Protecting Groundwater for Health

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Managing the Quality of Drinking-water Sources

Edited by Oliver Schmoll, Guy Howard,
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World Health Organization

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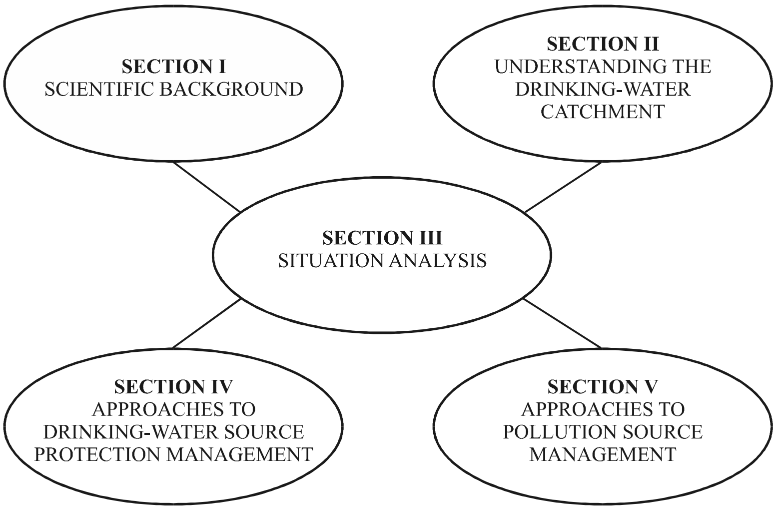
Structure of this book

This book is a tool for developing strategies to protect groundwater for health by managing the quality of drinking-water sources. For this purpose it provides different points of entry. As illustrated in the Figure below, the book consists of five sections.



Structure of Protecting Groundwater for Health

Section I covers the scientific background needed to understand which pathogens and chemicals are relevant to human health, how they are transported in the underground and how they may be reduced, removed or retarded (Chapters 3 and 4). The criteria for inclusion of agents in this overview are their relevance to human health and their relevance in groundwater. Further the concept of groundwater recharge areas is introduced in Chapter 2, and basic hydrological and hydrogeological background information is provided. The section is concluded by Chapter 5 which introduces socio-economic and institutional considerations relevant to developing the protection of groundwater resources.

Section II provides background information for characterizing and understanding the drinking-water catchment. The chapters in this section explain how conditions and human activities in the catchment may lead to the occurrence of pathogens or hazardous substances in groundwater. The section begins with general guidance on collecting information (Chapter 6). Chapter 7 discusses assessing the socio-economic and institutional setting as a necessary basis for choosing and implementing feasible management actions. Chapter 8 outlines the background and information required for understanding the hydrogeological conditions determining the likelihood of pollutants to reach aquifers. Chapters 9-13 address the range of human activities potentially releasing pollutants to the underground, i.e. agriculture, sanitation practices, industry, mining, military sites, waste disposal and traffic. These chapters end with checklists highlighting the type of information needed about the setting and the human activities in it for assessing health hazards potentially affecting groundwater.

Section III provides conceptual guidance on prioritizing both hazards and management responses. Chapter 14 describes how information on the hydrogeological conditions, particularly on aquifer vulnerability, can be related to human activities in the drinking-water catchment area in order to assess the potential for pollutants emitted from these activities to reach the aquifer. Chapter 15 discusses how to prioritize pollutants according to their public health burden as well as to their likelihood of long-term accumulation in the aquifer. It also addresses the need to consider the socio-economic context in choosing feasible options from the range of technically appropriate management responses for protection, control or remediation.

Section IV provides an overview of the potential management actions that may be taken to protect drinking-water sources. These begin with their integration into a comprehensive Water Safety Plan that covers all supply steps from catchment to consumer (Chapter 16). Two chapters specifically cover protection of the drinking-water source: Chapter 17 at the scale of designating and managing groundwater protection zones in the catchment and Chapter 18 at the scale of protecting wellheads. Lastly, Chapter 19 addresses the management of groundwater abstraction in order to avoid impacts upon quality and quantity and thus on human health.

Section V provides an overview of control measures to prevent pollution from human activities in the catchment, beginning with the overarching issues of policy, land-use planning and implementation of management options for protecting groundwater (Chapter 20). Chapters 21-25 follow with overviews of the specific management approaches that help avoid groundwater pollution from the range of human activities in the catchment, i.e. agriculture, sanitation practices, industry, mining, military sites, waste disposal and traffic.

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Acronyms and abbreviations

ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
ASS	acid sulphate soils
BAT	best available technology
BC MAFF	British Columbia Ministry for Agriculture, Fisheries & Forestries, Canada
BGS	British Geological Survey
BMP(s)	best management practice(s)
BOD	biochemical oxygen demand
BTEX	benzene, toluene, ethylbenzene, xylene
C&D	construction and demolition
CCTV	close circuit television
cDCE	cis-dichloroethene
cf`	contamination factor
CJD	Creutzfeldt-Jakob disease
COD	chemical oxygen demand
CSOs	combined sewer overflows
CTC	carbon tetrachloride/tetrachloromethane
CVM	contingent valuation methodologies
CW	chemical warfare
2,4-D	(2,4-dichlorophenoxy)acetic acid
DALY	Disability Affected Life Years
2,4-DB	(2,4-dichlorophenoxy)butyric acid
1,2-DCA	1,2-dichloroethane

1,2-DCB	1,2-dichlorobenzene
1,4-DCB	1,4-dichlorobenzene
1,1-DCE	1,1-dichloroethene
DCM	dichloromethane
DDT	dichlorodiphenyltrichloroethane
DFID	Department for International Development, UK
DNAPL	dense non-aqueous phase liquid
DNB	dinitrobenzene
DNT	dinitrotoluene
DOC	dissolved organic carbon
DOE	Department of the Environment
DWI	Drinking Water Inspectorate
EA	Environment Agency
EDCs	endocrine disrupting chemicals/compounds
EDTA	ethylendiamine tetraacetic acid
EED	Environmental Engineering Division
EIA(S)	Environmental Impact Assessment (Study)
EU	European Union
FS	faecal streptococci
FAO	Food and Agriculture Organization
GIS	Geographical Information System
GDWQ	*Guidelines for Drinking-water Quality*, WHO
HACCP	Hazard Analysis and Critical Control Points
GV	guideline value
Hb	haemoglobin
HCB	hexachlorobenze
HD	mustard gas
HIV	human immunodeficiency virus
HMX	High Melting Explosive cyclotetramethylenetetranitramine
IARC	International Agency for Research on Cancer
ICPE	International Commissions for the Protection of the Elbe
ICPR	International Commissions for the Protection of the Rhine
IDWSSD	International Drinking Water Supply and Sanitation Decade
ISL	in situ leaching
IUPAC	International Union of Pure Applied Chemistry
LNAPLs	light non-aqueous phase liquid
LWS	Lenzburg water supply
MCPA	(4-chloro-2-methylphenoxy)acetic acid
MCPP	2-(4-chloro-2-methylphenoxy)propanoic acid (mecoprop)
MDG	Millennium Development Goal
metHb	methaemoglobin
MNA	monitored natural attenuation
MSW	municipal solid waste
MTBE	methyl tertiary-butyl ether
NA	natural attenuation
NAPL	non aqueous phase liquid
NCRP	National Council on Radiation Protection Measurements, USA
NGOs	non-governmental organizations
NRC	National Research Council, USA

NSW	New South Wales, Australia
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCE	perchloroethylene/tetrachloroethene
PCP	pentachlorophenol
PCPs	personal care products
PCR	polymerase chain reaction
PHAST	participating hygiene and sanitation transformation
POPs	persistent organic pollutants
PPP	purchasing power parity
RDX	Royal Dutch Explosive cyclotrimethylenetetranitramine
REC	Regional Environmental Council
RNA	ribonucleic acid
SHI	Sanitary Hazard Index
SPA	Source Protection Areas
2,4,5-T	(2,4,5-tricholorophenoxy)acetic acid
TCA	trichloroethane
TCE	trichloroethene
TCM	trichloromethane
tDCE	trans-dichloroethene
TDS	total dissolved solids
TeCE	tetrachloroethene
TNT	trinitrotoluene
TON	total organic nitrogen
2,4,5-TP	(2,4,5-tricholorophenoxy)propanoic acid (fenoprop)
TTC	thermotolerant coliforms
UNDP	United Nations Development Programme
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
UNICEF	United Nations International Children's Emergency Fund
UNESCO	United Nations Educational, Scientific and Cultural Organization
UNSCEAR	United Nations Scientific Committee of Effects of Atomic Radiation
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VBNC	viable but non-culturable
VC	vinyl chloride
VFAs	volatile fatty acids
VOC	volatile organic compounds
WEDC	Water Engineering and Development Centre, University of Loughborough, United Kingdom
WHO	World Health Organization
WMO	World Meteorological Organization
WSP	Water Safety Plan
γ-HCH	1α,2α,3β,4α,5α,6β-hexachlorocyclohexane (lindane)

Section I

Scientific background

1

Groundwater and public health

G. Howard, J. Bartram, S. Pedley, O. Schmoll, I. Chorus and P. Berger

Water-related disease remains one of the major health concerns in the world. Diarrhoeal diseases, which are largely derived from poor water and sanitation, accounted for 1.8 million deaths in 2002 and contributed around 62 million Disability Adjusted Life Years per annum (WHO, 2004a). On a global scale, this places diarrhoeal disease as the sixth highest cause of mortality and third in the list of morbidity and it is estimated that 3.7 per cent of the global disease burden is derived from poor water, sanitation and hygiene (Prüss-Üstün *et al.*, 2004). This health burden is primarily borne by the populations in developing countries and by children.

At 2002 estimates, roughly one-sixth of humanity (1.1 billion people) lack access to any form of improved water supply within 1 kilometre of their home, and approximately 40 per cent of humanity (2.6 billion people) lack access to some form of improved excreta disposal (WHO and UNICEF, 2004). These figures relate to the clear definitions provided in the updated Global Water Supply and Sanitation Assessment Report and are shown in Table 1.1 below.

If the quality of water or sanitation were taken into account, these numbers of people without access to water supplies and sanitation would increase even further.

Endemic and epidemic disease derived from poor water supply affects all nations. Outbreaks of waterborne disease continue to occur in both developed and developing

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countries, leading to loss of life, avoidable disease and economic costs to individuals and communities. The improvement of water quality control strategies, in conjunction with improvements in excreta disposal and personal hygiene can be expected to deliver substantial health gains in the population.

Table 1.1. Definition of improved and unimproved water supply and sanitation facilities (WHO and UNICEF, 2000)

Water supply		**Sanitation**	
Improved	Unimproved	Improved	Unimproved
Household connection	Unprotected well	Connection to a public sewer	Service or bucket latrines (excreta removed manually)
Public standpipe	Unprotected spring	Connection to a septic system	
Boreholes	Vendor-provided water	Pour-flush latrine	Public latrines
Protected dug well	Bottled water	Simple pit latrine	Latrines with an open pit
Protected spring	Tanker-truck provided water	Ventilated improved pit latrine	
Rainwater collection			

This monograph provides information on strategies for the protection of groundwater sources used for drinking-water as a component of an integrated approach to drinking-water safety management (WHO, 2004b). The importance of source protection as the first stage of managing water quality has been an important component in both national and international efforts. In their *Guidelines for Drinking-water Quality*, WHO (2004b and previous editions) emphasize the need for effective source protection.

The focus of this monograph is the public health aspects of groundwater protection. It does not address environmental concerns, such as ecological protection. The control of some pollutants, whilst of little importance for health, may be very important to environmental protection. For guidance on these areas, readers should consult appropriate texts such as Chapman (1996).

1.1 GROUNDWATER AS A SOURCE OF DRINKING-WATER

Groundwater is the water contained beneath the surface in rocks and soil, and is the water that accumulates underground in aquifers. Groundwater constitutes 97 per cent of global freshwater and is an important source of drinking-water in many regions of the world. In many parts of the world groundwater sources are the single most important supply for the production of drinking-water, particularly in areas with limited or polluted surface water sources. For many communities it may be the only economically viable option. This is in part because groundwater is typically of more stable quality and better microbial quality than surface waters. Groundwaters often require little or no treatment to be suitable for drinking whereas surface waters generally need to be treated, often extensively. There are many examples of groundwater being distributed without treatment. It is vital therefore that the quality of groundwater is protected if public health is not to be compromised.

National statistics for the use of groundwater as a source of drinking-water are sparse, but the importance of this resource is highlighted by figures published in Europe and the USA. The proportion of groundwater in drinking-water supplies in some European countries is illustrated in Table 1.2 and for the USA in Table 1.3. The data show that reliance upon groundwater varies considerably between countries; for example, Norway takes only 13 per cent of its drinking-water from groundwater sources, whereas Austria and Denmark use groundwater resources almost exclusively for drinking-water supply. A global estimate of one-third of the world's population depending on groundwater supply is given by Falkenmark (2005).

Table 1.2. Proportion of groundwater in drinking-water supplies in selected European countries (EEA, 1999; UNECE, 1999)

Country	Proportion	Country	Proportion
Austria	99%	Bulgaria	60%
Denmark	98%	Finland	57%
Hungary	95%	France	56%
Switzerland	83%	Greece	50%
Portugal	80%	Sweden	49%
Slovak Republic	80%	Czech Republic	43%
Italy	80%	United Kingdom	28%
Germany	72%	Spain	21%
Netherlands	68%	Norway	13%

The data from the USA demonstrates the importance of groundwater particularly for smaller supplies, reflecting the generally limited treatment requirements. However, this has implications for control of public health risks as the management and maintenance of smaller supplies is often weaker than for larger, utility operated supplies (Bartram, 1999).

Table 1.3. Proportion of groundwater in drinking-water supplies in the USA by size of supply (US EPA, 2004)

Population served	Proportion groundwater	Proportion surface water
<500	89%	11%
500-1000	78%	22%
1001-3300	70%	30%
3301-10 000	57%	43%
10 000-50 000	43%	57%
>50 000	26%	74%

Within countries the usage of groundwater may also vary substantially, depending on the terrain and access to alternative water sources. For instance, in the USA it ranges from 25 per cent or less in Colorado and Kentucky to more than 95 per cent in Hawaii and Idaho. In rural areas of the USA, 96 per cent of domestic water comes from groundwater. In the United Kingdom, although the national average for groundwater usage is 28 per cent, the southern counties of England depend more heavily on groundwater than the northern counties, Wales and Scotland.

In Latin America, many of the continent's largest cities – Mexico City, Mexico, Lima, Peru, Buenos Aires, Argentina and Santiago de Chile, Chile – obtain a significant proportion of their municipal water supply from groundwater. In India, China, Bangladesh, Thailand, Indonesia and Viet Nam more than 50 per cent of potable supplies are provided from groundwater. In Africa and Asia, most of the largest cities use surface water, but many millions of people in rural areas and low-income peri-urban communities are dependent on groundwater. These populations are most vulnerable to waterborne disease. Pedley and Howard (1997) estimate that as much as 80 per cent of the drinking-water used by these communities is abstracted from groundwater sources.

Where it is available, groundwater frequently has important advantages over surface water. It may be conveniently available close to where it is required, can be developed at comparatively low cost and in stages to keep pace with rising demand. Although small, simple surface water supplies can be achieved relatively cheaply and pumping groundwater from deep aquifers may create significant operating costs, overall the capital costs associated with groundwater development are usually lower than with large-scale surface water supplies. For the latter, large, short-term capital investments in storage reservoirs often produce large, step-wise increments in water availability and temporary excess capacity that is gradually overtaken by the continuing rising demand for water. An additional disadvantage in some circumstances is that surface water reservoirs may have multiple, sometimes conflicting functions – water supply, flood control, irrigation, hydroelectric power and recreation – and cannot always be operated for the optimum benefit of water supply.

Furthermore, aquifers are often well protected by layers of soil and sediment, which effectively filter rainwater as it percolates though them, thus removing particles, pathogenic microorganisms and many chemical constituents. Therefore it is generally assumed to be a relatively safe drinking-water source.

However, groundwater has been termed the 'hidden sea' – *sea* because of the large amount of it, and *hidden* because it is not visible, thus pollution pathways and processes are not readily perceived (Chapelle, 1997). This highlights a key issue in the use of aquifers as drinking-water source, showing that particular attention is needed to ascertain whether the general assumption of groundwater being safe to drink is valid in individual settings. As discussed below, understanding the source-pathway-receptor relationship in any particular setting is critical to determine whether pollution will occur.

Whilst there is a large volume of groundwater in this 'hidden sea', its replenishment occurs slowly – at rates varying between locations. Over-exploitation therefore readily occurs, bringing with it additional quality concerns.

1.2 THE PUBLIC HEALTH AND SOCIOECONOMIC CONTEXT OF GROUNDWATER PROTECTION

The use of groundwater as a source of drinking-water is often preferred because of its generally good microbial quality in its natural state. Nevertheless, it is readily contaminated and outbreaks of disease from contaminated groundwater sources are reported from countries at all levels of economic development. Some groundwaters naturally contain constituents of health concern: fluoride and arsenic in particular. However, understanding the impact of groundwater on public health is often difficult and the interpretation of health data complex. This is made more difficult as many water supplies that use groundwater are small and outbreaks or background levels of disease are unlikely to be detected, especially in countries with limited health surveillance. Furthermore, in outbreaks of infectious disease, it is often not possible to identify the cause of the outbreak and many risk factors are typically involved.

Throughout the world, there is evidence of contaminated groundwater leading to outbreaks of disease and contributing to background endemic disease in situations where groundwater sources used for drinking have become contaminated. However, diarrhoeal disease transmission is also commonly due to poor excreta disposal practices and the improvement of sanitation is a key intervention to reduce disease transmission (Esrey *et al.,* 1991; Curtis *et al*., 2000). Furthermore, water that is of good quality at its source may be re-contaminated during withdrawal, transport and household storage. This may then require subsequent treatment and safe storage of water in the home (Sobsey, 2002).

Ensuring that water sources are microbially safe is important to reduce health burdens. However, a balance in investment must be maintained to ensure that other interventions, also important in reducing disease, are implemented. Diverting resources away from excreta disposal, improved hygiene practices in order to achieve very good quality water in sources may be counter-productive (Esrey, 1996). Balancing investment decisions for public health gain from water supply and sanitation investment is complex and does not simply reflect current knowledge (or lack of) regarding health benefits, but also the demands and priorities of the population (Briscoe, 1996).

Groundwater is generally of good microbial quality, but may become rapidly contaminated if protective measures at the point of abstraction are not implemented and well maintained. Further problems are caused by the creation of pathways that short-circuit the protective measures and natural layers offering greatest attenuation, for instance abandoned wells and leaking sewers. Pollution may also occur in areas of recharge, with persistent and mobile pollutants representing the principal risks.

The control of the microbial quality of drinking-water should be the first priority in all countries, given the immediate and potentially devastating consequences of waterborne infectious disease (WHO, 2004b). However, in some settings the control of chemical quality of groundwater may also be a priority, particularly in response to locally important natural constituents such as fluoride and arsenic. Furthermore, hazardous industrial chemicals and pesticides which can accumulate over time may potentially render a source unusable. The scale, impact and the often lack of feasible clean-up technologies for some chemical contamination in groundwater means that they should receive require priority for preventative and remedial strategies.

Groundwater also has a socioeconomic value. It is often a lower cost option than surface water as the treatment requirements are typically much lower. In many countries, groundwater is also more widely available for use in drinking-water supply. This may provide significant advantages to communities in obtaining affordable water supplies, which may have benefits in terms of promoting greater volumes of water used for hygiene and other purposes. The natural quality of groundwater also makes its use valued in industry, and it may provide environmental benefits through recharge of streams and rivers or for the growth of vegetation. These other benefits reinforce the need for its protection.

The actions taken to protect and conserve groundwater will also create costs to society, through lost opportunity costs for productive uses of land and increased production costs caused by pollution containment and treatment requirements. When developing protection plans and strategies, the cost of implementing such measures should be taken into consideration, as well as the cost of not protecting groundwater, in order for balanced decisions to be made.

1.3 GROUNDWATER QUANTITY

The interrelated issues of groundwater quality and quantity can best be addressed by management approaches encompassing entire groundwater recharge areas or groundwater catchments. These units are appropriate both for assessing pollution potential and for developing management approaches for protection and remediation.

