unexpected interaction of seemingly safe components or methods of operations under exceptional conditions, to be anticipated and recognised.

The principal subcomponent activities of a HAZOP study are:

(i) Division of the chemical process unit into sections identification of critical process equipments from hazard considerations;

(ii) Likely process parameter deviations in critical process equipments;

(iii) The likely causes for the deviations;

(iv) Implications of the causes on the individual equipments;

(v) Assessment of the capabilities of control instruments/indicators/alarms;

(vi) Search for off-site hazard potential;

(vii) Preliminary classification of identified hazards;

(viii) Reclassification after technical discussions/relevant data acquisition/process analysis;

(ix) Attempts for narrowing down the hazardous events; and

(x) Quantification of the risks through FT/consequence analysis.

HAZOP which involves several subcomponent activities is to be carried out by multidisciplinary teams of experienced technical personnel possessing detailed knowledge of both the design and operations of chemical process plant. The study team should include experts from production, technical and engineering services, process control and instrumentation, research and development and safety departments. The team should be able to gather reliable data on failure rates of process equipments. The most appropriate time to commence a HAZOP study is at the design freeze stage when the design is firmed up and detailed engineering is in progress.

Fault tree analysis

The Fault Tree approach to system safety is an excellent tool for identifying and correcting system defects, and can be very effectively utilised in conjunction with a HAZOP study (Lee, *et al.*, 1985). The method is based on the promise that a loss incident or an accident has one or more causes/events/conditions which are deviations from the normal or planned state of the system. If only one such event or condition is sufficient to cause an accident, then the probability of its occurrence is equal to the probability of this cause event. If two or more independent events are required, then by the multiplication law, the probability of an accident is equal to the product of the probability of these events. Because probabilities are expressed as fractions (10^{-1}-10^{-7} per hour), the requirement for each additional cause event reduces the probability of an accident by several orders of magnitude. This principle is exploited in FTA to provide interlocks to prevent catastrophic reaction incidents.

Data reliability plays a crucial role in FTA of chemical process industries (Powers and Tompkins, 1974). Constructing fault tree is an instructive procedure requiring system and environment dependent data. Table 1 show typical failure data useful for process industries. It should be supplemented to system dependent data applicable to a particular plant and its environment. Human failure rates deserve special attention since human beings are less reliable by at least three orders of magnitude at repetitive and programmable tasks.

Table 1: Major Chemical Accidents during 1974-88

Year	Place	Nature of accident	Consequences	
			Death	Injuries
1974	Decatur, USA	Propane explosion	7	152
1974	Flixborough, UK	Explosion in caprolactum plant	28	89
1975	Beek, Netherlands	Propylene explosion	14	107
1976	Seveso, Italy	Runaway reaction, dioxin/TCDD emission	— long term effects	193
1977	Cartagenia, Columbia	Ammonia release	30	25
1978	Chicago, USA	Hydrogen sulphide release	8	29
1978	Santa Cruz, Mexico	Methane fire	52	—
1978	Xilatopec, Mexico	Gas explosion in transit	100	150
1978	Los Alfaques	Propylene transport accident	216	200
1979	Three Mile Island, USA	Nuclear reactor accident; 200,000 evacuated		
1979	Novosibirsk, USSR	Chemical plant accident	300	
1980	Sommerville, USA	PCl_3 accident during rail transportation	—	300
1981	Tacoa, Venezuela	Oil explosion	145	
1982	Taff, USA	Acrolein explosion; 17,000 evacuated		
1984	Sao Paulo, Brazil	Petrol pipeline explosion	508	
1984	Ixhuatepec, Mexico	LPG tank explosion	452	4,248
1984	Bhopal, India	Runaway reaction of stored MIC in pesticide plant	2,500	'000s
1986	Chernobyl, USSR	Nuclear reactor accident, 90,000 evacuated, transboundary fall-out in Europe	325	300
1986	Devnya, Bulgaria	Fire in a chemical complex	17	19
1986	Schweizerhalle, Switzerland	Fire-related spill of toxic chemicals. Rhine river pollution and ecological damage		
1988	North Sea, UK	Piper Alpha oil rig explosion	166	

Consequence analysis

For each credible event in a chemical processes system, consequence analysis can be made. It is based on specially evolved consequence modelling techniques. From such an analysis, the most hazardous events can be identified and safety measures suggested (van Deelan, 1987).

Risk rating techniques

These techniques rank the hazards of various plant units at the early stages of project design. These rankings can be used to layout a plant logically, determine spacing distances between various plant units and buildings, specify ventilation requirements and suggest fire fighting and other safety requirements in different sections of a plant. The initial calculations are made with no credit given for safety features. The approach to RR techniques is flexible and can easily be modified to suit specific problems or local requirements. They are normally offered as suitable starting points in safety analysis.

Hazard analysis for siting industries

Traditionally, the location and siting of chemical plants are determined by economic, market, labour, transportation, water, energy and associated factors. For installations that process hazardous, flammable and toxic materials, hazard analysis is a convenient tool in ensuring the safety of employees and the neighbouring community by providing adequate spacing within and between hazardous plants and the neighbouring community. These analysis may also stimulate designers to reduce inventories of hazardous materials, pipeline sizes and failure probabilities. Applying hazard analysis in the early planning stage of a chemical plant may provide a useful quantitative assessment of alternative layouts for hazardous plants. The technique can readily be computerized allowing easy checks and layout modifications and spacing provisions throughout the evolution of the project.

CONCLUSIONS

The paper has attempted to present two relevant dimensions to the Symposium theme: (i) the environmental effects of major chemical accidents; and (ii) possible ways of preventing the accidents. Given that modern society's needs are propelling fast technological developments, human and environmental consequences are to be anticipated. Technological disasters are becoming a source of major concern to all countries, developed or developing. As research in chemical and material synthesis finds advantages in exploring extremely high temperatures and extremely high pressures (Pimental Report, 1985) our goal must be to continually upgrade intrinsic safety in industrial innovation and reduce the probability of accidents and their subsequent impacts to the maximum extent possible.

Chemical safety has also assumed global dimensions calling for international cooperation in the transfer of hazardous chemical technologies. A systematic and comprehensive effort should be mounted to analyse previous chemical accidents and widely disseminate the information in the industry. For example there were four accidents in the process industries similar to the one which occurred in the Seveso plant.

There is also need for increased attention to analytical procedures and properties of chemicals. In Bhopal the threat of a second toxic release was looming large until correct analytical procedures were developed to establish the quality of MIC in the second tank for safe processing. In this experience the importance of correct analytical methods and its availability in a time of crisis was acutely felt.

Finally, there is need to promote research on chemical safety on a continuing basis, and to encourage radically fresh thinking in the planning and siting of chemical industries.

These and other initiatives may substantially contribute to reducing threats from chemical accidents for human lives and the environment.

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ATMOSPHERIC MODELLING

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The possible consequences of global warming have raised so much concern that United Nations has sponsored an effort to develop cooperative mitigation strategies for greenhouse phenomenon. The global temperatures and precipitation with increased levels of carbon dioxide and other greenhouse gases have become a subject matter of deep concern. While actual measurements enable the temperature profile existing at any particular time, modelling has become necessary to predict global warming effects. Even if such predictions are prone to large margin of errors, they are required for the development of mitigation strategies for global warming and risk is too large not to look for means of mitigation.

The various atmospheric modellers employ one-, two- or three dimensional models with varying levels of sophistications and demand on computer time. One dimensional models compute the composition of atmosphere as a global average varying only with the altitude. The two dimensional models calculate changes with both latitude and altitude. In the three dimensional models, Earth's surface is divided into 800-11000 grid points and atmosphere over each grid point is divided into five to fifteen layers. Projections far into the future using three dimensional models are prohibitively expensive due to the time required on super computers. Although spacial resolution in the global climate is often inadequate, such models do produce accurate simulation of some phenomena. Comparisons of simulated data with the total ozone mapping made on Nimbus 7 satellite has raised significant issues in the predictability of atmospheric models in general. Most of these models contain about 160 chemical reactions and more than 40 reactive species. Each time a reaction rate is remeasured, a new species or reaction discovered or a new product for a known reaction identified, the models need further refinement, especially if prediction far into the future is required. However, for short term applications such as the regulation of traffic in a crowded city, simpler models with the required level of reliability do exist. Since the species with long lifetimes such as $CFCl_3$ or CF_2Cl_2 with 73 and 110 years respectively seem to hold more threat to global climate, it has become essential to examine the lifetimes of relevant chemical species and even some airborne dust and inorganic materials. In this presentation, the Status of Art in atmospheric modelling and its possible role in policy making would be highlighted.

HUMAN INFLUENCE ON ATMOSPHERIC CONSTITUENTS : TODAY'S CONCERN

Atmospheric temperature has played a key role in the evolution of intelligent life on the Earth. A remarkable feature is that minor constituents present in parts per million or billion levels dominate the atmospheric properties. Especially, the atmospheric temperature is sensitive to levels and nature of trace gases in the environment. In the evolution of atmosphere, supernova explosions are known to have altered the concentrations of such minor atmospheric constituents. Climatic changes are believed to have led even to the extinction of several life species in the past and the climate is known to be influenced by trace gases as discussed by Mitra (1980).

The human activities have attained such proportions that their influence on the atmospheric constituents has now become apparent. Therefore, the response of the atmosphere to human influences has not only become relevant but also necessarily a matter of deep concern. Human impact on climate can arise out of alterations in the biosphere as well as atmospheric constituents. There are now increasing emissions of pollutants which persist in the atmosphere for long periods and can give rise to global problems. There are also steady discharges of pollutants with shorter atmospheric residence times which can contribute to an imbalance of the environment in the region.

Gaseous pollutants listed in Table 1 with longer atmospheric lifetimes are capable of diffusion into various atmospheric layers extending from 10-50 km above the Earth's surface (Hileman, 1989). The gases listed in Table 1 are now known to perturb the global thermal environment. The oxides of sulphur and nitrogen formed from the combustion of fossil fuel possess shorter atmospheric lifetimes and contribute

TABLE 1: Concentrations, Lifetimes of Greenhouse Gases

	Atmospheric concentration, ppm (volume)	Atmospheric lifetime
Carbon dioxide	350	~500 years[a]
Ozone	0.02-10	less than a few hours[b]
Methane	1.7	7-10 years
Nitrous oxide	0.31	150 years
CFC-11 ($CFCl_3$)	2.3×10^{-4}	75 years
CFC-12 (CF_2Cl_2)	3.8×10^{-4}	110 years

[a] Combined lifetime for atmosphere, biosphere, and upper ocean.

[b] Although lifetime of ozone itself is less than a few hours, lifetime of O_2 (ozone + oxygen atoms) depends strongly on location, varying from about an hour in the upper stratosphere to months in the lower stratosphere to hours to days in the troposphere.

Source : Department of Energy.

to acid rain. A summary of the levels of annual transfer rates of various elements into the environment resulting from human activities is included in Table 2. There is discharge of both solid and liquid wastes and gaseous emissions.

TABLE 2: Elemental Composition of Aerosols and the Annual Transfer Rates of Elements

Elements	Aerosol composition[a,b]	Annual transfer combustion	Rate mining[c]
Al	54-8000	2800	134000
As	0.5-80	1.5	47
Be	0.3-8	0.28	1.1
Ca	600-20000	420	~83000
Cd	1-47	0.065	7.7
Cr	4-180	2.8	~2500
Cu	8-1100	4.6	6190
Fe	100-14000	2200	680000
Hg	1-14	8.4	8.4
Mn	2-380	14	24600
Mo	0.2-12	0.8	76
Ni	0.4-230	5.6	560
Pb	30-7700	183	3340
Sb	0.2-91	0.28	75
Se	1-9	3	1.04
Si	120-18000	8400	380000
Sn	0.3-160	0.54	178
Ti	4-580	140	~1000
Zn	9-2500	22	4040

[a] typical composition at London.
[b] in mg/kg dust.
[c] 106 kg/year.

ATMOSPHERIC MODELS FOR ASSESSMENT OF HUMAN IMPACT

There is little that humans could do to alter the influence of the Sun on the Earth. However, there are now indications that additions to atmospheric constituents resulting from human activities may have an impact on climatic cycles as well as the biosphere around a specific region in the globe. Therefore, there are attempts being made to assess:

(i) The trends in the climatic changes occurring over centuries to delineate any superimposed effects of human activities and

(ii) The dangers of industrial activities to regional atmospheric conditions and life population.

An attempt has now been made to selectively review the atmospheric modelling approaches to both global and regional scenarios. Although basic principles involved in the two types of model systems are similar, the dimensions of the problem vary markedly. Whereas regional models deal with emissions from point and continuous sources, the human impact on climatic changes is expected as a result of steady discharges of constituents exhibiting long atmospheric residence time over extended periods.

GLOBAL WARMING : A CAUSE FOR ALARM

The greenhouse effects of trace gases in the environment participate in the thermal regulation of the atmosphere. The thermal radiation environment of the Earth is undergoing a perturbation due to variations in greenhouse effects. Minor variations in temperature of the Earth can well lead to significant changes in the biosphere and geobiochemical cycle of the planet.

A simplistic model representing the energy transfers based on radiative-convective modes along one dimension namely vertical distance from the Earth and the importance of trace gases is depicted in Figure 1.

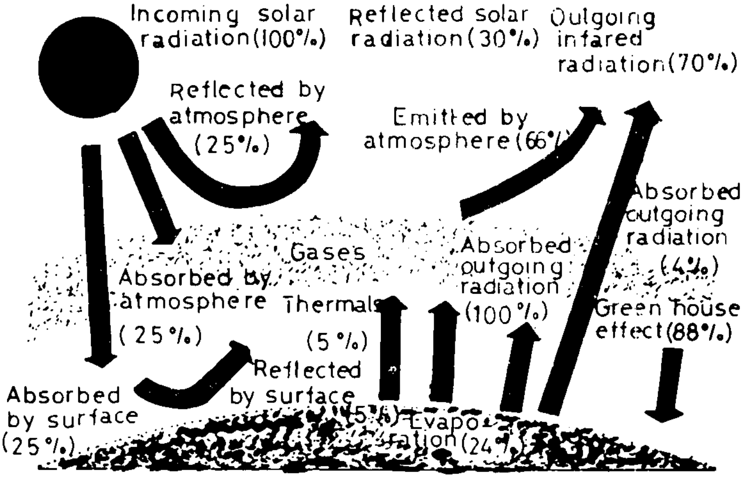

Fig. 1. Heat budget of atmosphere.

Several independent analyses of the Earth's surface temperature over the past century have shown that the past 10 years have been the warmest decade on record (Hileman, 1989). Although there are controversies on the possible consequences of the greenhouse effect, alarming consequences to global warming have been predicted (Global Change Report No. 4, 1988). A warming rate of 3.5° to 4.5° C over the next century has been predicted. Although the magnitude of the increase may seem small, even a change of 1°C can be severe and a global increase of 2°C is unprecedented in the era of human civilization.

Direct effect of global warming will be on ocean levels. Climatologists have generated various scenarios of temperature dependent ocean level increases and one such analysis is depicted in Figure 2 (Hileman, 1989; Ember *et al.*, 1986). With one-third of world's population living in coastal zones ocean level increases can endanger a vast section of human population. Therefore there is now a need to model the consequences of greenhouse warming effects which predict a slow but steady and alarming change. On the other hand, release of a toxic gas can impact the life system in the vicinity. The risk of such gas releases to the local environment needs also to be assessed, especially in view of a number of major industrial accidents in recent times.

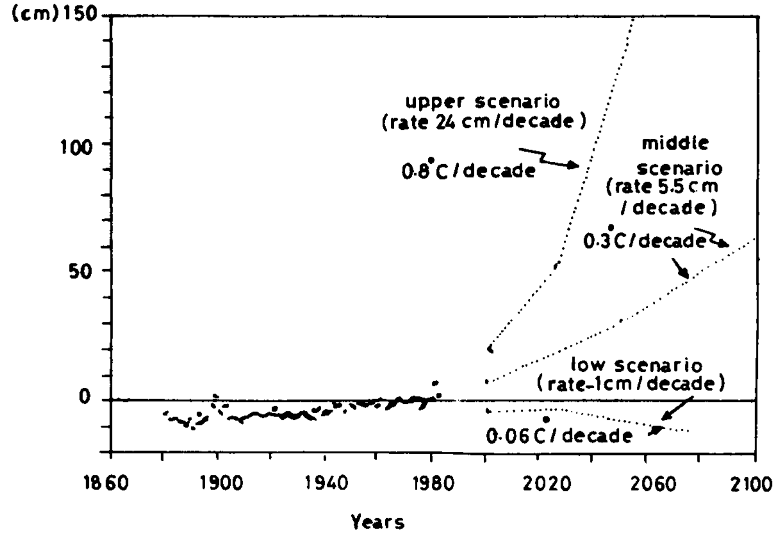

Fig. 2. Global sea-level change (cm).

MODELLING FOR RISK ASSESSMENT

A newer dimension has now become evident from recent industrial accidents such as those at Bhopal and Mexico city. Potential dangers of acutely toxic or combustible gas clouds to life systems are now obvious. The need for suitable safety/risk assessment is increasingly felt. Therefore mathematical models for atmospheric dispersion of toxic gas releases are attaining importance.

The basic difference between the two sets of risk assessment models namely those dealing with climatic changes on one hand and the immediate atmosphere on the other arises from the spatial and time frame considerations. Generally the mathematical models dealing with risk assessment of industrial gas releases deal with altitudes of 1-2 km and much higher concentrations of gases (Pasquill, 1980), whereas climate models need to deal with such greater heights as 10-40 km from the Earth's surface and concentration levels of ppm and ppb. There are very few problems concerning the action of pollutants on the environment that do not at some stage involve a consideration of how materials are mixed and dispersed in fluid. In other words, atmospheric modelling deals with the influence of various factors on dispersion and mass transfer (Pasquill, 1980).

SOME GENERAL CONSIDERATIONS IN RISK ASSESSMENT MODELS

Mathematical models to describe the dispersion of heavy gases (heavier than air) have been developed and extensive reviews have appeared (Griffiths, 1984; Havans, 1987). There are a number of mathematical models, but commonly they are used to estimate the concentration downwind of a pollutant source located in a mixing layer. Mixing layer is believed to extend upto 0.5-1.0 km above the Earth's surface. Meteorological conditions, undoubtedly would influence the mixing layer significantly. The flow of gases is affected by the frictional drag of the Earth's surface within the mixing layer. A progressive reduction wind-speed is expected as the altitude decreases from the top of the mixing layer. Another important factor contributing to mixing is the heating of air in contact with the ground, which is warmed by the Sun.

Consideration of the spatial distribution of an airborne material necessarily needs to take into account (i) the shape of the distribution of concentration at any given time and downward position, (ii) the dimensions of the diffusing cloud, and (iii) whether the material is lost by deposition or decomposition. Dispersion models for two idealized cases of discharges namely instantaneous and continuous can be represented as in Figure 3. In a homogeneous air stream, diffusion along the x-axis (the mean wind), y-axis (crosswind) and z-axis (vertical) directions needs to be

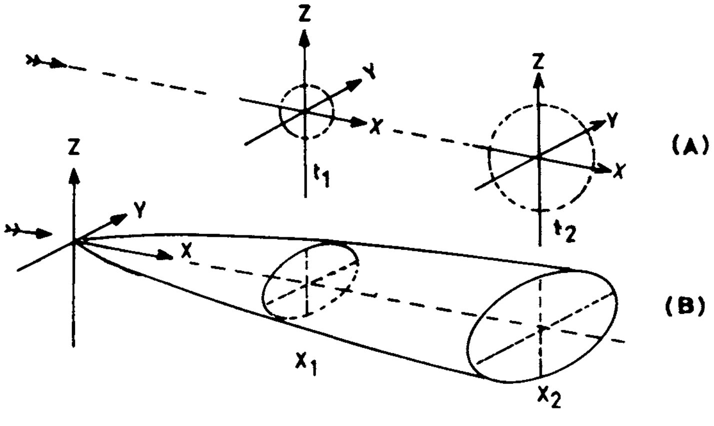

Fig. 3. Idealized representation of instantaneous (A) and continuous (B) sources.

considered (Pasquill, 1980). In case of an instantaneous point source, an equation of the general form as follows can be considered assuming exponential functions.

$$X\ (x, y, z, t) = A_1\ [\exp - (a|\ x\ |^p + b\ |y\ |^r + c\ |z\ |^s)]$$

where X is the concentration of the airborne material (unit of matter per unit volume), x,y,z are measured from a moving origin situated at the centre of the mass cloud. The quantities, p,r and s have positive values (Pasquill, 1980). In case of a continuous point source, applying continuity condition, equation of diffusion can be written as below:

$$X\ (x, y, z) = A_2 \exp\ [\ - (b|\ y\ |^r + c\ |z\ |^s\ )]$$

The above two equations define that zero concentration of the gas is observed only at infinity values of x, y and z. Therefore, these equations may be conveniently redefined as follows:

$$\int^{\propto}\int_{-\propto} \int xdxdydz = Q$$
$$\int^{\propto}\int_{-\propto} uXdydz = Q$$

An idealized formula recommended for the estimation of concentration at short range from a ground level continuous point source in neutral conditions can be written as below:

$$X\ (x, y, z) = \frac{Q_1}{2\Pi\ \sigma_y\sigma_z u} \exp\left|\frac{-y^2}{2\sigma_y^2}\right| \exp\left|\frac{-z^2}{2\sigma_z^2}\right|$$

where Q is the rate release of material and the quantities and σ_z are root mean square displacements (i.e. the standard deviations of the crosswind concentration distributions horizontally (y) and vertically (z) and u friction velocity. The values of σ_y and σ_z are evaluated on the basis of a correlation of data obtained from field experiments and needs to be categorized according to meteorological conditions including atmospheric stability (Pasquill, 1980; Havans, 1987).

Number of similarity and three dimensional models for estimating the assessment of risk from release of industrial gases have been reported already and many of them are being successfully used (Pasquill, 1980; Griffiths, 1984; Havans, 1987; Anita *et al.*, 1988). Essentially the gas dispersions to an altitude of say 0.5-1.0 km have been computed.

Changes occurring in the concentrations of gases beyond an altitude of 10 km are relatively minor. The concentrations of gases at such altitudes are so low that in three dimensional models used for industrial risk assessment the numerical diffusion errors in calculations cannot be easily overcome. However, even minor changes in the concentrations of trace gases present at such altitudes are known to influence the temperature of the planet significantly. Therefore, more elaborate models are necessary. Global changes due to greenhouse warming have become a matter of intensive study and search for suitable atmospheric models has become necessary.

GLOBAL CHANGES : ROLE OF GREENHOUSE GASES

The air, clouds, soils, vegetation and any form of material in the planet either reflect or absorb and re-emit a portion of the Sun's energy incident upon them. The bodies which absorb the energy radiate in the infrared region of the electromagnetic spectrum. Such an emitted energy is absorbed by some trace gases in the atmosphere, thus trapping a great proportion of the Sun's energy providing a greenhouse effect and a thermal radiation environment suitable to mankind.

The amounts of naturally occurring atmospheric trace gases such as carbon dioxide, methane and nitrous oxide and new radiatively important gases such as chlorofluorocarbons and other halocarbons are on the increase. The observed increases in the concentrations of carbon dioxide, methane, nitrous oxide and atmospheric halocarbons are as shown in Figure 4 (Ember *et al.*, 1986). It is now feared that such increases in greenhouse gases can aggravate the global warming effect.

Since the first systematic measurement of atmospheric carbon dioxide in 1958, its level has increased from 315 to 350 ppm. From the analysis of the air trapped in the ice cores of Antarctica, the preindustrial level has also been estimated to be 280 ppm. The current level of carbon dioxide appears to be the highest for the last 160,000 years (Hileman, 1989). Burning of fossil fuel and massive deforestation are the main reasons attributed for the changes in carbon dioxide levels.

Although the concentrations of the other trace gases such as methane, nitrous oxide, tropospheric ozone are much less relative to carbon dioxide, it is now estimated that they trap as much as 60 % of the energy trapped by carbon dioxide. Further, each molecule of other trace gases absorbs more infrared light than a carbon dioxide molecule. The combined greenhouse warming effect of other trace gases is believed to be equal to that of carbon dioxide. The role of methane, for instance, in greenhouse warming has received much attention in recent years, particularly because each molecule of methane is 15-30 times more effective than carbon dioxide molecule.

The possible interactions of some trace gases like nitrous oxide of halocarbons with tropospheric ozone raise further alarms. The Total Ozone Mapping Spectrometer housed in Nimbus 7 satellite has given valuable information on the trends of ozone levels in the atmosphere (Heath *et al.*, 1985; Ember *et al.*, 1986). The data based on tropospheric ozone levels is not complete and its effect on surface warming is complex. In upper troposphere it contributes more to surface warming than it does in the mid- or upper stratosphere.

Ozone depletion in the lower troposphere, in contrast, induces some surface cooling. Therefore, it becomes necessary in the case of ozone to examine the overall effects on surface warming by assessing the variations of the concentrations of the gas at various heights. Since there is an overall increase in global temperature, the possible roles of all the greenhouse gases have aroused much interest and concern. There is an attempt to estimate or predict the concentrations of greenhouse gases at different altitudes and latitudes. Particularly the ozone depletion in Antarctica has become a puzzle and the scientific opinion that the industrial activity in one part of the globe can influence markedly the ozone layer in another has made it necessary to take into account all relevant factors.

