CHAPTER 13

POLLUTION AND REMEDIATION OF POLLUTED GROUNDWATER

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Introduction

In this chapter, the environment and dynamics of groundwater are discussed in relation to polluting substances. The principal pollutants are identified, and an outline is given of the historical development of pollution, in scale and variety. The controls over the vulnerability of ground and groundwater to pollution are evaluated, and the concept of aquifer protection outlined. *The commonest pollutants are postulated to be hydrocarbons and their derivatives.* Detection of pollution is followed by remediation, and the commoner clean up processes are described. Case histories are introduced. The differences in the nature and scale of pollution in temperate as against semi-arid countries, and in densely populated as against sparsely populated terrain are discussed.

Overview

Groundwater contamination is perceived to be *the introduction of any substance that does not naturally occur in it. Pollution is the introduction of a substantial quantity of any such substance in concentrations over a level defined by a directive following national legislation. That level or maximum admissible concentration is variable between the receiving enviromnent and between governing bodies.*

Water enters the ground to finish up in subsurface storage and is then *groundwater.* If the host rock is permeable, it is an *aquife*r. Water moves through the ground as a fluid. It follows that other fluids, provided they are not too viscous, can follow the same paths. So groundwater, whether in aquifers or not, can be contaminated. Only in aquifers does it pose an immediate problem, but contaminants which enter an almost impermeable rock can gradually migrate into an aquifer. The quality of groundwater is affected by many influences other than human. The youngest groundwater has a composition approximating that of rainwater. The longer they are in contact with their host, the more solutes they will acquire, until they are saturated and at chemical equilibrium.

Historically, massive impacts on water quality have resulted from invasion by hydrocarbons that have leaked from natural storage in older lithological structures. Radioactive pollution of groundwater emanates from deposits of radioactive minerals. *Unstable or soluble substances such as volcanic dust* can be widely dispersed by winds. *Bedded evaporites* leach into groundwater.

Long before the human race got to work, the products of decay and excretion by animals and plants affected groundwater. Generally speaking, poor quality groundwater resulting from natural influences are tolerable in that populations have either avoided affected groundwater or have used surface resources.

The dividing line between polluted groundwater and that of naturally poor quality is not precise. Forest and wild fauna can cause poor quality groundwater but do not, by definition, introduce pollutants. On an adjoining farm vegetation and livestock create pollutants.

A prograding coastline in Africa is a combination of beach ridges and lagoons. The lagoons fill up with vegetation, silts and clays, and ultimately a lot of iron oxides. The resulting coastal plain is underlain by elongated sand aquifers bounded by iron-laden clays. If the groundwater moves naturally and slowly, poor quality water in significant quantities is not drawn in from the adjoining lagoon deposits. If a well-field is put in, pumping soon brings in iron in an acid environment, and the emerging water, on exposure to air, precipitates iron and clogs the system between water abstraction and public supply.

Evaporites in contact with groundwater, e g in the Middle East, are not a great nuisance until a strong vertical groundwater gradient is induced by pumping from a relatively distant, unpolluted aquifer, when dissolved sulphates migrate into the well-field area. There are many groundwater pollution risks in Botswana, exacerbated by these sandy soils, but in terms of per unit area of groundwater, these are less significant than in a densely populated terrain like the United Kingdom.

Aquifer Vulnerability

The degree to which groundwater is vulnerable to pollution is controlled by the ease or difficulty with which pollutants can reach the aquifers in which the groundwater is stored. Discussion now centres on pollutants derived from human activity. Generally though not always, pollutants come from the surface. They pass either in solution or in non-aqueous fluid flow downward through the unsaturated sub-soil through the partially saturated zone, into the groundwater.

The soil is a complex catalyst in which bacteria, air and humic acids play a part in attacking and breaking down or altering most organic and some inorganic substances. A thick well-developed soil is naturally more effective in halting further progress of pollutants than a thin soil.

The unsaturated sub-soil carries some bacteria and a lot of air. Fluids percolating through this zone are subject to further attack. The more impermeable, the more the progress of fluids is retarded, or even halted; and the thicker this zone, the longer is the fluid under attack.

In both the soil and sub-soil, degradation of contaminants is a natural chemical process which proceeds regardless of bacterial action. Within the aquifer, bacteria exist, and air sometimes exists. So groundwater, especially if it is moving, can further be purified by the action of both aerobic and anaerobic bacteria.