Excessive groundwater abstraction in relation to recharge will lead to depletion of the resource and competition between uses, e.g. between irrigation and drinking-water supply. Strong hydraulic gradients ensuing from abstraction can induce the formation of preferential flow paths, reducing the efficacy of attenuation processes, and thus lead to elevated concentrations of contaminants in groundwater. Furthermore, changes in groundwater levels induced by abstraction may change conditions in the subsurface environment substantially, e.g. redox conditions, and thus induce mobilization of natural or anthropogenic contaminants.

Groundwater quantity issues may have substantial impacts on human health. Lack of a safe water supply affects disease incidence for instance by restricting options for personal and household hygiene. Competing demands for groundwater, often for irrigation and sometimes for industry, may lead to shortage of groundwater for domestic use. In such situations it is important to ensure allocation of sufficient groundwater reserves for potable and domestic use and health authorities often play an important role in this. This monograph largely focuses on water quality issues, as these are of direct relevance to the provision of safe drinking-water. Quantity issues are therefore addressed in the context of their impact on groundwater quality.

This text is concerned with groundwater as a source of drinking-water supply. However, in many locations other uses, for example irrigation, account for the largest fraction of groundwater abstraction, and inter-sectoral collaboration may be needed to develop effective groundwater allocation schemes.

1.4 DISEASE DERIVED FROM GROUNDWATER USE

Groundwater contributes to local and global disease burdens through the transmission of infectious disease and from chemical hazards.

1.4.1 Infectious disease transmission through groundwater

The global incidence of waterborne disease is significant, though it can only be estimated since reliable data are not sufficiently available for direct assessment of disease cases (Prüss-Üstün *et al.*, 2004). The contribution of groundwater to the global incidence of waterborne disease cannot be assessed easily, as there are many competing transmission routes; confounding from socioeconomic and behavioural factors is typically high; definitions of outcome vary; and, exposure-risk relationships are often unclear (Esrey *et al.*, 1991; Payment and Hunter, 2001; Prüss and Havelaar, 2001). Many waterborne disease outbreaks could have been prevented by good understanding and management of groundwaters for health. Pathogen contamination has often been associated with simple deficiencies in sanitation but also with inadequate understanding of the processes of attenuation of disease agents in the subsurface.

The most comprehensive reports of waterborne disease outbreaks come from two countries, the USA and the United Kingdom, and some indications of the role of groundwater in the infectious diarrhoeal disease burden can be estimated in these countries (Craun, 1992; Hunter, 1997; Payment and Hunter, 2001; Craun *et al.*, 2003; 2004).

Lee *et al.* (2002) identified that of 39 outbreaks of waterborne disease in the USA between 1999 and 2000, 17 were due to consumption of untreated groundwater, although approximately half of these outbreaks were reported from individual water supplies, which are not operated by a utility and served less than 15 connections or less than 25 persons. A further eight were reported in non-community supplies, which serve facilities such as schools, factories and restaurants.

A detailed analysis of the incidence of waterborne disease in the USA was published in the mid-1980s by Craun (1985), which is still relevant. In his summary of data from the period between 1971 and 1982, Craun reports that untreated or inadequately treated groundwater was responsible for 51 per cent of all waterborne disease outbreaks and 40 per cent of all waterborne illness. A recent analysis of public health data in the USA showed little change to the epidemiology of disease outbreaks (Craun *et al.*, 1997). Between 1971 and 1994, 58 per cent of all waterborne outbreaks were caused by contaminated groundwater systems, although this is in part is due to the higher number of water supplies using groundwater than those using surface water.

Craun *et al.* (2003) report that for the period 1991-1998, 68 per cent of the outbreaks in public systems were associated with groundwater, an increase from previous reports (Craun, 1985; Craun *et al.*, 1997). However, this apparent increase is likely to be due in part to the introduction of the USA Surface Water Treatment Rule in 1991, which requires ‘conventional filtration’ of most surface water supplies. In general it appears that waterborne outbreaks in the USA decreased after 1991, with the introduction of more stringent monitoring and treatment requirements.

Craun *et al.* (2004) provide a detailed discussion of waterborne outbreaks in relation to zoonotic organisms (organisms with an animal as well as human reservoir) between 1971 and 2000 in the USA. They note that 751 outbreaks were reported linked to drinking-water supplies during this period, the majority (648) being linked to community (year-round public service) water supplies. The aetiology was either known or suspected in 89 per cent of the outbreaks and zoonotic agents caused 118 outbreaks in community systems representing 38 per cent of outbreaks associated with these systems and 56 per cent of those where aetiology was identified. The data show that the majority of illnesses and deaths were caused by zoonotic agents in the reported waterborne outbreaks.

The zoonotic agents of greatest importance were *Giardia*, *Campylobacter*, *Cryptosporidium*, *Salmonella*, and *E. coli* in outbreaks caused by contaminated drinking-water. The majority of outbreaks caused by zoonotic bacteria (71 per cent) and *Cryptosporidium* (53 per cent) were reported in groundwater supplies. The use of contaminated, untreated or poorly treated groundwater was responsible for 49 per cent of outbreaks caused by *Campylobacter*, *Salmonella*, *E. coli*, and *Yersinia*. Groundwater that was contaminated, untreated or poorly treated contributed 18 per cent of all outbreaks caused by *Giardia* and *Cryptosporidium*.

Kukkula *et al.* (1997) describe an outbreak of waterborne viral gastroenteritis in the Finnish municipality of Noormarkku that affected some 1500-3000 people, i.e. between 25 and 50 per cent of the exposed population. Laboratory investigations confirmed that adenovirus, Norwalk-like virus and group A and C rotaviruses were the principal causative agents. The source of the outbreak was thought to be a groundwater well situated on the embankment of a river polluted by sewage discharges. In 1974 an outbreak of acute gastrointestinal illness at Richmond Heights in Florida, USA was traced to a supply well that was continuously contaminated with sewage from a nearby septic tank (Weissman *et al*., 1976). The main aetiological agent was thought to be *Shigella sonnei*. During the outbreak approximately 1200 cases were recorded from a population of 6500.

Outbreaks of cryptosporidiosis have also been linked to groundwater sources, despite being usually regarded as a surface water problem. A large outbreak of cryptosporidiosis occurred in 1998 in Brush Creek, Texas, USA from the use of untreated groundwater drawn from the Edwards Plateau karst aquifer (Bergmire-Sweat *et al.*, 1999). There were 89 stool-confirmed cases and the estimated number of cases was between 1300 and 1500. This outbreak was associated with the consumption of water drawn from deep wells of over 30 m located more than 400 m from Brush Creek.

In 1997, epidemiological investigations traced an outbreak of cryptosporidiosis in the United Kingdom to water abstracted from a deep chalk borehole. Three hundred and forty five confirmed cases were recorded by the investigation team, who claimed this to be the largest outbreak linked to groundwater to have been reported (Willcocks *et al*., 1998). This incident has particular significance because the water used in the supply was drawn from a deep borehole and was filtered before distribution.

In the outbreak of *E. coli* O157:H7 and *Campylobacter* in Walkerton, Ontario in Canada in 2000, the original source of pathogens appears to have derived from contaminated surface water entering into a surface water body directly linked to an abstraction borehole (Health Canada, 2000). Although the series of events leading to the outbreak indicate a failure in subsequent treatment and management of water quality, better protection of groundwater would have reduced the potential for such an outbreak. An outbreak of *E. coli* O157:H7 occurred among attendees at the Washington Country Fair, New York, USA and was shown to be caused by consuming water from a contaminated shallow well that had no chlorination (CDC, 1999). A total of 951 people reported having diarrhoea after attending the fair and stool cultures from 116 people yielded *E .coli* O157:H7. This outbreak resulted in hospitalization of 65 people, 11 children developed haemolytic syndrome and two people died.

In developing countries evidence of the role of groundwater in causing disease outbreaks is more limited, although there have been numerous studies into the impact of drinking-water, sanitation and hygiene on diarrhoeal disease. In part the limited data on groundwater related outbreaks reflects the often limited capacity of local health surveillance systems to identify causal factors and because it is common that several factors may be implicated in the spread of disease. However, the limited data on outbreaks specifically linked to groundwater may also reflect that improved groundwater sources are generally of relatively good quality. Diarrhoeal disease related directly to drinking-water is most likely to result from consumption of poorly protected or unimproved groundwater sources, untreated or poorly treated surface water, contamination of distribution systems and recontamination of water during transport.

Pokhrel and Viraraghavan (2004) in a review of diarrhoeal disease in Nepal in relation to water and sanitation, cite examples from South Asia where contamination of groundwater supplies has led to outbreaks of disease.

A study of local populations in Kanpur, India recorded an overall incidence rate of waterborne disease of 80.1 per 1000 population (Trivedi *et al*., 1971). The communities in the study areas took water from shallow groundwater sources, analysis of which revealed that over 70 per cent of the wells were contaminated. Of the cases of waterborne disease investigated, the greatest proportion was of gastroenteritis, followed by dysentery.

In addition to outbreaks, there is some evidence of contaminated groundwater contributing to background levels of endemic diarrhoeal disease. For example, Nasinyama *et al.* (2000) showed that the use of protected springs in Kampala, Uganda which were in generally in poor condition was associated with higher rates of diarrhoea than the use of piped water supplies. Much of this disease burden is thought to occur in developing countries where the use of untreated water from shallow groundwater sources is common in both rural and peri-urban settlements (Pedley and Howard, 1997).

1.4.2 Chemical hazards

The risk to health from chemicals is typically lower than that from pathogens. The health effects of most, but not all, chemical hazards arise after prolonged exposure, and tend to be limited to specific geographical areas or particular water source types. Much remains to be understood about the epidemiology of diseases related to chemical hazards in water and the scale of disease burden remains uncertain. However, some data do exist. Craun *et al.* (2004) report that 11 per cent of waterborne outbreaks in the USA between 1971 and 2000 were associated with acute effects following ingestion of a chemical.

Ensuring that chemicals of health concern do not occur at significant concentrations in groundwaters implies understanding sources of pollution, aquifer vulnerability and specific attenuation processes as well as recognizing the importance of naturally-occurring chemicals of health concern. In groundwater, however, there are two contaminants in particular that represent particular hazards of concern: fluoride and arsenic.

Fluoride affects bone development and in excess leads to dental or, in extreme form, skeletal fluorosis. The latter is a painful debilitating disease that causes physical impairment. However, too little fluoride has also been associated with dental caries and other dental ill-health (WHO, 2004b). Drinking-water is the principal route of exposure to fluoride in most settings, although burning of high fluoride coal is a significant route of exposure in parts of China (Gu *et al.*, 1990).

Arsenic causes concern given the widespread occurrence in shallow groundwaters in Bangladesh, West Bengal, India and in groundwater in several other countries. The scale of arsenic contamination is most severe in the shallow groundwater of Bangladesh. At present, the total population exposed to elevated arsenic concentrations in drinking-water in Bangladesh remains uncertain, but is thought to be somewhere between 35 and 77 million and has been described as the largest recorded poisoning in history (Smith *et al.,* 2000; BGS and DPHE, 2001). Problems are also noted in countries as diverse as Mexico, Canada, Hungary and Ghana, although the source of arsenic and control strategies available vary. The true scale of the public health impact of arsenic in groundwater remains uncertain and the epidemiology is not fully understood.

In the case of Bangladesh, the lack of country-wide case-controlled studies makes estimating prevalence of arsenicosis difficult. In a recent evaluation of data collected by the DPHE-Unicef arsenic mitigation programmes, Rosenboom *et al.* (2004) found a prevalence rate of arsenicosis (keratosis, melanosis and de-pigmentation) of 0.78 per 1000 population exposed to elevated arsenic (above 50 µg/l) in 15 heavily affected Upazilas (an administrative unit in Bangladesh). These authors note, however, that the data were difficult to interpret and that exposure had been relatively short and therefore these numbers could increase. The lack of a national cancer prevalence study makes estimations outside small cross-section studies problematic.

Increasing numbers of countries in Asia are now identifying arsenic contamination of groundwater (including Cambodia, China, Laos, Myanmar, Nepal, Pakistan and Viet Nam). In India, increasing numbers of areas are being identified as arsenic affected beyond West Bengal (School of Environmental Studies, Javadpur University, 2004). This demonstrates that arsenic is an important contaminant for public health and concern is growing.

Other chemical contaminants of concern in groundwater may also lead to health problems. These include nitrate, uranium and selenium. Of these, nitrate is of concern as it is associated with an acute health effect (methaemoglobinaemia or infantile cyanosis). The scale of the health burden derived from nitrate remains uncertain although it has been suggested to cause significant health problems in some low-income countries where levels in groundwater reach extremely high values (Melian *et al.*, 1999). Nitrate is also of concern given that it is stable once in groundwater with reasonably high oxygen content, where it will not degrade. Thus it may accumulate to a long-term water resource problem that is expensive and difficult to remediate and whose effect may not be noticed until concentrations become critical.

1.5 GROUNDWATER IN THE CONTEXT OF INTERNATIONAL ACTIVITIES TO REDUCE WATER-RELATED DISEASE

The International Drinking Water Supply and Sanitation Decade (IDWSSD; 1980-1990) provided a sustained focus on the need for concerted efforts to accelerate activities to increase global access to safe water supply and to sanitation. The Rio Earth Summit (1992) placed water both as resource and as water supply on the priority agenda and the World Summit on Sustainable Development in 2002 also placed safe drinking-water as a key component of sustainable development. In September 2000, 189 UN Member States adopted the Millennium Development Goals (MDGs). Target 10 of the MDGs is to halve by 2015 the proportion of people without sustainable access to safe drinking-water and basic sanitation; the baseline for this target has been set as 1990. Other important initiatives have included a Protocol on Water and Health to the 1992 Convention on Use of Transboundary Watercourses and International Lakes (Box 1.1).

Box 1.1. The WHO-UNECE Protocol on Water and Health (UNECE and WHO, 1999)

The WHO-UNECE Protocol on Water and Health to the 1992 Convention on the Protection and Use of Transboundary Watercourses and International Lakes is an international legal instrument on the prevention, control and reduction of water-related diseases in Europe.

A major product of the Third European Ministerial Conference on Environment and Health (1999), the Protocol was signed at the Conference by 35 countries and represents the first major international legal approach for controlling water-related disease. It has become legally binding for the 16 countries that have ratified it in 2005. By adopting the Protocol, the signatories agreed to take all appropriate measures towards achieving:

- adequate supplies of wholesome drinking-water;
- adequate sanitation of a standard which sufficiently protects human health and the environment;
- effective protection of water resources used as sources of drinking-water and their related water ecosystems from pollution from other causes;
- adequate safeguards for human health against water-related diseases;
- effective systems for monitoring and responding to outbreaks or incidents of water-related diseases.

The Global Environmental Monitoring System Water programme, launched in 1977 by UNEP in collaboration with UNESCO, WHO and WMO, has the overall objective of observing and assessing global water quality issues in rivers, lakes and groundwater by collecting together and interpreting data from national monitoring networks. A first assessment of freshwater quality published in 1989 (Meybeck *et al.*, 1989) included discussion of links between water quality and health. The programme was reviewed and evaluated in 2001 with a view to enhancing its ability to contribute to inter-agency global programmes, including the Global International Waters Assessment and the UN-wide World Water Assessment Programme.

Recently, the World Bank has established a groundwater management advisory team (GW·MATE) to develop capacity and capability in groundwater resource management and quality protection through World Bank programmes and projects and through the activities of the Global Water Partnerships regional networks.

WHO's activities in support of safe drinking-water span across the range of its functions as a specialized agency of the UN system (Box 1.2).

Box 1.2. WHO activities related to safe drinking-water

Evidence and information: Burden of disease estimates (at global level and guidance on their conduct at other levels); and cost-effectiveness water interventions (generically at global level and guidance on their conduct at other levels).

Status and trends: Assessing coverage with access to improved sources of drinking-water, and to safe drinking-water (with UNICEF through the Joint Monitoring Programme).

Tools for good practice: Evidence-based guidance on effective (and ineffective) technologies, strategies and policies for health protection through water management.

Normative guidelines: Evidence-based and health-centred norms developed to assist development of effective national and regional regulations and standards.

Country cooperation: Intensive links to individual countries through its network of six regional offices, regional environment centres and country offices.

Research and testing: Encouraging and orienting research; developing and encouraging the application of protocols to increase harmonization, exchange and use of data. Publication with IWA of the Journal of Water and Health (http://www.iwapublishing.com/template.cfm?name=iwapwaterhealth).

Tools for disease reductions: Focussing especially on settings such as healthy cities, healthy villages, healthy schools.

1.6 GROUNDWATER IN THE WHO GUIDELINES FOR DRINKING-WATER QUALITY

Since 1958 WHO has published at about ten year intervals several editions of *International Standards for Drinking-water* and subsequently *Guidelines for Drinking-water Quality*. The third edition of the Guidelines, published in 2004, includes a substantial update of the approach towards the control of microbial hazards in particular based on a preventive management approach. In preparing the third edition of the Guidelines a series of state-of-the-art reviews was prepared on aspects of water quality management and human health (Box 1.3) of which *Protecting Groundwater for Health* is one.

In the overall context of the *Guidelines for Drinking-water Quality* (GDWQ), this monograph serves two purposes: it provides the background information on potential groundwater contamination as well as approaches to protection and remediation that were taken into account in developing the third edition of the GDWQ. Further, *Protecting Groundwater for Health* supplements it by providing comprehensive information on: assessing the potential for contamination of groundwater resources, prioritizing hazards and selecting management approaches appropriate to the specific socioeconomic and institutional conditions.

Box 1.3. State of the art reviews supporting the third edition of WHO *Guidelines for Drinking-water Quality* (selected titles)

Water Safety Plans: Managing Drinking-water Quality from Catchment to Consumer (Davison *et al*., 2005)

Safe Piped Water: Managing Microbial Water Quality in Piped Distribution Systems (Ainsworth, 2004)

Water Treatment and Pathogen Control: Process Efficiency in Achieving Safe Drinking-water (LeChevallier and Au, 2004)

Assessing Microbial Safety of Drinking-water: Improving Approaches and Methods (Dufour *et al*., 2003)

Quantifying Public Health Risks in the WHO Guidelines for Drinking-water Quality: A Burden of Disease Approach (Havelaar and Melse, 2003)

Rapid Assessment of Drinking-water Quality: A Handbook for Implementation (Howard *et al*., 2003)

Domestic Water Quantity, Service Level and Health (Howard and Bartram, 2003)

Managing Water in the Home: Accelerated Health Gains from Improved Water Supply (Sobsey, 2002)

Water Quality: Guidelines, Standards and Health: Assessment of Risk and Risk Management for Water-related Infectious Disease (Fewtrell and Bartram, 2001)

Chemical Safety of Drinking-water: Assessing Priorities for Risk Management (in preparation)

A central approach of the third edition of the GDWQ is the development of a reliable preventive safety management approach: a Framework for Safe Drinking-water, the three key requirements of which are described in Box 1.4. This includes the introduction of Water Safety Plans (WSPs) as a management tool for avoidance and control of groundwater contamination. These are described in Chapter 16 of this book.

Box 1.4. The three key requirements of WHO's Framework for Safe Drinking-water (WHO, 2004b)

1. *Health-based targets* based on an evaluation of health concerns.
2. Development of a *Water Safety Plan* (WSP) that includes:
    - *System assessment* to determine whether the water supply (from source through treatment to the point of consumption) as a whole can deliver water of a quality that meets the health based targets.
    - *Operational monitoring* of the control measures in the drinking-water supply that are of particular importance in securing drinking-water safety.
    - *Management plans* documenting the system assessment and monitoring plans and describing actions to be taken in normal operating and incident conditions, including upgrading, documentation and communication.
3. A system of *independent surveillance* that verifies that the above are operating properly.

This approach meets the need for developing an understanding of the key steps in the supply chain at which pollution may be introduced or prevented, increased or reduced. Effective management implies identifying these, ideally through a quantitative system assessment. The framework also includes identification of the appropriate measures to ensure that processes are operating within the bounds necessary to ensure safety. For drinking-water supply from groundwaters these controls may extend into the recharge area but may also relate to more immediate source protection measures, such as well-head protection. Some of the measures to verify safe operation of processes relevant to groundwater safety may be amenable to sophisticated approaches such as on-line monitoring of levels (e.g. of landfill effluents). Others (such as the ongoing integrity of a well plinth) are best approached through periodic inspection regimes.

1.7 REFERENCES

Ainsworth, R. (ed.) (2004) *Safe Piped Water: Managing Microbial Water Quality in Piped Distribution Systems*. WHO Drinking-water Quality Series, IWA Publishing, London. http://www.who.int/water_sanitation_health/dwq/924156251X/en/index.html (accessed January 11, 2006).