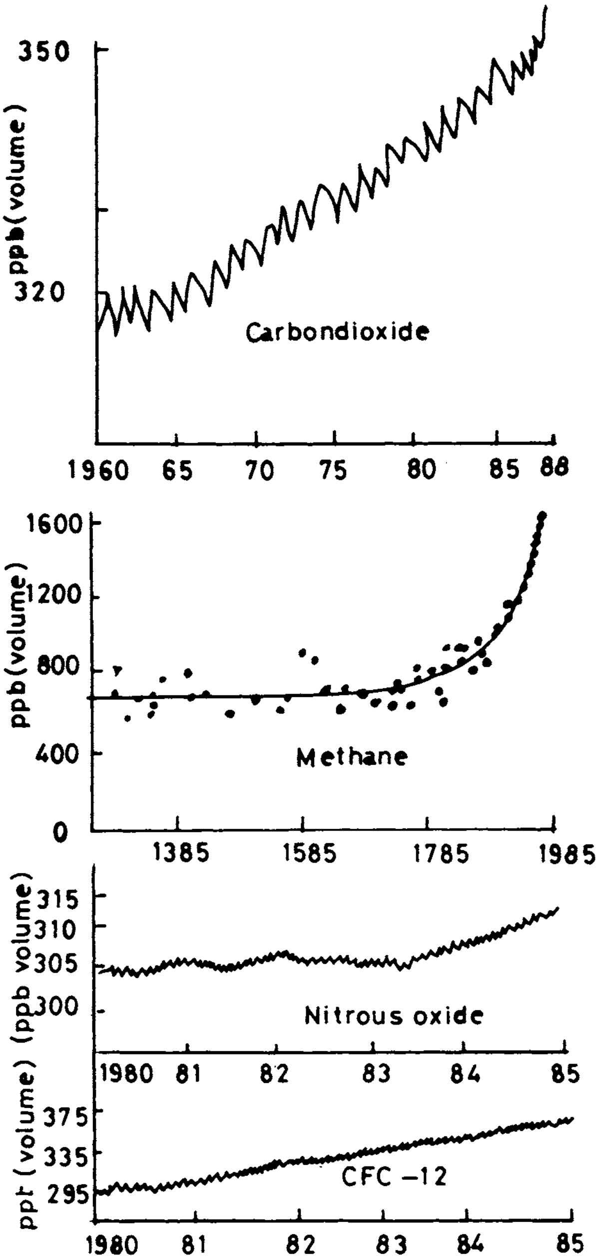

Fig. 4. Atmospheric concentrations of trace gases.

It is not surprising that in the last two years, the theory about greenhouse warming has been elevated to a matter of serious concern. Especially there is a growing concern on the level of ozone around 40 km above the Earth's surface. This is significant because the type of species involved in the depletion of ozone may vary depending on the altitude. Chlorine is thought to be destroying ozone at 40 km whereas nitrogen radicals are believed to be important at the altitudes of 12-30 km. The ozone depletion in the stratosphere is considered an early warning of the further climatic changes to come. There is now a sufficient evidence by way of direct measurements for the depletion of ozone layer over Antarctica.

ANTARCTIC OZONE PUZZLE

Data collected from Solar Backscatter Ultra Violet and Total Ozone Mapping Spectrometer (TOMS) aboard Nimbus 7 satellite showed unambiguously the more rapid depletion of ozone at the rates of 2.5 % over Antarctica, 1.5 % over the tropics and negligible over other areas. The seasonal variations in the ozone hole levels over the Antarctica have caused much discussion (Zurer, 1987; Hileman, 1989).

The observed variations in ozone levels over Antarctica have been analysed in terms of natural phenomena taking into account hydrodynamic and air current characteristics. Theories have been proposed that Antarctic ozone hole is a natural phenomenon. However, some environmentalists argue that the hole is a consequence of chlorofluorocarbons (Hills *et al.*, 1987; De Zafre *et al.*, 1987; Solomon *et al.*, 1987). In order to explain the loss of ozone at the altitudes of 12-20 km above Antarctica, where chlorine is expected to be in the inactive form for ozone depletion, a complex series of heterogeneous reactions has also been proposed (Rowland *et al.*, 1987). A photochemical process involving HOCl has been invoked as shown in the Table 3.

TABLE 3: Ozone Depletion Pathways Resulting from HOCl Photochemistry

$H_2O + ClONO_2$	$\longrightarrow$	$HOCl + HNO_3$	(1)
$HOCl + h\upsilon$	$\longrightarrow$	$Cl + OH$	(2)
$Cl + O_3$	$\longrightarrow$	$ClO + O_2$	(3)
$HO + O_3$	$\longrightarrow$	$HO_2 + O_2$	(4)
$ClO + HO_2$	$\longrightarrow$	$HOCl + O_2$	(5)

While the real causes for the ozone depletion over the Antarctica remain a puzzle, the need to examine the possible effects of such depletions on the global climate is being increasingly recognized. Climate modelling has aroused both scientific and public interest.

CLIMATE CHANGE : WHY TO MODEL ?

Modelling of the climate change has attained importance in recent years for several reasons. These are:

(i) Difficulties in explaining the observed statistical trend of global warming on the basis of chance and meteorological perturbations;

(ii) The discovery of a stratospheric ozone hole over Antarctica;

(iii) Possibilities that the ozone hole over Antarctica may have been caused by the release of chlorofluorocarbons and other man-made alterations to the environment;

(iv) The unprecedented increase in concentrations of the greenhouse gases; and

(v) The hope that with better understanding of the climate changes, a suitable mitigation strategy can be evolved if the models can give rise to reliable predictions.

There has been an increase in the remote sensing capability and substantial improvement in the range of devices for monitoring the atmospheric changes. There are controversies on the capabilities of the currently used climate models to discern man-made alterations from natural variations in climate but not on the need for modelling.

CURRENT CLIMATE MODELS : VARIOUS TYPES

Various factors in atmospheric models

The regions 35 km above the Earth's surface are considered to be photochemically controlled and the dynamical processes seem to be relevant in case of lower stratosphere. Factors such as the movement of air from the equator towards the poles or the upward transport of trace gases from the troposphere lying upto about 12 km above the Earth's surface are of prime importance in atmospheric modelling.

The most realistic computer models of the atmosphere need to consider photochemistry, radiation and transport of mass and heat as well as the coupling among the above three processes. Photochemistry is influenced by the nature of chemical species present in the atmosphere. The type and amount of photochemically relevant atmospheric constituents are now known to vary with the altitude and the location. The radiation incident upon the Earth from the Sun is also subject to major variations. The intensity and the wavelength of light incident upon the Earth's environment vary with time of the day, season, latitude and presence of greenhouse gases including ozone. The amount of solar radiation reaching Earth and Earth's changing orientation to the Sun have been important causes for climatic changes in the history of the planet throughout.

Changes in the Sun's irradiance are important. No scientific theory seems to exist to predict the future changes in the solar output. It is, however, recognised that the Earth's disposition with respect to the Sun varies cyclically over time. A periodicity of 41,000 years has been estimated in the tilting of the Earth towards the Sun from 22 to 24.5° and back again. The month when Earth is closest to the Sun varies over the cycles of 19,000-24,000 years and currently January is believed to be the month when the Earth is in its closest position with respect to the Sun.

Variations in the shape of the Earth's orbit from being nearly circular to being elliptical with a periodicity of 100,000 years have been reported (Hileman, 1989). The climatic cycles caused by such orbital factors and inconsistency of the Sun as a radiation source are superimposed over any atmospheric perturbations resulting from human interventions. It is now believed that orbital changes alone would not cause vast climate shifts (Hileman, 1989). Feedbacks such as changes in Earth's reflectivity, dustiness of the atmosphere, the carbon dioxide and methane contents in the environment act together with orbtial changes to enhance global warming and cooling. Although some of the increase in carbon dioxide content in recent years has been attributed to human activities, the possible effects on the carbon dioxide levels of the atmosphere due to the striking of an extinction bolide onto a shallow marine carbonate rich sedimentary section have been assessed (O'Keffe and Aherms, 1989). It has been predicted that the impact of such a bolide (~KM in radius) onto a carbonate rich terrain would increase the carbon dioxide content by a factor of two to ten, which in turn could give rise to increase of global temperature by 2 to 10K and for periods of 104 to 105 years. In other words, natural processes of such large magnitudes are superimposed over the perturbations due to human impacts. In addition, most atmospheric models need to consider as many as 160 chemical reactions and the participation of more than 40 chemical species. With such complexities, atmospheric modelers are forced to rely on simplifications and make approximations.

Different climate models and their approaches

Most of currently used atmospheric models can be categorised as one-, two-and three dimensional types. One dimensional models compute the composition of the atmosphere as a global average varying only with altitude. The two dimensional models calculate changes with both altitude and latitude giving a longitudinal average. Three dimensional models are more realistic although they need considerable computer capability. The number of parameters and spatial resolution attempted in three dimensional models are large.

Future predictions using three dimensional values over extended periods of time are hence prohibitively expensive. However, such models are often used to calculate the global temperatures and the precipitation levels. In these models, the Earth's surface is divided into 800 to 11000 rectangles or grid points. The atmosphere over each grid point is divided into different layers ranging from a total of 5 to 15. The flow and mixing of atmospheric gases from each of these cells into adjacent cells is calculated using the basic laws of thermodynamics and hydrodynamics.

The laws of conservation of mass, energy and momentum are applied and the gas laws are taken into account. The transfer of electromagnetic radiation through a heterogeneous gaseous medium is related to incoming solar radiation and changes in the contents of each cell. The reflectivity of various surfaces such as ice, snow, oceans, clouds and vegetated lands is included. Equations are solved to estimate winds, temperature, sunlight, relative humidity and precipitation for each point on the globe. In order to predict the effect of doubling of carbon dioxide and other trace gases on the atmosphere, the amounts of such gases are deliberately doubled and various scenarios are developed using three dimensional models. Variations in surface temperatures and alterations in cloud cover, wind and precipitation patterns are calculated.

In view of the increase of global mean tropospheric concentration of CFC-11 and CFC-12, respectively ~230 parts per and ~395 parts per 10^{12} by volume, there is now an effort to model the release and consequences of such gaseous emissions (Hammitt *et al.*, 1987; Wigley, 1988). A simple two-box model comprising an atmosphere box and delayed release box has been developed. The model equations are:

$$\frac{dM}{dt} = P_a + P_{na} + P - \frac{M}{\tau}$$

$$\frac{dD}{dt} = (1 - \alpha)\, P_{na} - D$$

where P_a/P_{na} are the aerosol/non-aerosol production rates, M and D are the masses in the atmosphere and delay boxes is the fraction of non-aerosols released directly to the atmosphere, alpha is the annual fraction of the delay box that leaks into the atmosphere and τ is the lifetime. Substituting rates of 0.25 and 0.15 for CFC-11 and 0.15 and 0.25 for CFC-12, various scenarios could be developed. The values of τ have been estimated as 75 and 111 yr. for CFC-11 and CFC-12 respectively. Different scenarios have been developed assuming that future concentration of CFC-12 and CFC-11 continue to increase asymptotically. A case where a cut-back in the production level of 1986 by 20 % was also assumed and the CFC levels computed. Production limits of ~19 % (CFC-11) and 15 % (CFC-12) of the 1986 values have been predicted to be required to stabilize the CFC concentration at the current levels. The greenhouse effect implications of various scenarios of CFC levels in the atmosphere have been analysed using radiative transfer models. The linear dependence of the direct radiative forcing perturbations (Q) on the concentration of C as in equations CFC-11; $\Delta Q = 0.00027C$ and CFC-12; $\Delta Q = 0.00031C$ has been assumed. For various values of α, β and τ, contribution of CFC-12 expected upto 2050 have been computed using mathematical models (Hammitt *et al.*, 1987; Wigley, 1988). The importance of the compliance of Montreal protocol on substances that deplete the ozone layer has been emphasised (Wigley, 1988).

Success of climate models and authentication

The currently used atmospheric models enable the prediction of summer and winter temperature extremes for large areas on the Earth. Calculated temperatures for various levels of the atmosphere of Mars and Venus, where coupling to well developed biosphere is not relevant, are in close agreement with the values observed. Furthermore, the models have been able to simulate the temperature conditions that prevailed during Mesozoic Era and glacial/interglacial cycles. Experimental evidence for the temperatures of the past have been obtained from studies on ocean sediments and ice cores in Antarctica.

Some general limitations of climate models

All the atmospheric models developed so far have some basic limitations and one of them is the lack of required spatial resolution. A variety of atmospheric chemistry and physics occurs within the atmosphere over each grid point. For instance, storm fronts, mountainous ranges, urban/industrial pollution, atmospheric chemical reactions, changes in cloud type vary on spatial scales which are smaller than the sizes of the grid cells used by atmospheric modelers.

Accurate predictions of greenhouse warming involves understanding interactions among inconstant Sun and the highly complex systems of the atmosphere, biosphere and geosphere. Changes in one system such as the growth of phytoplankton or trees can produce a variety of effects on the atmosphere, some of which would produce warming and the others cooling. In other words, it is difficult to allow for feedback systems in climate modelling. Especially, the most important feedback system is the ocean and the understanding of its dynamics in light of greenhouse effects is crucial to assess the extent of global warming due to greenhouse perturbations. The analysis of the temperature conditions during "Younger dryers" cold event between 11-10 Kyr has led to a belief that heat budget of the high altitude North Atlantic produced changes over land. General Circulation Model (GCM) results support the dominant role of sea-surface temperature fluctuations in forcing high altitude climate change (Broecker *et al.*, 1985; Overpeck *et al.*, 1989). The importance of sea-surface interactions and their possible role in season changes in tropics have been much realised. Upwelling of nutrient rich water along the coasts of Arabian sea due to seasonal reversals in the surface circulation has been analysed. The role of particle flux pattern and the atmospheric dust fall out on the biological productivity along the coastal lines is now recognized (Nair, 1989). In this context, the particulate emission of many trace metal ions due to human activities and the resulting atmospheric fall out needs careful investigation and a modelling effort.

Changes of tropical sea-air interaction processes over a period of 30 years during 1949-1979 have been assessed using experimental measurements of sea-surface temperature, sea-air temperature differential, scalar wind speed, saturation defect etc. (Flohn and Kapala, 1989). Tropical circulation changes have been predicted on the basis of this study. A warming of the tropical troposphere by 1°C has been predicted to be associated with more frequent deep convections in oceans with sea-surface temperatures >27.5° . This is expected to cause the release of more latent heat into the atmosphere. The physical role of water vapour due to phase changes has been attributed to be more important than even its greenhouse effect. A positive feedback resulting from additional energy inputs may lead to the acceleration of delayed ocean warming in lone altitudes (Flohn and Kapala, 1989). Thus the mathematical models need to necessarily take into account the complex processes resulting from sea-air interactions and the associated feedback responses. Currently used models need to take into account more fully the effects of ocean dynamics.

The prediction of the effect of global warming on the ecosystem, water supplies, agriculture and sea level changes is acutely more difficult at the global level. However, regional impacts can be assessed, although only with difficulty.

MITIGATION STRATEGIES

Global warming is now a phenomenon of much concern. Measurement of atmospheric trace gas levels gives valuable clues regarding trends in atmospheric and climatic changes. Modelling is perhaps a means to seek forewarnings of any catastrophe to come. It is possible to argue that the climatic models require further refinements, at least when the global changes are to be considered and the level of spatial resolution required is higher. The predictions made by the currently used models may be subject to large margin of errors. However, the risk of not acting on the possible alternatives to contain the global warming is too large to permit any complacency.

There is perhaps little that human kind could do to alter the weather cycle of the globe arising from natural phenomena. However, when the fear of the human impact on the weather cycle has arisen, it is necessary to evolve appropriate mitigation strategies against man-made global warming. There are still controversies on the beginning of the human impact on climatic change, but not on the potential danger resulting from some of the pollutants emitted by the industrialized world. Climate models may be prone to errors, but a blind and passive waiting is unacceptably foolish. There is now a need to discuss possible strategies to:

(i) Enhance capability to predict more accurately;
(ii) Measure and quantify the climatic perturbations; and
(iii) Evolve a global action plan for arresting the rapid increases in greenhouse gases.

Any discussion without support from a well conceived action plan and commitment could serve no purpose. There is an increasing recognition for the need to contain the global change. This is obvious from the jump in the federal funds for research on global change in USA by 42 % over the 1989 level. It is an area calling for interdisciplinary research inputs and committed political will of Nations to preserve the planet from impending adverse climatic changes.

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URBAN AIR POLLUTION MODELLING

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There is a range of urban air pollution models currently in use. Rollback and simple box models give crude estimates of the overall emission reductions required to avoid violations of long-term exposure health standards fors low-reacting pollutants. Gaussian plume models are used to predict both short-term and long-term exposures to pollutants arising from motor vehicles and large point sources such as power stations and mills. Multi-box models such as the ATDL model are used to predict long-term exposures from particulate pollution arising from a variety of point and area sources. Statistical models may be combined with these estimates to predict the number of violations of short-term exposure standards. Numerical grid square models are used to simulate photochemical smog episodes. In all instances, the models usually do not accurately predict the time of occurrence and location of the maximum pollution episodes. If the requirement of time and space pairing of predictions and observations is relaxed, then the models usually can predict the worst case pollution levels to within a factor of two, the best that can be expected from any model, given the inherent statistical uncertainty in air pollution measurements. However, many models require detailed data sets which are not always available, and severe local problems such as sea breeze effects and complex terrain complicate model performance and increase these problems.

INTRODUCTION

The purpose of this paper is to critically examine air quality models for urban areas. There are many reviews which cover the broad spectrum of air quality models, including Hanna (1978, 1982), Drake *et al.* (1979), Turner(1979), Simpson and Hanna (1982), Hayes and Moore (1986), and Seinfeld (1988). This paper summarises these reviews. The classification of models chosen in this review is shown in Table 1.

Air quality models, sometimes termed air quality simulation models, are mathematical descriptions of the atmospheric transport, diffusion and chemical reactions of pollutants. They operate on sets of input data characterising the emissions, topography and meteorology of a region and produce outputs that describe the air quality of the region.

The air quality models can be classified as prognostic (that is, based on the fundamental physicochemical principles governing air pollution), and as diagnostic (that is, statistical descriptions of observed air quality data).

TABLE 1: Different Model Types

Generic model type	Number of sources	Area types	Pollutants	Terrain complexity	Required resolution
Grid					
a. Region-oriented	Multiple source	Urban Rural	O_3, HC, CO, NO_2 (1-hour), SO_2 (3- and 24-hour), TSP	Simple Complex	Temporal Spatial
b. Specific-source oriented	Single source	Rural	O_3, HC, CO, NO_2 (1-hour), SO_2 (3- and 24-hour), TSP	Simple Complex	Temporal
Trajectory					
a. Region-oriented	Multiple source	Urban	O_3, HC, CO, NO_2 (1-hour), SO_2 (3- and 24-hour), TSP	Simple	Temporal Spatial (Limited)
b. Specific-source oriented	Single source	Urban Rural	O_3, HC, CO, NO_2 (1-hour), SO_2 (3- and 24-hour)	Simple Complex (Limited)	Temporal Spatial (Limited)
Gaussian					
a. Long-term-averaging	Multiple source Single source	Urban Rural	SO_2 (annual), TSP, NO_2 (annual)*	Simple	Temporal
b. Short-term-averaging	Multiple source Single source	Urban Rural	SO_2 (3- and 24-hour), CO, TSP, NO_2 (1-hour)*	Simple Complex (Limited)	Temporal Spatial
REFINED/SCREENING USAGE					
Isopleth	Multiple source	Urban	O_3, HC, NO_2 (1-hour)	Simple	Temporal (Limited)
SCREENING USAGE					
Rollback	Multiple source Single source	Urban	O_3, HC, NO_2 SO_2, CO, TSP	Simple	—
Box	Multiple source	Urban	O_3, HC, CO, NO_2 (1-hour), SO_2 (3- and 24-hour), TSP	Simple Complex (Limited)	Temporal

* Only of NO_2 is taken to be total NO_x.

A general way to formally classify models is the following:

(i) Models that provide point solutions directly. They are explicitly solved for the air quality property under consideration, typically the (expected) pollutant concentration, and can be applied in a straightforward manner to any location in the region of interest without having to estimate concentrations at other locations. They include analytical formulae, the most common example being the Gaussian equation; and

(ii) Models that provide solutions only through (numerical) calculations over one-, two-, or three-dimensional domains. Photochemical air quality models fall in this category.

Air quality standards are written in terms of concentrations. In the USA, national ambient air quality standards (NAAQS) are set at a level determined to be appropriate to protect public health and well-being. Models are used for planning and assessing the attainment of these standards.

MODELS FOR NON-REACTIVE POLLUTANTS

First, the models for non-reactive or slowly reacting pollutants are considered. The conservation of mass equation for an inert pollutant is given by:

$$\frac{\partial X}{\partial t} + \left(\bar{u} \frac{\partial X}{\partial x} + \bar{v} \frac{\partial X}{\partial y} + \bar{w} \frac{\partial X}{\partial z} \right) =$$

$$- \frac{\partial}{\partial x} < u'X' > - \frac{\partial}{\partial y} < v'X' > - \frac{\partial}{\partial z} < w'X' > + S \qquad \ldots (1)$$

where <...> refers to an ensemble average; X is the ensemble average of the concentration of the pollutant; $\bar{u}$, $\bar{v}$, and $\bar{w}$ are the mean wind speeds in the x-, y-and z-directions respectively; u', v' and w' are the corresponding random components of wind speed; X' is the random component of the concentration of the pollutant; and S refers to the source strength of the pollutants. The first three terms on the right-hand side of equation (1) refer to so-called turbulent diffusion. These terms are usually replaced by the gradient-transport representation, yielding an equation of the form:

$$\frac{\partial x}{\partial t} + \left(\bar{u} \frac{\partial X}{\partial x} + \bar{v} \frac{\partial X}{\partial y} + \bar{w} \frac{\partial X}{\partial z} \right) = \frac{\partial}{\partial x} K_x \frac{\partial X}{\partial x} + \frac{\partial}{\partial y} K_y \frac{\partial X}{\partial y} + \frac{\partial}{\partial z} K_z \frac{\partial X}{\partial z} + S \qquad \ldots (2)$$

where K_x, K_y and K_z are referred to as the eddy diffusivity coefficients for turbulent diffusion in the x-, y- and z-directions respectively.

Gaussian methods

If the turbulence is homogeneous and stationary and only a point source is considered, then there is an analytic solution to equation (2), the Gaussian expression:

$$X\ (x, y, z) = \frac{Q}{2\pi\sigma_y\sigma_z\bar{u}} \exp\ (-\ y^2/2\ \sigma_y^2)\ \exp\ \{-\ (H - z)^2/2\ \sigma_z^2\}$$

$$+ \exp\ \{\ -\ (H + z)^2/2\ \sigma_z^2\} \qquad \ldots (3)$$

where Q is the source strength (mass emission rate), $\bar{u}$ the mean wind speed, σ_ψ and σ_z the standard deviations in concentration in the crosswind (y) and vertical (z) directions respectively, and H the effective height of emission. The wind is assumed to be in the x-direction. Veigele and Head (1978) have summarised assumptions needed to derive equation (3) from equation (2). The expression in equation (3) depicts a plume of effluent moving away from the source. Pasquill (1974) has reviewed relevant observational data regarding the validity of such a representation of pollution. The plume model is widely used for point sources and is also applied to line and area sources. Instead of viewing the pollutants as forming a plume, another approach adopted involves visualising "puffs" of pollutant which follow air trajectories and diffuse in a Gaussian manner. Conceptually, such a model is more widely applicable than the plume model, as light and variable meteorological conditions could be more easily treated, although the performance in practice is not always significantly better (e.g. see Lorimer, 1988).

Box models

Box models are the simplest of the numerical models. The region to be modelled is treated as a single cell, or box, bounded by the ground on the bottom, the inversion base (or some other upper limit to mixing) on the top, and the east-west and north-south boundaries on the sides. The box may enclose an area of the order of several hundred square kilometres. Primarypollutants are emitted into the box by the various sources located within the modelled region, undergoing uniform and instantaneous mixing. The ventilation characteristics of the modelled region are represented, though only grossly, by specification of a characteristic wind speed and rate of rise of the upper boundary.

Fundamental to the box model concept is the assumption that pollutant concentrations in a volume of air, a "box", are spatially homogeneous and instantaneously mixed. Under this assumption, pollutant concentrations can be described by a simple balance among the rates at which they are transported in and out of the air volume, their rates of emission from sources within the volume, the rate at which the volume expands or contracts, the rates at which pollutants flow out the top of the volume, and the rates at which pollutants react chemically or decay.

Because of the formulation, box models can predict, at best, only the temporal variation of the average regional concentration for each pollutant species. Consequently, they are capable of addressing only multiple-source regional questions. Since box models lack spatial resolution, they cannot be used in situations where the meteorological or emissions patterns vary significantly across the modelling region. The combined effects of local emissions patterns and meteorological conditions generally give rise to significant spatial variations in pollutant concentrations.

Grid, trajectory and particle-in-cell methods

Grid models derive concentration levels by solving equation (2) numerically, using a horizontal, rectangular grid and a number of vertical levels. Conceptually, apart from the vertical levels, this approach appears to be similar to the multi-box-model one. However, there is an important difference in that grid models can consider horizontal diffusion explicitly.

Since a fixed grid is used, such an approach is referred to as Eulerian. Since the most serious errors in a numerical solution of equation (2) occur in the advection terms (the second term in square brackets on the left-hand side), then some people have suggested a Lagrangian approach where a cell is allowed to move through the atmosphere. The basic equation is now:

$$\frac{dx}{dt} = \frac{\partial}{\partial x} K_x \frac{\partial X}{\partial x} + \frac{\partial}{\partial y} K_y \frac{\partial X}{\partial y} + \frac{\partial}{\partial z} K_z \frac{\partial X}{\partial z} + S \qquad \ldots (4)$$

However, the cell would be distorted as it moves through the atmosphere due to local wind shear, and a distorted co-ordinate system is difficult to work with. So, instead of considering a continuous grid of cells, a single cell is considered and, using equation (4), the change in concentration in the cell may be calculated as it moves along the air trajectory. Models based on this formulation are referred to as "trajectory" models.