Aquifer vulnerability is strongly influenced by the various thicknesses of soil and types of substrate - thin soils often provide little protection against bacterial invasion.

Well-head Vulnerability

The vulnerability of groundwater in a well-field can be controlled by defined constraints to invasion by pollutants at the well-head. The essential difference between aquifer vulnerability and well-head vulnerability is that the first is almost constant and the second varies with the controls imposed, the size and disposition of the well-field, and the pollutants present.

Well-head Protection Areas (WHPAs) are defined fairly uniformly world wide, and are based on the time taken for groundwater to migrate from potential pollutants, and the distance travelled. WHPAs comprise the following:

- A small, fenced operational courtyard, wherein only essential activities are permitted;
- An inner source protection zone, to protect against pathogens. In Europe this is a 50 day zone; in Botswana where soils are thin and temperatures high, a 100 day zone or a minimum distance of 100m radius from the borehole is preferred;
- An intermediate fracture flow protection zone applied in Botswana to dominating fracture porous aquifers, and the control is 1 km radius; and
- An outer source protection zone, corresponding to an arbitrary 100 year catchment.

Exclusion, Detection and Remediation of the Principal Pollutants

For the purpose of the discussions in this chapter, pollutants may be grouped as follows:

- Relatively insoluble non-aqueous phase liquids;

☐ Polluting solutes in water; and
☐ Pathogens.

Two types of pollutant origin are distinguished:

☐ **Point source** eg: a septic tank or chemical factory leak; and
☐ **Diffuse source** eg: fertiliser spreading and pesticide spraying.

Point source pollution contaminates aquifers in pulses, especially if the host rock is a mixture of permeable and impermeable material behind which pollutants get trapped. It will be readily appreciated that the punch of a point source is more invasive than a more gentle, widespread attack.

Non-Aqueous Phase Liquids.

Most non-aqueous phase liquids are hydrocarbons and hydrocarbon derivatives. They are classified as lighter than water (**Light Non Aqueous Phase Liquids** or LNAPLs) or denser than water (**Dense Non Aqueous Phase Liquids** or DNAPLs). Mercifully most non-aqueous phase liquids are of the light variety and hence sit on the groundwater surface.

Dense liquids that lie under the water on the aquifer floor are often difficult to locate. If the floor is irregular the liquid accumulates in pools, which must be defined before the liquid can be removed. Of all fluids, apart from water, petroleum and spills thereof are the commonest, simply because in the current consumer society lifestyle, hydrocarbons are at present the cheapest source of energy. With a bit of luck, the future will see hydrocarbons displaced but meanwhile the movement of petroleum products from source to point of use will inevitably generate spills.

Spills of petroleum are accidental and infrequent, but they occur at points rather than diffusely, and in considerable volume (as tanker spillages or long lasting leaks) so they penetrate the soil, the first and major line of defence. Leakage from underground storage tanks, though relatively small in volume, is one of the most common causes of hydrocarbon pollution. Usually the pollutant has reached the aquifer before it is detected, typically by taste, in borehole water supplies. Prevention of such spillage is simply achieved, by providing protection where the risk of spillage is high.

A hydrocarbon spillage forms a pancake on the water table, its *disposition* related to the polluting source and the hydraulic gradient, its *thickness* related to its viscosity, and its *extent* related to the hydraulic gradient and to the duration of the spillage. The pancake is underlain by a zone of polluted groundwater, where the water has absorbed as much pollutant as it can. This is not much, but is the indicator that pollution exists. A 'smear' zone of residual hydrocarbons is left above the pancake as the rest of the water level fluctuates.

Like most organic compounds, petroleum is vulnerable to oxidation and in time and with access to air the lighter hydrocarbons will decompose to carbon dioxide and will evaporate. Viscous hydrocarbons will slowly separate into lighter components and heavy tars which are as resistant to decomposition as tarmac on a road. But their relatively high viscosity inhibits the downward movement of heavy hydrocarbons into an aquifer. Given that leaving nature to run its course belongs to a spacious age long past, the measures now employed to clean up a hydrocarbon spill are any or all of the following:

(a) Bulk Removal of the Host Material in the Vadose (unsaturated) Zone

The more viscous fraction of the spillage lags behind the migrating mass in the zone of downward percolation, and can often be dug out. The host is removed to be 'farmed' as in ground pollution.