Bartram, J.K. (1999) Effective monitoring of small drinking water supplies. In *Providing Safe Drinking Water in Small Systems: Technology, Operations and Economics*, (eds. J.A. Cotruvo, G.F. Craun and N. Hearne), pp. 353-365, Lewis Publishers, Washington DC.

Bergmire-Sweat, D., Wilson, K., Marengo, L., Lee, Y.M., MacKenzie, W.R., Morgan, J., Von Alt, K., Bennett, T., Tsang, V.C.W. and Furness, B. (1999) Cryptosporidiosis in Brush Creek:

Describing the epidemiology and causes of a large outbreak in Texas, 1998. In *Proc. Internat. Conf. on Emerging Infectious Diseases*, Milwaukee, WI, AWWA, Denver, Colorado.

BGS and DPHE (2001) *Arsenic Contamination of Groundwater in Bangladesh*. BGS Technical Report WC/00/19.

Briscoe, J. (1996) Financing water and sanitation services: the old and new challenges. *Water Supply*, **14**(3/4), 1-17.

CDC (1999) Outbreak of *Escherichia coli* O157:H7 and *Camplyobacter* among attendees of the Washington County Fair – New York 1999. *Morbidity and Mortality Weekly Report*, **48**(36), 803-804.

Chapelle, F.H. (1997) *The Hidden Sea: ground water, springs and wells*. Geoscience Press Inc., Arizona.

Chapman, D. (ed.) (1996) *Water Quality Assessments*. E&F Spon, London.

Craun, G.F. (1985) A summary of waterborne illness transmitted through contaminated groundwater. *J. Environ. Health*, **48**, 122-127.

Craun, G.F. (1992) Waterborne disease outbreaks in the United States of America: causes and prevention. *World Health Statistics Q.*, **45**(2-3), 192-199.

Craun, G.F., Berger, P.S. and Calderon, R.L. (1997) Coliform bacteria and waterborne disease outbreaks. *JAWWA*, **89**, 96-104.

Craun, G.F., Calderon, R.L. and Nwachuku, N. (2003) Causes of Waterborne Outbreaks Reported in the United States, 1991-1998. In *Drinking Water and Infectious Disease, Establishing the Links*, (eds. P. Hunter, M. Waite and E. Rochi), pp. 105- 117, CRC Press and IWA Publishing, Boca Raton, Florida.

Craun, G.F., Calderon R.L. and Craun, M.F. (2004) Waterborne Outbreaks Caused by Zoonotic Pathogens in the United States. In *Waterborne Zoonoses: Identification, causes and control*, (eds. J.A. Cotruvo, A. Dufour, G. Rees, J. Bartram, R. Carr, D.O. Cliver, G.F. Craun, R. Fayer and V.P.J. Gannon), pp. 120-135, WHO, IWA Publishing, London.

Curtis, V., Cairncross, S. and Yonli, R. (2000) Domestic hygiene and diarrhoea - pinpointing the problem. *Tropical Medicine and Internat. Health*, **5**(1), 22-32.

Davison, A., Howard, G., Stevens, M., Callan, P., Fewtrell, L., Deere, D. and Bartram, J. (2005) *Water Safety Plans: Managing Drinking-water Quality from Catchment to Consumer*. World Health Organization, Geneva. http://www.who.int/water_sanitation_health/dwq/wsp0506/en/index.html (accessed on January 11, 2006).

Dufour, A., Snozzi, M., Koster, W., Bartram, J., Ronchi, E. and Fewtrell, L. (eds.) (2003) *Assessing Microbial Safety of Drinking-water: Improving Approaches and Methods*. WHO Drinking-water Quality Series, IWA Publishing, London http://www.who.int/water_sanitation_health/dwq/9241546301/en/index.html (accessed on January 11, 2006).

EEA (1999) *Groundwater Quality and Quantity in Europe*. Environmental Assessment Report, No. 3.

Esrey, S.A., Potash, J.B., Roberts, L. and Shiff, C. (1991) Effects of improved water supply and sanitation on ascariasis, diarrhoea, dracunculiasis, hookworm infection, schistosomiasis, and trachoma. *Bulletin of the WHO*, **69**(5), 609-621.

Esrey, S.A. (1996) Water, wastes and well-being: a multi-country study. *Am. J. Epidemiology*, **143**(6), 608-623.

Gu, S.L., Ji, R.D. and Cao, S.R. (1990) The physical and chemical characteristics of particles in indoor air where high fluoride coal burning takes place. *Biomed. Environ. Sci.*, **3**(4), 384-390.

Falkenmark, M. (2005) Water usability degradation – economist wisdom or societal madness? *Water International*, **30**(2), 136-146.

Fewtrell, L. and Bartram, J. (eds.) (2001) *Water Quality: Guidelines, Standards and Health: Assessment of Risk and Risk Management for Water-related Infectious Disease.* IWA Publishing, London.

Havelaar, A.H. and Melse, J.M. (2003) *Quantifying Public Health Risks in the WHO Guidelines for Drinking-water Quality: A Burden of Disease Approach*. RIVM report 734301022/2003, Bilthoven. http://www.who.int/water_sanitation_health/dwq/quantifyinghealthrisks/en/index.html (accessed January 11, 2006).

Health Canada (2000) Waterborne outbreak of gastroenteritis associated with a contaminated municipal water supply, Walkerton, Ontario, May-June 2000. *Canada Communicable Disease Report*, **26**(20), 170-173.

Howard, G. and Bartram, J. (2003) *Domestic Water Quantity, Service Level and Health*. World Health Organization, Geneva. http://www.who.int/water_sanitation_health/diseases/wsh0302/en/index.html (accessed January 11, 2006).

Howard, G., Ince, M. and Smith, M. (2003) *Rapid Assessment of Drinking-water Quality: A Handbook for Implementation*. Water, Engineering and Development Centre (WEDC), Loughborough.

Hunter, P.R. (1997) *Waterborne Disease: Epidemiology and Ecology*, John Wiley & Sons, Chichester, New York.

Kukkula, M., Arstila, P., Klossner, M.L., Maunula, L., Bonsdorff, C.H. and Jaatinen, P. (1997) Waterborne outbreak of viral gastroenteritis. *Scandinavian J. Infectious Disease*, **29**, 415-418.

LeChevallier, M.W. and Au, K.-K. (2004) *Water Treatment and Pathogen Control: Process Efficiency in Achieving Safe Drinking-water.* WHO Drinking-water Quality Series, IWA Publishing, London. http://www.who.int/water_sanitation_health/dwq/9241562552/en/index.html (accessed January 11, 2006).

Lee, S.H., Levy, D.A., Craun, G.F., Beach, M.J. and Calderon, R.L. (2002) Surveillance for waterborne-disease outbreaks - United States, 1999-2000. *CDC Morbidity and Mortality Weekly Report*, **51**(SS-8), www.cdc.gov.mmwr/PDF/SS/SS5108.pdf (accessed April 29, 2005).

Melian, R., Myrlian, N., Gouriev, A., Moraru, C. and Radstake, F. (1999) Groundwater quality and rural drinking-water supplies in the Republic of Moldova. *Hydrogeology J.* **7**, 188-196.

Meybeck, M., Chapman, D. and Helmer, R. (1989) *Global Freshwater Quality: a first assessment*. Published for WHO/UNEP by Blackwell Scientific, Oxford.

Nasinyama, G.W., McEwen, S.A., Wilson, J.B., Waltner-Towers, D., Gyles, C.L. and Opuda-Asibo, J. (2000) Risk factors for acute diarrhoea among inhabitants of Kampala District, Uganda. *SA Medical J.* **90**(90), 891-898.

Payment, P. and Hunter, P.R. (2001) Endemic and epidemic infectious intestinal disease and its relationship to drinking water. In *Water Quality: guidelines, standards and health*, (eds. L. Fewtrell and J. Bartram), pp. 61-88, IWA Publishing, London.

Pedley, S. and Howard, G. (1997) The public health implications of microbiological contamination of groundwater. *Q. J. Eng. Geol.*, **30**, 179-188.

Pokhrel, D. and Viraraghavan, T. (2004) Diarrhoeal disease in Nepal vis-à-vis water supply and sanitation status. *J. Water and Health*, **2**(2), 71-81.

Prüss, A. and Havelaar, A. (2001) The global burden of disease study and applications in water, sanitation and hygiene. In *Water Quality: guidelines, standards and health*, (eds. L. Fewtrell and J. Bartram), pp. 43-59, IWA Publishing, London.

Prüss-Üstün, A., Kay, D., Fewtell, L. and Bartram, J. (2004) Unsafe water, sanitation and hygiene. In: *Comparative Quantification of Health Risks: Global and Regional Burden of Disease Attributable to Selected Major Risk Factors*, (eds. Ezzati, M., Lopez, A. D., Rodgers, A. and Murray, C. J. L), Volume 2, pp. 1321-1352, World Health Organization, Geneva..

Rosenboom, J.W., Ahmed, K.M., Pfaff, A. and Madajewicz, M. (2004) Arsenic in 15 Upazilas of Bangladesh: Water supplies, health and behaviour. *Report prepared for APSU, Unicef and DPHE*, Dhaka.

School of Environmental Studies (2004). Javadpur Univeristy, Kolkatta, West Bengal, www.soesju.org/arsenic/ (accessed April 29, 2005).

Smith, A.H., Lingas, E.O. and Rahman, M. (2000) Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bulletin of the WHO*, **78**(9), 1093-1103.

Sobsey, M.D. (2002) *Managing Water in the Home: accelerated health gains from improved water supply*. World Health Organization, Geneva. http://www.who.int/water_sanitation_health/dwq/wsh0207/en/index.html (accessed January 11, 2006).

Trivedi, B.K., Gandhi, H.S. and Shukla, M.K. (1971) Bacteriological water quality and the incidence of waterborne diseases in a rural population. *Indian J. Med. Sciences*, **25**, 795-801.

UNECE (1999) *Inventory of Transboundary Groundwaters*. UNECE Task Force on Monitoring and Assessment. Guidelines on monitoring of transboundary groundwaters, vol. 1, Supporting Technical Documents.

UNECE and WHO (1999) Protocol on Water and Health to the 1992 Convention on the Protection and use of Transboundary Watercourses and International Lakes. http://www.euro.who.int/Document/Peh-ehp/ProtocolWater.pdf (accessed January 11, 2006).

US EPA (2004) www.epa.gov/safewater/electronic/presentations/sdwq/pt4/sdwa57.html (accessed April 29, 2005).

Weissman, J.B., Craun, G.F., Lawrence, D.N., Pollard, R.A., Suslow, M.S. and Gangarosa, E.J. (1976) An epidemic of gastroenteritis traced to a contaminated public water supply. *Am. J. Epidemiology*, **103**, 319-398.

Willocks, L., Crampin, A., Milne, L., Seng, C., Susman, M., Gair, R., Moulsdale, M., Shafi, S., Wall, R., Wiggins, R. and Lightfoot, N. (1998) A large outbreak of cryptosporidiosis associated with a public water supply from a deep chalk borehole. Outbreak Investigation Team. *Communicable Disease and Public Health*, **1**, 239-243.

WHO (2004a) *World Health Report 2004*. WHO, Geneva.

WHO (2004b) *Guidelines for Drinking-Water Quality: Recommendations*. 3rd edn, vol 1, WHO, Geneva.

WHO and UNICEF (2000) *Global Water Supply and Sanitation Assessment 2000 Report*. WHO, Geneva and UNICEF, New York.

2

Groundwater occurrence and hydrogeological environments

J. Chilton and K.-P. Seiler

Many people are surprised to discover that groundwater is widely and heavily used throughout the world. During severe droughts in arid regions of the world, newspapers and television carry dramatic pictures of dry wells in rural communities and people walking long distances for small amounts of household water. However, groundwater usage is important in both humid and arid regions, and it can be a revelation that many cities are dependent on groundwater and use such large volumes of groundwater in their public water supplies.

One reason for this general lack of awareness is that groundwater is usually a hidden resource, out of sight and therefore out of mind. It is, nevertheless, as valuable an asset in water supply terms as rivers, lakes and reservoirs, and deserves to be equally protected. As a consequence of this lack of awareness, the main features of groundwater systems are poorly known or even misunderstood. To provide the necessary basic knowledge of hydrogeology for the reader to fully appreciate the rest of the monograph, this chapter aims to rectify the situation by placing place groundwater in its appropriate context within the wider water cycle. It then summarizes the ways in which groundwater occurs and moves, and how it is replenished. The characteristics of the main types of geological settings are described so that the reader is able to see how different hydrogeological environments vary in their response to the pressures of water abstraction and pollution.

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This knowledge will be used to help guide the information requirements outlined in Chapter 8. In relation to the overall source-pathway-receptor approach to the assessment of pollution this chapter is mainly focussed on the pathway through groundwater systems to the receptor, and should be read in this context.

Providing an adequate technical basis would be difficult without defining at least some of the most important terms related to groundwater and pollution. The most important definitions are highlighted through the chapter and key concepts illustrated by figures. A short list of suitable standard texts which can provide further details for the interested reader is given at the end of the chapter, along with the references actually quoted.

2.1 GROUNDWATER IN THE HYDROLOGICAL SYSTEM

2.1.1 The hydrological cycle

The continuous movement of water between oceans, atmosphere and land is known as the hydrological cycle (Figure 2.1). Considering the freshwater component of the system, which is the part of greatest significance for this monograph, inflow is from precipitation in the form of rainfall and from melting snow and ice. Outflow occurs primarily as stream flow or runoff and as evapotranspiration, a combination of evaporation from water surfaces and the soil and transpiration from soil moisture by plants. Precipitation reaches streams and rivers both on the land surface as overland flow to tributary channels, and also by subsurface routes as interflow and baseflow following infiltration to the soil. Part of the precipitation that infiltrates deeply into the ground may accumulate above an impermeable bed and saturate the available pore spaces to form an underground body of water, called an aquifer. The water contained in aquifers contributes to the groundwater component of the cycle (Figure 2.1), from which natural discharge reaches streams and rivers, wetlands and the oceans.

Figure 2.1 simplifies the hydrological cycle, illustrating only its natural components. There are few areas of the world in which the cycle has not been interfered with and modified by human settlement and associated activities. Large urban areas alter the processes of infiltration and drainage (e.g. Lerner *et al.*, 1990; Lerner, 1997), as do big irrigation schemes. Negative and costly impacts of waterlogging and salinity are widely experienced where excess infiltration from irrigation with diverted surface water raises groundwater levels beneath the irrigated land. This is seen most dramatically in the lower Indus Valley in Pakistan. Estimates of the area affected vary, but of 16.1 million ha irrigated, some 4.6 million ha are affected to some extent by waterlogging and salinity, of which perhaps 2 million ha have suffered serious deterioration (Ghassemi *et al.*, 1995). Engineering works for flood control, irrigation, hydropower and navigation can all change the surface water component of the cycle locally but sometimes dramatically, and groundwater abstraction can intercept discharge to rivers, wetlands and the oceans. An example of modification of the hydrological cycle that clearly has the potential to cause negative health impacts is the uncontrolled discharge of untreated urban wastewater or industrial effluents to surface water or groundwater. Modifying the hydrological cycle by human intervention also implies changing pollutant pathways and transport mechanisms, and these changes must be understood in developing strategies for protecting the health of water users.

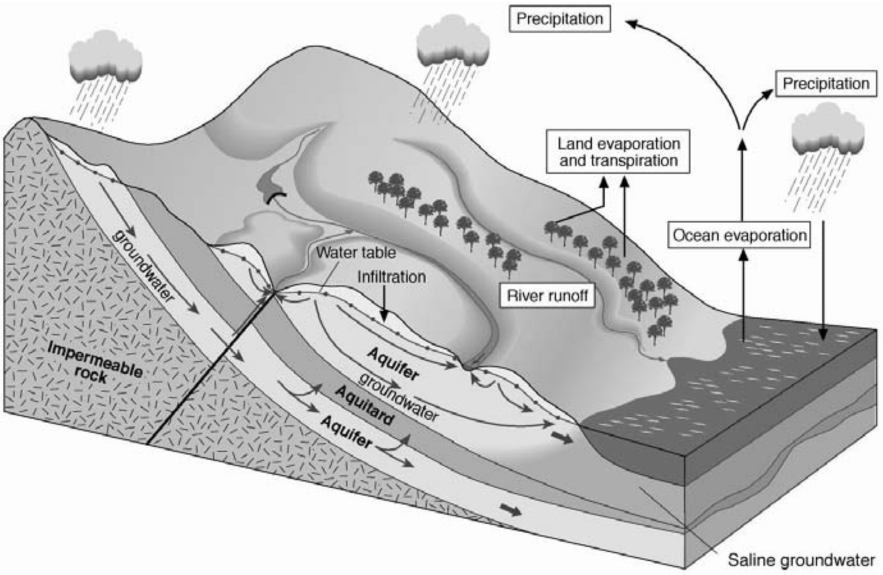


Figure 2.1. The natural hydrological cycle (modified from Morris *et al.*, 2003).

DEF ▶ *Aquifers are layers of rock or sediments which are sufficiently porous to store water and permeable enough to allow water to flow through them in economically viable quantities.*

The river basin or catchment is the geographical expression of the hydrological cycle, and the spatial unit within which water resource balances can be estimated and through which pollutants are transported within the cycle. Figure 2.1 demonstrates that both surface water and subsurface processes occur. This means that the river basin or sub-basin, and all of the activities within it, should be the unit or basis for the management of water resources, rather than political or administrative subdivisions. River Basin Management Plans are, therefore, an essential feature of the European Union (EU) Water Framework Directive (EC, 2000), which is intended to establish the overall approach to long-term management of water resources by EU Member States. It also follows that catchments can contain land from more than one or indeed several countries and transboundary or multi-national authorities, such as for the Rhine, Danube, Zambezi and others, have been established to oversee their management. Thus a key principle is that:

NOTE ▶ *The catchment boundaries of a river basin or sub-basin should define the management unit for water resources, rather than administrative or political boundaries.*

2.1.2 Groundwater in the hydrological cycle

While the definition of groundwater as the water contained beneath the surface in rocks and soil is conceptually simple and convenient, in practice the picture is a little more complex, and confusion can arise. The water beneath the ground surface includes that contained in the soil, that in the intermediate unsaturated zone below the soil, that comprising the capillary fringe and that below the water table (Figure 2.2). The soil is commonly understood to comprise the broken down and weathered rock and decaying plant debris at the ground surface. The region between the soil and the water table is commonly referred to as the unsaturated zone or sometimes the vadose zone.

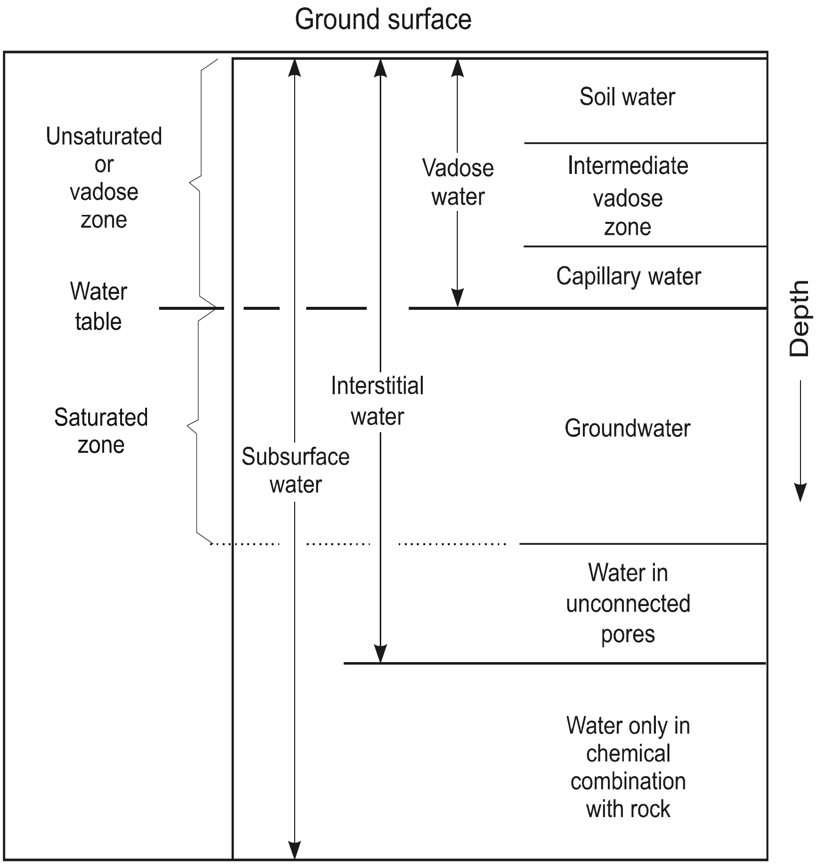


Figure 2.2. Classification of subsurface water (modified from Driscoll, 1986)

DEF ▶ *The* ***unsaturated zone*** *contains both air and water, while in the* ***saturated zone*** *all of the voids are full of water. The* ***water table*** *marks the boundary between the two, and is the surface at which fluid pressure is exactly equal to atmospheric pressure.*

Strictly speaking, therefore, groundwater refers only to water in the saturated zone beneath the water table, and the total water column beneath the earth's surface is usually called subsurface water (Figure 2.2). In practice, of course, the saturated and unsaturated zones are connected, and the position of the water table fluctuates seasonally, from year to year and with the effects of groundwater abstraction.