Since the required three-dimensional local wind data are usually non-existent, only horizontal wind fields can be used in the models. For a single cell, the turbulent diffusion term is ignored (quite often) or approximated from external data. The use of multiple cells requires approximations to avoid cell distortion, usually by ignoring wind shear. Seinfeld (1988) details these problems quite explicitly.

The errors inherent in smoothing the wind field and neglecting diffusion limit the applicability of such models. Also, the interpretation of the solution poses a problem, since observations against which model predictions are compared are only collected at a fixed point, while the model solutions refer to moving cells. Problems with the assumptions made in deriving grid and trajectory models are summarised in Table 2.

To avoid the difficulties of the Eulerian and Lagrangian formulations, a particle-in-cell (PIC) method has been suggested (e.g. Sklarew *et al.*, 1971). In this method, the mass of the pollutants is separated into individual elements and the centroids of these discrete masses ("particles") are tracked. Eulerian cells are used to define mass averages (concentrations) based upon the number of particles in each cell at a given time. There are no distorted Lagrangian cells, yet the errors associated with first-order Eulerian methods are avoided.

Some models also try to predict the dynamic behaviour of the wind and temperature fields through the primitive equations (e.g. see Seinfeld, 1988). This introduces more numerical error into the calculations due to the increased number of calculations required and their increased uncertainties in input data.

TABLE 2: Assumptions Made in Deriving Grid and Trajectory Models (after Liu and Seinfeld, 1975)

Model	Assumption	Magnitude of errors introduced (for typical urban conditions)	Possibility of rectification
Trajectory	Neglect of horizontal diffusion	Slight	Rectification not needed
	Neglect of vertical component of wind	Can be substantial	Excellent (but at the xpense of longer computing times and more data handling)
	Neglect of wind shear	Can be substantial	Difficult
Grid	Neglect of errors introduced through discretization	Substantial	Good (incorporation of more suitable techniques)

Rollback models

Rollback models assume that the pollutant concentrations are directly—though not necessarily linearly—proportional to emissions according to some simple relationship. Consequently, the emissions control requirements are presumed proportional to the amount by which the peak pollutant concentration exceeds the standards. The non-linearity of atmospheric processes limits the usefulness of such models to a screening role in which a first rough estimate is made of the emission controls required. Rollback methods lack spatial resolution and so are most useful for regional analysis of areas with many well-distributed sources of various types (e.g. see DeNevers and Morris, 1975).

PHOTOCHEMICAL MODELS

Photochemical models have the additional simulation problem of chemical reactions.

The EKMA model

The US Environmental Protection Agency recommends two approaches for formulating State Implementation Plans to achieve the NAAQS for ozone. The first of these is the so-called city-specific Empirical Kinetic ModellingApproach (EKMA) (e.g. see Seinfeld, 1988). The other approach is the use of grid-based photochemical air quality models. The EKMA method was developed as a procedure to relate levels of peak ozone to levels of reactive non-methane organic compounds and oxides of nitrogen. The method utilises a set of isopleths that depict peak ozone concentrations as a function of the following parameters:

(i) Morning concentrations of ROG (reactive organic gases) and NO_2 (which may include precursors transported from upwind sources);

(ii) Emissions of ROG, NO_2 and other species occurring during the day;

(iii) Meteorological conditions; and

(iv) Reactivity of different ROG mixtures.

The ozone isopleths are developed through computer simulations using various assumed starting levels of ROG and NO_2. The isopleths are used to compute the percent reduction in emissions that is needed to lower the measured peak ozone to the NAAQS of 0.12 ppm.

The conceptual basis of the EKMA model is the trajectory model. This formulation assumes a parcel or column of air to be advected through an urban area based on the transport winds—usually the surface winds. The ROG and NO_2 within the column react chemically in accordance with the kinetic mechanism that is used in the model. A computer program has been developed to generate the ozone isopleths.

It is now widely recognised that the EKMA method is only appropriate for those regions that have a clearly definable urban core and a simple travel path to the point of downwind ozone maxima. Seinfeld (1988) states that the method should not be applied to a number of situations, especially the development control strategies for single or small groups of emission sources. Nevertheless, because the EKMA model or any trajectory model can contain the most detailed and up-to-date chemical mechanism, and at the same time retain its computational efficiency, it is well-suited to assess quickly the effectof ROG and NO_2 emission changes on ozone levels based on realistic chemistry.

Grid-based photochemical models

Various types of gridded photochemical air quality models have been developed. They differ primarily in the number of atmospheric processes accounted for, the level of sophistication in their treatment of these processes, and the numerical procedures used to solve the governing system of equations. Examples of grid-based or airshed models that have been used to evaluate ozone control strategies are the Systems Applications Inc. Urban Airshed Model(UAM), the LIRAQ Model, and the California Institute of Technology Model (e.g. see Seinfeld, 1988).

Gas phase chemical reaction mechanisms for the atmospheric organic/NO_2 system have, as a result of many years of smog chamber and laboratory kinetic studies, reached a fairly advanced state of development. Available chemical mechanisms can be classified as *explicit* (or *detailed*) and as *reduced* (or *lumped*). Explicit mechanisms aim to account for the detailed actual chemistry of each species and intermediate. Typically, they involve several hundred reaction steps and are too lengthy to be incorporated in three-dimensional atmospheric models. For this reason, reduced or lumped mechanisms, generally involving fewer than 100 reactions, have been developed as systematic approximations of the detailed chemistry that is described by the explicit mechanisms.

As a result of EPA-funded programmes, two up-to-date chemical mechanisms for the formation of ozone in urban areas are presently available, one developed and tested by SAPRC/ERT (Statewide Air Pollution Research Center), and the second, the CBM-IV by Systems Applications Inc. (e.g. see Seinfeld, 1988). Both of these chemical mechanisms have been tested against the smog chamber data from the University of California, Riverside, and the University of North Carolina chamber facilities. The predictions of each of these chemical mechanisms agree with these environmental chamber data to within about 30 percent for ozone maxima and show varying levels of "reasonable agreement" for other measurements, and despite somewhat different approaches, both must be judged to be equivalently "good" at this stage. Results of comparison of the CBM-X and SAPRC/ERT mechanism are presented in Seinfeld (1988).

The CSIRO IER model

Recently, the CSIRO Division of Coal Technology, Australia, has released a model which appears to be a significant improvement on the EKMA model. This model (e.g. see Johnson, 1984) is based on the integrated empirical rate (IER) model of ozone formation. This model incorporates a new measure of smog intensity, namely primary smog product concentration [PSP]. [PSP] is a measure of the amount of molecular oxygen dissociated by the smog reactions and its use greatly simplifies the description of smog formation. The model is derived from extensive measurements of smog formation in outdoor smog chambers from ambient concentrations of precursors.

MODEL APPLICATIONS

Gaussian plume models

In spite of the simplifying assumptions made in deriving the Gaussian plume formula and its weak verification by observational data, the formula given by equation (3) is widely employed; indeed, it is the basis for the United States Environmental Protection Agency (USEPA) models recommended for use by air quality managers (e.g. see Tikvart, 1978). One undoubted reason for this is the simplicity

TABLE 3: Summary of Characteristics of EPA Gaussian Plume Models

Model	Reference	Predictions
Air Quality Display Model (AQDM)	TRW Systems Group (1969)	Monthly to yearly averages, shorter times using Larsen (1971) method
Climatological Dispersion Model (CDM/CDMQC)	Busse and Zimmerman (1973), Brubaker *et al.* (1977)	Monthly to yearly averages, shorter times using Larsen method (then referred to as (CDMQC)
Gaussian-Plume Multiple Source Air Quality Algorithm (RAM)	Turner and Novak (1978)	Hourly to daily averages
Single Source (CRSTER) Model	USEPA (1977)	Maximum concentrations from 1-hour to 24-hour averaging times, frequency distributions of concentrations
Texas Episodic Model (TEM)	Porter and Christiansen (1976)	10-minute to 24-hour averages
PTMAX, PTDIS and PTMTP	Turner and Busse (1973)	PTMAX considers maximum concentrations, PTDIS all concentrations, PTMP multiple sources
PAL	Petersen (1978)	1- to 24-hour concentrations from point, area and line sources

of the formula; it requires little data to be collected for its use compared to other models which seek to improve on it.

The best known of the Gaussian plume models are listed in Table 3 and are part of the UNAMAP (User's Network for Applied Modelling of Air Pollution) system developed by the United States Environmental Protection Agency. Briggs (1975) has reviewed various plume-rise models and points out that plume rise is confidently predicted only for stable conditions.

Gifford (1976) has shown how the various schemes for σ_y and σ_z values are related and suggests that the interpolation formulas derived by Briggs (1974) incorporate the best features of these schemes (see Table 4).

Hanna *et al.* (1977) have reviewed the different stability classification schemes and corresponding σ curves. Both reviews recommend that, wherever possible, the data for the standard deviations of wind direction, σ_θ and σ_ϕ, be used to compute σ_y and σ_z; the stability-classification-scheme approach should only be used when these data are not available. For instance, Carrasand Williams (1984) have identified new dispersion formulae appropriate for Australian conditions, especially tropical situations.

If a line source is viewed as an indefinite number of point sources, each yielding pollutant concentrations given by equation (3), then the pollutant concentration from a line source is obtained by integrating in the horizontal direction (y-direction). This is the basic assumption in most Gaussian plume approaches to line sources; for example, HIWAY (Zimmerman and Thompson, 1975) and the GM model (Chock, 1978) assumes line sources of infinite length. Sistla *et al.* (1979) conclude that models such as these yield reasonable estimates of CO and particulate pollutants, as have Darling *et al.* (1977) in their review of 13 models.

TABLE 4: Briggs' Formulas (1974) [Formulas Recommended by Briggs for $\sigma_y(x)$ and $\sigma_z(x)$; $10^2 < x < 10^4$ m]

Pasquill type	σ_y, m	σ_z, m
Rural conditions		
A	$0.22x\ (1 + 0.0001x)^{1/2}$	$0.20x$
B	$0.16x\ (1 + 0.0001x)^{1/2}$	$0.12x$
C	$0.11x\ (1 + 0.0001x)^{1/2}$	$0.08x\ (1 + 0.0002x)^{1/2}$
D	$0.08x\ (1 + 0.0001x)^{1/2}$	$0.06x\ (1 + 0.0015x)$
E	$0.06x\ (1 + 0.0001x)^{1/2}$	$0.03x\ (1 + 0.0003x)^{-1}$
F	$0.04x\ (1 + 0.0001x)^{1/2}$	$0.016x\ (1 + 0.0003x)^{-1}$
Urban conditions		
A-B	$0.32x\ (1 + 0.0004x)^{-1/2}$	$0.024x\ (1 + 0.001x)^{1/2}$
C	$0.22x\ (1 + 0.0004x)^{-1/2}$	$0.20x$
D	$0.16x\ (1 + 0.0004x)^{-1/2}$	$0.14x\ (1 + 0.0003x)^{-1/2}$
E-F	$0.11x\ (1 + 0.0004x)^{-1/2}$	$0.08x\ (1 + 0.0015x)^{-1/2}$

One of the major criticisms in using Gaussian plume models is the difficulty in incorporating deposition and settling effects. There are ways of incorporating deposition effects in the Gaussian plume model and Horst (1979) has reviewed a number of such models.

In Table 3, AQDM, CDM/CDMQ, RAM, TEM and PAL are urban models which consider pollution from a variety of sources. TEM uses the Gaussian plume approach for point sources and the Gifford-Hanna approach for area sources which is examined in the next section. RAM is used to calculate hourly to daily pollutant concentrations for point and area sources, and the computation of σ_y is explicitly incorporated using equation (3); it is used for urban or rural areas (different stability schemes for each) and for flat, level terrain. PAL is similar to RAM, but includes line sources such as highways as well and is not designated for use for entire urban areas, but rather for portions thereof, such as shopping centres, airports and large parking areas; level terrain is assumed. None of these models allows for complex terrain effects. VALLEY (Burt, 1977) is a Gaussian plume model for point and area sources in complex terrain, but only accounts for complex terrain effects quite crudely.

An AMS position paper on the accuracy of Gaussian models is summarised in Table 5, following Drake *et al.* (1979), and concludes that agreement between prediction and observation to no more than a factor of two should be expected.

TABLE 5: Estimates of Accuracy for Diffusion Calculations (after Drake *et al.*, 1979)

Circumstances	Accuracy
POINT SOURCES	
Ideal conditions: near field (< 1 km), short averaging times (min to hr), flat terrain, steady meteorology, surface source	10% to 20%
Same as above, except for elevated sources	20% to 40%
Real-world applications: meteorological parameters reasonably well known and steady with no exceptional circumstances	Factor of two
Exceptional circumstances: wakes, buoyant plumes; varied surfaces, such as forests, cities, shorelines, rough terrain; extreme stable and unstable conditions; distances > 10 to 20 km	Poorer than factor of two; may be as poor as a factor of 10, or more
URBAN AREA SOURCES	
Ideal source and meteorological input data and conditions	10% to 20%
Real-world applications with no exceptional circumstances	Factor of two

The ATDL model has been developed by Gifford and Hanna (1971, 1973) and Hanna(1971), and is applied to urban area sources in which the emissions are assumed to be uniform over grid squares (of typical size 1-10 km). The pollutant is assumed to be well mixed to a height which is not the inversion layer, but given by vertical diffusion parameters varying with stability conditions.

Gifford and Hanna (1975) have suggested that the ATDL model works best for long-term averaged concentration values while, for short-term simulations, information about initial values of pollutant concentration should be used for calibration of the model—calibration is also recommended for long-term averages if the data are available. The application of the model to the prediction of annual TSP (total suspended solids) levels in Brisbane is shown in Figure 1. Where monitoring occurs in the grid squares, the accuracy appears to be within a factor of two (Simpson *et al.*, 1987).

An urban model which also combines all types of sources and is calibrated using Gaussian plume models in the Smeared Concentration Approximation (SCA) model

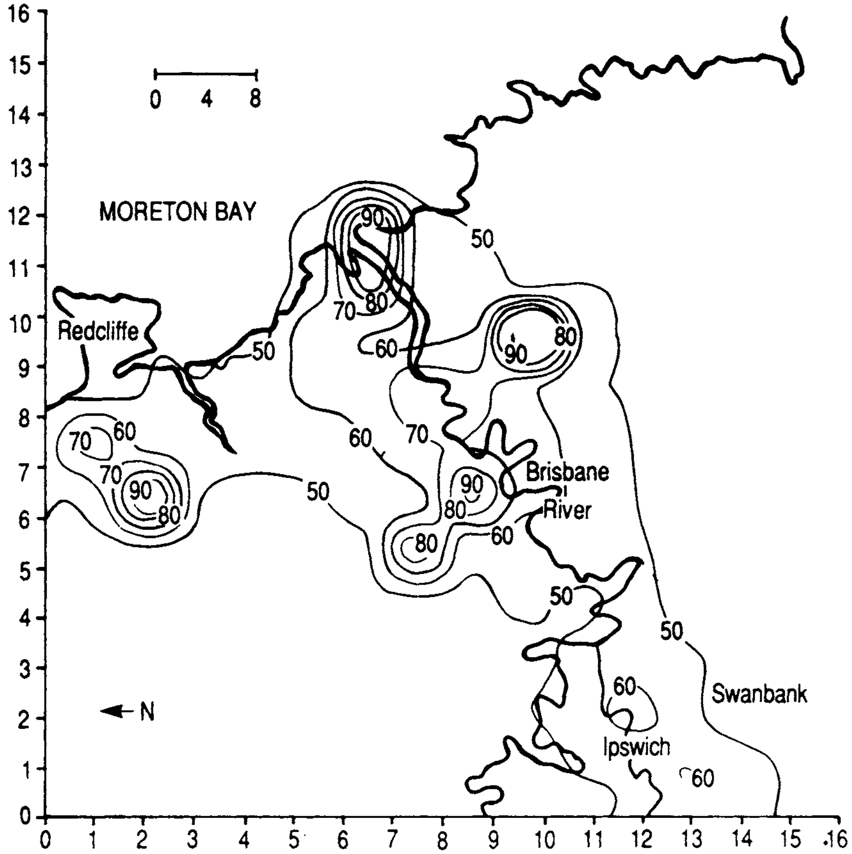

Fig. 1. Contour plot of mean total suspended solids (TSP) estimates (Simpson *et al.*, 1987).

(Dennis, 1978, 1980). This model has been used in both Europe andAustralia (e.g. see James *et al.*, 1985) as a convenient method for incorporating air quality objectives into integrated regional economic environmental planning strategies.

Model performance measures

In 1980, under a co-operative agreement with the EPA, the AMS held a workshop on dispersion model performance at Woods Hole, Massachusetts to discuss current practices in the evaluation of dispersion model performance.

to recommend performance evaluation measures, and, if possible, to set performance standards for these models (Fox, 1981). Workshop discussion resulted in the recommendation of a set of performance measures to be used for evaluating the performance of different dispersion models.

The following measures of difference were suggested: the bias (average) of the difference (observed-predicted); the variance of the difference (noise); and the gross variability (gross error) of the difference.

These are actually related measures, because the sum of the square of the bias plus the variance equals the square of the gross variability. The following measures of correlation were suggested: time, space, and time and space combined. The recent reviews on model performance attempt to use these measures where possible.

The nature of current National Ambient Air Quality Standards and Prevention of Significant Deterioration increments requires that an extreme concentration value (highest, second highest) be estimated by models. Workshop participants agreed that the accuracy of highest or second highest estimates is expected to be poor and difficult to evaluate statistically. Statistical evaluations have greater meaning when applied to a relatively larger number of values than to one or two extremes. Generally, statistical evaluations applied to an upper percentile (2% or 5%) of the predicted values are more informative than those applied to only the highest or second highest prediction. Evaluations applied to estimates of mean performance will supply more information about overall model performance than will evaluations applied to extremes only. The workshop participants, therefore, recommended that the statistical form of standards and increments be changed to consider the upper 2% to 5% of concentrations rather than one or two extreme values.

Hayes and Moore (1986) present a comparative analysis of the results of 15 air quality model performance evaluation studies involving 35 rural, urban, complex-terrain and regional models. Of the 35 models studied, most (25) were Gaussian in formulation, including five long-term climatological models, three of which performed only long-term calculations (AQDM, CDM and TCM) and two of which make both long- and short-term estimates (MSDM and ERTAQ). The remaining ten models were numerical first-order-closure models (including three rural models, one complex-terrain model, and six regional models). The model applications focus on slowly or non-reactive pollutants, principally sulfur dioxide (SO_2) and TSP. Among study findings are the following:

(i) Flat-terrain rural models nearly always predict the second highest concentrations within a factor of two (often less), with no evidence of systematic overprediction or underprediction, but some models may underpredict the highest concentrations by more than a factor of two at distances far downwind (> 20 km);

(ii) None of the models accurately predicts spatial patterns of $\leq$ 24-hour-averaged concentrations, and while increasing the averaging time from 24 hr to annual improves performance for some models, it does not appear to do so for flat-terrain rural models; and

(iii) While some models appear to predict more frequent concentrations (e.g. 5th or 10th high, 95th percentile) better than they do the highest concentrations (e.g. 2nd high), no overall systematic tendency is evident.

Combined deterministic statistical models

Since it is now acknowledged that urban models need to simulate concentrations frequency distributions in order to examine whether standards have been violated, a recent modelling approach has combined the deterministic ATDL model with assumptions about the form of the statistical distribution (e.g. see Simpson and Miles, 1989; Miles and Simpson, 1988).

To extend the ATDL model output to include annual maximum ground-level concentrations, and other statistics within the frequency distribution for the pollutant, a methodology has been developed over recent years which allows accurate estimates of pollutant concentrations corresponding to any statistic of the frequency distribution to be made, thereby relating the probability of exceeding set standards to control strategies. The generalised methodology developed has been outlined by the following steps:

(i) Assume/identify a statistical distribution for the air pollution concentrations;

(ii) Develop a deterministic model from available data, to predict a range of percentiles of air pollutant concentrations;

(iii) From the results in (ii), estimate the parameters of the statistical distribution assumed in (i); and

(iv) Using the parameters derived in (iii), construct a statistical distribution of air pollutant concentrations from which the estimates of high pollution levels can be obtained.

The results for the study in Brisbane are shown in Figure 2.

Photochemical models

Seinfeld (1988) has summarised recent reviews of photochemical model performance as follows.

The overall accuracy of photochemical grid-model ozone predictions is currently about 35 percent when predictions and observations are paired in time and space. The errors in single-day simulations are somewhat less than for multiple-day runs. On the whole, grid-model ozone predictions tend to be biased low. Of the 63 single-day simulations surveyed, 70 percent exhibit a tendency toward underprediction of ozone. However, much of this trend may be due to "paired" comparisons; when the requirement for pairing in time and space is dropped, much of the underestimation disappears, which simply means that peak predicted values occur at somewhat different

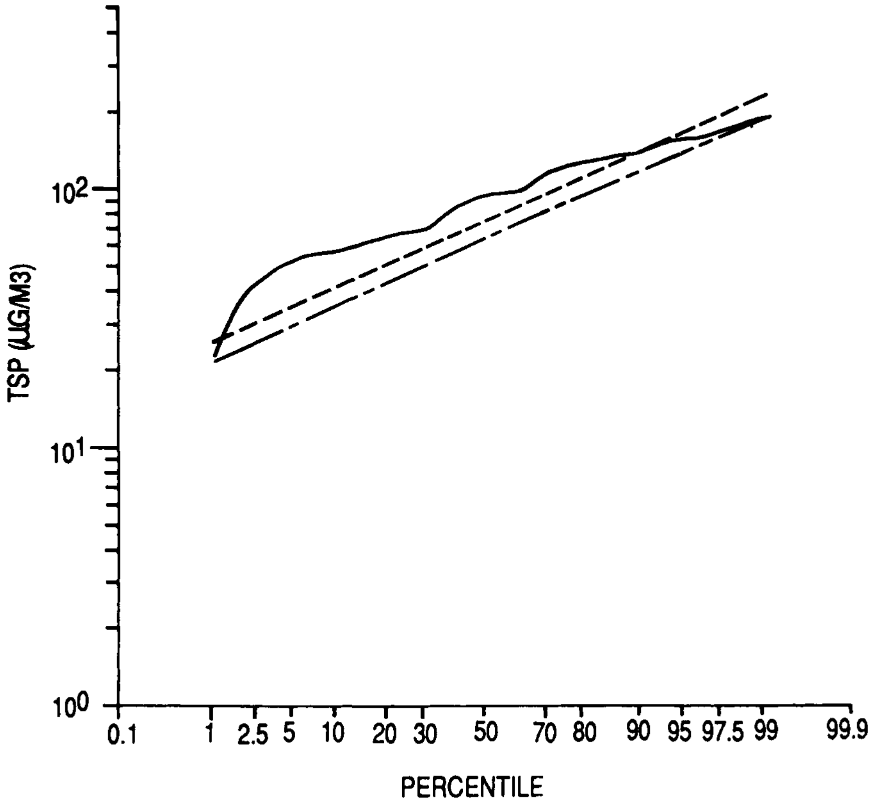

Fig. 2. Plot of predicted concentrations, using both Jamboree Heights (— —) and ratio (- - - -) background corrections, compared with observed TSP (——) concentrations for Woolloongabba, Queensland, Australia, 1978-1979 (Simpson *et al.*, 1987).

times and locations than those measured. For example, relaxing the requirement for time/space pairing in St Louis simulations reduced the bias from –32 percent to +4 percent (Seinfeld, 1988). Part of the difficulty in matching ozone maxima at the correct time and location is due to the inherent difficulties in reconstructing the meteorological and emissions fields on the day in question. Seinfeld (1988) concludes that grid-based photochemical air quality models with up-to-date chemistry, wind-field treatment, and numerical techniques have reached a level of accuracy that may be difficult to improve upon in the near future.

The most important application of the photochemical models is in predicting the consequences of various smog control policies. The approach adopted, in part because of these model predictions, is mainly to control the emissions of hydrocarbon precursors and not NO_x (e.g. see Chock and Heuss, 1987). However, it is by no means clear that this approach is working (e.g. see Lindsay *et al.*, 1989). Given the rising NO_x levels in all industrialised countries, this gives some cause for alarm and perhaps a re-examination of the control approaches being adopted.

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RECENT TRENDS IN ENVIRONMENTAL MANAGEMENT IN THE ASIA-PACIFIC REGION

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For many years, the major environmental problems in the Asia-Pacific region stemmed from the relative lack of development and inadequate infrastructure facilities. In short, poverty itself seemed polluting. Therefore, countries of the region have generally considered economic growth and industrialisation as key development priorities and concern for the protection of the environment has been regarded as of secondary importance. This very process of accelerated development brought to the fore many environmental problems and considerable impact on their resource potential.

Desiring to cope with the gradually rising environmental costs of economic development as well as to maintain adequate balance, Governments of the region have responded in a decisive manner to evolve policies and programmes to prevent environmental degradation. However, the measures adopted were essentially of the problem-responsive type constituting a restorative action, which have been found to be expensive, inconvenient, time-consuming and sometimes insoluble in economic terms.

The countries of the Asia-Pacific region are now in the midst of an enhanced economic development involving natural resources. The challenges ahead to cope with the complex environmental problems are, therefore, formidable which require competent environmental management to achieve sustainable development.

This paper discusses the improved concepts, techniques, institutional arrangements and comprehensive approaches that are being adopted in the region for the management of the environment.

INTRODUCTION

The Asia-Pacific region, comprising over half of the world's population, displays vast diversity in the types and degree of interaction and direct dependency on the natural environment. Nevertheless, the people and countries in the region are experiencing similar desires and difficulties in their social and economic development. The similarity is that development relies on a natural resources base which can sustain development only if it is properly used and managed. The region has wide variations in climate, geology, soils, vegetation, culture and social structure. Apart from high population density, the region includes some of the poorest countries, consisting of about 500 million people below the poverty line (US $ 70 per capita per annum). About 72 percent of the population is rural, 54 percent depending on agriculture and 18 percent on livestock based activities.