(b) Removal by Pumping from a Borehole

A scavenger pump placed in a borehole opposite the pancake removes a mixture of hydrocarbon and water to a chambered tank at the surface, whence the oil is skimmed off and the water ducted to a lagoon for final oxidation. To make the hydrocarbon to flow towards the scavenger, a deep pump removes a limited amount of groundwater, creating a gradient. This has the added benefit of stopping further lateral migration of the pollutant. Water can also be passed through activated carbon filters and re-injected, though this is more commonly undertaken in remediating a chlorinated hydrocarbon spill

(c) Decomposition of the Hydrocarbon to Carbon Dioxide by Injecting Air

This is mainly effective in removing tainted water. Air is constantly pumped into the polluted groundwater; the soil gas immediately above the water table is analysed for carbon dixoide and the regression plotted. As time goes by, the carbon dioxide decreases more and more until the permissible concentration of pollutant is achieved. Air injection not only oxidises the hydrocarbon but also provides the oxygen required for aerobic bacteria to degrade the hydrocarbons.

(d) Decomposition of the Hydrocarbons by Injecting Bacteria and/or Nutrients

Bacteria are routinely present in hydrocarbons and will ordinarily attack pollutants present in the hydrocarbons. Whether introducing more bacteria significantly speeds up the process is a debated question, as the bacteria - which naturally degrade the pollutant - rapidly multiply when the correct 'food' and environment exist. Introducing nutrients is also practised, and is also a debated question.

Major spillages do not appear to have occurred in Botswana. A spillage at Artesia (North of Gaborone on the Francistown Road) occurred in November 1996. There was some concern that a well-field less than 20 km away near Mmamabula would be affected, but though no remedial measures appear to have been taken, there have been no reports of groundwater pollution. Beneath the thin cover of Kalahari sands the Karoo sandstones aquifers do not appear to have been invaded. Though the soils are thin it may be that the Kalahari sands have exerted an attenuating influence.

(e) Halogenated Hydrocarbons

Modified hydrocarbons are used in industry, mainly as solvents. It is difficult in practice to prevent the used material from leaking into the ground, and until quite recently the accumulations of generations of heedless leakage were unnoticed. Most are LNAPLs and are dealt with in a way similar to that applied to petroleum.

(f) Polluting Solutes in Water

This group comprises the following:

- Faecal and vegetative material;
- Industrial chemicals;
- Heavy metals in storm water from quarries, mines, settlement lagoons, highways etc;
- Salt; and
- Soluble agricultural chemicals.

Faecal and Vegetative Material

In Botswana, rotting vegetation is an almost negligible source of pollution. The widespread use of pit latrines, however, is a strong potential threat. Excrement bypasses the soil profile and the only protection against bacterial invasion of groundwater is attenuation in the unsaturated zone. Nitrates can also build up in groundwater to an undesirable level. The remedy is to encourage the use of sealed and improved latrines.

Industrial Chemicals

Risks relating to industrial chemicals are restricted to industrial zones, which in Botswana are few. The principal sources are solvents, and acid and alkaline wastes. For example, breweries use much caustic soda and resulting effluents can destroy the soil structure before wreaking havoc in the groundwater. The remedy is to treat the effluent on site.

Salt is widely used in northern latitudes where it is spread on roads to inhibit icing; it reaches storm drains and is difficult to exclude from the groundwater. Needless to say, there is no problem in Botswana in this respect.

Soluble Agricultural Chemicals

Fertilisers tend to be widely and excessively used in non-organic farming situations. The object is to provide nutrients to the root zone of growing crops. Nitrate is derived from fertilisers as well as from animal and vegetation remnants and national directives on water quality imposes a limit, in the range 30 to 50 mg/l. In Botswana the limit is rather higher. The risk is not from ingestion of nitrate itself but in the gut it tends to reduce to nitrite, which is a carcinogenic. Where the unsaturated zone is thick nitrate is mostly degraded to nitrogen, but more generally the remedy is to educate the users of fertiliser into using minimal quantities despite the blandishments of the manufacturers.

Finally, a startling thought. Water can pollute groundwater. If hot water from a factory, or power plant, is discharged into the ground, it changes the bacterial types and quantities, it can enable some dormant pathogens to energise and multiply and can change the dissolved solid concentration. If the water is continuously recirculated, the effect can be serious. This has happened in the Cheshire plain of United Kingdom. Even water at an ambient temperature can contaminate not groundwater but the host - the aquifer. A strong rise in water level following artificial recharge can lead to the groundwater coming into contact with pollutants previously out of reach

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