Appreciating this distinction is especially important in relation to protecting groundwater from pollutants originating from activities at the surface. Such pollutants can either be retained in the soil or they may be carried downwards by infiltrating water, depending on the physicochemical properties of both the soil material and of the pollutants. The soil, and the unsaturated zone beneath it, can be considered to serve as a reactive filter, delaying or even removing pollutants by the range of processes described in Chapters 3 and 4. The properties of the materials comprising the soil and the unsaturated zone are, therefore, critical factors in defining the vulnerability of groundwater to pollution, as described in Chapter 8.

In volume terms, groundwater is the most important component of the active terrestrial hydrological cycle, as shown in Table 2.1. Excluding the 97.5 per cent of water of high salinity contained in the oceans and seas, groundwater accounts for about one third of the freshwater resources of the world (UNESCO, 1999). If the water permanently contained in the polar ice caps and glaciers is also excluded, then groundwater accounts for nearly all of the useable freshwater. Even if consideration is further limited to the most active and accessible groundwater bodies, which were estimated by Lvovitch (1972) at 4 x 10^6 km^3, then they still constitute 95 per cent of the total freshwater. Lakes, swamps, reservoirs and rivers account for 3.5 per cent and soil moisture for 1.5 per cent (Freeze and Cherry, 1979). The dominant role of groundwater resources is clear, their use is fundamental to human life and economic activity, and their proper management and protection are correspondingly vital.

Table 2.1. Estimated water balance of the world (modified from Nace, 1971 and UNESCO, 1999)

Parameter	**Surface area (10^6 km^2)**	**Volume (10^6 km^3)**	**Volume (%)**	**Residence time**
Oceans and seas	361	1,370	97	~ 4000 years
Groundwater	130	8	0.5	Weeks - 100 000 years
Icecaps and glaciers	17.8	27	2	10-100 000 years
Lakes and reservoirs	1.55	0.13	<0.01	~ 10 years
Soil moisture	130	0.07	<0.01	2 weeks - several years
Atmospheric water	504	0.01	<0.01	~ 10 days
Swamps	<0.1	<0.01	<0.01	1-10 years
River channels	<0.1	<0.01	<0.01	~ 2 weeks
Biospheric water	<0.1	<0.01	<0.01	~ 1 week

The last column of Table 2.1 provides an indication of the range of residence times of water in the various compartments of the hydrological cycle. The great variation in residence times in freshwater bodies is also illustrated in Figure 2.3, which emphasizes the generally slow movement and long residence time of most groundwaters compared to surface waters.

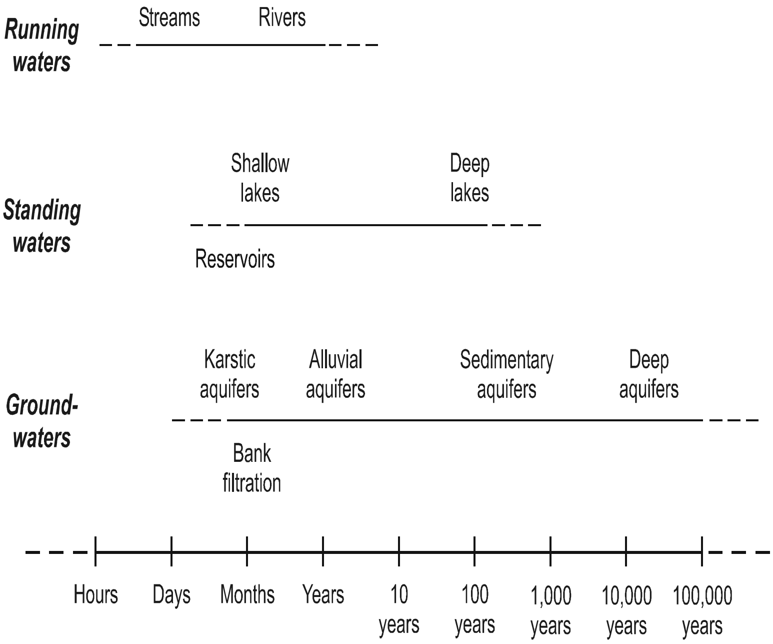


Figure 2.3. Water residence time in inland freshwater bodies (modified from Meybeck *et al.*, 1989)

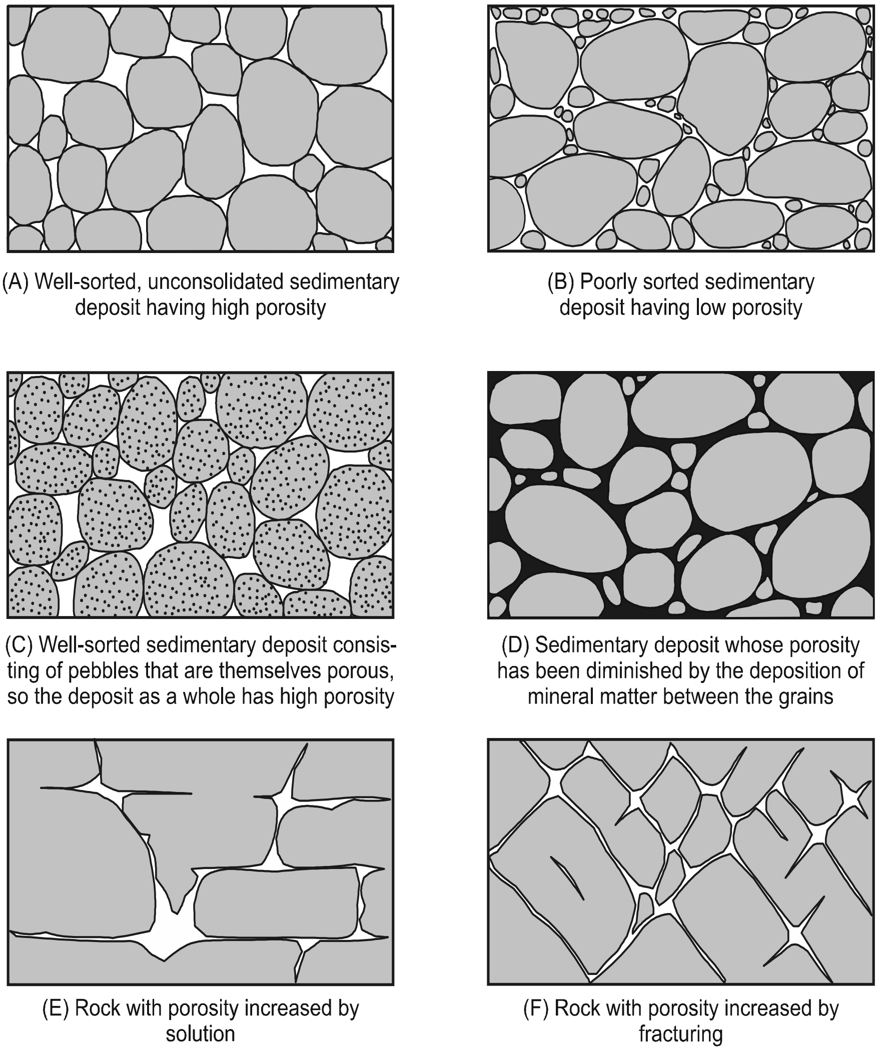
2.2 GROUNDWATER OCCURRENCE AND MOVEMENT

2.2.1 Groundwater occurrence and storage

Some groundwater occurs in most geological formations because nearly all rocks in the uppermost part of the earth's crust, of whatever type, origin or age, possess openings called pores or voids. Geologists traditionally subdivide rock formations into three classes according to their origins and methods of formation:

Sedimentary rocks are formed by deposition of material, usually under water from lakes, rivers and the sea, and more rarely from the wind. In unconsolidated, granular materials such as sands and gravels, the voids are the spaces between the grains (Figure 2.4A). These may become consolidated physically by compaction and chemically by cementation (Figure 2.4D) to form typical sedimentary rocks such as sandstone, limestone and shale, with much reduced voids between the grains.

Igneous rocks have been formed from molten geological material rising from great depth and cooling to form crystalline rocks either below the ground or at the land surface. The former include rocks such as granites and many volcanic lavas such as basalts. The latter are associated with various types of volcanic eruptions and include lavas and hot ashes. Most igneous rocks are strongly consolidated and, being crystalline, usually have few voids between the grains.


(A) Well-sorted, unconsolidated sedimentary deposit having high porosity

(B) Poorly sorted sedimentary deposit having low porosity

(C) Well-sorted sedimentary deposit consisting of pebbles that are themselves porous, so the deposit as a whole has high porosity

(D) Sedimentary deposit whose porosity has been diminished by the deposition of mineral matter between the grains

(E) Rock with porosity increased by solution

(F) Rock with porosity increased by fracturing

Figure 2.4. Rock texture and porosity of typical aquifer materials (based on Todd, 1980)

Metamorphic rocks have been formed by deep burial, compaction, melting and alteration or re-crystallization of other rocks during periods of intense geological activity.

Metamorphic rocks include gneisses and slates and are also normally consolidated, with few void spaces in the matrix between the grains.

In the more consolidated rocks, such as lavas, gneisses and granites, the only void spaces may be fractures resulting from cooling or stresses due to movement of the earth's crust in the form of folding and faulting. These fractures may be completely closed or have very small and not very extensive or interconnected openings of relatively narrow aperture (Figure 2.4F). Weathering and decomposition of igneous and metamorphic rocks may significantly increase the void spaces in both matrix and fractures. Fractures may be enlarged into open fissures as a result of solution by the flowing groundwater (Figure 2.4E). Limestone, largely made up of calcium carbonate, and evaporates composed of gypsum and other salts, are particularly susceptible to active solution, which can produce the caverns, swallow holes and other characteristic features of karstic aquifers. It is worthwhile becoming aware of the main geological terms, as geological maps are likely to be one of the main sources of information required to characterize a catchment or area of investigation (Chapter 8), but also noting the following important distinction:

NOTE ▶ *A geologist's principal subdivision of rock types is according to origin, whereas hydrogeologists first classify aquifers as unconsolidated or consolidated and hence whether water is stored and moves mainly between the grains of the rock matrix or through fractures.*

The volume of water that can be contained in the rock depends on the proportion of these openings or pores in a given volume of rock, and this is termed porosity of the rock.

DEF ▶ *The porosity of a geological material is the ratio of the volume of the voids to the total volume, expressed as a decimal fraction or percentage.*

Increasing pore space results in higher porosity and greater potential to store water. Typical porosity ranges are shown in Table 2.2 for common geological materials, emphasizing the division between unconsolidated and consolidated referred to above.

Not all of the water contained in fully saturated pore spaces can be abstracted by wells and boreholes and used. Under the influence of gravity when, for example, the water level falls, some of the water drains from the pores but some remains, held by surface tension and molecular effects. The ratio of the water that drains by gravity from an initially saturated rock mass to its own total volume is defined as the specific yield of the material, and typical values are also shown in Table 2.2.

Table 2.2. Porosity and specific yield of geological materials (Freeze and Cherry, 1979; Driscoll, 1986; Domenico and Schwartz, 1998)

Material	Porosity	Specific yield
Unconsolidated sediments		
Gravel	0.25-0.35	0.16-0.23
Coarse sand	0.30-0.45	0.1-0.22
Fine sand	0.26-0.5	0.1-0.25
Silt	0.35-0.5	0.05-0.1
Clay	0.45-0.55	0.01-0.03
Sand and gravel	0.2-0.3	0.1-0.2
Glacial till	0.2-0.3	0.05-0.15
Consolidated sediments		
Sandstone	0.05-0.3	0.03-0.15
Siltstone	0.2-0.4	0.05-0.1
Limestone and dolomite	0.01-0.25	0.005-0.1
Karstic limestone	0.05-0.35	0.02-0.15
Shale	0.01-0.1	0.005-0.05
Igneous and metamorphic rocks		
Vesicular basalt	0.1-0.4	0.05-0.15
Fractured basalt	0.05-0.3	0.02-0.1
Tuff	0.1-0.55	0.05-0.2
Fresh granite and gneiss	0.0001-0.03	<0.001
Weathered granite and gneiss	0.05-0.25	0.005-0.05

Another important way of distinguishing aquifers and the way in which groundwater occurs, when considering both its development and protection, is shown in Figure 2.5. In the figure an unconfined aquifer is one in which the upper limit of the zone in which all the pore spaces are fully saturated, i.e. the water table, is at atmospheric pressure. At any depth below the water table the water pressure is greater than atmospheric, and at any point above, the water pressure is less than atmospheric. In contrast, at greater depths, the effective thickness of an aquifer often extends between two impermeable layers (Figure 2.5).

DEF ▶ *Materials through which water can pass easily are said to be **permeable** and those that scarcely allow water to pass or only with difficulty are described as **impermeable**.*

If the overlying layer has low permeability and restricts the movement of water, then it is known as an aquitard and causes the aquifer beneath to be partially or semi confined. If the overlying layer has such low permeability that it prevents water movement through it, then the aquifer is fully confined. In these situations, at any point in the confined aquifer, the water pressure is greater than atmospheric, because of the elevation of the outcrop receiving recharge. If a borehole is drilled through the confining layer into the aquifer, water rises up the borehole to a level that balances the pressure in the aquifer. An imaginary surface joining the water level in boreholes in a confined aquifer is called the potentiometric surface, which can be above or below the groundwater surface in the overlying unconfined aquifer (Figure 2.5). If the pressure in a confined aquifer is such that the potentiometric surface is above ground level, then a drilled borehole will overflow (Figure 2.5). For a phreatic aquifer, which is the first unconfined aquifer to be formed below the surface, the potentiometric surface and groundwater surface correspond, and this is called the water table.

From the groundwater development point of view, unconfined aquifers are often favoured because their storage properties make them more efficient for exploitation than confined aquifers, and they are likely to be shallower and therefore cheaper to drill into and pump from. On the other hand:

NOTE ▶ *A confined aquifer which has even a modest overlying sequence of less permeable clay strata is likely to be much less vulnerable to pollution than an unconfined aquifer.*

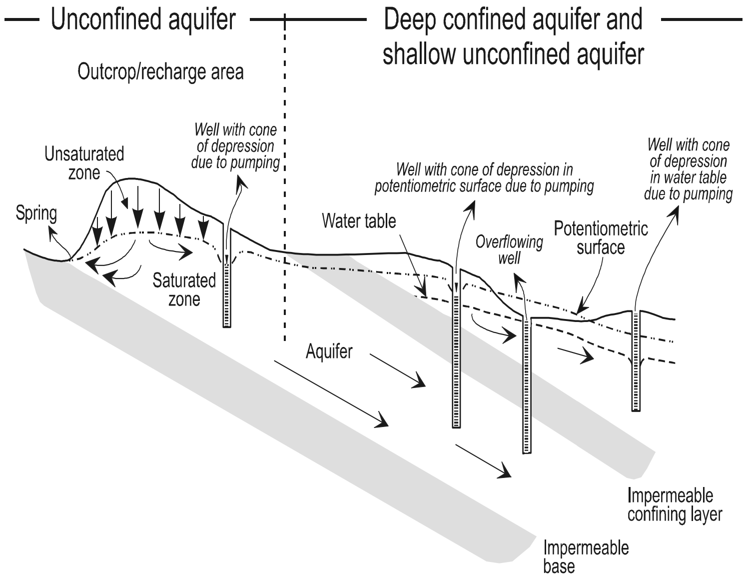


Figure 2.5. Schematic cross-section illustrating confined and unconfined aquifers

2.2.2 Groundwater movement

Groundwater is not usually static but moves slowly through aquifers. However, it needs a source of energy to do so, which is provided by the hydraulic head represented by the height of the water level in an observation well or borehole in the aquifer. The total hydraulic head is made up of two components, the elevation head being the height of the midpoint of the section of the borehole or well that is open to the aquifer, and the pressure head, which is the height of the column of water above this midpoint. The first component thus reflects location and topographic position and the second reflects conditions in the aquifer, including seasonal and longer-term changes in water levels. Hydraulic heads are normally measured with respect to an arbitrary datum, which is often sea level. To obtain a more comprehensive description of these rather difficult concepts, the reader should refer to standard hydrogeological text books such as Freeze and Cherry (1979), Price (1996) or Domenico and Schwartz (1998). For an understanding of groundwater movement for the present purposes, however, it is sufficient to know that groundwater moves from regions of high head to regions of low head.

The flow of groundwater through an aquifer is governed by Darcy's Law, which states that the rate of flow is directly proportional to the hydraulic gradient:

$$Q/A = q = - K\,(h_1 - h_2)/l = - K\,\Delta h/\Delta l \qquad \text{(Eqn. 2.1)}$$

where Q is the rate of flow through area A under a hydraulic gradient $\Delta h/\Delta l$ which is the difference in hydraulic heads (h_1 - h_2) between two measuring points, and q is the volumetric flow per unit surface area. The direction of groundwater flow in an aquifer is at right angles to lines of equal head. A simple experimental apparatus used to demonstrate Darcy's Law is shown in Figure 2.6, indicating also the elevation and pressure components of hydraulic head referred to above. The equation for Darcy's Law is conventionally written with a minus sign because flow is in the direction of decreasing hydraulic heads.

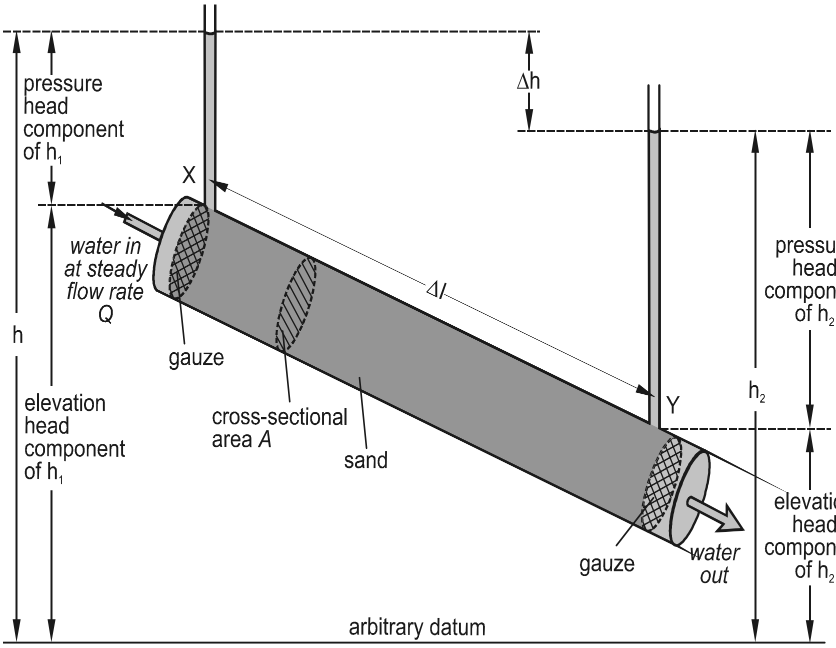


Figure 2.6. Experimental apparatus to demonstrate Darcy's Law (modified from Price, 1996)

The constant of proportionality in the equation, K, has dimensions of length/time because the hydraulic gradient is dimensionless. This parameter is known as hydraulic conductivity, and is a measure of the ease with which water flows through the sand contained in the cylinder in the laboratory experiment or through the various materials that form aquifers and aquicludes. The similarity between Darcy's Law and other important laws of physics governing the flow of both electricity and heat should be noted. The ease with which water can flow through a rock mass depends on a combination of the size of the pores and the degree to which they are interconnected. These features determine the overall permeability of the rock. For clean, granular materials, hydraulic conductivity increases with grain size. Typical ranges of hydraulic conductivity for the main types of geological materials are shown in Figure 2.7.