The cultural heritage of the region is wide-ranging and includes in many countries significant architectural treasures and other historical monuments dating thousands of years back. The value and influence of this heritage is no longer limited to the region. As a major centre of attraction for visitors from all over the world, it makes a significant contribution to a flourishing tourist industry which is an important source of employment and foreign exchange for many countries. However, the intrinsic value of this heritage to people of the region is not primarily touristic or economic. It is deeply rooted in the spiritual and social values of the communities and reinforces their sense of cultural identity and spiritual harmony. Thus cultural heritage plays an important unifying role and provides a code of social conduct.

The natural heritage of the region ranges from the elephant and rhino, many species of primates, the panda, tigers, leopards and lions, birds of paradise and parrots, corals and associated wealth of colourful coral fishes, etc., and also includes various vegetative formations, such as almost pure dipterocarp forest and other rain forests.

The economic benefits that flow from this natural heritage range from daily agricultural activities for the production of food, fuelwood and trade commodities such as spices, vegetable oil, fibres, etc., to large-scale commercial exploitation of timber. It is estimated that the region provides about 70 percent of the world's tropical forest. The fauna of the region is, among other things, a major source of daily sustenance especially for the rural population. A closely related aspect is the use to which various species of plants have served the people of this region in traditional medicine and other related uses.

Freshwater and marine resources are also daily source of food and revenue for individuals and governments of the region. Indeed the island nature of many of the countries and their limited surface area compel them to be heavily dependent on marine resources for food. Small and large scale fisheries, including industries based on this resource, can be considered as important as agriculture-based activities in providing employment.

The region is also rich in a variety of minerals containing some of the largest deposits in the world. There are huge reserves of iron and manganese ores, rare metal-bearing pegmatites, deposits of chromite, copper, nickel, cobalt, lead and zinc, gold, platinum, uranium, asbestos, graphite, magnesite and some other non-fuel minerals. Significant supplies of fuel minerals, petroleum, natural gas and coal, are found in the region. About 60 percent of the world's resources of tin ores are found in East Asia. The main reserves of graphite are concentrated in Sri Lanka, India and Republic of Korea. More than 30 percent of the world reserves of zirconium and the largest reserves of muscovite are in India. Iron ores are abundant though irregularly distributed throughout the region, with total resources estimated at 163,000 million tons. Economic deposits of chromite are found in India, Iran, Pakistan and the Philippines, the latter country being the world's most important producer of refractory grade chromite.

The total estimated reserves of manganese in the region are about 500 million tons, mostly in Australia, India and China. Combined deposits of tungsten from East Asia and Australia account for over 75 percent of total world resources. The region's reserves of antimony constitute over 3 million tons or some 60 percent of the world's total. Though sizeable copper deposits are not common in the region, the Philippines ranks among the 10 leading copper-producing countries in the world. Total resources of bauxite in the region are estimated at 7000 million tons, the bulk of which is in Australia, China, India and Indonesia. About 8 percent of the world's production of phosphate rock are from the Asia-Pacific region mainly from China, Australia, Christmas Island, Nauru, Ocean Island and Vietnam. Finally the region contains natural gas reserves and about 20 percent of the world's coal reserves.

The Asia-Pacific region has the potential of becoming one of the fastest growing regions of the world with an estimated population of 3.4 billion by the year 2000. In many countries of the region, the population pressure or poorly managed or wasteful use of resources has led to degradation and depletion of key resources. With future population pressures and increased rates of national development, the demands on natural resources will increase and, unless exploitation is managed so that renewable resources are used on a sustained basis and non-renewal resources used wisely and conservatively, the natural resource base will be severely degraded.

Recent study done by ESCAP (1983) does in fact provide a clear indication of these possible future trends. If preventive measures are not taken swiftly or stepped up, the Asia-Pacific region could, over the next fifteen years, lose 70 percent of the tropical forests and 10 percent of its gene pool; the damage caused by the floods, the use of pesticides, and industrial pollution could be doubled; nearly 20 million square kilometers of land could be affected by desertification. Devastation of this scale would constitute a threat not only to the living conditions of hundreds of millions of people, but also to the very foundations of development, i.e. water, arable land, fuelwood, marine resources and the inhabitable environment.

ENVIRONMENTAL ISSUES

For many years, the major environmental problems in the Asia- Pacific region stemmed from the relative lack of development and inadequate infrastructure facilities, -in short, poverty itself seemed polluting. Therefore countries of the region have generally considered economic growth and industrialisation as key development priorities and concern for protection of the environment has been regarded as of secondary importance. Hence, the situation in many of the countries of the region, until recently, was that concern over environmental quality became ignored in the process of marshalling resources to meet priority development goals. Higher agricultural productivity, maximising incomes and boosting living standards, balanced development among states and improved health care are but a few of these goals. Development thus proceeded apace, with industrialisation being the favoured path for accelerated socio-economic growth through increases in output, income and job opportunities. This very process of rapid development spanning mining, forestry, estate development, agriculture, land settlement, urbanisation and industrialisation brought to the fore problems of a second order, namely, damage and disruption to the environment, which not only bagan to emerge but to gain in significance from year to year. Of particular concern are:

- Rural-urban drift contributing to urban concentration and congestion with enormous pressure on water supplies, waste disposal and other public services as well as giving rise to serious squatter problems;
- Polluting emissions, both gaseous and liquid, from a wide range of vehicular traffic and industries, including agro-based ones such as palm oil and rubber processing facilities;
- Particulate matter, such as smoke emissions from stacks and vehicle exhaust, and dust from quarrying;
- High ambient lead levels of concentrations 2 to 4 times higher than the allowable ambient level, at busy road junctions in urban areas;
- Occurrence of haze coupled with long dry spell leading to localised high temperatures especially in the urban setting and resulting in poor visibility and interruption of flight schedules;
- High noise levels measured at the boundary of many residential buildings and schools located at new main roads;
- Erosion and sedimentation of rivers and canals, arising from housing, land settlement, urbanisation and infrastructure construction and logging, causing perennial and recurring floods;
- Excessive deforestation and logging, shifting cultivation and dam construction for irrigation and hydropower projects which disrupt and dislocate traditional human settlements andwildlife;
- Desertification;
- Mining and industrial effluents polluting rivers and inland waterways, resulting in fishkill in river systems and limiting the availability of water of appropriate quality for future growth;
- Discharge of untreated sewage into watercourses;
- Oil spills and the discharge of wastes from ships near coastal areas causing fishkill, loss of other marine life and oil contaminated beaches;
- Indiscriminate dumping of solid wastes, poor refuse collection system and rampant littering;
- Misuse of fertilizers, pesticides and herbicides in agriculture;
- The build-up of dangerous pesticide residues in fish and other marine biota and adverse impacts through the food chain;

- Indiscriminate disposal and dumping of toxic and hazardous wastes generated by industries;
- Increased emissions of oxides of sulphur and nitrogen produced by the combustion of fossil fuel leading to acid rain and photochemical smog;
- Depletion of the ozone layer and accompanied threat of incresed ultra-violet radiation at the surface of the earth;
- Increased concentration of carbon dioxide and the possibility of unpredictable changes in climate due to the 'greenhouse' effect; and
- Increase in fallout of trace metals, potentially toxic to humans and other organisms due to industrial activities, and the large number of organic micropollutants being transported long distances and deposited along with acid rain, toxic metals and other pollutants.

ENVIRONMENTAL MANAGEMENT IN THE ASIA-PACIFIC

Desiring to cope with the gradually rising environmental costs of economic development as well as to maintain adequate balance, governments in the Asia-Pacific region have taken cognizance of the environmental issues and responded in a decisive manner to evolve policies and programmes to alleviate environmental degradation.

Several approaches have been adopted in the region to deal with environmental protection depending on the gravity of the problems. The traditional approach, however, has been for environment-related issues to be routinely reviewed by several departments connected with resource development or conservation. In many cases, these departments did not have any statutory powers and the approach was found to be most unsatisfactory. The next development was the designation of a specific committee/department among the ministries to look after environmental issues. Subsequent requirements for specialised needs and skills have ultimately led to the creation of a fulltime environmental ministry, agency or board.

There has been a continuing upsurge of high level, full time environmental agencies in the region since 1977 (ESCAP, 1984). Almost all the countries in East Asia, South Asia and South East Asia have established separate Agencies or Ministries in charge of environmental matters. In the Pacific, however, institutionalisation of environmental concerns has been slow. Most of the countries in the region have no specific agency dealing with environmental protection. As of now, however, Cook Islands has a Directorate of Conservation; Papua New Guinea, a Ministry of Environmental Conservation; the Trust Territory of the Pacific Islands, an Environmental Protection Board. In Vanuatu, an Environment Unit is planned to be created in the Ministry of Lands, Mines and Energy (Asian Development Bank, 1987).

During the past decade, a priority task in the efforts of the countries of the region to achieve a balance between development and the environment was to deal with environmental problems that had accumulated over the years through restorative measures backed by systematic enforcement of the various legislations while developing strategies to forestall future environmental problems.

Generally, legislation includes a statement of policy, goals, objectives and priority targets. In certain instances, it covers a variety of aspects of the environment, while in others it merely establishes the enabling acts and defines the scope and functions of the central environmental agency and provides a procedure whereby environmental considerations can be fed into decision-making procedures.

The countries of the region have undertaken a variety of legislative measures for environmental protection. A survey undertaken by ESCAP (Legislative Development. Vol 1: Summary) revealed that these are often sectoral in character. The survey indicated that environmental legislations in the region generally cover the areas of land-use, air and water quality, environmental impact assessment, noise, solid wastes, industrial waste disposal, coastal zone management, forests, parks and wildlife, hazardous substances, mineral development and cultural environment. Some countries have developed general environmental protection policies. Sometimes, these general environmental policies are predicated on the relevant provisions of the national constitution so that they truly reflect a permanent national commitment to improving the environment.

Legislation regarding Environmental Impact Assessment (EIA) occupies an important place in the environmental management undertaken by these countries. However, it has been found that except for countries such as Australia, Philippines with specific legislation on EIA, countries such as Hongkong, Malaysia, Papua New Guinea, Republic of Korea, Sri Lanka and Thailand have no specific legislation on EIA, but they rely heavily on the provisions of general environmental protection legislation (which often includes EIA) for the purpose of carrying out EIA of development projects. In other countries such as Bangladesh, Fiji, India, Indonesia, Nepal, Pakistan and Samoa, informal procedures are resorted to for the incorporation of environmental considerations into the planning of selected sites and projects, particularly in the case of major industries and other large-scale development undertakings. There are also many countries in the region without any requirement of EIA. Inadequacy of information on the environmental conditions and environmental protection needs of these countries could be a reason for the absence of EIA requirement.

Inadequate implementation and enforcement have so far appeared to be a critical shortcoming in many countries of the region. These shortcomings are often the result of the prevalence of factors such as poverty and inadequate and insufficient trained manpower, funds and equipment.

Logically it would be sensible to work out a proper environmental plan to be carried out within the 'general planning framework' before any pollution control work is carried out. However, in the context of most of the countries of the Asia-Pacific region, having due regard to the necessary lead time required to evolve a sound plan (data collection, resources, trained manpower, etc.) and urgency of enforcing anti-pollution measures, immediate action was called for. In this sense, pollution control has been the main activity in the programme of the Environmental Protection Agencies of the region for protection of the environment and enhancement of its quality.

The sustained environmental improvement efforts to date have made significant inroads into the problems identified at the start of the decade. Consciousness of environmental changes and appreciation of their bearing on social and economic well-being have grown significantly. Formal education, technical training, mass media, and non-government organisations and citizen groups have all played a role in this process of building environmental awareness. There has also been some progress in terms of greater access to information on environmental problems and prospects, administrative and legislative means of organising and implementing action, methodological guidance in assessment and analysis of environmental changes and measures, and training and technical co-operation to deal with environmental matters. Regional co-operation to deal with shared environmental problems has also increased. Environmental aspects have begun to be seen in clearer perspective in various sectors of development, such as, food and agriculture, health, industry and human settlements.

Public involvement in environmental debate and action has increased, support, both at scientific and grassroot levels for action to arrest environmental degradation has grown in the face of increasing negative ramifications of industrialisation, urbanisation, population growth and significant changes in forests, rangelands and farmlands.

The preservation of representative samples of the region's natural forest ecosystem with its constituent flora and fauna has continued to be accorded due importance. Such natural forest habitats are indispensable as they play a truly significant role in the preservation of watershed; in the maintenance of hydrological cycle while serving as a permanent source of scientific, cultural and recreational value.

THE CHALLENGES AND NEW STRATEGIES IN ENVIRONMENTAL MANAGEMENT

The achievements todate in terms of measures for overcoming environmental problems do not by any means represent the complete answer in tackling the whole gamut of environmental issues. The measures adopted have been essentially of the problem-responsive type amounting to 'pollute first and clean later' policy which have been found to be expensive, inconvenient, time-consuming and sometimes, insoluble in economic terms.

The countries of the Asia-Pacific region have no choice but to forge ahead with economic development for self-reliance and to raise the standard of living of the people to a satisfactory level. With greater experience, more thorough investigation of past projects and increased understanding of natural systems, it is now apparent that many development projects can and do have significant, and often unanticipated effects on the natural environment and the use made of it and that these effects can add to the real costs or affect the real benefits of the undertaking.

Increasingly it is now being recognised that, even if the direct and measurable economic costs and benefits of the projects remain of prime importance for the majority of the proposals, the effects on the natural environment which are not included in the economic sums cannot be ignored if allocative efficiency is to be maximised.

It is therefore crucial for developing countries such as those of the region to protect the source of their present wealth and those that are likely to be familiar in the future on the principle that renewable resources can best be extracted from a healthy environment. In addition, these countries must be constantly aware that their basic resources are finite and thus farsighted resource husbandry is of paramount importance.

This has, in recent years, led to some serious rethinking on the directions and pace of future development efforts. Whilst the concern with the human environment can only reinforce the commitment to development, it should serve, however to provide new dimensions to the development concept itself. The concept should have as its aim the satisfaction of human needs without destroying the environment from which these needs are generated. In this respect, therefore, in view of the interactions that exist between resource development and environmental quality, environmental management should be understood to mean prudent management of the quality and quantity of the natural resources.

As a result, the view which has been gaining ground in the developing countries considers environment decisions as organically linked to development decisions. While pollution and conservation are not unimportant from the point of view of environmental management, its major concern is with optimal resource use, resource maintenance and enhancement. Indeed, development with efficient environmental management can help to generate the resources and the means for sustainable development, given rational use and application of advances in science and technology.

In the context of the Asia-Pacific region, as the prospects of a long-run, abundant supply of natural resources are dim, and technological innovations are inadequate, discrete and unpredictable, the countries of the region have to take a serious look at the resource limitations, especially renewable resources, and tailor the development efforts suitably. This does not imply sacrificing development itself. What it does imply, though, is that patterns of resource development and resource use have to be restructured by adopting policies of resource management which are innovative and imaginative, and focus on employment and efficiently organised productive activities while treating environment as an important parameter.

Further, since the development of natural resources will be a continuing process which involves intentional changes to the environment through the various activities, it must be accompanied by conscious efforts in guiding these environmental changes so that the sustaining of economic growth will serve the purpose of providing a better standard of living not only in the material sense, but also in the value of life itself. The task of guiding these changes must be carried out through a proper long-term management of the resources by maintaining an equilibrium between the modes of resources and the rising needs.

The challenges ahead to cope with the complex environmental problems are, therefore, formidable which require competent environmental management to achieve sustainable development.

In the light of the above concept of environment and development, the countries of the Asia-Pacific region are beginning to adopt an environmental management strategy which essentially consists of the following components:

- Appropriate Environmental Policy;
- Integrated Economic and Environmental Planning; and
- Regional Co-operation.

Appropriate Environmental Policy

Environmentalism has grown out of the contradictions between modern economic activity and the regenerative capacities of natural systems. Such contradictions are characterised by the emergence of environmental problems and environmental values. The result is a confrontation between environmental advocates and affected parties and the vested interests of development. The policy system is principally a mechanism for conflict resolution, generating policy instruments that are the operational guidelines that define the actions of the implementation system.

Accelerated development in the developing countries could enhance their capacity to improve their environment. The environmental implications of poverty and underdevelopment and the inter-relationships between development, environment, population and resource must be taken into account in the process of development. It is essential to avoid environmental degradation and give future generations the benefits of sound environment. There is a need to ensure an economic development which is environmentally sustainable over the long run and which protects the ecological balance.

In order to inculcate a greater understanding of the close relationship between development and the environment, governments of the region have formulated comprehensive environmental policies reflecting the recognition of their responsibility and strong commitment to manage all the resources of the nation in a manner which with due concern for the welfare of the future generations maximises the quality of life for all. Such a policy statement is broader in scope than the underlying policies of any laws and legislations with regard to environmental quality which in essence would chiefly be concerned with the control of various pollutants. It would also extend to other environmental tangibles and intangibles covering such diverse subjects as soil and water conservation, flood control, wildlife, national parks, cultural aspects, aesthetic values, health, recreation and tourism, and town and country planning.

The environmental policies of the countries of the region are generally consistent with the concept of sustainable development. Some of the significant features of the policies include the following elements:

- Maintain the quality of the environment relative to the needs and aspirations of the growing population;
- Preserve the country's unique and diverse cultural and natural heritage;
- Minimise the impact of growing population and human activities relating to mineral exploitation, deforestation, agriculture, urbanisation, tourism, and the development of other resources both renewable and non-renewable, on the environment through restorative and preventive measures;

- Balance the goals of socio-economic development and the need to bring the benefits of development to a wide spectrum of the population with the preservation and protection of the environment through proper environmental management; and
- Promote greater co-operation and increased co-ordination in environmental management at all levels of the governments.

The environmental policies have enunciated definite goals to achieve sustainable development, support and promote general welfare, and to create and maintain conditions under which man's activities and nature can co-exist in harmony. The responsibility of the environmental decision-maker and planner is to serve the major goals outlined in the environmental policy. This complex management task requires the environmental manager to be aware of and to recognise the key factors which constrain his activities. These factors can be identified as social, technical, political, legal, ecological and economic. An understanding of these inter-relationships requires multi- disciplinary knowledge and an inter-disciplinary, integrated planning approach to develop public policy programmes that enhance and achieve the politically desired quality of life.

Integrated Economic and Environmental Planning

In the past, there has been a tendency to equate development with the more narrowly conceived objective of economic growth as measured by the rise in gross national product or by physical indicators alone. When natural environment was considered, it was often viewed as an economic constraint on development. Flooding, slope stability, soil structure, and seismic activity were seen as environmental factors affecting the cost of development but usually subject to satisfactory engineering solutions. The lack of attention to environmental factors in development planning has led to significant environmental degradation, irreversible loss of precious ecological and other natural resources, and in many instances hazard to life and property, unanticipated social costs, loss of amenity and quality of life. In addition, when development planning has concentrated on overall economic growth, socio-economic disparities have led to the creation of urban slums and attendant neglect of basic environmental amenities such as water supply and sanitation. Disparities between urban and rural areas have intensified migration from rural areas to urban slums.

Underlying othe importance of striking a balance between development and the environment is the need to place more emphasis on preventive approach to environmental management than on curative measures. Accordingly there has emerged a clear need to modify the traditional methodology and approach of project evaluation adopted by development planners and decision-makers that are based purely on economic considerations, in order that environmental dimension is incorporated into the development planning process from the outset.

In this respect, a more expedient approach used by the countries of the Asia-Pacific region has been to adopt the environmental impact assessment (EIA) process by which individual projects were carefully examined for environmental implications following the lead by the industrialised countries. The EIA requirement has indeed been the most powerful tool of the developing countries for influencing development decisions and it is expected that this would continue to be the case for the next decade or so.

The EIA process concentrates on individual projects, although occasional attempts have been made to conduct EIAs for overall development programmes. The EIA process could not be expected to give adequate attention to regional environmental needs. Past experience has shown that despite the use of environmental impact assessments and other techniques, major economic development projects have caused unacceptable environmental degradation.

Detailed environmental investigation is usually only possible at the appraisal stage, often in conjunction with a pre-feasibility study or feasibility study. Quite commonly, the environmental specialist is given inadequate time to prepare an environmental impact assessment for a multi-million dollar project. Thus, the environmental input is too little or too late, and by that time such a project would have been included in the national development plan and/or annual budget and it becomes difficult to prevent the project from proceeding.

Attention has since been directed to bringing about better planning which is environmentally as well as economically sound, i.e., Economic-cum-Environmental (E-c-E) planning. When development planning is done on this basis, the role of the EIA can be limited to local environmental effects, whereas without such planning, the EIA must deal also with macro environmental effects but can rarely do so effectively. The EIA process is no substitute for proper regional planning.

Figures 1 and 2 sum up the evolutionary processes of E-c-E planning in the countries of the Asia-Pacific region.

The objectives of integrated economic-cum-environmental planning is to prepare good plans which directwise investment decisions, thus contributing to sustainable development and benefiting the whole population. A 'good' plan is one which enables economic, social, natural resource, and environmental objectives to be satisfied; identifies development strategies which enable all the objectives to be satisfied; and identifies development and projects which are consistent with and facilitates the stated objectives and strategies.

Projects with varying degrees of integration were undertaken in Indonesia, Republic of Korea, Philippines and Thailand. The first project to comprehensively integrate environmental factors into regional economic development planning was the Songkhla Lake Basin Planning Study in Thailand. The process is shown in Figure 3. The steps involved in Regional Environmental Development Planning Process is shown in Figure 4.

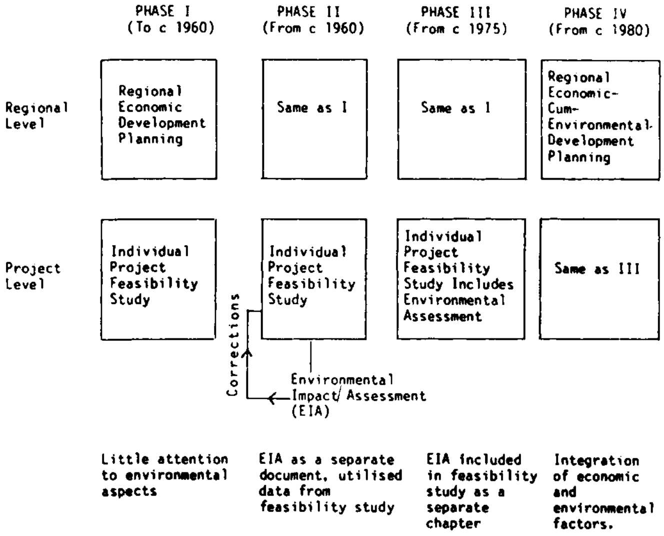

Fig. 1. Evolution of Economic-cum-environmental Planning
[*Source* : Environment Unit, Asian Development Bank].

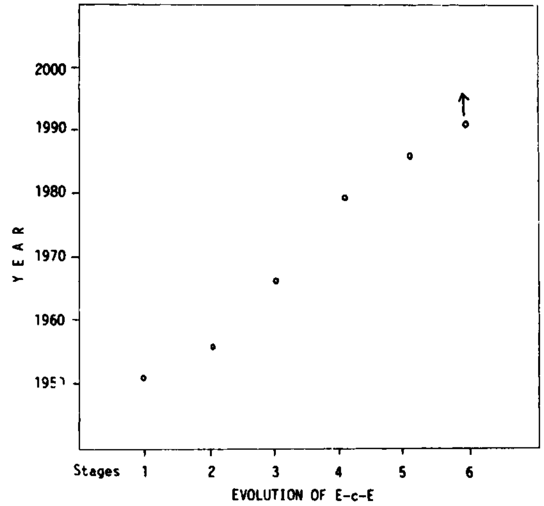

Fig. 2. Schematic illustration of economic-cum-environmental development planning in the Asia-Pacific region. [*Stages* : 1. Conventional Regional Development Planning; 2. Regional Economic Development Planning; 3. Environmental Impact Assessment (EIA) (Project oriented); 4. Environmental Profiles (beginning efforts at incorporating environmental inputs into development planning); 5. Regional Environmental Development Planning; and 6. Regional Economic-cum-Environmental Planning].
[*Source* : Environment Unit, Asian Development Bank].

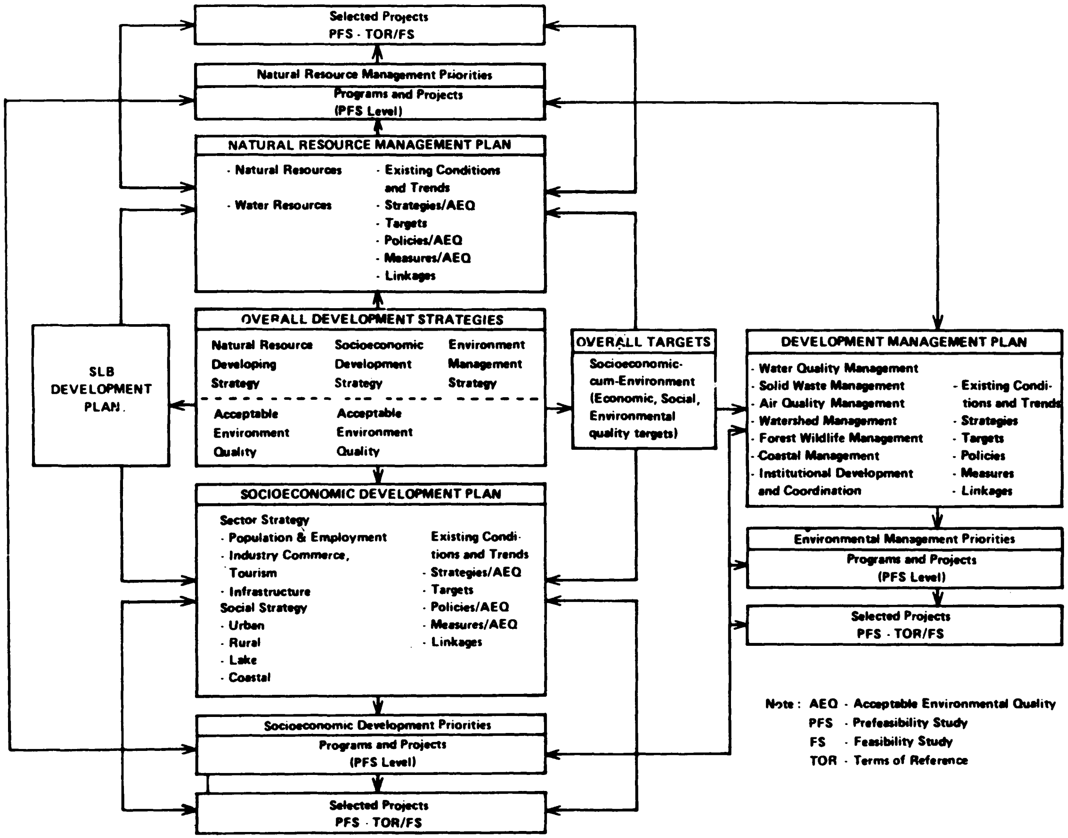

Fig. 3. Integrated Economic-cum-Environmental Development plan for Songkhla Project
[*Source* : Environment Unit, Asian Development Bank].

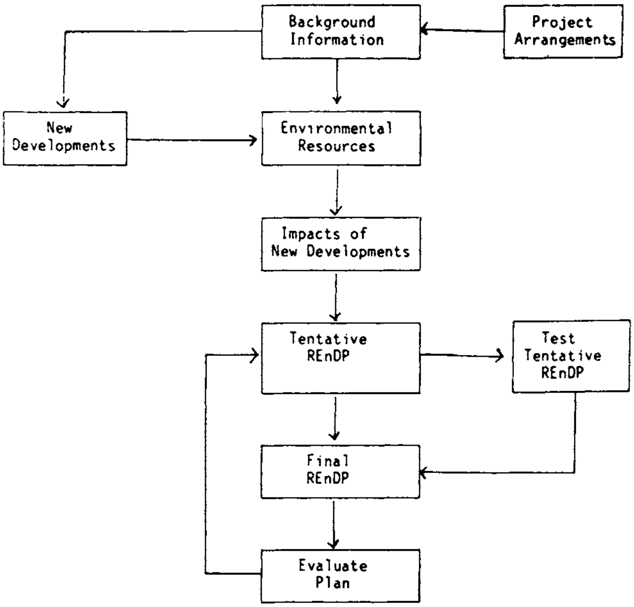

Fig. 4. Steps involved in regional environmental development planning process [*Source* : Environment Unit, Asian Development Bank].

The evolution of regional environmental development planning in Asia has been gradual with several different approaches being tried. The chronological sequence of some of the most significant projects is as follows (Asian Development Bank, 1988):

(1) Philippines — *Laguna Lake Basin* : Basin wide water quality management plan (1978).

(2) Philippines — *Palawan Integrated Area Development* : Regional environmental development plan for the Island of Palawan (1983).

(3) South Korea — *Han River Basin* : Regional environmental development plan (1984).

(4) Thailand — *Songkhla Lake Basin Planning Study* : Economic-cum-environmental planning (1985).

(5) Thailand — *Eastern Seaboard Planning Study* : Comprehensive regional environmental development plan (1986).

(6) Indonesia — *Segara Anakan* : Regional environmental development plan (1986).

(7) Malaysia — *Klang Valley* : Regional environmental development planning (1987).

(8) Thailand — *Samutprakarn Project* : Regional environmental development planning (1987).

Regional Co-operation

The task of environmental management is so vast and complex that in order to accomplish it, it must be shared. The environmental problems are all-encompassing and transcend national boundaries. In this respect, regional co-operation in the Asia-Pacific region has been very pronounced in the broad field of environmental protection and management since the early seventies through regional seminars and meetings to foster inter-state collective measures for tackling environmental problems in the region. An Asian Plan of Action for the Human Environment was adopted in Bangkok in 1973.

Effective implementation of this broad regional Action Plan was hampered by the marked diversity of country and sub-regional situations in the region and this had led to the adoption in recent past of sub-regional environment action programmes. Todate the following sub-regional programmes have been established:

- ASEAN Environment Programme (ASEP) established in 1978 and comprising Brunei Darussalam, Indonesia, Malaysia, the Philippines, Singapore and Thailand;
- South Pacific Regional Environmental Programme (SPREP) established in 1980 encompassing 22 countries and dependent territories, containing nearly five million people of three main ethenic groups—Melanesian, Polynesian and Micronesian—who are scattered over some 30 million square kilometers, of which less than two percent is land;
- South Asia Co-operative Environment Programme (SACEP) established in 1981 and involving Afghanistan, Bangladesh, Bhutan, Burma, India, Iran, Maldives, Nepal, Pakistan and Sri Lanka; and

The priority areas identified for action under the three sub-regional programmes share broad characteristics and objectives while being adapted to respective sub-regional situations. Technical co-operation stimulated by these sub-regional programmes has enabled the countries to learn from each other in their common endeavour to promote environmentally sound development in the region.

ASEAN Environment programme (ASEP)

ASEAN, in all modesty, can be numbered among the success stories in regional co-operation in the field of environmental management. The past eleven years have reconfirmed the exemplary spirit of co-operation among ASEAN Countries on environment. During this period ASEAN has completed two phases of intensive environmental programme and embarked on its third phase in 1988.

The ASEAN Ministers on the environment met in Bangkok for the second time in November 1984 and reiterated their commitment to the protection of the ASEAN environment and the safeguarding of its natural resources in order to make them available for sustained economic development. The Ministers declared (Bangkok

Declaration on the ASEAN Environment, 1984) the need to strengthen and enhance the regional co-operation in the field of environmental protection to meet the increasing and challenging environmental problems of the ASEAN Region in the decade ahead. In this respect, they redefined the Development Strategy of the ASEAN countries to include an integrated approach entailing advance or forward planning in the environmentally related activities with a view to incorporating the environmental dimension into development planning right at the base level in order to achieve sustainable development and long-term conservation of the assets and at the same time improving the quality of life for all.

In order to achieve the above objectives the Ministers have issued definite policy guidelines for application throughout the ASEAN region. The basic elements of the policy guidelines can be summarised as follows:

(i) Foster the development of macro economic-cum-environmental development plans which can be accommodated by the environmental carrying capacity of the region;

(ii) Continue and strengthen the use of EIA process for individual projects, both government and private sector, that are likely to produce significant environmental impacts;

(iii) Establish environmental units in the planning divisions of major project implementing agencies to ensure that environmental consciousness permeates planners and decision-makers so that development policy and planning in all sectors reflect systematic consideration of the environment;

(iv) Evolve criteria for augmentation of renewable resources and economical use of non-renewable resources;

(v) Prepare an optimal land-use pattern and zoning plan;

(vi) Develop new and practicable approaches for preserving forests, wild life and other ecological systems in the face of continuing population pressure;

(vii) Adopt practicable methods for ensuring reasonable technology for waste management and wherever practicable adopt low-waste and non-waste technology and more effective re-use and recycling of wastes in production;

(viii) Develop a Toxic and Hazardous Waste Control Programme and stimulate efforts by government agencies and industry to develop suitable systems for control;

(ix) Increase efforts to provide water-borne sewerage systems with central sewage treatment facilities at least for the major towns;

(x) Provide environmental training of personnel involved in decision-making on projects, programmes, policies and plans with emphasis on cause and effect relationship that exist between an individual's environment and his health;

(xi) Develop a comprehensive environmental information system to facilitate decision-making; and

(xii) Promote government-industry co-operation.

The enunciation of policy guidelines in environmental management for the first time by the Ministers in charge of the environment at this meeting is a step in the right direction and this has certainly made the ASEAN Environmental Programme more meaningful and effective.

South Pacific Regional Environmental Programme (SPREP)

The Action Plan for the SPREP is intended to provide a framework for environmentally-sound planning and management suited to the needs and conditions of the countries and people from the region, and to enhance their own environmental capabilities. The principal objective of the Action Plan is to help the countries of the South Pacific to maintain and improve their shared environment and to enhance their capacity to provide a present and future resource base to support the needs and maintain the quality of life of the people.

The more specific objectives of the plan are:

(i) Assessment of the state of the environment in the region including the impacts of man's activities on land, fresh water, lagoons, reefs and the ocean; the effects of these on the quality of man's environment, and the human conditions which have led to these impacts;

(ii) The development of management methods suited to the environment of the region which will maintain or enhance environmental quality while utilising resources on a sustainable basis;

(iii) The improvement of national legislation and the development of regional agreements to provide for responsible and effective management of the environment; and

(iv) The strengthening of national and regional capabilities, institutional arrangements and financial support which will enable the Action Plan to be put into effect efficiently and economically.

The Action Plan has identified some sixty areas of environmental assessment, management and legislation for SPREP to initiate activities. All components for the Action Plan are interdependent and together provide a framework for comprehensive action which should contribute to both the protection and continued development of the region.

The implementation of the Action Plan and its co-ordination is in the hands of four organisations: The South Pacific Commission (SPC), the Economic and Social Commission for Asia and the Pacific (ESCAP), and the United Nations Environment Programme (UNEP), with SPC hosting the SPREP Secretariat.

South Asia Co-operative Environment Programme (SACEP)

The big change in South Asia's protection of the shared environment is the greater co-operation among the South Asian neighbours, culminating in the establishment of the South Asia Co-operative Environment Programme. Without losing sight of the benefits of technology and third party assistance, the SACEP countries have placed priority on co-operative schemes to tackle the myriad of environmental problems that have arisen in the region.

SACEP will aim to bring about better management of the environment in the region, particularly through eliminating the wasteful use of natural resources. Some of the main functions of the programme are to promote co-operative activities to solve major environmental problems of economic development, to facilitate the exchange of information and expertise among countries on environmental issues, to use local resources for implementing projects, and to encourage support from interested donor countries and other sources.

Three principal bodies share the responsibility for SACEP's programmes. They are the governing council—the policy-making and review body comprising ministerial-rank representatives from all SACEP countries; the Consultative Committee in charge of facilitating the programmes and policies formulated by the Council through close informal co-operation, and the dissemination of SACEP information; and the Secretariat which assists the Council, the Committee and individual countries in carrying out their respective environmental responsibilities.

While extreme poverty has made the environmental problems of South Asia diffused and often indefinable, environmental impact assessment and cost benefit analysis, the protection of the regional seas, resource management, environmental education and training, environmental legislation and energy have been identified as the priority areas in environmental management.

CONCLUSIONS

The assaults on the environment of the Asia-Pacific region are both many and varied in nature, arising from the countrys' rapidly developing economy. In response, measures have been taken, within the constraints of competing policy priorities and claims on resources to protect and enhance the quality of the environment within manageable proportion on a scale of priorities.

Although much has been achieved, the task is far from being complete. It is regionally recognised that the environmental issues will become more complex, in the decade ahead, and require more competent environmental management. In this regard, the Asia-Pacific region is poised to adopt a preventive approach to environmental protection. For this purpose, it is apparent that incorporation of environmental dimension into the development planning process is emerging as the effective environmental management strategy for the region together with enhanced regional co-operation to manage shared environmental issues.

In addition, the countries of the region have begun to realise that environmental management, far from being a handicap, can actually contribute to the success of resource development programmes. In fact, it has become evident that the environmental protection approach is a resource management concept while economic development is generally pursued as a resource use concept, and that the whole objective of integrating environmental planning with development is to absorb the resource management ideas into the process of planning for resource use.

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THE INTERNATIONAL GLOBAL ATMOSPHERIC CHEMISTRY PROGRAMME

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The International Global Atmospheric Chemistry (IGAC) Program is a core project of the International Geosphere Biosphere Program (IGBP) and seeks to understand quantitatively the chemical and physical processes that determine atmospheric composition. IGAC provides a response to the growing international concern about rapid atmospheric changes and their potential impact to mankind.

The IGAC plan has adopted six major foci. These are:

(i) Natural variability and anthropogenic perturbations of the marine atmosphere;

(ii) Natural variability and anthropogenic perturbations of tropical atmospheric chemistry;

(iii) The role of polar regions in changing atmospheric composition;

(iv) The role of Boreal regions in changing atmospheric composition;

(v) Global distributions, transformations, trends and modelling; and

(vi) International support activities.

An outline of the major regional foci are given. For each region, the research is shaped by the characteristics of these parts of the globe and their susceptibility to change. These six IGAC foci are intended, collectively, to address areas of greatest current uncertainty and/or perceived importance.

INTRODUCTION

The global atmosphere is chemically complex and evolving; it possesses fundamental chemical connections to the oceans, the solid Earth, and most importantly to the biota. The atmospheric concentrations of several trace gases are observed to be increasing over the globe at rates that are leading to important changes in both the chemical and radiative properties of the global atmosphere. The challenge and responsibility that faces us today is to understand quantitatively the chemical, physical, and biological processes that determine atmospheric composition and to use this knowledge to address the past and future evolution of the Earth's atmosphere.

The International Global Atmospheric Chemistry (IGAC) Programme has been created, under the auspices of the Commission on Atmospheric Chemistry and Global Pollution (CACGP) of the International Association of Meteorology and Atmospheric Physics (IAMAP), in response to the growing international concern about these rapid atmospheric chemical changes and their potential impact on mankind. This programme, while emphasising atmospheric composition and chemistry, recognizes that the Earth's atmosphere, oceans, land, and biota form an interacting system that collectively determine the global environment and its susceptibility to change. The International Geosphere Biosphere Programme (IGBP) is a broad-ranging interdisciplinary international undertaking that addresses all major aspects of this latter interactive system. The IGAC Programme is a Core Project of the broader interdisciplinary programme of IGBP, providing the important atmospheric chemistry component and recognizing its linkages with the biosphere and human activities.

The overall goal of IGAC is to measure, understand, and thereby predict changes now and over the next century in the chemistry of the global atmosphere with particular emphasis on changes affecting the oxidising power of the atmosphere, the impact of atmospheric composition on climate, and the interactions of atmospheric chemistry with the biota. This goal is broad and encompasses several urgent environmental issues including the increasing acidity of rainfall, the depletion of stratospheric ozone, the greenhouse warming due to accumulation of trace gases, and the biological damage from increased oxidant levels.

In many cases the IGAC Programme will build on existing national programmes. It is not intended to replace these programmes but to provide the international cooperation whereby essential scientific endeavours can be accomplished that involve large demands for man-power, technology, geographic coverage, or monetary resources beyond the capability of any single nation.

The IGAC plan, which is described in this paper, has adopted six major foci. Each of these foci addresses important problems in global atmospheric chemistry whose solution requires international cooperation.These foci are intended collectively to address areas of greatest current uncertainty and/or perceived importance. They are not intended to be exclusive and we expect further foci will be added as time proceeds.

The implementation of the IGAC Programme will be guided by the IGAC Steering Committee (contact names and addresses are provided in the Appendix). Each of the IGAC projects will have a Scientific Coordination Committee responsible for planning and conduct of the project. The urgency of the issues addressed by IGAC suggests an immediate start on each of these projects. For some projects this start will involve development of detailed plans for action while for others that are in a greater stage of readiness the work will commence immediately.

Funding of work within the IGAC projects will largely come from individual national programmes although mechanisms for funding activities in nations without significant available resources will be sought.

GLOBAL ATMOSPHERIC CHANGE AND THE GOALS OF IGAC

The Earth's atmosphere is a vital natural resource that until recently appeared unaffected by human activities, except on local scales. However, during the past decades, it has become abundantly clear that the worldwide strongly growing anthropogenic activities have impacts on the atmosphere over large areas of the continents, and even globally. Through industrial and agricultural activities, humans are moving millions of tons of chemicals into the atmosphere, where they are chemically processed and from where the products of reactions are transferred back to the Earth's surface. The rates of these transfers are now so large, and the products of the chemical reactions so hazardous, that the atmosphere, vegetation, land and oceans can no longer cope with the assault.

Worldwide, the amounts of numerous key chemicals are increasing above their natural background levels in the atmosphere: of special importance are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). Simultaneously, synthetic chemicals like chlorofluorocarbons (CFCs) are building up and causing a man-made loss in the stratospheric ozone layer; the concentration of ozone in the stratosphere is now decreasing. Moreover, the sizes of these changes are not small. Convincing data from the gases trapped in polar ice cores tell us that the present CO_2, CH_4, and N_2O concentrations are unprecedented, at least for the Earth of the last 160,000 years, see Figure 1. Continued increasing trends are elevating these concentrations to ever more uncharted territories. Simultaneously, there are demonstrable human-caused disturbances to the global cycles of essential nutrient elements like carbon, nitrogen and sulfur.

There are even sharper changes occurring on less than worldwide scales but still in large regions. Air pollutants such as ozone and sulfur and nitrogen oxides from combustion of coal and oil are afflicting many regions, with losses of air quality, photochemical smog formation, acid rain, damage to crops and other plants, and detrimental impacts on soils, forests and lakes.

Scientists have learned remarkable things about the roles of chemicals in the atmosphere and how our climate and the ozone layer are controlled. Chemicals present in minute amounts are now known to have important influences far beyond what their small amounts in the air would suggest. Trace gases like CO_2, CH_4, N_2O, O_3 and the CFCs are very effective greenhouse gases that alter the energy balance of our planet and hence its climate. Similarly, extremely small amounts of chemicals can destroy the stratospheric ozone layer and that protects us from the Sun's ultraviolet radiation.

The kinds of atmospheric changes that are happening now and the speed of those changes demand attention. It is essential that we accelerate research in the science of the environment. We now recognize that interdisciplinary approaches to the problems are essential. Collaboration between such diverse specialists as plant physiologists, marine chemists, microbiologists, cloud physicists, boundary layer dynamicists, meteorologists, oceanographers and photochemists are required to understand adequately both the vital interactions among the Earth's component systems

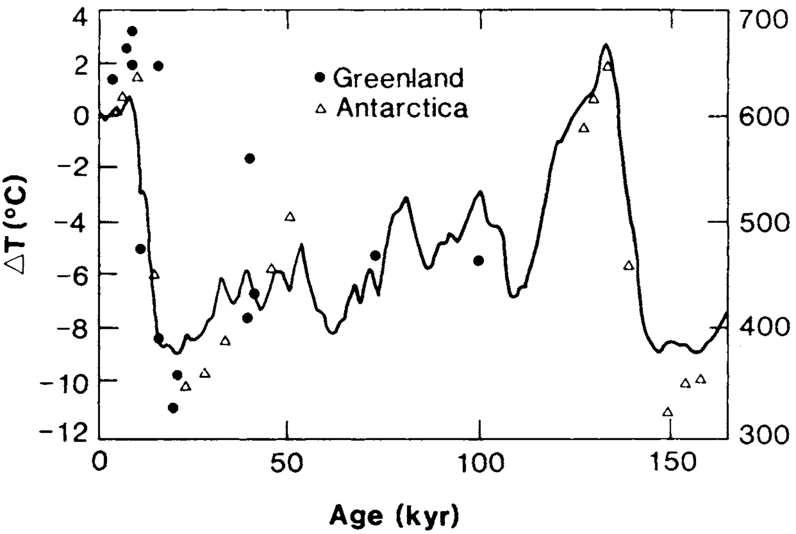

Fig. 1. Methane concentrations (ppb by volume) from ice cores plotted as age of air before present. Solid circles are data from Greenland ice cores, and triangles represent data from Antarctic ice cores. The solid line is the isotope based temperature. The data show that methane increased from about 320 ppb to 620 ppb between the end of the next to last glaciation and the subsequent interglacial period, about 160,000 to 120,000 years ago. These changes suggest that exposing and warming ice-covered soils produced more methane as glaciers retreated. The data also show that contemporary methane levels and their rate of increase are unprecedented, at least during the last 160,000 years. (Reprinted from R.J. Cicerone and R.S. Oremland, Biogeochemical Aspects of Atmospheric Methane, Global Biogeochemical Cycles, Vol 2, p 301, 1988).

and the complex processes taking place in the atmosphere itself. A basic scientific goal for this research is to observe and quantify the changes that are under way now. Another basic goal is to develop enough understanding, as quickly as possible, to permit predictions to be made so that environmental damage can be restricted, avoided, or reversed in the future. With such predictive capability in hand, sensible management of resources and the environment can be undertaken to maintain a habitable planet for a growing human population.

National programmes addressing global atmospheric chemistry now exist in several countries. However, the scope and nature of the needed research dictates that international collaborative efforts be developed urgently; no one nation or group alone possesses or can develop the scientific expertise, advanced instrumentation, remote sensing capabilities and platforms for all of the measurements that are required.

The International Global Atmospheric Chemistry (IGAC) Programme has been formed in response to growing concern in many countries about these observed and predicted chemical changes in the global atmosphere and their potential impacts on humanity. Atmospheric chemistry in addition plays a very important role in a larger interactive global system comprised of the atmosphere, oceans, land and biota that determines the global environment and its susceptibility to change. The IGAC Programme is therefore intended to be a vital contributor to the International Geosphere Biosphere Programme (IGBP) of the International Council of Scientific Unions (ICSU), that addresses this overall global system.

The present study will focus on plans for scientific study of the chemistry of the troposphere. There is a vital existing base of research in the stratosphere that has been coordinated under the Middle Atmosphere Programme (MAP). Plans for new research in upper atmospheric chemistry are presently being formulated as part of the Middle Atmosphere Responses to Changes (MARC) programme jointly sponsored by the International Association of Meteorology and Atmospheric Physics (IAMAP) and the International Association of Aeronomy and Geomagnetism (IAAG). We emphasise that the division of atmospheric chemistry into tropospheric and upper atmospheric components is an artificial one and the IGAC Steering Committee intends to cooperate with, and review the development of the MARC programmes to ensure that vital investigations involving chemical and dynamical interactions between the upper and lower atmosphere receive appropriate attention. The IGAC goals pertain to the entire atmosphere and an objective of the IGAC Steering Committee is to develop an integrated plan comprising the present document and the relevant MARC plans augmented and/or modified where necessary.

IGAC goals

The goals of the International Global Atmospheric Chemistry Programme are:

(i) To develop a fundamental understanding of the chemical processes that determine the chemical composition of the atmosphere;

(ii) To understand the interactions between atmospheric chemical composition and biological and climatic processes;

(iii) To predict the impact of natural and anthropogenic forcings on the chemical composition of the atmosphere; and

(iv) To provide the necessary knowledge for the proper maintenance of the biosphere and climate.

These goals address our understanding of several anthropogenic pressures leading to ubiquitous stresses on the biosphere, such as:

(i) Increasing acidification of precipitation, see Figure 2;

(ii) Increasing oxidant concentration in surface air;

(iii) Warming due to increases in the concentrations of trace gases involved in the greenhouse effect; and

(iv) Alteration of biospheric exchange fluxes due to land use and climatic changes.

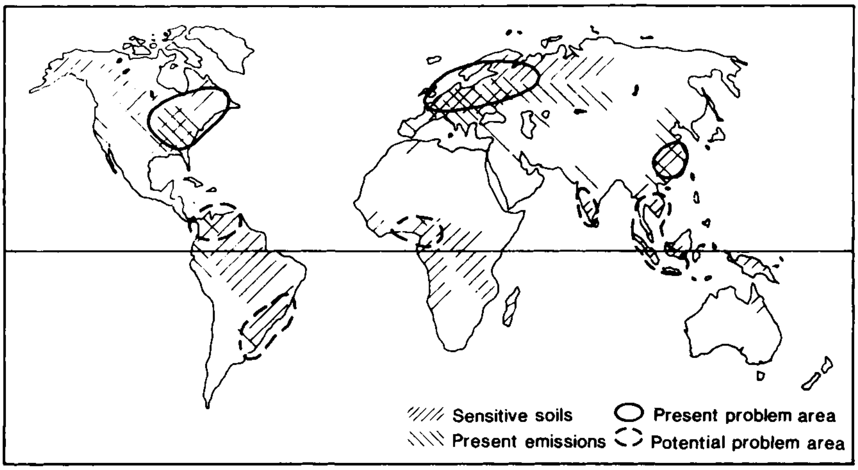

Fig. 2. Rough estimates of (a) the sesitivity of soils to surface water acidification due to acid deposition; and (b) present emission of acidifying compounds from human activities. Areas circled by solid lines represent a combination of a and b and are thus problem areas today. Areas encircled by dashed lines represent a combination of sensitive soils and regions with projected rapid increases in emissions due to increasing industrialisation and population growth. Such areas are potential future problem areas of acid deposition. (Reprinted with permission from Rodhe *et al.*, 1988, Acidification and regional air pollution in the tropics. In "Acidification in Tropical Countries", eds H.Rodhe and R.Herrera. SCOPE 36, John Wiley and Sons Ltd.).

To achieve these goals a programme of fundamental research is needed to measure and understand:

(i) Global distributions and trends;

(ii) Surface exchange processes;

(iii) Gas-phase chemical reactions; and

(iv) Multiphase processes.

To aid understanding and to predict future changes we need to formulate regional and global models for simulating the tropospheric chemical system and its interaction with marine and terrestrial ecosystems.

IGAC foci

The varying soil, water, vegetation, fauna and climate of different regions over the globe cause marked differences in trace gas emission rates, trace gas composition, photochemical activity and chemical removal rates over the Earth. Because of this and for logistical reasons, we have found it convenient to focus the research activities in IGAC on a number of specific regions, that are of special importance in atmospheric chemistry. For each region, the research is shaped by the characteristics of these parts of the globe and their susceptibility to change. The major regional foci are:

1. Natural Variability and Anthropogenic Perturbations of the Marine Atmosphere

The oceans cover about 70% of the planet and act as both a source and sink of many important atmospheric constituents. In the marine atmosphere chemical species of continental origin are processed without disturbances of new anthropogenic inputs. The marine atmosphere is, therefore, also a favourable area to study transformation processes in detail. The complexity of the marine atmospheric cycle of one species, sulfur, is shown in Figure 3. Three IGAC projects are proposed to address this environment and perturbations to it due to continental emissions:

(i) North Atlantic Regional Study;
(ii) Marine Gas Emissions, Atmospheric Chemistry and Climate; and
(iii) East Asian—North Pacific Regional Study.