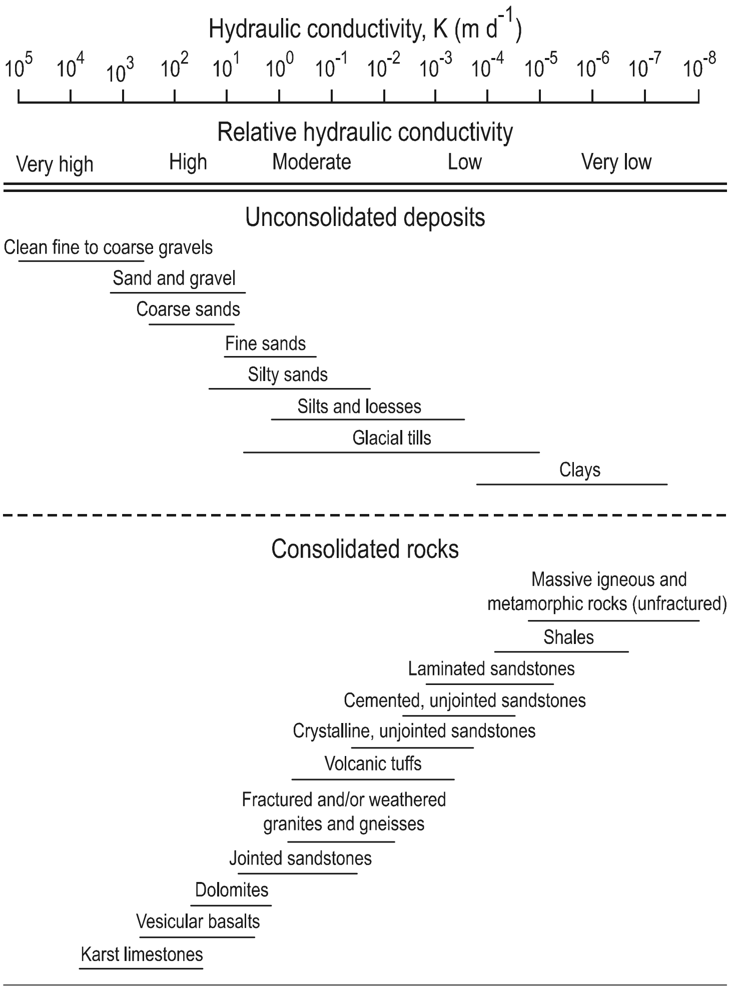


Figure 2.7. Range of hydraulic conductivity (K) values for geological materials (based on Driscoll, 1986 and Todd, 1980)

Darcy's Law can be written in several forms. By substituting q in the equation, it is possible to determine the specific discharge per unit area, if the volumetric flux Q is divided by the full cross-sectional area (A in Figure 2.6). However, this area includes both solids and voids, although clearly flow can only take place through the voids or pore spaces. A more realistic linear pore velocity, v, the volumetric flow rate per area of connected pore space can be calculated if the porosity is known. Thus we can define:

$$v = -q/n = -Ki/n \qquad \text{(Eqn. 2.2)}$$

Where i is conventionally used to represent the hydraulic gradient $\Delta h/\Delta l$. To make this calculation, it is necessary to know the effective or dynamic porosity n_e, which represents the proportion of the total porosity that is involved in groundwater movement. This is difficult to measure, but for unconfined aquifers is probably close to the specific yield values given in Table 2.2.

DEF ▶ *The effective porosity is defined as the proportion of the total volume that consists of interconnected pores able to transmit fluids.*

Thus most materials in which intergranular flow predominates have effective porosities of 0.15 to 0.25, so in these types of aquifers the actual groundwater flow velocity is four to six times the specific discharge. The linear velocity will always be greater than the specific discharge, and increases with decreasing effective porosity. This average velocity in the direction of groundwater flow does not represent the true velocity of water particles through the pore spaces. These microscopic velocities are generally greater because the intergranular flow pathways are irregular and tortuous and longer than the average linear macroscopic pathway. The average linear velocity, *v*, is a key parameter in groundwater protection, as it defines the travel times for water and solutes within aquifers. For unconsolidated granular aquifers, typical natural groundwater flow velocities range from a few mm/d for silts and fine sands to 5-10 m/d for the clean and coarse gravels.

Darcy's Law provides a valid description of the flow of groundwater in most naturally occurring hydrogeological conditions i.e. for fractured rocks as well as granular materials. Fractured rocks are characterized by low porosity and localized high hydraulic conductivity, and very high flow velocities of up to several kilometres per day may result (Orth *et al.*, 1997; US EPA, 1997), especially where a small number of fractures are enlarged by solution (Figure 2.4E). Extensive development of solution in limestone areas can result in karst terrain, which is typified by channels, sinkholes, depressions and caves, into which all traces of surface flow may disappear. Such conditions can be very favourable for groundwater supplies from springs and boreholes, but aquifers of this type are often highly vulnerable to all types of pollution (Malard *et al.*, 1994).

Groundwater flow may occur through the spaces between the grains or through fractures (Figure 2.4) or a combination of the two in, for example, a jointed sandstone or limestone. Hydrogeologists commonly refer to these as dual-porosity aquifers, because they have primary porosity and permeability from the intergranular pores and additional secondary porosity and permeability provided by the fracture systems. The presence of highly fractured rocks should immediately warn of the risk of rapid transport over large distances. The occurrence of potential contaminant sources close to water supplies in such environments should be considered to provide a very high risk of pollution.

The characteristic properties of an aquifer to store and transmit groundwater are normally deduced from the interpretation of pumping tests performed on wells or boreholes (Price, 1996) or by introducing inert tracers into groundwater flow systems and observing their transport (Becker *et al.*, 1998; Käss, 1998). Determinations of aquifer parameters are often difficult and expensive, and information is usually available for at most a few specific locations in an aquifer. However, most geological materials are far from uniform laterally or with depth. As an example, sediments such as river alluvium, deltas and glacial deposits may contain alternating fine and coarse layers, clay lenses, sand channels and many other features and structures which reflect the complex history of deposition. These geological variations mean that aquifers are rarely homogeneous, in which the properties are the same irrespective of position in the aquifer, but more often heterogeneous, with varying properties. Obtaining or selecting aquifer parameters that can apply to and be representative of a whole aquifer or catchment is often, therefore, a difficult task for a hydrogeologist. Describing and quantifying groundwater flow is not as straightforward as a summary text such as this might suggest to the reader, especially in aquifers with complex patterns of fracture flow. However, distinguishing whether intergranular or fracture flow predominates for any aquifer of interest is fundamental to understanding the hydrogeology, which is in turn the basis for developing, managing and protecting groundwater.

NOTE ▶ *Whatever the source of pollution and type of pollutant, understanding the way groundwater occurs and moves is crucial to:*
(1) setting up groundwater protection policies;
(2) establishing water quality monitoring systems;
(3) designing pollution control or aquifer remediation measures.

2.3 GROUNDWATER DISCHARGE AND RECHARGE

It is important to distinguish between infiltration of precipitation and groundwater recharge. Thus looking back at the hydrological cycle in Figure 2.1, when rain falls, some infiltrates into the soil. Much of this moisture is taken up by the roots of plants and is subject to evapotranspiration from the soil zone, and some becomes interflow drainage to streams and rivers. Only a part of the infiltration becomes recharge and moves deeper into the subsurface under gravity, and in arid and semi-arid areas this may be a very small proportion indeed. This distinction becomes very important when considering the estimation of recharge in Chapter 8. Thus conceptually and for estimation purposes:

DEF ▶ ***groundwater recharge*** *should be defined as the downward flow of water reaching the water table and replenishing groundwater resources*

---

and should be distinguished from infiltration. The latter includes all of the water entering the ground from rainfall or other sources but by no means does all of this become groundwater recharge.

In the subsoil and rock closest to the ground surface, the pore spaces are partly filled with air and partly with water. This was defined as the unsaturated or vadose zone in Figure 2.2, and can vary in depth from nothing to tens of metres. In the unsaturated zone, soil, air and water are in contact and may react with each other, which can be important in the evolution of the hydrochemistry of the water. In the uppermost part of the unsaturated zone, some upward movement occurs in response to seasonal evapotranspiration requirements. Below this, in humid areas, movement in the unsaturated zone is dominantly vertically downwards. The most recent water arriving from the soil displaces downwards the whole column of water already in the unsaturated zone, rather like the movement of a piston, so that the water at the base of the column reaches the water table. For parts of the year, particularly when the weather is dry and no new percolating water passes below the soil, the 'piston' moves very slowly or not at all. In times of heavy rainfall and substantial infiltration, downward movement may be more strongly established.

By sampling the unsaturated zone water to obtain vertical profiles and repeat profiles of tracers such as bromide, nitrate and tritium, average rates of movement of less than 5 m/yr and often less than 1 m/yr have been measured in temperate regions (Wellings, 1984; Geake and Foster, 1989; Barraclough *et al*., 1994). This means that it could take 20 years or more for infiltrating water to reach a water table 20 m below the ground surface. It is common for the water table to be in the range 10 to 50 m below ground, and the unsaturated zone component of the pollutant pathway can therefore be substantial. In semi-arid regions, recharge can be much less and downward displacement correspondingly very slow (Edmunds and Gaye, 1994). In the most arid areas, the unsaturated zone may only act as a temporary storage reservoir in which water that percolates downwards after occasional heavy rain does not reach the water table but is instead drawn upwards and returns to the atmosphere by evapotranspiration from plants. Residence times in the unsaturated zone thus depend on the thickness and the rate of recharge, and can vary from almost nothing to tens or hundreds of years.

The above applies to aquifers in which downward movement of recharging water takes place only through the intergranular matrix. In fractured and dual porosity aquifer materials, much more rapid, preferential flow to the water table may occur, especially after heavy rainfall. This component of flow can carry pollutants from the ground surface much more quickly, allowing little or no time for attenuation, and such aquifers can be highly vulnerable to pollution.

All subsurface freshwater must have a source of recharge, even if it was long ago. This comes either by direct infiltration of rainfall or snowmelt, or from rivers and lakes. Now that the hydrological cycle has been interfered with as a result of human activities, recharge can also be derived from canals, reservoirs, irrigated land, water mains and sewerage systems in urban areas, mining waste, sewage lagoons, in fact any artificial water body that is in connection with the subsurface. Artificial recharge, which is becoming an increasingly important resource management option, can also introduce water of different origin and quality into aquifers. This of course means that groundwater recharge is not always of the same good quality as infiltrating rainfall, which itself may be contaminated by acid rain or atmospheric acid deposition.

2.4 GROUNDWATER FLOW SYSTEMS

In many aquifers, the hydraulic head reflects the topographic surface of the ground, and groundwater therefore moves from elevated regions where recharge occurs to discharge zones at lower elevations. Thus within the context of the overall cycle shown in Figure 2.1 and the source-pathway-receptor concept, the groundwater flow system (Figure 2.8) is a useful way of describing the physical occurrence, movement and hydrochemical evolution of groundwater.

DEF ▶ *A groundwater flow system is a discrete, closed three-dimensional system containing flow paths from the point at which recharging water enters an aquifer to the topographically lower point at which it leaves the aquifer.*

Infiltration of rainfall on high ground occurs in a recharge area in which the hydraulic head decreases with depth, and net saturated flow is downwards away from the water table and laterally towards areas of lower hydraulic head (A in Figure 2.8). After moving slowly through the aquifer down the hydraulic gradient (B in Figure 2.8), groundwater leaves the aquifer by springs, wetlands, baseflow to rivers (C in Figure 2.8) or discharge to lakes or the oceans. These are known as groundwater discharge areas, and at C (in Figure 2.8) the hydraulic head increases with depth and the net saturated zone flow is upwards towards the water table. In a recharge area, the water table can be at depth, with a considerable thickness of unsaturated zone above it. In a discharge area, the water table is usually at, or very near to, the ground surface. Rivers, canals, lakes and reservoirs may either discharge to or receive recharge from groundwater, and the relationship may change seasonally or over a longer time span or along the course of a single river.

While in many cases groundwater and surface water catchments have more or less the same boundaries, this is not always the case. Seasonally due to recharge, and in response to heavy abstraction, groundwater catchment boundaries may deviate significantly from surface water catchments. In deep aquifers, or sequences of more than one layered aquifer, groundwater recharge may come from great distances and deep groundwater flow may have little relationship to the overlying surface water system. In most cases, however, if there is no information it is a reasonable first estimate to assume surface water and groundwater catchments are similar and that groundwater flow patterns are likely to be a subdued reflection of the surface topography.

In large, deep aquifers, groundwater is likely to move slowly, at rates of a few metres per year, from recharge to discharge area over tens or hundreds of kilometres. This may take hundreds or thousands of years, and typical order-of-magnitude values from time of recharge to point of discharge are indicated in Figure 2.8. Hydrogeologists can confirm these by isotopic dating techniques (Kendal and McDonnel, 1998; Edmunds and Smedley, 2000). In small, shallow aquifers, recharge and discharge areas may be much closer or even adjacent to each other, and residence times can be restricted to a few months or years. In arid and semi-arid regions, groundwater discharge areas are often characterized by poor quality groundwater, particularly with high salinity. Groundwater discharge may be from seepages or salt marshes with distinctive vegetation, known as salinas or playas, in which evapotranspiration at high rates for long periods of time has led to a build-up in salinity.

While the flow system in Figure 2.8 is a useful general illustration, in many cases groundwater does not flow uniformly through the entire thickness of an aquifer, but instead flows predominantly at shallow depths close to the water table (Seiler and Lindner, 1995). In unconsolidated aquifers, both hydraulic conductivity and porosity usually decrease with depth due to consolidation and compaction. In fractured aquifers too, the hydraulic conductivity and porosity provided by the fracture system would be expected to decline with depth as the fractures become less open. This general but variable and not easily predicted decline in groundwater flow properties with depth often restricts the flow and pollutant pathway to the most permeable, near-surface parts of the aquifer. Further, the zone of seasonal water table fluctuation is often where the most active solution of fractures occurs and this helps to enhance the flow dominance of the uppermost part of the saturated aquifer.

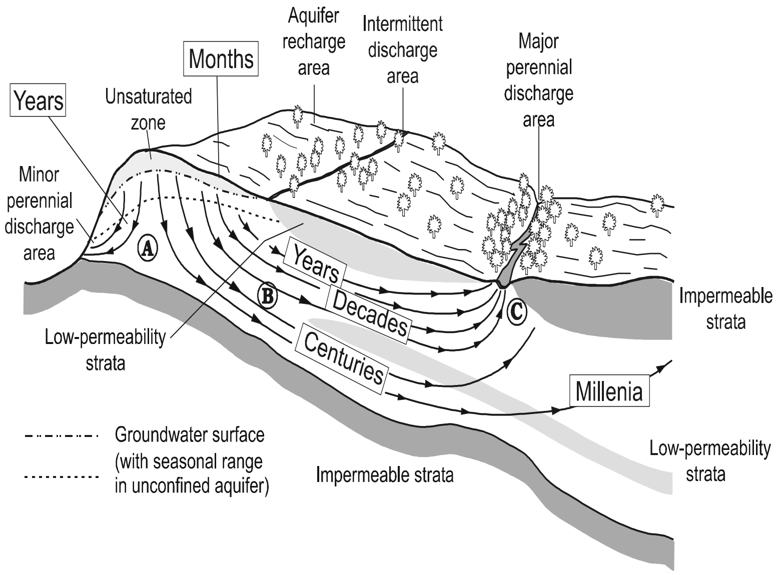


Figure 2.8. Schematic groundwater flow system (modified from Foster *et al.*, 2000)

Given the high porosity values in the upper part of Table 2.2, it can be seen that most types of aquifer, provided they are at least a few metres thick, can contain large volumes of water. Many aquifers are, of course, much thicker, ranging up to several hundred metres. Even in humid areas, recharge comprises only a proportion of the total rainfall and a simple calculation will show that, for typical annual recharge volumes equivalent to tens to a few hundreds of millimetres, the total volume of groundwater in storage in the aquifer is many times larger than the annual recharge. Aquifers are generally, therefore, high storage, low recharge systems with substantial capacity for dilution of incoming pollutants, except in the situations of restricted shallow flow referred to immediately above. In these cases, incoming recharge may be distributed far from evenly through the aquifer, and the resulting groundwater volume available for dilution may be much less than the total storage of the aquifer.

2.5 GEOLOGICAL ENVIRONMENTS AND AQUIFER TYPES

As described above, the natural subsurface geological environment provides the dominant control over the occurrence and movement of groundwater and hence defines which rock types form good aquifers. However, geodiversity and the consequent hydrogeological variability are poorly appreciated by many of those working in water protection and management. The variability both between and within hydrogeological environments can have a profound impact on how aquifers respond to the pressures imposed upon them. Further, if an aquifer is to be protected and managed, it is important to understand the groundwater flow system to be able to assess the susceptibility of the aquifer to these external changes and the types and timescales of the likely responses.

While almost all geological materials contain some water and many different rocks can form useful aquifers, nevertheless it is possible to develop a summary of the most common aquifer types and hydrogeological environments (Table 2.3). This classification is a useful overall basis for helping to identify the major potential concerns for protection and management of groundwater. The general subdivision in Table 2.3 takes into account both the rock type and the geological environment in which the rocks were formed. While such a broad classification is useful, it inevitably involves some simplifications of the true breadth of subsurface geological variation and complexity. The classification shown in Table 2.3, or slight variations of it, proved useful as a basis for discussion of groundwater quality monitoring (Chilton, 1996) and provided the hydrogeological framework within which the management of groundwater in urban areas (Foster *et al.*, 1998) and the development and management of groundwater in rural areas (Foster *et al.*, 2000) can be set. Each of the seven subdivisions is briefly described below.

Major alluvial and coastal plain sediments

The first subdivision (Table 2.3), covers a broad range of materials and lateral and vertical scales. At one end of the scale are extensive sequences of coastal, river and deltaic alluvium, sometimes hundreds of metres thick. These unconsolidated sedimentary deposits form some of the most important aquifers in the world, in which very large volumes of groundwater are stored and from which large quantities of water are pumped for water supply and irrigation. Examples include the Lower Indus and Ganges-Brahmaputra valleys, the Mekong, the Tigris-Euphrates, the north European plain and the Nile valley. Many of the world's largest cities such as Bangkok, Beijing, Cairo, Calcutta, Dhaka, Hanoi, Lima, Madras and Shanghai are located on such deposits and are supplied by groundwater drawn from unconsolidated strata.

These aquifers can cover large areas and contain enormous volumes of water. As an example, aquifers within the unconsolidated sediments underlying the Huang-Hai-Hai Plain of eastern China, which covers an area of 350 000 km^2, provide the potable water requirements for nearly 160 million people and also enough to irrigate some 20 million ha of land. The sediments are of Quaternary age and are typically 200-400 m thick. Groundwater in these sediments can be subdivided into three types: an upper unconfined freshwater zone, a middle saline water zone and a lower confined aquifer. The total volume of groundwater stored exceeds 2 000 000 million m^3, whilst usable groundwater resources have been estimated at more than 49 000 million m^3/a. Other unconsolidated sedimentary aquifers may be much less extensive but can still store sufficient volumes of groundwater to be important sources of water supply. The coastal plain around Jakarta and the Nile valley at Cairo are examples. Smaller but still locally-important aquifers are provided by river valley and coastal plain sediments of more limited lateral extent and depth, and aquifers of much more restricted size and extent may occur in upland river valleys as river terraces.

Aquifers in unconsolidated strata are rarely simple homogeneous systems but typically consist of alternating permeable layers of productive sands and gravels separated by less permeable aquitard layers of clay and silt, reflecting the complex history of deposition. In such sequences, the shallowest aquifer may be the easiest and cheapest to exploit, but is likely to be the most vulnerable to pollution. The presence of aquitards may produce complex groundwater flow patterns, but the permeable horizons may still have a degree of hydraulic continuity, such that pumping from one layer will affect the others, producing significant vertical head gradients and consequent leakage.

The high porosity of unconsolidated sediments, typically in the range 0.25 to 0.35, and the generally low horizontal hydraulic gradients in the major alluvial plains means that groundwater velocities are very low, usually in the range 0.003-0.1 m d^{-1}. These low velocities combined with the significant distances travelled (tens to hundreds of kilometres) indicate that much of the deeper groundwater in thick alluvial sequences is derived from recharge several hundred to several thousand years ago, and the term 'fossil' has sometimes been used to describe deep, old groundwater.