2. Natural Variability and Anthropogenic Perturbations of Tropical Atmospheric Chemistry

Tropical continental areas play an important role in the chemistry of the global atmosphere and its oxidising power. Large emissions of gases and particles are associated with rain forest and savanna regions and many tropical areas are experiencing rapid land use change. Four IGAC projects are proposed to address the tropics and their changes due to human activities:

(i) Biosphere-Atmosphere Trace Gas Exchange in the Tropics;
(ii) Deposition of Biogeochemically Important Trace Species;
(iii) Impact of Tropical Biomass Burning on the World Atmosphere; and
(iv) Chemical Transformations in Tropical Atmospheres and their Interaction with the Biosphere.

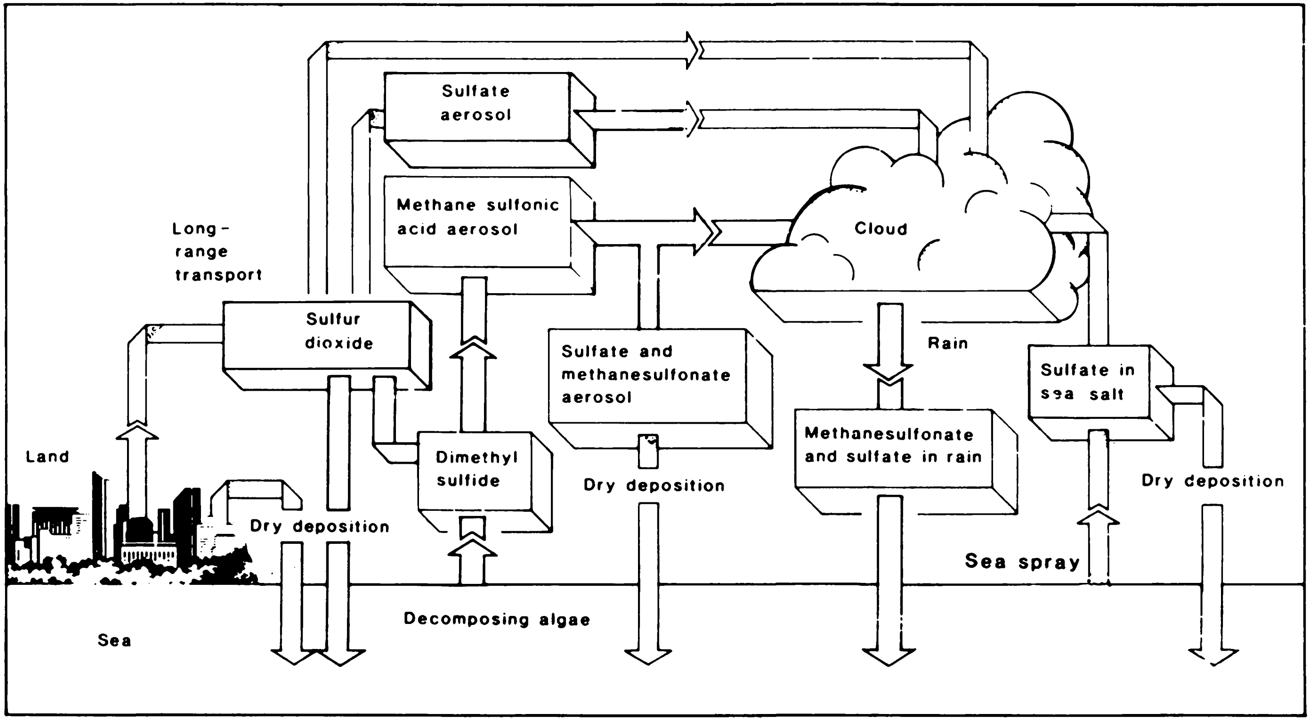

Fig. 3. The atmospheric sulfur cycle over the Southern Ocean. A major pathway (shaded) links cloud formation with algae in the sea. Decomposing algae produce dimethyl sulfide gas, which after emission to the atmosphere, turns into particles of methane sulfonic acid and sulfuric acid. These sulfur particles provide nucleii for cloud droplets to form around (Reprinted from CSIRO Division of Atmospheric Research Annual Report, 1983-1985).

3. *The Role of Polar Regions in Changing Atmospheric Composition*

The Arctic and Antarctic regions play important roles in atmospheric chemistry involving long-range transport of anthropogenic pollutants, exchange of trace gases between the atmosphere and snow/ice surfaces, atmospheric chemistry in a seasonal light/dark atmosphere and the concentration and storage of atmospheric constituents in ice, see Figure 4. These regions have a special sensitivity to anthropogenic emissions (e.g. ozone destruction by halocarbon decomposition products, albedo changes due to soot particles). The polar regions are especially important because the expected greenhouse warming of the Earth is most pronounced at high latitudes during the winter half year. Two IGAC projects are proposed for these regions:

(i) Polar Atmospheric Chemistry; and

(ii) Polar Air-Snow Experiments.

4. *The Role of Boreal Regions in Changing Atmospheric Composition*

An understanding of the cycling of trace gases between the asmosphere and ecosystems in the boreal region is of special importance for assessing the impact of a coming climate change on these cycles and how fluxes from this region alter climate (e.g. through positive feedback mechanisms). This arises because these regions both contain major carbon reservoirs that may be very sensitive to the effects of future climate change, see Figure 5, and are predicted to experience very large effects of a change in the climate. One IGAC project is proposed for these boreal and subantarctic regions:

(i) Northern Wetlands Study.

5. *Global Distributions, Transformations, Trends and Modelling*

The differences in the composition of the atmosphere over the globe and the short- and long-term variations in this composition reflect the net effect of all the relevant atmosphere processes: emissions, circulation, transformation and removal. The global distributions and trends of chemically and radiatively important species are signatures not only of atmospheric changes but also of the fundamental processes underlying them see Figure 6. The IGAC Programme has four projects addressing this important globally integrating research area, involving a ground-based network, aircraft-based surveys, experimental studies, and relevant theory and modelling:

(i) Global Tropospheric Ozone Network;

(ii) Global Atmospheric Chemical Survey;

(iii) The Chemical and Physical Evolution of Cloud Condensation Nucleii as Controllers of Cloud Properties; and

(iv) Development of Global Emission Inventories.

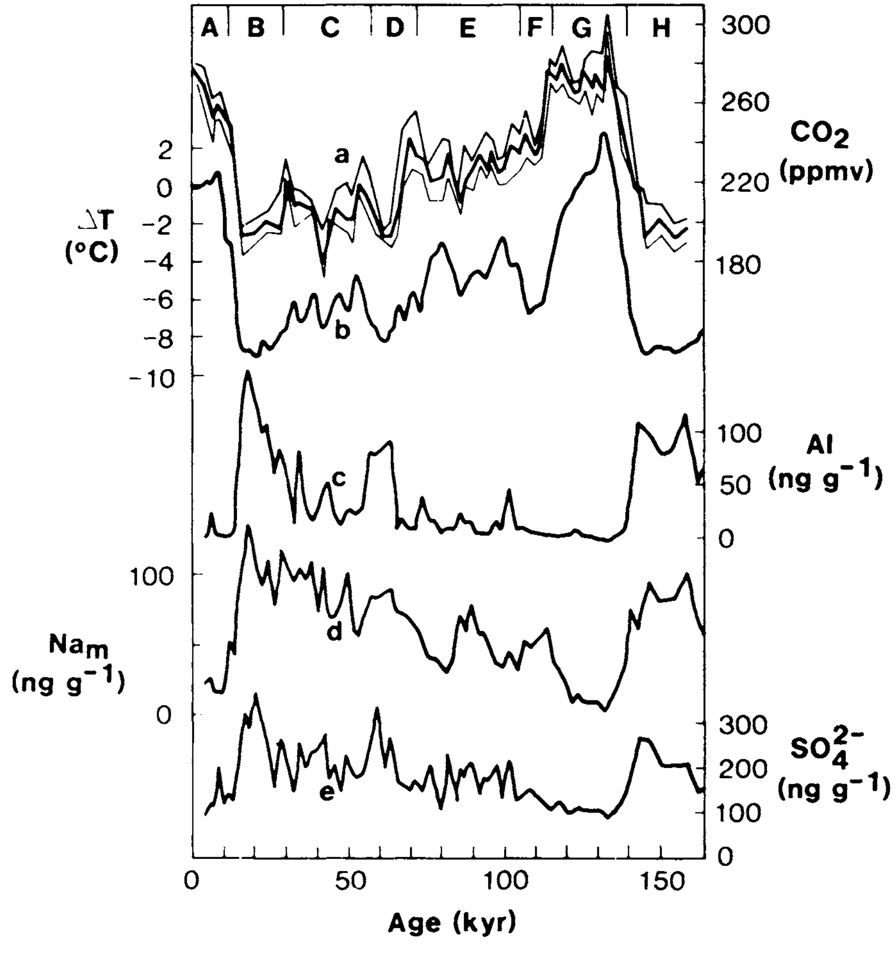

Fig. 4. Vostok ice core records; (a) CO_2 concentrations (ppmv) with envelope of uncertainty; (b) Smoothed Vostok isotope temperature record; (c) Aluminium content; (d) Marine sodium content; and (e) Sulfate content. The Vostok records show a large variation on an 100,000 year timescale with changes of isotope-based temperature and CO_2 of the order of 10°C and 70 ppmv respectively. Ice deposited during the coldest times is characterised by high concentrations of marine and terrestrial aerosols; these peaks likely reflect strengthened sources and meridional transport during full glacial conditions. There is no indication of long term relationship between volcanism, as indicated by sulfate, and climate. (Reprinted with permission from Lorius *et al.*, 1988, Long-term climatic and environmental records from antarctic ice, in "Contribution of Geophysics to Climate Change Studies", eds. A. Berger and R. R. Dickinson, Geophysical Monograph, AGU, Washington DC. USA).

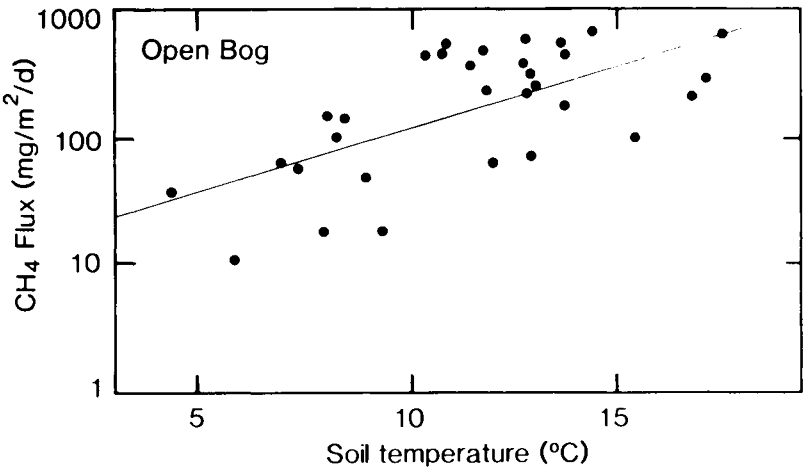

Fig. 5. Effect of soil temperature on methane emissions to the atmosphere from an open bog in the Marcell Experimental Forest, Minnesota (Reprinted from R.C. Harris, 1989, Historical Trends in Atmospheric Methane Concentration and the Temperature Sensitivity of Outgasing from Boreal and Polar Regions, in "Ozone Depletion, Greenhouse Gases and Climate Change", National Academy Press, Washington DC, USA).

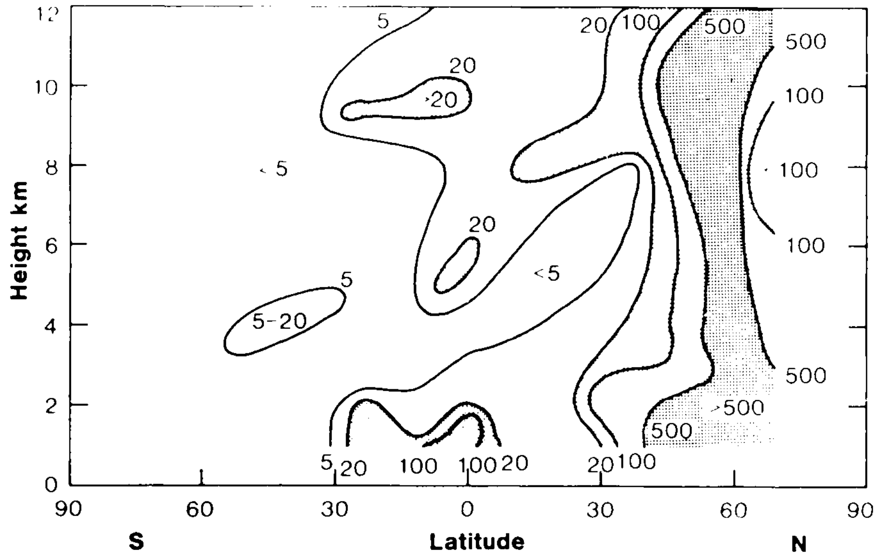

Fig. 6. Two dimensional distribution of isopentane concentration measured during the southward arm of the STRATOZ III flight from Sondestrom, Greenland to Punta Arenas, Chile. Such global distributions of key species are needed to define the oxidation capacity of the atmosphere (Reprinted with permission from D.H.Ehhalt and J.Rudolph (1987). Die globale Verteilung von Stickoxid und Kohlenwasserstoffen in der Troposphare. Jahresbericht 1986/87 der Kernforschungsanlage Julich GmbH).

6. *International Support Activities*

Scientific programmes of the scope of IGAC require, for their success, an essential support infrastructure. Three international supporting activities are proposed for IGAC:

(i) Education in Atmospheric Chemistry and Global Change;

(ii) Communication (IGAC Newsletter); and

(iii) Intercalibrations and Intercomparisons.

These six IGAC foci are intended collectively to address areas of greatest current uncertainty and/or perceived importance. They are not intended to be exclusive and we anticipate further foci will be added as time proceeds. For each of the above foci specific scientific goals and one or more specific scientific projects that address these goals, have been identified. These projects, that are defined in the following chapters, may consist of several phases and have been categorised according to their state of readiness.

Proposed scientific investigations relevant to these foci will in many cases build on existing national programmes. IGAC is not intended to replace these programmes but to provide the strategy whereby essential scientific endeavours can be accomplished that involve large demands for manpower, technology, geographic coverage, or monetary resources beyond the capability of any single nation.

The specific research activities proposed in IGAC have important common elements that must be emphasised. First, theory and modelling are an integral part of each of the IGAC foci. A whole heirarchy of models are required for the successful pursuit of the IGAC projects. Theory and modelling are important in the planning phases to identify the species to be measured and the locations, spatial resolutions and frequency of these measurements. Techniques for chemical data synthesis and analysis using diagnostic models and inverse methods need further development in order to deduce more accurate quantitative information on emissions, transformations and loss rates from global data sets. Valid theories and improved models are needed in the areas of surface exchange, stratosphere-troposphere exchange, gas-phase chemical and photochemical mechanisms, cloud and precipitation chemistry, hydrometeor-gas-aerosol interactions and aerosol physics.

A major challenge in this area is the development of global chemical transport models (GCTMs). This task, that requires accurate models of atmospheric dynamics, will require cooperation between the World Climate Research Programme (WCRP) and IGAC. This cooperation should be fruitful for both programmes. Specifically, while IGAC chemical modelling will be dependent on progress in general circulation modelling in WCRP, we also expect atmospheric tracers measured in IGAC to provide an important test of the predicted circulations in these models.

A second common element in many IGAC scientific investigations involves the laboratory determinations of fundamental molecular properties including absorption cross-sections, rate constants and homogeneous and heterogeneous reaction mechanisms. Such studies form the underpinning for instrumental design, data interpretation and development of new chemical theories.

A third common element involves new instrument development. Major challenges are provided by the need to accurately measure highly reactive free radicals (OH etc.), a wide variety of inorganic and organic compounds at concentrations sometimes as low as 1 part in 10^{12} in air, and key aerosol properties. Both in situ and remote sensing techniques are needed in IGAC to provide both local and global measurements of these key atmospheric constituents.

STRUCTURES OF IGAC, MODE OF OPERATION AND RELATIONSHIP TO IGBP AND OTHER INTERNATIONAL SCIENTIFIC ORGANISATIONS

The International Global Atmospheric Chemistry (IGAC) Programme has been created during 1983-87 in response to the growing concern over the rapid changes observed in the Earth's atmosphere during the past decade, and from their obvious potential for impact on human activities. The IGAC Programme has been developed and is directed by the Commission on Atmospheric Chemistry and Global Pollution (CACGP), an international commission of the International Association of Meteorology and Atmospheric Physics (IAMAP), an association of the International Council of Scientific Unions (ICSU). The CACGP has been in existence for several decades, including some years under a different name, and was originally formed because of general scientific concern about problems relating to atmospheric chemistry, including the emission, transport and final fate of various chemical species added to the atmosphere by the activities of man.

Representation in CACGP has always been intended to be global in coverage, and now includes members from all areas of the world with active programs in atmospheric chemistry. The current members of CACGP are listed in the Appendix.

The overall plan for IGAC is to develop research programmes of broad regional or global extent in that the most advantageous approaches require the participation of personnel and equipment from many countries. Initial projects for IGAC have been defined during the Dookie (Australia) Conference in November, 1988, and an IGAC Steering Committee has been appointed to furnish oversight for these. In the coming years, it will be the responsibility of the IGAC Steering Committee and the individual scientific project coordinating committees to develop detailed project proposals at scientific workshops. These Committees will also carry the responsibility for finding ways to implement and carry out the projects. Neither IGAC nor CACGP has direct funding capability or responsibility for the proposed activities, but rather they serve as initiators and coordinators of the programs. Participation in IGAC is open to all interested scientists, and is strongly encouraged, because the extent and complexity of the problems under consideration require the participation of scientists with wide varieties of experience and skills.

The major problems in atmospheric chemistry usually have important components, e.g. biological, that lie outside the traditional, albeit somewhat vague, boundaries of chemistry and meteorology. Effective research requires coordination and interaction with other parts of the scientific community and partnership with commissions in other branches of ICSU. The major importance of many environmental problems, as recognised in the 1980s, has caused the formation of a special interdisciplinary programme, the International Geosphere Biosphere Programme (IGBP). IGAC has a special relationship with IGBP.

A BRIEF OUTLINE OF THE IGBP AND ITS SPECIAL RELATIONSHIP WITH IGAC

IGBP Objectives

To describe and understand the interactive physical, chemical and biological processes that regulate the Total Earth System, the unique environment that it provides for life, the changes that are occurring in this system, and the manner in which they are influenced by human actions on timescales of decades to centuries.

Goal

With improved understanding of the system, the primary goal of the programme is to advance our ability to predict change in the global environment. This capability will build upon the results of physical models of the Earth System by incorporating understanding of relevant biogeochemical processes.

Initial Objectives

To obtain the information that is necessary to understand more completely the cycling of key elements among the terrestrial and marine ecosystems and the atmosphere, taking into consideration the natural and anthropogenic factors affecting these cycles and the interactive effects of climate-induced feedback within and between biosphere, oceans and atmosphere.

The special committee (SC-IGBP), which directs IGBP, recognizes that many activities outside the direct coordination of the SC-IGBP are as essential to the overall "Global Change Programme" as the "core Global Change Projects" directly coordinated by the SC-IGBP. The CACGP of IAMAP has, therefore, been invited, and agreed, to accept the task to develop the IGAC Programme as an atmospheric chemistry core project of the overall "Global Change Programme".

Projects developed by the IGAC Programme, that contains substantial biological components, should be developed in close cooperation and coordination with the SC-IGBP to promote the effective involvement of the biological community. For this purpose, it will be necessary to establish especially close links between the CACGP/IGAC Committee and the IGBP Coordinating Panels on the Terrestrial Biosphere-Atmospheric Chemistry and Marine Biosphere-Atmosphere Interactions.

OTHER INTERNATIONAL SCIENTIFIC ORGANISATIONS

The International Union of Pure and Applied Chemistry (IUPAC) has a Commission on Atmospheric Chemistry within its Applied Chemistry Division. There is a designated person for liaison between the Commission and IGAC/CACGP.

The aim of the IUPAC Commission on Atmospheric Chemistry is "to identify problems related to the chemistry of the atmosphere and to advise and cooperate in international activities designed to address these problems. The commission is concerned with indoor/workplace air quality, urban and regional environment as well as the global atmosphere. Among other considerations it will be necessary to review and harmonise the sampling and analytical procedures for studying atmospheric chemistry."

IUPAC also has a Commission of Chemical Research Applied to World Needs, (CHEMRAWN). This commission has a current interest in the chemistry of the atmosphere and its impact on global change, and through the IUPAC Commission on Atmospheric Chemistry has contact with IGAC.

IGAC has established links with the WMO BAPMoN Programme and joint talks were conducted at the Dookie Workshop. Eight of the IGAC Projects involve scientists who also participate in BAPMoN activities. The collaboration of these two programmes should considerably enhance long term global atmospheric chemistry studies.

Plans for new research in upper atmospheric chemistry are presently being formulated as part of the Middle Atmosphere Responses to Changes (MARC) programme jointly sponsored by the International Association of Meteorology and Atmospheric Physics (IAMAP) and the International Association of Aeronomy and Geomagnetism (IAGA). The IGAC Steering Committee intends to cooperate with, and review the development of the MARC programmes to ensure that vital investigations involving chemical and dynamical interactions between the upper and lower atmosphere receive appropriate attention.

There is cooperation between the World Climate Research Programme (WCRP) and IGAC on the development of global chemical transport models (GCTMs). This cooperation should be fruitful for both programmes. Specifically, while IGAC chemical modelling will be dependent on progress in general circulation modelling in WCRP, we also expect atmospheric tracers measured in IGAC to provide an important test of the predicted circulations in these models.

The development and implementation of the IGAC tropospheric ozone project is closely coordinated with the World Meteorological Organization and the IAMAP International Ozone Commission who have traditional interests in this area. One illustration of the changing nature of tropospheric ozone is shown in Figure 7.

The development of remote sensing techniques for tropospheric composition in IGAC will be explored in coordination with the International Radiation Commission. Both the International Commission on Cloud Physics and the International Radiation Commission have parallel projects on aerosols and clouds in the International Aerosol Climatology Project, IACP, and the International Satellite

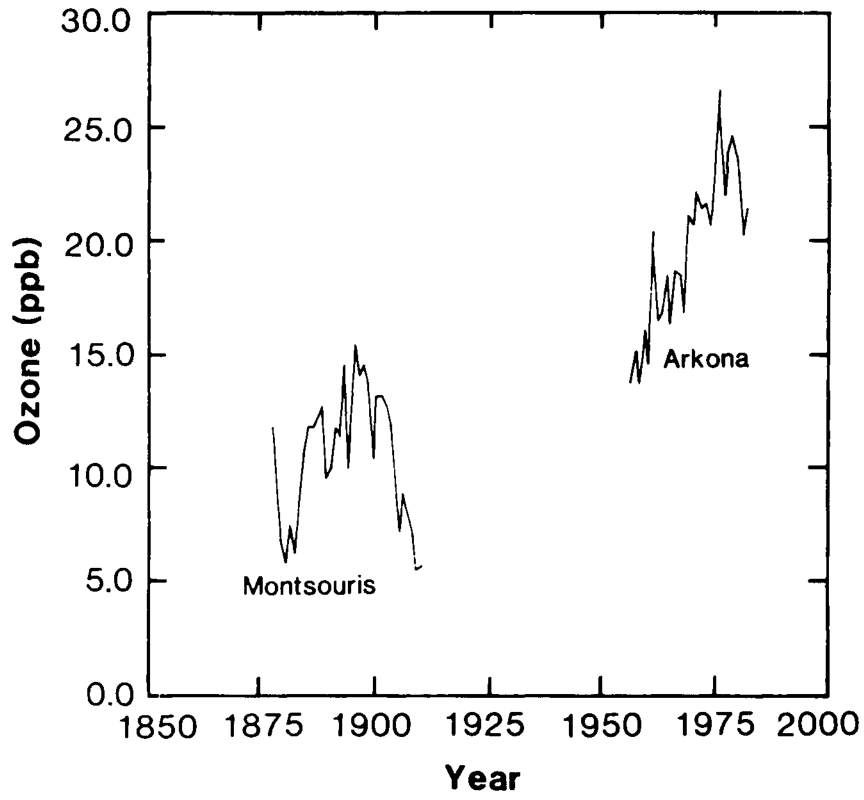

Fig. 7. Annual averages of ozone mixing ratio at Montsouris, near Paris (1876 - 1910) adjusted for SO_2 interference and at Arkona in the Baltic (1956-1983). Such unique reconstructions of past records, and comparisons of present records, are only possible with detailed documentation about experimental technique and comprehensive intercomparisons of measurement techniques (Reprinted with permission from A. Volz and D. Kley, 1988, Evaluation of the Montsouris series of ozone measurements made in the nineteenth century. *Nature*, Vol 332, p. 242).

Cloud Climatology Project, ISCCP, respectively. IGAC Projects are designed to interface with these and these Commissions are represented on the IGAC projects.

IGAC Marine studies will be conducted in cooperation with the JGOFS Programme of the Scientific Committee on Ocean Research (SCOR) and the Polar studies with Scientific Committee on Antarctic Research (SCAR).

THE HISTORY OF IGAC

The history of IGAC is one small part of the history of international programmes of research and monitoring of atmospheric composition.