Intermontane alluvial and volcanic systems

Aquifers of this type include some volcanic lavas and pyroclastic rocks, together with alluvial-volcanic and alluvial fan deposits. They are typically associated with rapidly infilled and faulted troughs or basins within mountain regions (Table 2.3). Hydraulic conductivities and porosities are generally high but variable. When combined with the above average rainfall that is often found in the mountainous climatic regimes where many of these environments are found, valuable aquifers occur and are capable of supporting substantial borehole yields. Additional recharge to groundwater often occurs where surface water flowing from the surrounding mountain slopes infiltrates into the highly permeable valley-fill deposits, especially through the alluvial fans and colluvial deposits found on valley margins. Examples of this environment include Mexico City, Guatemala City, San Salvador, Managua and San José in Central America, the Kathmandu Valley in Nepal, Bandung and Yogyakarta in Indonesia, Davao in the Philippines and Sana'a in Yemen. In these mountainous areas, flat land is limited and highly valuable, and is often densely populated. Restrictions on available land for settlement will often result in groundwater abstraction for potable supplies in the basin occurring within densely populated areas, with significant implications for water quality. Furthermore, the concentration of population and the consequent high water demand can result in groundwater abstraction exceeding the safe yield of the aquifer. Long-term decline in groundwater levels and/or contamination of groundwater can result, as for example in Mexico City (NRC, 1995), the Kathmandu Valley (Khadka, 1991) and the Sana'a Valley (Alderwish and Dottridge, 1999).

Consolidated sedimentary aquifers

Important aquifers occur within consolidated sedimentary strata, principally sandstone and limestone (Table 2.3). These can be broadly subdivided into younger, Tertiary formations and older Mesozoic or Palaeozoic formations. Globally, although their distribution is irregular, they are widespread and common being found both in mountain belts such as the Alpine-Himalayan, Andean, Urals and North American cordilleras and in lowlands and plateau areas such as northern Europe and central China.

Sandstones have been formed when sandy marine or continental sediments were buried and compacted to form consolidated rocks. The degree of consolidation generally increases with depth and age of the rocks. Thus the younger, Tertiary sandstones usually retain some degree of primary porosity between the sand grains and are typically of low to moderate permeability. In the older, Mesozoic or Palaeozoic formations with more strongly developed cementing of the grains, the primary porosity may have become largely eliminated. Pre-Tertiary sandstones can range from friable to highly indurated depending on the degree of cementation, and in the latter cases it is the secondary porosity resulting from the development of fractures which can provide adequate permeability and storage for such rocks to form productive aquifers.

Limestones exhibiting solution enhancement of such fractures (called karst) are widespread and can be prolific aquifers, although well yields are highly variable in time and space. For instance, in northern China, karst limestones occupy an area of 800 000 km^2, are typically 300-600 m thick and their groundwater resources have been estimated at 12 800 million m^3 yr^{-1}. In southern China, karst limestones are even more extensive where they cover an area of 1 400 000 km^2, with groundwater resources estimated at 190 000 million m^3 yr^{-1}. Similar, highly permeable limestones occur throughout southern Europe, including along the coast of the Adriatic Sea region from which the karst name derives, in the Middle East and in the USA.

Recent coastal calcareous formations

These formations form important local aquifers. Examples, which include Florida, Jamaica, Cuba, Hispaniola and numerous other islands in the Caribbean, the Yucatan peninsula of Mexico, the Cebu limestone of the Philippines, and the Jaffna limestone in Sri Lanka, provide important sources of potable water for the people living there and for irrigation. Their high to very high permeability derives not only from initially high primary porosities (due to the sedimentary environment of deposition), but also from fractures that have been enhanced by solution. This can produce rapid groundwater movement with velocities frequently in excess of 100 m d^{-1}. The high infiltration capacity of these strata often precludes surface drainage systems and very often groundwater is the only available source of water supply in these environments.

These characteristics have important implications for protecting groundwater quality. Soils can be very thin and water movement from the soil to the water table via fissures is often so rapid that these formations are highly vulnerable to pollution. In addition, being coastal, the aquifers are usually underlain by seawater, often at shallow depths. Excessive abstraction of groundwater, with a consequent lowering of the water table, may induce saline intrusion by lateral movement of the freshwater/seawater interface inland or local upconing and contamination of the fresh groundwater body from below.

Glacial formations

Deposits of glacial and fluvioglacial origin comprise small but locally important aquifers not only in temperate zones of the world but also at altitude in the mountain ranges of the Andes and Himalayas. Ice-transported sediments are commonly unsorted mixtures of all grain sizes from clay to boulders, typically have low permeabilities and act as aquitards or aquicludes. Their geographical distribution is often limited, as they tend to occur in regions of active erosion. In contrast, water-sorted sediments, laid down from glacial melt-waters, include the sands and gravels of kames and eskers, which can form restricted but highly productive aquifer systems. These can sometimes be more extensive, as in the coalescing gravel outwash plains of North America, the eastern Andes and the Himalayas/Pamir/Tienshan cordilleras, or quite narrow and sinuous, as in the glacial channels of the North German Plain and the Great Lakes.

The environment of deposition, from melt-water streams and the upper reaches of braided rivers makes for highly variable lithology. As a result, multiple aquifers are typical, comprising complex systems in which lenses of highly permeable sands and gravels are partly separated vertically and laterally from each other by lower-permeability fine sands, silts and clays. The resultant ‘patchy’ aquifer can be very productive, but hydraulic continuity between different lenses means that mobile persistent contaminants are able to penetrate to significant depths.

In many glacial areas, the underlying bedrock consists of ancient, hard and unweathered granites and gneisses, which are very unpromising as aquifers. In these terrains, even the small sedimentary aquifers referred to above can provide vital but potentially quite vulnerable water supplies to the small and scattered communities in such regions. Sometimes these aquifers are used for urban supply, either directly by means of boreholes, or as prefilters for high volume riverbank intakes via infiltration galleries or collector wells. Examples include Cincinnati and Lincoln (USA), Berlin and Düsseldorf (Germany), and Vilnius (Lithuania).

Loessic plateau deposits

Fine windblown deposits, called loess, form an important aquifer in China. Although loess is found elsewhere, such as in Argentina and north of the Black Sea, thick deposits are almost entirely restricted to north central China where they cover an area in excess of 600 000 km^2. Of this, some 440 000 km^2 is continuously covered with a thickness of between 100 and 300 m. The loess covers a vast plateau at elevations of between 400 and 2 400 m above sea level. The loess plateau supports a population of 64 million and 7.3 million ha of cultivated land and is dependent on groundwater for domestic water and irrigation in this semi-arid region. The distinctive geomorphological features and geological characteristics produce a complex groundwater system. The loessic plateau aquifers are frequently cut through by gullies and ravines, so that the plateaux form a series of independent water circulation systems. The deposits are generally of low permeability and the presence of palaeo-soils produces a layered aquifer; the deeper zones being partly confined. The water table is often quite deep (30-50 m below surface).

Extensive volcanic terrains

One of the largest and most important areas of volcanic lava flows occurs in the central and western parts of India, where the Deccan basalts cover more than 500 000 km^2. Other extensive volcanic terrains occur in North and Central America, Central and East Africa, and many islands are entirely or predominantly of volcanic origin, such as Hawaii, Iceland, the Canary Islands (Spain) and some of the Caribbean islands. Older lavas such as the Deccan basalts can often be largely impermeable in the rock mass, but younger basalts can provide very large springs. Individual lava flows can be up to 100 m thick, and although the more massive flows are often impermeable, extensive jointing allows water to infiltrate and move through them. The junctions between flows can form highly productive aquifers, because of the cooling cracks and joints, and development of rubble zones caused when the rough surface of the lava is covered by the chilled base of the next flow, weathering and soil in the period of time between successive flows. Extensive lava tubes may be formed where lava drains from beneath a cooled and congealed surface. It is the combination of these features that make the Deccan basalts and other such volcanic rocks important and locally productive aquifers. Other materials are thrown out as volcanic clouds, which sometimes settle as ash deposits or become welded tuffs. The mineralogy and chemistry of the volcanic rocks and their viscosity and gas content determine the precise nature of the volcanic eruptions and resulting rocks. Alternating sequences of ashes and lavas, in which the lavas act as conduits for groundwater flow and the intervening ashes provide the storage, characterize the important aquifer systems of Costa Rica, Nicaragua and El Salvador.

Weathered basement complex

These aquifers are found in ancient crystalline rocks of Precambrian or Lower Palaeozoic age. In sub-Saharan Africa, such rocks cover 40 per cent of the total land area and some 220 million people live on them. Groundwater flow and storage occurs in restricted fractures in the fresh bedrock, but usually more extensively in the superficial weathered layers. The processes of weathering and disaggregation can enhance both porosity and permeability (Chilton and Foster, 1995). Because these ancient rocks occupy stable, continental shield areas, there has been plenty of opportunity for prolonged periods of weathering, and the zone of weathering tends to be better developed and thicker in tropical regions where such processes are more active. As a result, the weathered zone can be as much as 60 m thick, but more commonly in the range of 20 to 30 m. Groundwater velocities in weathered and fractured bedrock aquifers can be very variable.

Even with the beneficial effects of weathering, the volumes of water stored within these aquifers are generally limited, hydraulic conductivities are low, borehole yields modest and groundwater is used mostly for providing potable water supplies for rural communities and small towns, and for small-scale supplementary irrigation. Larger cities located on such formations, such as Kampala in Uganda, may find it difficult to abstract the large quantities of water needed for urban supply and also to dispose of wastewater on-site to the subsurface in a sanitary manner.

Table 2.3. Summary of characteristics of principal hydrogeological environments

Hydrogeological environment	Lithology	Geological description and origin	Groundwater flow regime	Natural groundwater flow rates (m/d)
Major alluvial and coastal plain sediments	Gravels, sands, silts and clays	Unconsolidated deposits of major rivers, deltas and shallow seas, high primary porosity and permeability. Very extensive and thick aquifers	Intergranular	2-10 in gravels, 0.05-1 in sands, 0.001-0.1 in silts
Intermontane alluvial and volcanic systems	Pebbles, gravels, sands and clays, sometimes inter-bedded with lavas and volcanic ashes	Rapid infilling of faulted troughs and basins in mountain regions; unconsolidated, primary porosity and/or permeability usually high for fan sediments and ashes, but lavas and lacustrine deposits are often poor aquifers or confining aquitards. Less extensive but can be thick	Intergranular, fracture in lavas and cemented ashes	0.001-10
Consolidated sedimentary aquifers	Sandstones	Marine or continental deposits buried, compacted and cemented to form consolidated rocks; degree of consolidation generally increases with depth/age of deposition. Primary porosity moderate to poor but secondary porosity introduced by fractures can be significant	Intergranular and fracture	0.001-0.1
	Limestones	Deposited from skeletal material (shell fragments, reefs, reef detritus) in shallow seas and compacted to form consolidated rocks; often have fractures which may be enlarged by solution processes to form characteristic topography, cavities and tunnel systems known as karst	Dominant fracture with variable intergranular component	0.001-0.1 in matrix, up to 1000 in karst fissures
Recent coastal calcareous formations	Limestones and calcareous sands	Usually composed of coral limestones, shellbanks, chemically precipitated oolites and calcareous oozes; often loosely cemented; porosity and permeability can be exceptionally high, especially if fractures are solution-enhanced	Intergranular and fracture	0.01-0.1 in matrix, up to 2000 in karst

Hydrogeological environment	**Lithology**	**Geological description and origin**	**Groundwater flow regime**	**Natural groundwater flow rates (m/d)**
Glacial formations	Boulders, pebbles, gravels, sands, silts and clays	Ice-transported sediments are commonly unsorted and have low permeability, but water-sorted sediments such as melt-water and outwash deposits often have high porosity and permeability. Can be thin, patchy and shallow	Intergranular	0.001-0.1 in tills, much higher in sands and gravels
Loessic plateau deposits	Silts, fine sands and sandy clays	Usually well-sorted windblown deposits of silt and fine sand, with some sandy clay deposits of secondary fluvial origin; low permeability. Can be extensive and thick but divided into blocks by deep gullies	Intergranular	0.001-0.01
Extensive volcanic terrains	Lavas, tuffs and ashes	Extensive basaltic lava flows or ashes and tuffs from more explosive eruptions. Primary porosity only in ashes and the less welded tuffs and at junctions of lavas. Joints and fractures in lavas. Variable potential, decreasing with age	Fracture with variable intergranular	0.001-10
Weathered basement complex	Crystalline rocks, granites, gneisses, schists	Decomposition of older igneous or metamorphic rocks can produce a weathered mantle of variable thickness, moderate porosity but generally low permeability, underlain by fresher rock which may be fractured; the combination results in a low potential but important very widespread but shallow aquifer system	Dominantly intergranular in weathered zone, fracture below	0.001-0.1

2.6 REFERENCES

Because many of the basic concepts about groundwater occurrence and movement are likely to be new to many of the readers of this monograph, and this introductory discussion may not have done them justice, the following three standard texts can be used to provide additional material if required:

Domenico, P.A. and Schwartz, F.W. (1998) *Physical and Chemical Hydrogeology*, 2nd edn, John Wiley, New York.

Freeze, R.A. and Cherry, J.A. (1979) *Groundwater*, Prentice Hall, Englewood Cliffs, New Jersey.

Price, M. (1996) *Introducing Groundwater*, 2nd edn, Chapman and Hall, London.

Additional references quoted in the chapter:

Alderwish, A.M. and Dottridge, J. (1999) Urban recharge and its influence on groundwater quality in Sana'a, Yemen. In *Groundwater in the Urban Environment: Selected city profiles*, (ed. P.J. Chilton), pp. 85-90, Balkema, Rotterdam.

Barraclough, D., Gardner, C.M.K., Wellings, S.R. and Cooper, J.D. (1994) A tracer investigation into the importance of fissure flow in the unsaturated zone of the British Upper Chalk. *J. Hydrology*, **156**, 459-469.

Becker, M.W., Reimus, P.W. and Vilks, P. (1998) Transport and attenuation of carboxylate-modified latex microspheres in fractured rock, laboratory and field tracer tests. *Ground Water*, **37**(3), 387-395.

Chilton, P.J. (1996) Groundwater. In *Water Quality Assessments: A guide to the use of biota, sediments and water in environmental monitoring*, 2nd edn, (ed. D. Chapman), pp. 413-510, E & FN Spon, London.

Chilton, P.J. and Foster, S.S.D. (1995) Hydrogeological characterization and water supply potential of basement aquifers in tropical Africa. *Hydrogeology J.*, **3**, 36-49.

Driscoll, F.G. (1986) *Groundwater and Wells*, 2nd edn, Johnson Division, St Paul, Minnesota.

Edmunds, W.M. and Gaye, C.B. (1994) Estimating the spatial variability of groundwater recharge in the Sahel using chloride. *J. Hydrology*, **156**, 47-59.

Edmunds, W.M. and Smedley, P.L. (2000) Residence times indicators in groundwater: the East Midlands Triassic sandstone aquifer. *Appl. Geochem.*, **15**, 737-752.

European Community 2000: Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, *Official Journal of the European Communities*, **L327,** Brussels.

Foster, S.S.D., Chilton, P.J., Moench, M., Cardy, F. and Schiffler, M. (2000) *Groundwater in Rural Development: facing the challenges of supply and resource sustainability*, World Bank Technical Paper No. 463, Washington, DC.

Foster, S.S.D., Lawrence, A.R. and Morris B.L. (1998) *Groundwater in Urban Development: assessing management needs and formulating policy strategies*, World Bank Technical Paper No. 390, Washington, DC.

Geake, A.K. and Foster, S.S.D. (1989) Sequential isotope and solute profiling of the unsaturated zone of the British Chalk. *Hydrological Sci. J.*, **34**, 79-95.

Ghassemi, F., Jakeman, A.J. and Nix, H.A. (1995) *Stalinization of Land and Water Resources*, University of New South Wales Press, Sydney.

Käss, W. (1998) *Tracing Techniques in Geohydrology*, Balkema, Rotterdam.

Kendal, C. and McDonnel, J.J. (1998) *Isotope Tracers in Catchment Hydrology*, Elsevier, Amsterdam.

Khadka, M.S. (1991) Nepal: Groundwater Quality. In *Groundwater Quality Monitoring in Asia and the Pacific*, UN-ESCAP, Water Resources Series No 70, Bangkok.

Lerner, D.N. (1997) Too much or too little: Recharge in urban areas. In *Groundwater in the Urban Environment: Problems, processes and management*, (eds. P.J. Chilton *et al.*) pp. 41-47, Balkema, Rotterdam.

Lerner, D.N., Issar, A. and Simmers, I. (1990) *Groundwater Recharge: A guide to understanding and estimating natural recharge*, Heisse, Hannover.

Lvovitch, M.I. (1972) World water balance: general report. In IAHS/UNESCO/ WMO *Proc. of Symposium on World Water Balance*, Reading, 1970, pp. 401-415, IAHS, Wallingford.

Malard, F., Reygrobellet, J-L., and Soulie, M. (1994) Transport and retention of faecal bacteria at sewage-polluted fractured rock sites. J. Environ. Qual., 23, 1352-1363.

Meybeck, M., Chapman, D.V. and Helmer, R. (eds.) (1989) Global Freshwater Quality: A first assessment, GEMS Global Environment Monitoring System, WHO/UNEP, Blackwell, Oxford.

Morris, B.L. Lawrence, A.R., Chilton, P.J., Adams, B., Calow, R. and Klinck, B.A. (2003) Groundwater and its Susceptibility to Degradation: A global assessment of the problem and options for management. Early Warning Report Series, RS 03-3, UNEP, Nairobi.

Nace, R.L. (ed) (1971) Scientific Framework of World Water Balance, Technical Papers in Hydrology 7, UNESCO, Paris.

NRC (1995) Mexico City's Water Supply: Improving the outlook for sustainability, NRC, National Academy Press, Washington, DC.

Orth, J.P., Netter, R. and Merkl, G. (1997) Bacterial and chemical contaminant transport tests in a confined karst aquifer (Danube Valley, Swabian Jura, Germany). In *Karst Water and Environmental Impacts*, (eds. G. Gunay and A.I. Johnson) Balkema, Rotterdam.

Seiler, K-P. and Lindner, W. (1995) Near surface and deep groundwater. *J. Hydrology*, **165**, 33-44.

Todd, D.K. (1980) *Groundwater Hydrology*, 2nd edn, John Wiley, New York.

UNESCO (1999) *World Water Resources at the Beginning of the 21st Century*, CD version, UNESCO, Paris.

US EPA (1997) *Guidelines for Wellhead and Spring Protection in Carbonate Rocks*, EPA 904-B-97-0003, Washington, DC.

Wellings, S.R. (1984) Recharge of the upper chalk aquifer at a site in Hampshire, England. *J. Hydrology*, **69**, 275-285.

3

Pathogens: Health relevance, transport and attenuation

S. Pedley, M. Yates, J.F. Schijven, J. West,
G. Howard and M. Barrett

This chapter will summarize current knowledge about the distribution of pathogens in groundwater and the factors that control their transport and attenuation. The aim is to provide a level of information and interpretation that will allow public health specialists and water resource managers to estimate risks to the groundwater from microbial contaminants derived from sources described in Section II of this monograph, for example, agricultural and urban sources.

Many factors, some environmental and others linked to the properties of the organism, control the survival and transport of microorganisms in the subsurface. However, it is important to consider that often the factors perceived to be of importance have been studied in isolation using controlled laboratory experiments and the conclusions then extrapolated to predict the fate of pathogens in the environment. This process is known as upscaling and is itself the subject of current research. In contrast, very few studies have attempted to examine the effect of multiple factors interacting in the natural environment. Current knowledge therefore offers a number of guiding principles about the transport and attenuation of pathogens in groundwater, but the

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complex interaction of factors controlling the fate of pathogens is poorly understood and difficult to predict in some environments.