The International Geophysical Year (IGY), 1957-1959, heralded the first global multiphase, multispecies study of atmospheric composition, with background measurements of CO_2, tropospheric O_3, aerosols, composition of precipitation, radionuclides and many other things. Background atmospheric observatories were set up in such remote clean air locations as Mauna Loa, Hawaii and at several places in Antarctica. Fortunately some of the work initiated as part of IGY was not stopped with the completion of IGY and so we have some long term records that are invaluable today, e.g. CO_2, antarctic total O_3.

A network for global total ozone measurements was initiated in the 1930s and received much impetus from IGY. This total ozone network continued to grow during the 1960s through the activities of WMO and the IAMAP International Ozone Commission, to the global ozone observing system (GO_3OS) today. During the 1970s the issue of man-made destruction of the ozone layer by nitrogen and chlorine compounds emerged. As well as the IAMAP and WMO activities, the Middle Atmosphere Programme (MAP), of SCOSTEP was an international scientific response to this problem. Now there exist the UN Convention for the Protection of the Ozone Layer and the 1986 Montreal Protocol on Substances that Deplete the Ozone Layer.

In the 1950s a European network for the Chemical Composition of Air and Precipitation was established. Data from this network provided the first view of regional air pollution problems. By 1970 the problems of trans-national pollution of sulfur and nitrogen oxides and acid rain were recognized and the precipitation chemistry network was supplemented by EUROTRAC and EMEP today.

The International Atomic Energy Agency (IAEA) in cooperation with the WMO has since 1961 conducted a worldwide survey of hydrogen and oxygen isotopes in precipitation, in order to provide data for hydrological applications of environmental isotopes. More recently the IAEA has provided data on the chemical composition of these precipitation samples to the station operators.

Around 1970 scientists in CSIRO and NOAA recognized the need for long term high quality multiconstituent monitoring of background atmospheric composition. This was given tremendous impetus with the intergovernmental Stockholm Conference on the Human Environment in 1972. The UNEP Global Environmental Monitoring System (GEMS) and the WMO Baseline Air Pollution Monitoring Network (BAPMoN) were initiated. Mauna Loa, Cape Grim, and similar observatories took up the challenge.

By 1980 it had become clear that the chemistry of the atmosphere was being perturbed over large regions, even globally. The acidity of precipitation, chlorine-catalysed destruction of stratospheric ozone, the continued increase in atmospheric carbon dioxide concentrations and the altered cycling of major nutrient elements were clear signs of global changes. Scientists from around the world recognised that the scope of human activities had become large enough that each of these perturbations could grow and that other unanticipated problems were quite likely. A particularly sobering realisation concerned the chemistry of the troposphere. This was that the presence of surfaces (oceans, clouds, plants, soils) and the interactions of the lower atmosphere with the global biota makes tropospheric chemistry even more complex than that of the stratosphere.

Concern over how to approach the complexities of atmospheric perturbations and the growing need for information that could lead to minimising future perturbations, led to a study by the US National Academy of Sciences. In 1984 their report "Global Tropospheric Chemistry: A Plan for Action" was published; it analysed the scope of the scientific issues and the likelihood of successful research. This report concluded that an major focussed research thrust was both necessary and feasible, and that an experimental framework for understanding the biogeochemical cycling of materials into and through the atmosphere was needed, due to evidence that the atmosphere, soils, oceans, plants and microbes comprise an interlocking system. An intellectually and physically broader approach, than had been applied to urban and regional pollution problems, was needed.

The US NAS/NRC Global Tropospheric Chemistry Report adopted three main goals: (i) to obtain quantitative understanding of the cycling of tropospheric chemicals globally, (ii) to develop a capability to predict future changes in atmospheric chemistry, and (iii) to use these capabilities to provide the information necessary for societal decisions to maintain a stable atmosphere. To achieve these goals would obviously require the best efforts of scientists from many individual nations and their combined efforts would be truly international.

The scientific community responded very positively to this first report and in 1985 and 1986 a broader research planning effort was conducted. This involved about 150 scientists (one third international) over a one year period and produced the 1987 report "Global Tropospheric Chemistry: Plans for the US Research Effort". The main goals of the 1984 NAS/NRC report were embraced and two sharper foci were advanced:

(i) Understanding the oxidising capacity of the atmosphere; and
(ii) The roles of atmospheric chemistry in influencing the Earth's climate.

Five main areas of research were proposed:

(i) Global distributions and trends;
(ii) Biological and surface exchange;
(iii) Gas-phase transformations;
(iv) Multi-phase processes; and
(v) Theoretical modelling and prediction.

These US planning activities both stimulated and were stimulated by international scientific activities occurring at the same time.

In the early 1980s the ICSU was developing the International Geosphere Biosphere Programme. Independently in 1983 the IAMAP Commission on Atmospheric Chemistry and Global Pollution (CACGP) began considering a coordinated research programme in atmospheric chemistry during its international symposium at Oxford, England. Following two years of discussions and evaluation of this idea by a small group of commission members, CACGP agreed at the IAMAP General Assembly in Honolulu in 1985 to pursue vigorously the idea of such a programme. A special commission meeting was convened in Stockholm in September, 1986 for the sole purpose of discussing such a programme in depth. At the end of the Stockholm meeting CACGP agreed to coordinate the development of the International Global Atmospheric Chemistry Programme.

Planning for the IGAC Programme continued during the workshop held at the CACGP's Sixth International Symposium on Global Tropospheric Chemistry held at Peterborough, Ontario, Canada, August 1987. This meeting identified research initiatives and international activities that are particularly amenable to international cooperation, and provided guidelines for the organisation of the more extensive one week planning meeting held in Dookie, Australia, November, 1988. The result of the Dookie meeting are contained elsewhere in this report.

This IGAC Programme is being undertaken by CACGP with the cooperation of and input from other IAMAP Commissions including the International Radiation Commission, the International Ozone Commission, the International Commission on Cloud Physics and the Commission on Climate.

Looking forward, it is the wish of those involved that during the coming years IGAC, along with IGBP, BAPMoN, JGOFS, GO_3OS, MARC, WCRP and other international scientific endeavours, work together to understand global change in a holistic way to provide the information required by society for the wise use of our atmosphere and global environment.

APPENDIX

Copies of the IGAC Report can be obtained from the following distribution points:

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CHEMISTRY AND THE ENVIRONMENT: SCOPE FOR REGIONAL AND INTERNATIONAL COOPERATION

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While chemistry, over the years, has made immense contribution to human wellbeing, it also has added to some major world problems such as pollution, global warming, acid rain, deforestation, ozone layer depletion and increased risk of cancer. These are currently subjects of global concern. Such concern, although more evident in more advanced countries, but concrete actions, to combat these problems now, are lacking worldwide and at best are patchy. There is need to develop political awareness to these issues in the less advanced countries. There is also considerable scope for initiating further national, regional and international cooperative action to avert the future risks, as currently predicted, to the world community. Towards this end, an outline ten year regional and global programme, under the Commonwealth auspices, with an initial outlay of US $ 1 million per annum is suggested to complement other ongoing efforts.

INTRODUCTION

An understanding of the chemical changes in the environment is an area of fundamental importance. This is linked not only to man's quest for knowing how and when life began, but also to ensuring future continuity of life. The chemistry of the environment is therefore both a subject of great fascination and a matter of practical reality.

Since the beginning of time, the chemistry of the environment has been undergoing changes due to evolutionary processes and natural activities. Such changes have been enhanced and altered by human activities. In pursuit of its developmental objectives, human interventions often brought about dramatic changes to the environment encompassing land, water, air and even outer atmosphere. It is now evident that major changes to the environment have taken place over the last hundred years (Ramasami *et al.*, 1988) and most of these changes are in the directions that predict dramatic imbalances in the ecosphere.

To satisfy human desire for knowledge, and to meet demands for new and better products, the chemical sciences are undergoing phenomenal advances. Much of human progress to date, be it in meeting basic needs such as food, fuel, clothing, shelter and potable water or for satisfying comfort and recreational needs, is dependent on advances in chemical sciences.

Nevertheless, there is also a darker side of this bright picture. Developmental activities, including those in chemistry have made adverse contributions in a number of ways. Desertification, deforestation, acid rain, global warming, pollution of land, air and water, increased risk of cancer and other diseases are all part of the negative spin-offs of development. The continuation of life, as we know at present, is now at risk. Therefore, a new perception of development has become imperative. Development must be sound, sustainable and ecologically balanced. Developmental issues and their impacts are long term and global and should be considered as such. Current problems should be tackled on a global basis. There is, therefore, considerable scope for regional and international cooperation on issues such as chemistry and the environment.

The need for such cooperation is urgent. It has to be pursued on a multidisciplinary basis, with appropriate attention to both scientific and policy issues. Considerable political awareness of environmental issues in the West is now evident (Communique, 1989). There is a need to increase similar awareness in developing countries. Time is therefore opportune to strengthen ongoing national, regional and global efforts on chemistry and the environment and to embark on new ones, so that current forecasts of dire future consequences of this planet can be averted.

ISSUES OF CURRENT CONCERN

Issues of current concern are well known. It is encouraging to see the worldwide awareness on environmental issues. Environmental concerns, more popularly known as "green issue", have achieved political respectability in the West.

A succinct but an eloquent overview of major issues related to Chemistry and the Environment has been presented in the paper by Ramasami *et al.* (1988). The paper provides a good basis for considering specific areas for future cooperative action. Only three concerns, the greenhouse effect, acidity in fresh water and depletion of the ozone layer are briefly mentioned below as illustrations of the potential magnitude of such problems.

The greenhouse effect (Global warming)

The earth is warming up due to carbon dioxide and other greenhouse gases from power stations, vehicle exhausts and other sites where fossil fuel is burnt. Such global warming will melt huge ice sheets in Antarctica. It is estimated that by the year 2050, as a result of global warming, the sea level may rise by up to 5-7m, although current scientific consensus is more conservative and is in the range of 20 cm to 1.4m. Nearly one third of all human beings live within 60 km of coast line. A rise in the sea level of even half a meter could therefore have profound effects on habitation patterns, causing many people to move and many of the world's most important cities and ports to come under threat of flood. Whatever may be the actual rise, it is certain that large chunks of land will be under water if the potential threat of global warming is not contained and minimized. Although reliable predictions of regional climate do not exist, there is consistent scientific consensus that a significant global climate change will be induced due to man's activities. Another fear of global warming, apart from large scale flooding, is reduction in rainfall in summer, and greater evaporation of water both in winter and in summer. The net effect in Britain, as estimated by the British Institute of Hydrology recently could be a 40% reduction in the amount of water collecting in British reservoirs.

Acidity in fresh water

Atmospheric pollution, apart from global warming also leads to increasing the acidity in fresh water. As reported by the British Government's Acid Water Research Group (HMSO, 1989) in April 1989, Britain should restrict emission of sulfur dioxide to half of what they were in 1984 to improve the acidity of stream water. Reduction of around 30% in discharges of overall atmospheric pollution will hold acidity at present level. Only a reduction of 90% in emissions of sulfur dioxide and nitrogen oxides would neutralize surface water almost completely. The report warns that even with major curbs "the response to any deposition reduction will be delayed by up to several decades and some water may never recover".

Depletion of the ozone layer

Deterioration of the ozone due to the release of, in the main, chloro-fluorocarbons constitutes another major threat to humanity. Life on earth is as much dependent on ozone as on oxygen and water. According to the UNEP (Anon., 1989b) overall ozone levels have not yet dropped, but measurements made during the Antarctic Spring have shown that levels there have fallen by 40% in just a few years creating a "hole" in the ozone veil. The thinning of the ozone layer will let in much more of the Sun's ultraviolet radiation, not only damaging agricultural yields and ocean ecosystems, but giving rise to a large increase in skin cancer and eye disease. About 100,000 people die of skin cancer annually and UNEP calculates that a 3% reduction in ozone would produce another 20,000 cases annually in the US alone.

REVIEW OF INTERNATIONAL AND REGIONAL ACTIVITIES

Although a full review of international and regional activities is beyond the scope of this paper. some mention of such activities is pertinent in the context of this paper.

International activities

In the United Nations system, a number of specialized agencies are involved in work related to environment, most notable amongst these is the United Nations Environment Programme (UNEP) established following the 1972 Stockholm Conference on Human Environment. UNEP undertakes wide ranging activities on environmental issues. During 1979-83 UNEP had a fruitful collaboration with the Commonwealth Science Council on a CSC project on Management of Water Hyacinth with Dr Thyagarajan as its Regional Coordinator and Professor Haider as the National Coordinator for Bangladesh. Both the authors of this paper were closely involved in the formulation and implementation of this project. There were a number of outcomes of this project aimed at exploring various ways of tackling an environmental problem, the fast growing water weed. The findings of the project were reported through a number of CSC publications and through the Proceedings (Thyagarajan, 1984) of the Conference on Management of Water Hyacinth held in Hyderabad in 1983 to mark the termination of this very successful and interesting regional project. In addition to UNEP, there are a number of other UN agencies such as FAO, WHO and WMO with activities related to the environment. Besides, there are a number of international agencies outside the UN system which are concerned with environment. In terms of developing public awareness internationally, Greenpeace movement is unparalleled. In terms of carrying out work of scientific significance, International Council of Scientific Unions (ICSU) and International Union of Pure and Applied Chemistry (IUPAC) deserve mention.

ICSU

The International Council of Scientific Unions (ICSU) has been studying the problem through its various Unions and its international interdisciplinary research programmes such as the International Geophysical Year (1957-58), the International Biological Programme (1964-74), the Upper Mantle Project (1961-70) and for a study of interactions between various parts of the biosphere and geosphere, the Global Change Programme which was launched in 1986 by the 21st ICSU General Assembly. ICSU has initiated special studies such as those on Radioactive Waste Disposal & Disposal of Toxic Wastes and those carried out by the Scientific Committee on Problems of the Environment (SCOPE) on Environmental Consequences of Nuclear War (ENVWAR) and on Toxic Chemicals (CHEMRAWN).

The Global Change Programme or the International Geosphere- Biosphere Programme as it is now called, will, in the words of Sir Kendrew, its President, "will certainly be the most ambitious, the most wide-ranging, and in its impact on our understanding of the future possibilities for mankind, the most important project that ICSU has ever undertaken. Its purpose is to study the progressive changes in the environment of the human species on this Earth, past and future, to identify their causes, natural or man-made; and to make informed predictions of the long term future and thus of the dangers to our well being and even to our survival; and to investigate ways of minimizing those dangers that may be open to human intervention. From the point of view of fundamental sciences it is the extended study of the dynamics of the whole Earth System—its geology, its oceans, its atmosphere and its climate, and the thin green layer on its surface that we call the biosphere; a scientific enquiry offering immense intellectual challenges and rewards. So the programme will be scientifically exciting as well as immensely significant in charting the future of our species. It will necessarily continue for many years and will require the collection and analysis of huge amounts of data of all kinds using the most sophisticated techniques and the most powerful computers. It will be a major endeavour of the scientific community in every country of the world".

The IGBP is being planned by a Special Committee appointed by the ICSU Executive Board under J J McCarthy as Chairman. A separate presentation on the IGBP is included in the programme of the workshop, so any further details on IGBP will not be given here.

IUPAC

The International Union of Pure and Applied Chemistry (IUPAC) has a number of ongoing and proposed projects on Global Atmospheric Chemistry (Anon., 1989a). These include:

(i) Glossary of terms on atmospheric chemistry;

(ii) Inventory of tropospheric sampling networks;

(iii) Evaluation and recommendation of units for use in atmospheric chemistry;

(iv) Global climatic changes caused by atmospheric trace gases and depletion of stratospheric ozone;

(v) Review of analytical methods for the measurement of contaminants in the work place;

(vi) Evaluation and compilation of Henry's Law constants as related to atmospheric chemistry;

(vii) Worldwide inventory of emissions; and

(viii) CHEMRAWN Conference on atmospheric chemistry. The aim is to approach atmospheric chemistry as one coherent system of reactions leading to different aspects such as acid deposition, the oxidant problem, the arctic ozone hole and global climatic change.

On the national level also the UN agencies have been helping some of the vulnerable countries in working out suitable mechanism to tackle environmental problems. For example, a project entitled "Establishment and Initial Operation of Major Accident Hazards Control Systems" was launched in India in December 1986 with total outlay of US $ 1.64 million with assistance of ILO. The objective of the project is to strengthen the national system for prevention of occupational accidents in industrial activities involving one or more hazardous substances and processes which have the potential to result in major accidents leading to serious injury inside or outside the industrial installations. The project will help in setting up, with ILO's advice, a Major Hazards Control Advisory Centre in the Central Labour Institute in Bombay. It is hoped that this Centre will then share its experience and facilities with countries of the region who may need it.

Regional Activities

There are various UN agencies which are active on environmental problems in this region. They include ESCAP and SPC.

With the assistance of UNDP, a South Asian regional project on 'Safety and Control of Toxic Chemicals & Pollutants' was launched in 1988 involving UNDP outlay of about one million dollars. Being executed by ILO/SEARO, the project covers Burma, India, Indonesia, Sri Lanka and Thailand. The project aims at developing coordinated national priority programmes for chemical safety and control of environmental health hazards by:

(i) Supporting national focal point institutions on intersectoral action needed for reviewing the existing legislation and control mechanisms and quality standards and establishing the required regulatory framework as well as developing operational procedures for management including information storage and retrieval systems, environmental monitoring and risk assessment and programme evaluation;

(ii) Providing training for upgrading the technical planning and managerial skills of the national staff; and

(iii) Establishing 'Poison Centres' at national level for handling information on anti-dotal treatment of acute toxicity cases and involving health workers at community level in activities related to control of health hazards of pesticides.

To appraise the status of Chemical Safety in the region, promote awareness and identify key priority areas for action, an inter-country workshop was recently organised on 'Chemical Safety in South East Asian Region' which was attended by centres of the region and leading experts from developing countries and IPCS/Geneva.

It is expected that on completion of the project, apart from emergence of a coordinated programme at national level, review of and improvement in the national legislation for chemical safety and environmental hazard control would have been effected and a national system for hazardous chemicals registration and licensing would have been established in the three major participating countries i.e. India, Indonesia & Thailand and a review made on the monitoring, assessment, inspection and enforcement procedure in all the five participating countries.

Strategy for prevention of chemical accidents and emergency measures and procedures to cope with chemical accidents would also be worked out through specific studies in India, Indonesia and Thailand.

POLITICAL AWARENESS

The western economies

In the western economies, environment has become an important issue and the topic has gained political respectability and is attracting political support at the highest level. It is, therefore, only natural that the subject was given such prominence in the recent deliberations of the heads of Government or State of seven major industrial nations (the US, Britain, France, West Germany, Canada, Japan and Italy) and the President of the Commission of European Communities (Communique, 1989). They recognized the world-wide awareness of the necessity to preserve the global ecological balance and expressed great concern at the growing pollution of air, lakes, rivers, oceans and seas; acid rain, dangerous substances; and the rapid desertification and deforestation. They felt that decisive action was urgently needed to understand and protect the earth's ecological balance and agreed to work together to achieve the common goals of preserving a healthy and balanced global environment in order to meet shared economic and social objectives and to carry out obligations to future generations. Their deliberations were wide ranging and included the following:

- *Scientific research*—All countries were urged to give further impetus to scientific research on environmental issues, to develop necessary technologies and to make clear evaluations of the economic costs and benefits of environmental policies. The persisting uncertainty on some of these issues should not unduly delay action. In this regard all countries should combine their efforts to improve observation and monitoring on a global scale;

- *Technology development and transfer*—International cooperation needs to be enhanced in the field of technology and technology transfer to reduce pollution or provide alternative solutions;

- *Role of industry*—Industry has a crucial role in preventing pollution at source, in waste minimization, in energy conservation, and in the design and marketing of cost-effective clean technologies;

- *Role of agriculture*—The agricultural sector must contribute to tackling problems such as water pollution, soil erosion and desertification;

- *Environment and development*—Environmental protection is integral to development. Environmental considerations must be taken into account in economic decision-making. For sustainable development, compatibility of economic growth and development with the protection of the environment was a prerequisite.

Intensified efforts for technological breakthrough are important to reconcile economic growth and environmental policies. World Bank and regional development banks were urged to integrate environmental considerations into their activities. International organisations such as the United Nations and OECD were asked to develop analytical techniques/environmental indicators to help governments assess appropriate economical measures to promote the quality of the environment. The 1992 UN Conference on Environment and Development was expected to give additional momentum to the protection of the global environment;

- *Developing countries*—Through use of economic incentives, including aid mechanisms developing countries should be assisted to deal with past damage and to encourage them to take environmentally desirable action. In some cases past debts should be written off in return for environmental action. The financial and technological requirements of developing countries to sustain the growth of their economies and to meet environmental challenges should be recognized;
- *Depletion of ozone layer*—This was alarming and called for prompt action. Production and consumption of chlorofluorocarbons as covered by the Montreal protocol should be terminated as soon as possible and not later than the year 2000. Specific attention should be given to the ozone depleting substances, not covered by the Montreal protocol. Development and use of suitable substances and technologies should be promoted. More emphasis should be given on projects that provide alternatives to chlorofluorocarbons;
- *Environment and climate*—There was a need to limit emissions of carbon dioxide and other greenhouse gases which threaten to induce climate change, endangering the environment and ultimately the economy. The work of the Intergovernmental Panel on Climate Change required support. The world-wide network of observatories for greenhouse gases should be strengthened and the World Meteorological Organization's initiative to establish a global climatological reference network to detect climate change should be supported. An umbrella convention on climate change should be concluded, energy efficiency increased, energy conservation promoted and relevant techniques and technologies developed. Nuclear power plants can limit output of greenhouse gases, provided highest safety standards for plant operation and waste management are ensured for which international cooperation is to be strengthened;
- *Deforestation*—Deforestation damages the atmosphere and must be reversed. To preserve the scale of the world forests suitable forest, management practices should be adopted. Relevant international organizations should complete reports on the state of world forests. Strong support should be given to the FAO's Tropical Forest Action Plan adopted in 1986. Financial and technical cooperation should be given to nations with tropical forests. Temperate forests, lakes and rivers should be protected against effects of acid rain;

- *Marine environment*—Indiscriminate dumping of polluting wastes in oceans was condemned. For sustainable management of the marine environment, international cooperation was needed in preserving it and in conserving the living resources of the sea. Relevant United Nations bodies were asked to prepare a report on the state of the world's oceans. National, regional and global capabilities to contain and alleviate the consequences of maritime oil spills need to be improved. All countries were urged to make better use of the latest monitoring and clean-up technologies and to adhere to and implement fully the international conventions for the prevention of oil pollution of the oceans. International Maritime Organization was requested to put forward proposals for further preventative action;
- *Environmental law*—The Italian Government will host in 1990 a forum on international law for the environment with scholars, scientific experts and officials to consider the need for a digest of existing rules and to give in-depth consideration to the legal aspects of environment at the international level;
- *International institutions*—Existing environment institutions within the UN system should be strengthened. UNEP requires strengthening and increased financial support. Establishment of a new institution within the UN system is worth considering;
- *Flood in Bangladesh*—There was an urgent need for effective, coordinated action by the international community to support Bangladesh to find technically, financially, economically and environmentally sound solutions to the recurring flood problems in Bangladesh; and
- *Desertification*—Political support was given to set up an observatory of the Saharan areas to monitor the development of that fragile region and to protect it more effectively.

Awareness in developing countries

Awareness in developing countries on environmental issues is at best patchy and limited, in the main, to the scientific communities. The overwhelming poverty, progressive worsening of their economic situation and their inability to cope with recurrent natural disasters leave little scope for these countries to develop a long term global perspective on environmental issues. Although, the vast majority of the world population lives in developing countries, in relative terms their contribution to global environmental problems at present is minor. However, as some of these countries make economic progress, become industrialized and achieve a higher standard of living for their population, unless adequate measures are taken, their contribution to the environmental problems will become significant. Their planned economic advancement will therefore be equally at the peril of their future population.

For the future survival of all nations, developed or developing, it is therefore essential that there is close, meaningful and sustained cooperation on a global scale from now, while there is still prospect for containing the problems at their present level, and give nature a chance to make a recovery however slow and long term it may be.

Developing country participation in international cooperative projects will require scientific, technological and financial input from developed countries. These needed to be forthcoming without protracted futile negotiations as in some other fields which leave developing countries tired, bewildered and withdrawn. Developed countries should also make conscious efforts and enact necessary laws nationally and internationally so that their environmental problems, for example, toxic wastes, are not exported to developing countries taking advantage of their ignorance, innocence or economic vulnerability. In the long term, this is only a useless and self-defeating measure.

Unlike countries in the West, where the population is better educated, and public opinion plays an important and often decisive role in shaping political view point and direction, in developing countries, the vast majority of the population is illiterate and preoccupied with managing a bare existence. They have little or no political influence, nor any collective concern on long term global issues. The scientific community is small, fragmented and unable to make any sustained and meaningful political impact. Political view point is often catalyzed by disasters rather than forecasts based on systematic learned assessments. External pressures particularly by donor countries or agencies are also able to influence political thinking. International collaboration can therefore play a vital role in developing a proper political attitude in developing countries on environmental issues which is important for tackling the environmental problems globally.

CONCLUSIONS

There is an urgent need and considerable scope for regional and international collaboration on environmental issues vis-a-vis chemistry and the environment. The international climate for initiating such endeavours is right as can be seen from the political support that is evident from the declarations of western governments and the encouragement and support currently received by international environmental agencies.

The foremost requirement for initiating a new regional and/or international activity would be to establish an appropriate framework which should be purposeful, effective and should strengthen and extend ongoing efforts. The Commonwealth Science Council with its successful track record of promoting scientific collaboration involving countries both within and beyond the Commonwealth and its ability to work in harmony with other agencies could provide an ideal framework for such an endeavour. This workshop may therefore wish to recommend to the Commonwealth Science Council to embark on a programme on Chemistry and the Environment. The Council's sponsorship of this workshop illustrates that the subject is among its priority areas. However, for the Council to deliberate on this idea, it will require an outline proposal indicating the scope, participating agencies, and their task allocation, coordination and review mechanisms, funding requirements and duration.

Any such proposal should ideally encompass both policy considerations and scientific issues, for instance:

Policy

This should include:

(i) Development of legal and administrative framework nationally and internationally; and

(ii) Development of environmental protection standards for limiting pollution on land, water and air.

Scientific Issues

The inputs should be:

(i) R & D

- Development of alternatives to chlorofluorocarbons.
- Improvement of energy efficiency, promoting energy conservation, reduction of the use of fossil fuels, development of alternative energy technologies and environmentally sound techniques and technologies.
- Limit toxic emissions. Safe handling, storage, transport and disposal of chemicals and toxic wastes.
- Risk analysis, risk minimization and safe handling and disposal of accidental emissions and spillages.
- Climatic change.
- Development of analytical techniques and methods.

(ii) Information/Data

- Production of a Newsletter.
- Production of safety literature, films and video (in English and in local language) and their wide distribution.
- Regional data banks on chemical hazards/accidents.
- Global Climatological Reference Network (WMO).
- World-wide network of observatories for greenhouse gases.
- Network for Environmental Technology Transfer.
- Development of Expert Systems on hazard control.

(iii) Training

- Safe handling, storage, transport and disposal of chemicals and toxic wastes.
- Risk analysis, risk minimization.

- Safe handling and disposal of accidental emissions and spillages.
- Environmental chemistry.
- Development and management of computer based systems.

For political sensitization, workshops involving policy makers and leading scientists would be of immense value as well as brief but well presented literature aimed at politicians so that they not only can understand the issues involved but also know what specific action that can be taken at the political level. Often such literature do not answer the second aspect, thereby creating a sense of awe and helplessness in the minds of the politicians.

The Commonwealth Science Council is well experienced in organizing regional and international workshops, conferences and training courses. It also has a broad mechanism for information dissemination which could be further strengthened to respond to new and specific demands.

A programme of this nature, of necessity, should be flexible and long term and should take into account current national, regional and international activities. The idea of duplication of efforts in this instance should not be regarded as entirely unnecessary. The problem is overwhelming and world response to date is fragmentary at best and concrete action usually postponed beyond the magic year 2000. Such a programme should be well funded and well coordinated. A ten year programme, with 3-5 yearly reviews with annual funding of about a million US dollars made up of local and external contribution would constitute a serious and a meaningful response to the current challenge faced by the global community of which the Commonwealth is an important and integral part. Apart from government departments, universities, research establishments and industries, participation of national, regional and international chemical societies would be of immense value and should actively be sought.

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REPORT ON PANEL DISCUSSION "SCOPE FOR REGIONAL AND INTERNATIONAL COOPERATION"

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A panel discussion as the final session of the Regional Symposium was chaired by Dr G. Thyagarajan. He made an introductory statement concerning hazard analysis, limits of detection in the measurement of environmental constituents, scope for regional and international cooperation and possible support from the Commonwealth Science Council.

Besides looking at the basic scientific aspects of the chemistry of the environment, the regional symposium was also expected to delineate the scope for regional and international cooperation. A position paper presented by Dr M.N.G.A. Khan and Mr K.N. Johry initiated discussions in this regard. He pointed out the regional activities of existing agencies, the need for political awareness as well as a new regional initiative on chemistry and the environment. Dr Khan drew attention to many issues of current concern such as, the greenhouse effect, acidity in freshwater and the depletion of the ozone layer. The importance of political awareness, particularly in the developing countries, was emphasized. However, the greatest need was seen to be generation of regional and international collaboration on environmental issues aimed at developing an appropriate framework with emphasis on both policy and scientific goals. Dr Khan suggested that the Commonwealth Science Council could play a useful role in promoting scientific collaboration between countries both within and beyond the Commonwealth. Such an Asia-Pacific network could operate for 10 years with 3-5 yearly reviews. Dr Thyagarajan invited proposals focussed on developing cheaper but effective techniques and training of personnel for the same.

An example of such a cooperative research proposal was then provided by Dr A.G. Darnley. He argued that there should be specific, identifiable projects such as a study of resource use and management. The importance and relevance of the International Geochemical Mapping Project was emphasized earlier by Dr Darnley in his presentation. Dr Darnley suggested that the Project could consider regional and international cooperation within its framework and deal with specific identifiable problems associated with resource use and management. He suggested that UNDP could be approached for this purpose.

The specific objectives of Geochemical Mapping Project relevant to the Asia-Pacific region could be:

(i) To enable less developed countries to know and understand the geochemistry of the natural surficial environment;

(ii) To facilitate the comparison of geochemical information between countries (and regions); and

(iii) To build scientific knowledge-base and competence through international linkages.

Data from such geochemical mapping provide a sound basis for gaining an understanding of the environmental processes and actions needed to protect the environment.

Following the above discussion Dr Thyagarajan invited participants to state the position of their respective countries on these issues.

Dr C. Kaluwin (Papua New Guinea) described the functions of the Papua New Guinea Environmental Awareness Programme and its role in attempting to control soil degradation and other environmental changes arising from afforestation, agriculture and mining. He pointed out that necessary legislation now exists to deal with environmental problems. This was essential as the country relies heavily on the environment for economic progress. Various government and university groups are looking after the environmental matter. Mining is an important activity in the country and the ventures at Ok Tedi and Bouganville have resulted in the transfer of significant amounts of chemicals and sediments to the aquatic system. The introduction of pesticides to control insects has been followed-up with effective monitoring mechanisms to determine safe application levels. In a number of instances, the pristine environment has been extensively modified requiring rehabilitation. Monitoring of sea level rise is being undertaken, presumably taking into account land rise from the sea due to volcanic activity.

Dr M. Mohinder Singh (Malaysia) observed that the position paper outlined by Dr Khan, though comprehensive, was rather broad in scope. He felt that such a programme would be difficult to implement because handling of environmental issues requires clear identification of problems and specific attention of small groups of countries or sub-regional groups. Dr Mohinder Singh commented that the Federation of Asian Chemical Societies (FACS) has a Working Group on the Environment which has not functioned very well. However, the Asian Network for Analytical and Inorganic Chemistry (ANAIC), a joint network activity of the FACS and UNESCO, was very effective because of the specific focus on activities. These areas of expertise need to be recognised in order to develop an effective regional environmental programme.

Dr T. Clarkson (New Zealand) made a number of comments noting that the Asia-Pacific region has many environmental problems. Dr Clarkson referred to the Montreal Protocol as an example of a global strategy for dealing with a significant environmental problem. This could set a precedent as the Protocol has been ratified by a large number of countries..

Dr Clarkson saw the following major problems in managing the environment:

(i) Difficulties in the transfer of information between developed and developing countries including low consumption rate countries;

(ii) A need to develop high quality data base;

(iii) Handling of information technology transfer and other criteria related to establishing environmental protection infrastructure;

(iv) The need to interact with existing programmes; and

(v) The need for sharing of knowledge and literature through conferences and meetings which could be less technical in content.

An important point raised during the discussions leading to the formulation of the Montreal Protocol was : "How to initiate technology transfer?" Dr Clarkson's view was that informal networks have real value and he urged scientists to establish such informal networks.

Dr G. Sidhu (India) observed that the effectiveness of the programme such as the one outlined by Dr Khan depended upon good data collection and proper development strategy. Both of these criteria were directly related to the subject of the Regional Symposium. Dr Sidhu felt that perhaps atmospheric studies were overemphasized. He was of the opinion that there is an acute need for research on converting carbon dioxide back to carbon via carbon monoxide. Also alternatives to chlorofluorocarbons (CFC's) are required for use as degreasing fluids. He was optimistic that the synthetic organic chemists have the competence to meet the challenge. Adequate financial resources would have to be generated to pay for research on disposal of organic wastes and reutilization of biomass wastes. Dr Sidhu saw the Commonwealth Science Council as essentially playing a catalytic role with particular attention to the preparation of discussion papers.

·Dr Jayamane (Sri Lanka) elaborated on a specific problem in Sri Lanka which is probably quite general in the Asia-Pacific region. An increase in the industrial activities in Sri Lanka has led to an increase in the effluents and environmental pollution. Dr Jayamane saw that the real problem was, how to achieve development without pollution.

Dr R. Adhikari (Nepal) saw the most basic problem in his country as land degradation. Lack of direction with respect to forest conservation has led to soil erosion. Continual felling of trees has caused scarcity of basic fuel resulting in further exploitation of trees. Nepal has imported cheaper technology and has been adversely affected by having to use poor quality equipment. Water pollution is a big problem in Nepal because of lack of adequate treatment facilities.

Dr H.L. Bami (India) emphasised the importance of environmental regulations and averred that the crux of the problem lies in building the technical infrastructure for enforcing the environmental regulations. Agreement on data between laboratories, he felt, is of considerable importance and he strongly stressed the need to ensure that such agreement is maintained.

Dr Shafiqul Alam (Bangladesh) emphasised the role of analytical chemistry in understanding environmental problems. Dr Bilqis Haque (Bangladesh) pleaded that Bangladesh be included in any regional programmes because of the environmental devastation affecting her country. Bangladesh, like many other countries in the world, is completely at the mercy of nature.

Dr B.N. Noller (Australia) outlined a possible role of the Federation of Asian Chemical Societies (FACS) and the Asian Coordinating Group for Chemistry (ACGC) in tackling regional environmental problems. The FACS, through its Working Group on the Environment, has interest in both water quality and atmospheric pollution and through the Asian Network for Analytical and Inorganic Chemistry is involved with marine analysis, quality assurance and food analysis apart from analytical chemistry itself. He saw the role of legislation in controlling environmental pollution as being of prime importance. In Australia, it has been possible to totally control the impact of mining on the surrounding environment through the application of very specific legislation. Such an example is the control of uranium mining on the Alligator Rivers Region, Northern Australia. This point regarding legislation has been mentioned previously but must be seen as the necessary first step in protecting the environment.

After some concluding comments by Dr Thyagarajan, Dr M.S. Chadha highlighted the possible future dividends arising from the Regional Symposium and proposed a vote of thanks to all the participants.

BIOGRAPHIES

G.P. Ayers

Dr Ayers received his B.Sc. Honours (1972) and Ph.D. (1976) from the Monash University, Melbourne. He started as a Research Scientist at the CSIRO Division of Cloud Physics, Sydney, in 1972 and in 1982 moved to the CSIRO Division of Atmospheric Research, Melbourne where he is currently Principal Research Scientist. Dr Ayers was invited to the Dahlem Conference on Atmospheric Chemistry at Berlin, 1982; the SCOPE Conference on Tropical Acidification at Caracas, Venezuela, 1986; and the BAPMoN Workshop on Background Monitoring at Sofia, Bulgaria, 1989. He is at present Coordinator of the IGAC Debit Project. Dr Ayers has considerable experience in the chemistry of rain and atmospheric transport processes and a strong interest in tropical acidification.

H.L. Bami

Dr Bami received his Ph.D. degree in organic chemistry (1949) from the Indian Institute of Science, Bangalore. He carried out post-doctoral research at the National Institutes of Health, Bethesda, USA including extensive study tours to institutions dealing with pesticides, drugs and forensic analysis in USA, UK and Europe. Dr Bami has held senior research, analytical and development positions at the Malaria Institute of India, Delhi; the Central Drugs Laboratory, Calcutta and the Synthetic Drugs Plant. He became Director, Central Forensic Science Laboratory, New Delhi in 1968 from where he retired in 1982. He is at present a consulting forensic scientist. Dr Bami has published nearly 100 research papers in addition to numerous reviews, several of which were presented at international meetings. Dr Bami is a Fellow of Royal Society of Chemistry, Institution of Chemists (India), Indian Standards Institution and Indian Academy of Forensic Sciences, and is professionally associated with a number of scientific bodies.

M.S. Chadha

Dr Mohindra S. Chadha obtained his Master's in chemistry (1951) from Panjab University and Ph.D. in organic chemistry (1955) from Cornell University, Ithaca, New York. He carried out post-doctoral research at Cornell and at the University of California, Berkeley. He was also a recipient of Senior Resident Research Associateship of NASA, USA. Dr Chadha's interests relate to bio-organic chemistry, biotechnology, chemical and biochemical evolution. He worked at the Bhabha Atomic Research Centre for 30 years and retired from there in 1988 as Director, Biochemical Group. Currently he is the Principal Investigator of two research projects in the area of chemical and biochemical evolution. Dr Chadha has published more than 100 research papers. He has edited or co-edited 5 symposium-proceedings. He is a fellow of a number of scientific bodies including National Academy of Sciences (India) and Indian National Science Academy.

T.S. Clarkson

Dr Clarkson is an atmospheric chemist for the New Zealand Meteorological Service. His principal research interests are in the measurement of trace components in the clean troposphere, particularly light hydrocarbons and fluorocarbons. He is also involved in monitoring of ozone. Although most of his monitoring activity has been in New Zealand, measurements are made from regular flights of a research aircraft throughout the southwest Pacific as far north as the Equator, and monitoring is also undertaken in Antarctica. Dr Clarkson has an active interest in the protection of the ozone layer and in 1987 was head of the New Zealand delegation participating in negotiations leading to the Montreal Protocol.

A.G. Darnley

Dr Arthur G. Darnley received Ph.D. from Cambridge University following research work as an exploration geologist in the Zambian Copperbelt. After 9 years with the Atomic Energy Division of the British Geological Survey he joined the Geological Survey of Canada (GSC) in 1966 as the Head of Remote Sensing Methods and was responsible for the development of airborne gamma-ray spectrometry. From 1971 to 1986 he was Director of GSC's Resource Geophysics and Geochemistry Division, where he initiated systematic national radiometric and geochemical surveys. He is currently Senior Advisor, GSC. He has been chairman of many international technical committees concerned with uranium exploration methods and standards, and served as Senior Advisor for mineral development projects in Brazil and Thailand. He has been General Chairman of international exploration conferences in Vienna in 1976, Ottawa in 1977 and Paris in 1982. Dr Darnley has published many papers pertaining to the application of geophysics and geochemistry to mineral exploration and geological mapping.

T.M. Florence

Dr Florence received his M.Sc. (1961) and D.Sc. (1974) from the University of New South Wales (NSW), Australia. His D.Sc. was the first ever awarded in analytical chemistry at an Australian University. He is currently Senior Principal Research Scientist and Manager of the Centre for Advanced Analytical Chemistry, CSIRO Division of Fuel Technology, Lucas Heights, NSW. Dr Florence's present research interests cover ecotoxicology, environmental chemistry, electroanalytical chemistry, free radical chemistry and occupational hygiene. He has published 150 scientific papers. He has been a visiting professor at the University of Gothenberg, Sweden, Chanchung Institute of Applied Chemistry, China and the University of Canterbury, England. He received the RACI Analytical Chemistry Division medal in 1985 and has given numerous invited plenary lectures at international conferences on analytical and environmental chemistry.

I.E. Galbally

Mr Ian Galbally received his B.Sc. from Monash University, Melbourne (1965) and M.Sc from University of Melbourne (1970). He joined the CSIRO Division of Atmospheric Research, Melbourne as a research scientist in 1967 and is currently Principal Research Scientist. Mr Galbally has been a member of several national and international committees including SCOPE/UNEP International Nitrogen Unit (1978-82); National Committee for the Environment, Australian Academy of Science (1980-82); Australian Department of Science and Technology, Cape Grim Baseline Air Pollution Monitoring Station Working Group (1978–present); International Ozone Commission IAMAP (1980–present); Scientific Advisory Committee SCOPE Biospheric Trace Gas Emission Project (1986–present); Commission on Atmospheric Chemistry and Global Pollution IAMAP (1987–present); Associate Editor, Journal of Atmospheric Chemistry (1983–present); and member of Editorial Board, Tellus (1987–present). Mr Ian Galbally has published 50 research papers and has edited 3 books. During the International Year of Peace (1985-86) Mr Galbally was requested to undertake reviews and original research on atmospheric aspects of nuclear war.

R.M. Gifford

Dr Gifford received B.Sc. (1965) from Nottingham University and Ph.D. (1969) from Cornell University, New York, USA. From 1969 to the present Dr Gifford has been a Research Scientist at CSIRO Division of Plant Industry, Canberra, Australia. He is presently Senior Principal Research Scientist and leader of the project on "Agriculture in relation to global atmospheric change" and has authored or co-authored about 70 research publications, reviews or chapters in the area of whole plant physiology, photosynthetic physiology, energetics of agriculture, carbon partitioning in plants and carbon dioxide effects on plants.

K.N. Johry

Mr K.N. Johry who specialised in inorganic chemistry, has been involved in International and Commonwealth Cooperation in Science & Technology for more than two decades. Starting as Science Attache at Indian Mission in London he, presently heads the International Cooperation Division of the Council of Scientific & Industrial Research at New Delhi. He has been closely involved in many of the Commonwealth regional collaborative programmes under CSC and in developing bilateral cooperation with major science agencies / academies in

Europe, USA and third world countries. He was, until recently, President of the Indian Society for Information Science.

M.N.G.A. Khan

Dr Khan received B.Sc. (1961) and M.Sc. (1963) from Bangladesh (formerely Pakistan) and Ph.D. (1969) from Australia. During 1964-1974 he worked for Bangladesh Atomic Energy Commission and during 1975-1987 for the Commonwealth Science Council. Dr Khan is a nuclear chemist and has extensive experience in developing and managing regional and commonwealth collaborative research activities in rural technology, standardization and metrology, alternative energy and science popularization. He has written both for the scientific journals and popular press. He is a Fellow of the Royal Society of Chemistry and a life member and patron of the Bangladesh Chemical Society and associate member of the International Union of Pure and Applied Chemistry. Dr Khan is now a Chemistry Lecturer at Loughton College of Further Education at Essex in England. Apart from science/chemical education, his current interests include S & T cooperation, chemical safety and science popularization.

A. Maheswaran

Mr A. Maheswaran has B.Sc. (Hons) and is a Chartered Chemist by profession. He is a Fellow of The Royal Society of Chemistry, London and the Malaysian Institute of Chemistry and a Fellow of the Institution of Water and Environmental Management. He retired as Director-General of Environment, Government of Malaysia in 1987 after 28 years in the field of environmental management. In view of his distinguished services, he was honoured by His Majesty the King of Malaysia with the title 'K.M.N.'. He was also awarded 'Gold Medal' by the Malaysian Institute of Chemistry for his contributions to the field of environment as a chemist. Mr Maheswaran was official representative of Malaysia at several conferences/meetings abroad which included Governing Council Sessions of the United Nations Environment Programme (UNEP). He has also actively participated in seminars and conferences and published numerous papers. At present he is an Environmental Consultant and has carried out several assignments including those by the United Nations Agencies, namely, WHO, UNDP, ESCAP, UNEP and World Bank.

T. McEwan

Dr McEwan received B.Sc. (1953), B.Sc. Honours in chemistry (1955) and M.Sc. (1959) from the University of Queensland, Australia and Ph.D. (1966) from Dalhousie University, Nova Scotia, Canada. He is a Fellow of the RACI (1974). From 1982-1988 Dr McEwan was Director, Biochemistry Branch, Queensland Department of Primary Industries and Acting Deputy Director, Division of Animal Industry and later Director of Animal Laboratories, in the same department till his retirement at the end of 1988. Dr McEwan represented his Department on the Water Quality Council of Queensland, the Agricultural Chemicals Committee

(Australian Government) and the Inter-departmental Committee on Chemical Contamination on Food. Outside Australia Dr McEwan has attended the Codex Committee on Pesticide Residues, The Hague (1986, 1987, 1988) as the Queensland representative; the Codex Committee on Residues of Veterinary Drugs in Food, Washington (1987); attended a Joint FAO/WHO Expert Committee on Food Additives in Rome (1987); acted as a consultant for FAO visiting Rome and various countries in East Africa (November 1980-81).

A.P. Mitra

Dr Mitra obtained his M.Sc. and Ph.D. in physics from Calcutta University under Prof. S.K. Mitra, FRS. He was Colombo Plan Fellow in the Division of Radiophysics, CSIRO, Australia (1951); Visiting Assistant Professor and Associate Professor in Engineering Research, Pennsylvania State University, USA (1952-54); Secretary, Radio Research Committee, National Physical Laboratory (NPL), CSIR (1954). He served the NPL from 1954 in various capacities and was Director of the Institute from 1982 onwards till February 1986 when he was appointed Director-General, CSIR and Secretary to the Government of India, Department of Scientific & Industrial Research, a position which he currently holds. Dr Mitra is a Fellow of the Royal Society of London and Fellow of numerous National and International Academies and Societies. He is recipient of innumerable awards, prizes and distinctions including Padma Bhushan awarded by President of India in 1989.

B.N. Noller

Dr Noller received B.Sc. (1971) and M. Chem. (1973) from the University of New South Wales, Australia and Ph.D. from the University of Tasmania (1978). Following a brief period at the Research School of Chemistry, Australian National University, Canberra, Dr. Noller became Research Scientist for analytical chemistry and environmental chemistry at the Alligator Rivers Region Research Institute, Jabiru, Northern Territory, Australia. Dr Noller is currently Senior Research Scientist and has undertaken research on the impact of uranium mining on the tropical ecosystem including several studies on natural physico-chemical processes in freshwater systems. Dr. Noller had represented the Royal Australian Chemical Institute at Federation of Asian Chemical Societies executive meetings and is currently Secretary-General, FACS.

G.I. Pearman

Dr Pearman received both his B.Sc Honours (1963) and Ph.D. (1968) in biology from the University of Western Australia. Following post-graduate research at Madison, Wisconsin. He joined CSIRO, Australia where he is currently Assistant Chief of the Division of Atmospheric Research. He is also coordinator of the CSIRO Climate Change Programme. His early work with CSIRO involved the measurement of CO_2 fluxes into wheat crops, and from this he developed a strong interest in the global carbon cycle. He was the main thrust behind the establishment of the Australian Baseline Monitoring Station in Tasmania. He was the editor of the

CSIRO book, Greenhouse: Planning for climate change. He is currently coordinator of the INRE programme. Dr Pearman has been the member of several national and international committees: Australian Academy of Science (1986); National Committee for the International Geosphere-Biosphere Programme (1987); Chairman, International Global Atmospheric Chemistry Programme (1987-88). In 1987, Dr Pearman was convenor of the Greenhouse 87 Conference held at Monash University. For his contribution to the science and management concerning greenhouse research, Dr Pearman was awarded the CSIRO Medal in 1988. He was elected to Fellowship of the Australian Academy of Science in 1989. For the work of his group in public communication, he received a United Nations Environment Programme Global 500 award in 1989.

T. Ramasami

Dr Ramasami obtained B. Tech. and M. Tech in leather technology from University of Madras and a Ph.D. in physical inorganic chemistry from the University of Leeds, UK. His research training includes homogeneous catalysis, inorganic reaction mechanisms and synthesis of coordination compounds and environmental chemistry. He is currently a senior scientist at the Central Leather Research Institute, Madras and heads Physical and Inorganic Chemistry and Biophysics Divisions. He has published 76 scientific papers and 27 other technical reports and articles.

G.S. Sidhu

Dr Gurbachan Singh Sidhu obtained M.Sc. and Ph.D. from Lucknow University in organic chemistry. He spent most of his research career (1949 to 1981) at the Central laboratories for Scientific and Industrial Research, Hyderabad, which was renamed as Regional Research Laboratory and subsequently as Indian Institute of Chemical Technology. Dr Sidhu was the Director of this Institute from 1963-1981. He became the Director-General, Council of Scientific and Industrial Research, New Delhi (1981-1984) and Chairman of the Board of Directors of National Research and Development Corporation (1981-1983). Dr Sidhu's R & D interests have centered around, naturally occurring quinones, industrial organic chemistry related to drugs, pesticides and intermediates and coal conversion. He is currently working as an independent Consultant.

R. Simpson

Dr Simpson is a Senior Lecturer in the Division of Australian Environmental Studies at Griffith University, Brisbane, Australia. He has worked as a Research Scientist in the CSIRO Division of Atmospheric Research and, since his arrival at Griffith University in 1976, has published widely in the air pollution literature. He is presently Secretary of the local branch of the Clean Air Society of Australia and New Zealand and will shortly publish a book on air pollution in Brisbane.

V. Subramanian

Mr Subramanian obtained M.Sc. in physics from Madras University in 1984. At present he is a Senior Research Fellow (CSIR) at Central Leather Research Institute, Madras working on mathematical modelling of different aspects in molecular physics. His main areas of interest are molecular mechanics and molecular orbital calculations. He teaches quantum mechanics, classical mechanics, mathematical physics and polymer physics to post-graduate students at the Madras University.

G. Thyagarajan

Dr Gopalakrishna Thyagarajan obtained M.Sc. and Ph.D. in organic chemistry from Osmania University, Hyderabad, India. He did his post-doctoral research in Organic Chemistry at the University of California, Berkeley, USA (1964-65) and was Visiting Scientist at the National Institutes of Health, Bethesda, MD, USA (1969-71). He held various positions in scientific research and science management at the Regional Research Laboratory (RRL) between 1957 and 1974. Since 1975 he has headed three of India's national laboratories in Jorhat, Hyderbad and Madras. Dr Thyagarajan's basic research publications which number over 75 are in the areas of organic synthesis, natural products chemistry and aquatic weeds. His contributions to industrial research pertain to pesticides, synthetic drugs, industrial chemicals and petroleum rheology. His current interests have extended to chemical safety and risk analysis and management of technological change. His contributions to Indian industrial development won him several coveted awards. Professional body affiliations include American Chemical Society, International Union of Pure and Applied Chemistry, International Science Policy Foundation, Indian Institution of Chemists (Fellow) and Royal Society of Chemistry, London (Fellow). Dr Thyagarajan is currently Science Adviser to the Commonwealth Secretary-General and Secretary, Commonwealth Science Council, London.

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