DEF ▶ ***Microorganisms*** *are microscopic organisms within the categories algae, bacteria, fungi, protozoa, viruses and subviral agents (Singleton and Sainsbury, 1999).*

Pathogens *are any microorganisms which by direct interaction with (infection of) another organism cause disease in that organism (Singleton and Sainsbury, 1999). The strict definition of a pathogen excludes those microorganisms that cause disease indirectly by the synthesis of a toxin that may subsequently be ingested by the victim. Several microorganisms implicated in food poisoning cause disease in this way: Clostridium perfringens and Staphylococcus aureus are examples of this group. Nevertheless, these microorganisms can be pathogens in the strict sense under different conditions.*

3.1 MICROBIAL PATHOGENS AND MICROBIAL INDICATOR ORGANISMS

The ability of a pathogen to inflict damage upon the host is controlled by a combination of factors, in particular the nature of the organism (for example its virulence) and the susceptibility of the host. Several factors combine to determine the susceptibility of the host, including age, nutritional status and immunity. Immunocompromised individuals, for example, are highly susceptible to infection by pathogens, whereas well-nourished young adults are typically less susceptible to infections.

DEF ▶ ***Virulence*** *is the capacity of a pathogen to cause disease, defined broadly in terms of the severity of the symptoms.* ***Infectivity*** *is the ability of a pathogen to become established on or within the tissue of a host.*

Water can be the vehicle for the transmission of many different types of pathogenic microorganism: some being natural aquatic organisms and some being introduced into the water from an infected host. Overall, the pathogens in water that are the main concern to public health originate in the faeces of humans and animals, and establish an infection when contaminated water is consumed by a susceptible host (Boxes 3.1 and 3.2). These are the classical waterborne pathogens (Table 3.1) that are transmitted by the faecal-oral route of infection (Figure 3.1). Waterborne pathogens can be classified into four broad groups according to their chemical, physical and physiological characteristics. Listed in order of increasing functional complexity the groups are viruses, bacteria, protozoa and helminths. In general, the transmission of helminths in groundwater is unlikely, although not impossible, due to the size of the organisms and their eggs. For this reason, and because public health concerns surrounding waterborne disease transmitted through groundwater have concentrated upon the other groups of microorganisms, helminths will not be discussed in this chapter. Within the other groups a large number of microbial pathogens are able to contaminate groundwater (Table 3.1).

Box 3.1. Health impacts of contaminated groundwater in Walkerton, Canada (based on Howard, 2001)

In May 2000, 6 people died and over 2000 others became ill in the small town of Walkerton, Canada, as a result of consuming groundwater contaminated by *E. coli* O157:H7 and *Campylobacter*. Walkerton was almost entirely dependent upon groundwater for domestic supply obtained from production wells varying from 15 to >70 m deep. These wells intercept limestones and dolomites. There was a history of detection of *E. coli* in a number of the wells, but this problem was regarded as being something that could be controlled by routine chlorination of the source water.

The first public health problems (diarrhoea, vomiting) were noted in the days following a particularly violent storm during which 100 mm of rain fell. Initially the problem was suspected as food poisoning and it was not until over a week later that well water was identified as the source and a boil-water alert was issued. *E. coli* O157:H7 and *Campylobacter* spp. were subsequently identified as the cause of the deaths. The source of the organisms was traced to a cattle farm close to one of the shallower production wells. It was initially suggested that storm water runoff conveyed the contaminants to the production wells. However, subsequent evidence indicates that the well contamination causing the outbreak had occurred before the storm event. The precise travel paths enabling the contaminants to enter the production wells (even the deepest of which was contaminated) remain a matter of speculation, although fissure flow in the limestone aquifer is an obvious candidate. It may be significant that there were abandoned production wells in the area that had not been properly sealed. Improperly abandoned boreholes may facilitate the rapid vertical mixing of contaminants entering at or near the surface.

It is clear that the public health impact was a result of the combination of inadequate protection and monitoring of the groundwater resource with a failure in treatment. This is not uncommon, Bramham in the United Kingdom being a further example (Lerner and Barrett, 1996). Clearly reliance on treatment (as a ‘single barrier’ approach) without other measures such as adequate groundwater protection is a higher risk approach than that of the ‘multi barrier’.

The types and numbers of the various pathogens will vary temporally and spatially depending upon the incidence of disease in the community, the known seasonality of human infections, and the characteristics of the aquifer systems. Furthermore, the microbial illnesses and the severity of the disease vary markedly with the organism.

NOTE ▶ *Although some enteric pathogens may circulate within a population all year round, many have a clearly defined seasonal distribution. For example, in temperate zones, the transmission of rotavirus takes place almost exclusively during cold weather.*

Box 3.2. Virus borne outbreaks of gastroenteritis in Wyoming, USA

In February 2001, episodes of acute gastroenteritis were reported to the Wyoming Department of Health among snowmobilers (Anderson *et al.*, 2003). The outbreak was believed to have been caused by noroviruses that could be identified from 8 of 13 stool samples as well as from groundwater samples of one well. A second outbreak of acute gastroenteritis occurred in Wyoming during October 2001 among persons who dined at a tourist saloon (Parshionikar *et al.*, 2003). A norovirus strain (genogroup I, subtype 3) was found in stool samples from three ill persons as well as in the water from the saloon's only well.

Although land use planning, water resource management, water treatment and disinfection are used to control the transmission of waterborne pathogens, the safety of a water source is frequently verified by testing for the presence of microbial parameters. A variety of pathogens may be present, and the different methods that are required to isolate each pathogen prohibit the direct examination of water samples for pathogens on a routine basis. Moreover, pathogens may not be detected due to low levels, or the lack of an appropriate detection method, but they may still be present at a density that represents an unacceptable level of risk. Furthermore, currently unknown and therefore undetectable pathogens may be present. To overcome this difficulty, a separate group of microorganisms is used as an indicator for the potential presence of pathogens. The common descriptive term for this group of organisms is faecal indicator organisms. Gleeson and Gray (1997) have published a thorough review of the application of faecal indicator organisms in water quality monitoring that may be consulted for further information. This group comprises the following:

- total coliform bacteria
- thermotolerant coliform bacteria
- *E. coli*
- faecal streptococci
- bacteriophage

Table 3.1. Pathogenic microorganisms of concern in groundwater (adapted from Macler and Merkle, 2000)

Organism	Associated health effects
Viruses	
Coxsackievirus	Fever, pharyngitis, rash, respiratory disease, diarrhoea, haemorrhagic conjunctivitis, myocarditis, pericarditis, aseptic meningitis, encephalitis, reactive insulin-dependent diabetes, hand, foot and mouth disease
Echovirus	Respiratory disease, aseptic meningitis, rash, fever
Norovirus (formerly Norwalk virus)	Gastroenteritis
Hepatitis A	Fever, nausea, jaundice, liver failure
Hepatitis E	Fever, nausea, jaundice, death
Rotavirus A and C	Gastroenteritis
Enteric adenovirus	Respiratory disease, haemorrhagic conjunctivitis, gastroenteritis
Calicivirus	Gastroenteritis
Astrovirus	Gastroenteritis
Bacteria	
Escherichia coli	Gastroenteritis, Haemolytic Uraemic Syndrome (enterotoxic *E. coli*)
Salmonella spp.	Enterocolitis, endocarditis, meningitis, pericarditis, reactive arthritis, pneumonia
Shigella spp.	Gastroenteritis, dysentery, reactive arthritis
Campylobacter jejuni	Gastroenteritis, Guillain-Barré syndrome
Yersinia spp.	Diarrhoea, reactive arthritis
Legionella spp.	Legionnaire's disease, Pontiac fever
Vibrio cholerae	Cholera
Protozoa	
Cryptosporidium parvum	Diarrhoea
Giardia lamblia	Chronic diarrhoea

NOTE ▶ *The coliform group of bacteria consists of several genera belonging to the family Enterobacteriaceae (Gleeson and Gray, 1997). The relatively limited number of biochemical and physiological attributes used to define the group (including growth at 37°C) means that its members include a heterogeneous mix of bacteria. Although the total coliform group will include bacteria of faecal origin it also includes species that are found in unpolluted environments. Thermotolerant coliforms are those bacteria from within the total coliform group that grow at 44°C. E. coli is a thermotolerant coliform.*

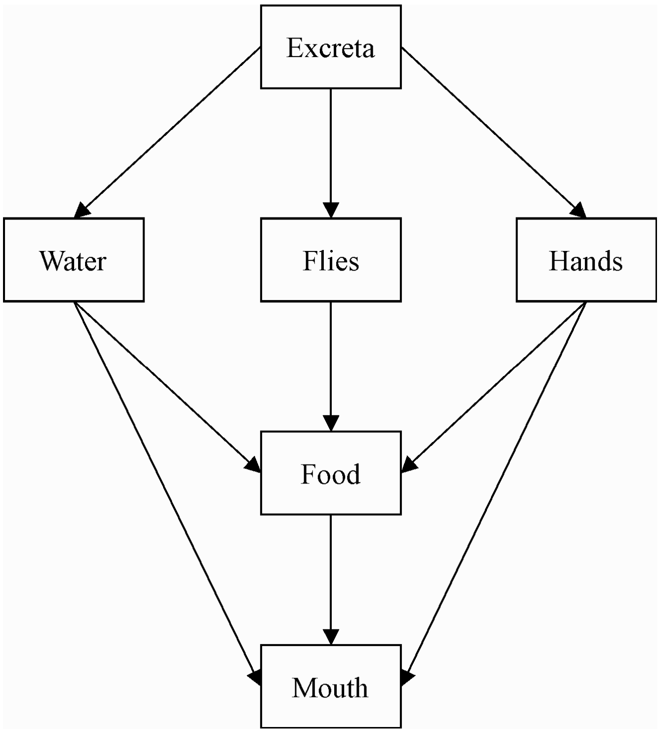

Figure 3.1. Principal elements of the faecal-oral route of disease transmission (Howard *et al.,* 2002)

An ideal microbial indicator of faecal pollution is easily detected, always present in faecal waste, and is more durable in the environment than most enteric pathogens. It should comprise a large percentage of the organisms in faecal waste, exceed the numbers of most enteric pathogens and be roughly proportional to the degree of pollution. Lastly, because indicator organisms should be absent unless faecal contamination is present, they should ideally not be present in drinking-water that is microbially safe for consumption. For many applications, 100 ml of water is used as the standard volume for analysis.

The durability of faecal indicator organisms in the subsurface is an important issue that has a direct bearing on the interpretation of water quality data. Ideally the faecal indicator organism should be removed from the environment at a slower rate than the most durable pathogen so that its potential for dispersal is greater. In practice, this situation will seldom arise. For the purpose of acting as surrogates for pathogens in groundwater tracer studies, other advantageous properties are the ease of preparing high numbers of the indicator and the ease of enumerating the indicator. These properties allow indicators to be used as a tool to identify and quantify removal processes in laboratory and field studies. The most important removal processes are inactivation or die-off, adsorption to the surface of the grains of the porous medium and physical filtration or straining when pore throats are too small to let a microorganism pass. Thus robust indicators are inactivated, adsorbed and strained not more than the pathogens they represent. The removal processes are described in more detail later in this chapter.

It is acknowledged that faecal indicator bacteria do not give absolute resolution to the presence/absence of pathogenic protozoa, bacteria and viruses. These diverse groups of microorganisms have highly variable transport and attenuation characteristics that cannot be wholly represented by the small group of indicator bacteria. However, the density of faecal indicator bacteria does provide a measure of probability of the presence of pathogens.

Faecal indicator bacteria are of limited use for predicting the presence or absence of viruses as viruses often survive significantly longer in groundwater systems. It is not practical to sample and analyse for all pathogenic viruses. As a result bacteriophage – viruses that infect bacteria – from faecal sources are often used to indicate the likely presence or absence of viruses in groundwater. Several groups of bacteriophage have been evaluated as indicator organisms although the focus of attention has been upon the coliphage group of viruses because they can be detected and quantified using relatively simple analytical methods.

Negatively charged bacteriophages, like MS2 and PRD1, have been found to be useful model viruses and have been used in many field and laboratory studies on subsurface transport of viruses (Schijven and Hassanizadeh, 2000). They attach poorly to most soils, and at low temperatures they inactivate at a low rate. PRD1 is relatively insensitive to higher temperatures or extreme pH. These bacteriophages have the same size and shape as many waterborne pathogenic viruses. They are easy to prepare in high numbers and are easy to detect. MS2 is an F-specific RNA bacteriophage. This group of bacteriophages may be naturally present in faecal contaminated water in numbers 10^2 to 10^4 times higher than enteroviruses (Havelaar *et al.*, 1993). However, F-specific bacteriophages are less stable (more temperature sensitive) than somatic coliphages. The latter are usually found in higher number in faecally contaminated water and are therefore also useful indicators.

3.2 DISTRIBUTION OF PATHOGENS AND FAECAL INDICATORS IN GROUNDWATER

Sources of faecal contamination in groundwater are discussed in Section II and potentially include leakage from on-site sanitation systems or sewers (Box 3.3), animal manures (Box 3.1), wastewater or sewage sludge applied in agriculture. The sources can be classified according to their origin. A point source has an identifiable source, such as a leaking septic tank, which may result in a well-defined plume. More difficult to control, and posing a greater risk to groundwater quality, are non-point sources. Non-point sources are larger in scale and produce relatively diffuse pollution originating from either widespread application of contaminated material or many smaller sources. The aggregate of point sources in a leaking sewerage system may, overall, represent a non-point source of contamination to groundwater (usually described as multi-point source of pollution).

Traditionally, hydrogeologists, and many public health scientists, have regarded groundwater as a relatively microbially safe source of drinking-water. Unlike surface waters, which are vulnerable to direct contamination from many sources, groundwater is often shielded from the immediate influence of contamination by the overlying soil and unsaturated zones as described in Chapter 2. In these zones, pathogenic microorganisms have been assumed to be attenuated by the prevailing physical, chemical and biological conditions in the environment. The risk of pathogens being transported into groundwater and producing a threat to public health was, therefore, considered to be low. Consequently, many groundwater sources are used for public supply with a minimum level of treatment, normally chlorination, or with no treatment at all.

The underlying rationale for restricted dispersion in the subsurface has some merit, but it is now known that microbial contamination of groundwater is more widespread than previously believed. Indeed, as was found with chemical contaminant studies, particularly in the 1980s, the more that it is looked for, the more it can be found. Tables 3.2 and 3.3 list some examples of studies that have demonstrated the occurrence of faecal indicators and enteroviruses in groundwater. Although there may be a bias in some of the studies, created by the deliberate selection of vulnerable sites, the data show that a significant percentage, up to 70 per cent in some regions, of groundwater sources contain one or more of the microbial indicators of faecal contamination.

Table 3.2. Occurrence of microbial faecal indicators in groundwater

Organism	Proportion of receptors positive (%)	Study location	Reference
Coliform bacteria	10	USA: 445 public supply wells	Abbaszadegan
Coliphage	21	USA: 444 public supply wells	*et al.*, 1998
Enterococci	9	USA: 355 public supply wells	
Somatic coliphage	50	USA: 30 public water supply wells	Lieberman *et al.*,
E. coli	50	judged to be vulnerable to faecal	1994
Enterococci	70	contamination	
Coliform bacteria	40	USA, Montana	Bauder *et al.*, 1991
E. coli	16-24	Canada, Province of Ontario:	Goss *et al.*, 1998
Faecal streptococci	12-24	farmstead domestic wells	
E. coli	60	Republic of Moldova, Balatina	Melian *et al.*, 1999
Faecal streptococci	50	and Carpini	
Thermotolerant coliforms and faecal streptococci	10-40	Finland: rural wells	Korhonen *et al.*, 1996

Table 3.3 shows the occurrence of pathogenic enteroviruses found in public water supply wells in the USA as defined by the Safe Drinking Water Act (US Government, 1996). Hydrogeological data from these studies were available on aquifer type as part of the study designs and were reviewed for accuracy by hydrogeologists. Limestone (karst), fractured bedrock (igneous and metamorphic rocks) and gravel (formed in high energy depositional environments with little or no sand or other fine grained materials) aquifers are defined as sensitive aquifers under the proposed Ground Water Rule (US EPA,

2000). If a public water supply well draws water from a sensitive aquifer, then the State must find the well sensitive to faecal contamination unless a hydrogeological barrier protects it. A hydrogeological barrier is defined as the physical, biological and chemical factors, singly or in combination, that protect a well from pathogenic organisms. In this proposal, a confining layer is one example of a hydrogeological barrier. If a hydrogeological barrier is present, then the State can nullify the determination that a system is located in a sensitive aquifer. If no suitable hydrogeological barrier exists, then the proposed Ground Water Rule requires the system to conduct faecal indicator source water monitoring.

Table 3.3. Occurrence of enteroviruses in public water supply wells in the USA

Sensitive wells [a]		**Non-sensitive wells**		**Samples per well**	**Average filtered volume (L)**	**Virus type (N_w)** [b]	**Reference**
N^+/N_w	*Positive*	*N^+/N_w*	*Positive*				
3/49	6%	2/10	20%	1	200-1000	Coxsackievirus B5 (1) Echovirus 13 (1) Echovirus 20 (1) Poliovirus 3 (1) [c] Reovirus (3)	Lindsey *et al.*, 2002
0/91	0%	0/0	-	1	1500		Banks and Battigelli, 2002
0/0	-	0[d]/27	0%	1	1500	Rotavirus (1) [d]	Banks *et al.*, 2001
0/92	0%	0/12	0%	1	200-300		Femmer *et al.*, 2000
1/96	1%	0/9	0%	2	200-300	Poliovirus 1 (1) [c]	Davis and Witt, 2000
1/96	1%	0/9	0%	2	200-300	Poliovirus 1 (1) [c]	Davis and Witt, 2000
6/12	50%	1/18	6%	12	6000	Coxsackievirus A7 (1) Coxsackievirus B1 (4) Coxsackievirus B3 (1) Coxsackievirus B4 (5) Coxsackievirus B5 (1) Echovirus 11 (2) Echovirus 15 (4) Echovirus 18 (2) Echovirus 21 (3) Echovirus 24 (2)	Lieberman *et al.*, 2002
0/31	0%	0/79	0%	4	Up to 1500		Doherty *et al.*, 1998

N^+ = number of positive enteroviruses by buffalo-green-monkey tissue culture; N_w = number of wells; a = sensitive wells are wells located in igneous or metamorphic rock aquifers or limestone aquifers or gravel aquifers with very low sand/fine grained content; b = serotyping results to confirm cell culture enteric virus positive samples (serological identification of all these samples was determined by Dan Dahling of the US EPA); c = possible laboratory contamination; d = positive by Rototest assay of RD cell lysate.

Lindsey *et al.* (2002) found enteric viruses in three sensitive aquifers and two that were not sensitive. In Tables 3.2 and 3.3, the data of Lieberman *et al.* (2002) are most meaningful because 12 samples were taken at monthly intervals from each well from 30 sites in the continental USA, the Virgin Islands and Puerto Rico. In addition, the sample volumes used in these studies were significantly larger than routine volumes: average

6000 litres, and maximum even up to 15 000 litres. This significantly increases the probability of detecting virus contamination of a well. Lieberman *et al.* (2002) found enteric viruses primarily in sensitive aquifers (i.e. karst, fractured bedrock and coarse gravel) but only once in a very shallow sand well (5 m deep; see also Dahling, 2002). One reason that as many as 7 of the 30 wells (24 per cent) were contaminated with enterovirus is because almost all wells were selected for enterovirus sampling only if they had a history of total coliform and somatic coliphage occurrence (see Table 3.2). Echovirus 11 was possibly coming from upgradient septic tanks. Viruses found in the karst wells must have travelled a long distance because no potential sources of contamination were near. One of the wells was located in a populated gravel flood plain with a nearby trailer park with septic tanks about 30 m away. In this well water, coxsackieviruses A7, B1 and B4, echoviruses 15, 18, 21 and 24 and reovirus were detected. Coxsackievirus B4 was also found in the water from a well in fractured basalt with septic tanks nearby.

Borchardt *et al.* (2003) studied the incidence of viruses in Wisconsin, USA private household wells located near seepage land application sites or in rural subdivisions served by septic systems. Fifty wells in seven hydrogeological areas were sampled four times over a year, once each season. Of the 50 wells, 4 (8 per cent) were found to be positive for viruses using analytical methods that detect the presence of the viral nucleic acid (reverse transcription PCR). Of these, three wells were positive for hepatitis A virus and the fourth well was positive for rotavirus and norovirus in one sample and for enterovirus in another sample. Culturable enteroviruses were not detected in any of the wells. Virus occurrence could not be associated statistically with faecal indicators (i.e. total coliforms, *E. coli*, faecal enterococci, F-specific RNA bacteriophages).

Clearly, the common perception that groundwater is *per se* a microbially safe source of drinking-water is inaccurate. Whilst usually the microbial contamination of groundwater is likely to be orders of magnitude lower than that of surface waters, it is now apparent that a significant percentage of groundwater sources are contaminated by microorganisms derived from faeces. As shown above, the known presence of infectious pathogenic viruses in some wells, for example, represents an unequivocal message that viruses are mobile in the subsurface, long-lived and capable of causing waterborne illness.

In the same way that surface waters may show rapid changes in the concentration of pathogens, distribution and concentration of pathogens and faecal indicator bacteria in groundwater sources is not static but also demonstrates fluctuation. Temporal and spatial variations are frequently observed that may be linked to seasonal changes in land use and changing weather patterns. For example, fluctuations in the levels of thermotolerant coliforms have been observed in proximity to wastewater irrigation sites in Mexico and in the United Kingdom. The distribution of enteric bacteria and viruses in urban groundwater has been observed to vary both horizontally and vertically (Box 3.3).

Box 3.3. Depth and extent of microbial contamination of groundwater in British urban sandstone aquifers (based on Powell *et al.*, 2000; 2001a; 2001b)

There are few published data on the microbial, and particularly viral, quality of United Kingdom groundwaters. This should not be taken as an indication of a general absence of contamination, rather as a lack of detailed monitoring studies. A number of workers have identified sewage contamination of the Triassic Sandstone aquifers in urban areas of the United Kingdom, derived from leaking sewers.

Powell and co-workers set out to determine the extent and penetration of microbial contaminants in the Triassic Sandstone aquifer underlying Birmingham and Nottingham in the United Kingdom. Five multilevel groundwater monitoring devices were installed into the aquifer, providing a total of some 50 depth-specific sampling points. Viral monitoring was undertaken using a glass wool trap for the concentration of enteric viruses from large volume groundwater samples.

The field data lead to four key findings:

- Sewer leakage-derived microbial contaminants are able to penetrate sandstone aquifers to significant depths (>90 m).
- Human enteric viruses, including pathogenic species are widespread in the aquifer.
- The species of sewage-derived human enteric viruses in groundwater are found to vary temporally, and in parallel with their predicted prevalence in the population. The dominant types found in March and June 2001 were Noroviruses and Coxsackievirus B4 respectively.
- Particular horizons at depth within the sandstone aquifer were found to be rapidly susceptible to microbial contamination (i.e. contaminant distribution is vertically and temporally heterogeneous).
- The Triassic Sandstone aquifer (and, by implication, other similar sandstone aquifers around the world), the second most important in the United Kingdom, is far more vulnerable to microbal contamination than previously assumed. This has public health implications where groundwater is consumed without adequate treatment.

Frequently, the microbial quality of shallow groundwater sources, including springs, will deteriorate after heavy rainfall as surface contamination is washed into the source directly and organisms in the unsaturated zone are mobilized by water percolating through the soil matrix (Box 3.1). Similarly, the relative proportions of indicator bacteria and pathogens, and of bacteria and viruses, will fluctuate such that the dominant species isolated at one time may be absent on subsequent sampling occasions (Box 3.4).

Box 3.4. Temporal fluctuations in microbial contamination of groundwater in Kampala, Uganda (based on Barrett *et al.*, 2000)

Sampling of 15 protected springs was undertaken in areas of high-density and low-density population (peri-urban) in Kampala, Uganda on three successive days (28-30 September 1999). The wet season was in progress, and rainfall occurred on every day of sampling. On the night of 28-29 September, a significantly heavier rainfall event took place. Analysis of the samples for faecal indicators, including thermotolerant coliforms and faecal streptococci, was undertaken. As shown by Figure 3.2, there was a clear pulse reaction of contamination in spring water within 12 hours of the major rainfall event.

A variety of metasedimentary rocks (e.g. quartzites and phyllites) underlie Kampala. Differential weathering has resulted in a pronounced topography with thin weathered mantles of limited extent containing shallow (2-20 m) groundwater flow systems that discharge to valley springs. These are fed by a combination of baseflow and seasonally derived interflow. Many of these springs are used, untreated, by lower income communities with limited access to higher service levels of piped water supply. Clearly the monitoring of protected springs for microbial contaminants in these localized groundwater flow systems must be interpreted in the context of rainfall events.

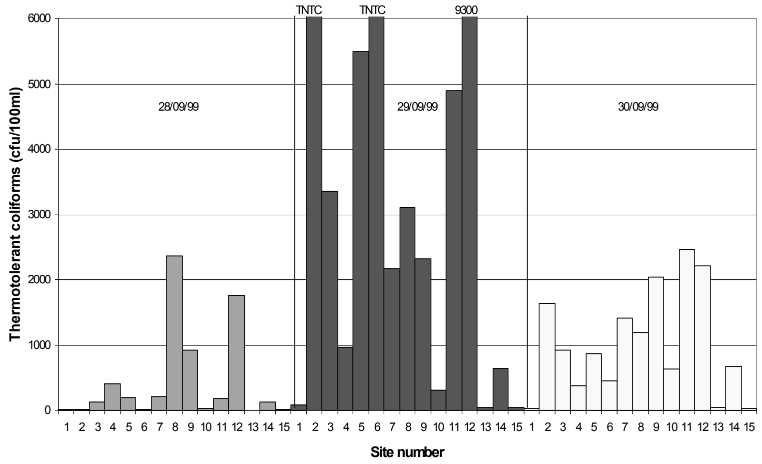

Figure 3.2. Effect of heavy rainfall on the microbial quality of spring water in Kampala, Uganda

3.3 TRANSPORT AND ATTENUATION OF MICROORGANISMS IN THE UNDERGROUND

Some, perhaps many, instances of groundwater receptor contamination will occur by rapid transport pathways accidentally introduced by human intervention and connecting the contamination source to the groundwater abstraction point. Such pathways could include inadequate sanitary completion of springs, wells and boreholes, the presence of a forgotten conduit connecting the source of contamination to the groundwater abstraction point, or voids and fractures in soils that allow direct ingress of contaminated materials. The implementation of management actions to reduce faecal contamination close to the abstraction point or the rehabilitation or improvement of the well or spring is usually sufficient to control access of pathogens to the water source (Section IV).

Rapid transport pathways cannot, however, explain all groundwater source contamination events and it is now widely accepted that the transport of microbial pathogens within groundwater systems is a significant mechanism for waterborne disease transmission. The remainder of this chapter deals with the factors that control the transport and attenuation of pathogens into and through groundwater.

3.3.1 Transport and attenuation of pathogens in the unsaturated zone

Hydrogeological processes in the unsaturated zone are complex and the behaviour of microorganisms is often difficult to predict. Nevertheless, the unsaturated zone can play an important role in retarding (and in some cases eliminating) pathogens and so must be considered when assessing aquifer vulnerability, as described in Chapter 8. Attenuation of pathogens is generally most effective in the uppermost soil layers where biological activity is greatest. The presence of protozoa and other predatory organisms, the rapid changes in soil moisture and temperature, competition from the established microbial community, and the effect of sunlight at the surface combine to reduce the level of pathogens within this zone. The effect of individual environmental factors will be discussed in a later section of this chapter.

The transport of pathogens from the surface into the subsurface requires the presence of moisture. Even during relatively dry periods, soil particles retain sufficient moisture over their surface for pathogens to migrate downwards into the subsurface. Under these conditions the main driving forces will be sedimentation, diffusion and bacterial motility. Within the thin film of moisture the organisms are brought into close contact with the surface of the particle, thus increasing the opportunity for adsorption to the particle surface and further retarding movement. If soil moisture decreases, the strength of the association between the organism and the particle surface will increase to a point where the organism is bound irreversibly to the surface. Passive binding to particle surfaces has been observed with some strains of virus, and it is believed that the strength of the bond can immobilize the virus and contain it at the point of interaction. It is possible that similar interactions occur with other groups of pathogens, but the processes are less well defined. Bacteria, for instance, synthesize extracellular substances that can enhance their attachment to surfaces and promote binding, suggesting that the process involves both passive and active processes. Whether alone, or in combination with the apparently protective effect of adsorption onto surfaces, soil moisture influences the persistence of microorganisms, in particular viruses. In laboratory experiments a soil moisture content of between 10 and 15 per cent was shown to be optimal for the survival of several strains of enteric virus (e.g. Bagdasaryan, 1964; Hurst *et al.,* 1980a; 1980b).

By contrast, an increase in the moisture content of the unsaturated zone may increase the vulnerability of the aquifer to pathogen contamination in two ways: by providing rapid transport pathways and by mobilizing adsorbed organisms. During periods of high recharge, for example during prolonged heavy rain, the intergranular spaces in the unsaturated zone become waterlogged and provide a hydraulic pathway for the rapid transport of pathogens. Where these intergranular spaces expand into fissures the downward migration of pathogens can be extremely rapid. For example, particles ranging in diameter from 0.1-6.0 µm have been found to move through 20 m of unsaturated chalk in less than 3 days by passage through horizontal and vertical fissures (Lawrence *et al.*, 1996). Moreover, the rapid movement of pathogens through fissures limits the potential for attenuation by adsorption to surfaces in the soil matrix.

In the interval between recharge events, the chemistry of the water in the unsaturated zone will change as it equilibrates with the soil matrix. In some soil types, these changes may favour the adsorption of microorganisms to surfaces in the soil matrix. A lowering in the ionic strength or salt content of the surrounding medium, which can occur during a rainfall event, may be sufficient to cause desorption of the organism allowing further migration into the soil. This phenomenon has been observed in laboratory experiments and there is evidence to suggest that it can occur in the field. Furthermore, some workers have noted that the virus particles that have desorbed from the soil surface have a reduced capacity to resorb when the environmental conditions become favourable. The implication of this observation is that virus particles that have been mobilized in the subsurface are unaffected by one of the principal methods of attenuation and are likely, therefore, to be dispersed over a much wider area than would be anticipated.

The size variability of microorganisms (Table 3.4) can, to an extent, control their mobility in the subsurface. Soil and rock pore sizes are also variable and the two ranges are known to overlap (Figure 3.3). Thus in soils that are composed of fine grain particles, typically clayey-silts, the pore space is sufficiently small (<4 µm) to physically prevent the passage of bacterial and protozoal pathogens into the subsurface. This removal process is called physical filtration or straining. Straining has been identified as the principal mechanism for controlling the migration of *Giardia* and *Cryptosporidium* species (*Cryptosporidium* oocysts: 4-6 µm; *Giardia* cysts: 7-14 µm) through these soil types; indeed, experience has shown that up to 99 per cent of *Cryptosporidium* oocysts are retained in the upper layers of the soil. However, the isolation of *Cryptosporidium* and *Giardia* from a small but significant number of groundwater sources in the USA (Hancock *et al.*, 1998) and the United Kingdom indicates that the protective effect of the soil layer is frequently evaded, probably by migration through preferential pathways or bypassing; for example, from sewers that are often located below the soil zone.

Several studies demonstrate a considerable degree of variability between the inactivation or die-off rates of different groups of pathogens, and between inactivation rates of the same organism in different environments. However, as a general rule, enteric viruses persist longer in soils than bacteria. Among the enteric viruses, hepatitis A virus appears to be the most resistant to inactivation in soil (Sobsey *et al.*, 1986) and, in laboratory experiments, shows a lower capacity for adsorption to particle surfaces. The oocysts of *Cryptosporidium* are highly resistant to environmental stress and it has been estimated that they could be detected after 12 months in soil.

Table 3.4. Approximate sizes of selected microorganisms

Class	Microorganism	Size
Virus	Bacteriophage	0.02-0.2 μm diameter
	Poliovirus	0.03 μm diameter
Bacteria	Bacterial spores (*Bacillus*, clostridia)	1 μm
	E. coli	0.5 μm x 1.0 μm x 2.0 μm
	Salmonella typhi	0.6 μm x 0.7 μm x 2.5 μm
	Shigella spp.	0.4 μm x 0.6 μm x 2.5 μm
Protozoa	*Cryptosporidium* oocysts	4.0-6.0 μm diameter
	Giardia	7.0-14.0 μm diameter
	Enteroamoeba histolitica	20-25 μm diameter

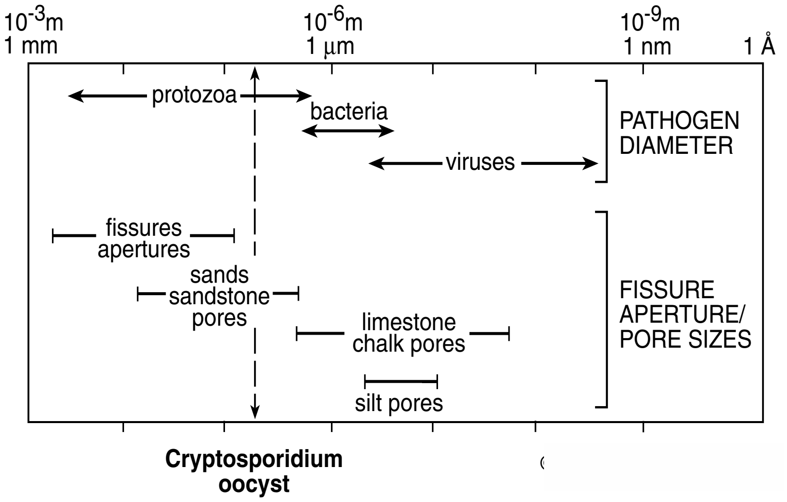

Figure 3.3. Pathogen diameters compared to aquifer matrix diameters (ARGOSS, 2001; British Geological Survey ©NERC)

Some of the factors that contribute to reduced inactivation rates in the unsaturated zone are known (lower temperatures, increased moisture, pH, reduced exposure to sunlight, organic matter and the nature of the pathogen) but the relative contribution of each factor at any field site is difficult to predict, and may be site specific. In these circumstances, the tendency of hydrogeologists and public health microbiologists is to construct general risk assessment models based upon laboratory and field experience. At their most sophisticated, the models comprise computer simulations of pathogen transport (for example Yates and Yates, 1988), but also used are simple tables and diagrams linking risk to the main observable features of the environment. One such model has been constructed by Romero (1972); a second has been developed to accompany guidelines for assessing the risk to groundwater from on-site sanitation (ARGOSS, 2001). However, the problem with such an approach is that only a qualitative indication for risk levels is given without any definition of what is meant by a high or low risk level. The actual useful information from this approach is a rough indication of a relative probability for pathogenic microorganisms to reach groundwater. Table 3.5 shows the different classes of lithology that were defined in decreasing order of ability to limit transport of microorganisms.

Table 3.5. Limitation of the transport of microorganisms by the lithology of the unsaturated zone in decreasing order (top to bottom) (based on ARGOSS, 2001)

Lithology of the unsaturated zone
Fine sand, silt and clay
Weathered basement (soft not consolidated)
Medium clean sand
Coarse sand and gravels
Consolidated rock

Shallow groundwater (<5 m) is assumed to be at the highest probability of contamination irrespective of the lithology of the unsaturated zone. As the depth to the water table increases so the capacity of the unsaturated zone to attenuate microorganisms will also increase, although this will depend upon the composition and structure of the unsaturated zone. For example, fine silts and clays will strongly adsorb bacteria and viruses and also effectively filter out the larger pathogenic microorganisms. Thus the probability of reaching groundwater at greater than five m depth is very low. By contrast, fracture flow through consolidated rock creates a relatively high probability of reaching groundwater even at depths of over 10 m.

In summary, maximizing the residence times in the unsaturated zone has been proposed as the key mechanism for eliminating bacteria and viruses (Lewis *et al.*, 1982) and, in general, this principle is robust. However, there are exceptions, for example:

- The variability in the nature and thickness of the unsaturated zone overlying aquifers means that the residence times may not always be adequate to attenuate all pathogens. In particular, during periods of high recharge, an aquifer may be vulnerable to contamination by pathogens that are transported rapidly through the waterlogged intergranular spaces in the unsaturated zone.
- Where the flow is intergranular within the unsaturated zone there is greater potential for contact with the soil/rock particles and hence greater potential for retention, both sorptive and filtering. However, if excessive loading takes place the filtering effect may lead to a blocking of the pores. The resulting reduction in hydraulic conductivity may reduce the effectiveness of the unsaturated zone to retard contaminants if the clogging forces recharge water into vertical fissures where rapid downward movement can occur.
- The structure of the unsaturated zone is seldom uniform and fissures may exist permanently or develop in any environment when the unsaturated zone dries out. The presence of fissures will always increase the vulnerability of the groundwater to contamination from the surface, and it should be considered that although the soil conditions may facilitate the adsorption and attenuation of pathogens, the existence of bypass channels may offset the protective effect of the soil.

3.3.2 Transport and attenuation of pathogens in the saturated zone

On reaching the saturated zone, microbial contaminants are subject to the same processes of attenuation that are described in Section 3.3.1 but under conditions of natural or artificially induced flow. Thus die-off, adsorption, filtration, predation and dilution all contribute to the attenuation of pathogens in the saturated zone. Due to the heterogeneous nature of aquifer material there may be large variations in hydraulic conductivity and this can significantly influence the movement of microorganisms in the aquifer. Microorganisms are transported in groundwater by advection, dispersion and diffusion, which are defined in Chapter 4. The result is a migration and spreading of the contaminant concentration in space and time. This may result in contamination of increasingly large aquifer volumes as the pollutant moves downgradient. Although the transport of pathogens in some aquifer types can be both rapid and extensive, there are several factors that may attenuate pathogens in groundwater (Table 3.6).

Table 3.6. Factors affecting transport and attenuation of microorganisms in groundwater (adapted from West *et al.*, 1998)

Characteristics of the microorganism	Aquifer/soil (environment) properties
Size	Groundwater flow velocity
Shape	Dispersion
Density	Pore size (intergranular or fracture)
Inactivation rate (die-off)	Kinematic/effective porosity
(Ir)reversible adsorption	Organic carbon content (solid)
Physical filtration	Temperature
	Chemical properties of groundwater (pH, etc.)
	Mineral composition of aquifer/soil material
	Predatory microflora (bacteria, fungi, algae, etc.)
	Moisture content
	Pressure

From the perspective of groundwater management and the estimation of pathogens at the point of abstraction (receptor), highly fractured and karstic aquifers represent a particular problem. As discussed in Chapter 2, groundwater flow through fractured systems may be very rapid, and the potential for microorganisms to be attenuated by interaction with the aquifer matrix is much reduced, although not entirely absent. Consequently, the inactivation rate of the pathogen and the groundwater flow rate will primarily control dispersal in these aquifer systems. Three referenced studies will help to illustrate the potential for rapid pathogen transport in highly fractured aquifers:

- The migration of bacteriophage in a chalk aquifer in the south of England was investigated by Skilton and Wheeler (1988, 1989). They injected three strains of bacteriophage into piezometers that intersected the water table and then collected samples at different sites downgradient to determine the extent of movement. Very high velocities were observed at one site due to the fact that the majority of the water flow is through fissures, fractures, solution openings and cavities. All three phage types were detected 355 m from the injection site approximately 5 hours after introduction. It is noteworthy that viable phage were still being recovered more than 150 days after they were injected into the aquifer.

- Mahler *et al.* (2000) cite the work of Batsch and colleagues who reported the detection of injected bacteria 14 km from the injection site, having been transported at a velocity of about 250 m/h. Mahler's own studies (Mahler *et al.*, 2000) in a karstic aquifer located in the South of France have confirmed the very rapid transport of faecal indicator bacteria in these systems.
- Lee (1993) investigated the contamination of a water supply well by *Giardia* spp. and *Cryptosporidium* spp. in a karstic environment. The karstic nature of the study area provided the potential for rapid infiltration of surface waters to the water table and subsequent transport of the organisms to the well through fractures and fissures. This connection was confirmed by the study. An analysis of particle size revealed that the full range of particle sizes found in the surface waters was not present in the well; there was a cut-off at both high and low ranges. The author concluded that there had been adsorption of smaller particles and straining of larger ones. The size range of the particles that were transported through the system included *Giardia* and *Cryptosporidium*.

These observations have significant implications for the public health risk associated with water abstracted from highly fractured and karstic aquifers. Not only can viral, bacterial and protozoan pathogens be transported rapidly over great distances, but also the groundwater flow pattern between the source and receptor can be very difficult to predict due to the many interconnected fractures in the aquifer. It is possible that well designed tracer studies and groundwater flow models can help to define the potential limits of pathogen dispersion in a highly fractured aquifer; however, with the current uncertainties surrounding pathogen attenuation in groundwater it is prudent to assume that where these aquifer types are exposed to sources of pathogens they are at high risk of contamination over a wide area.

In other aquifer types, the radius of migration from the source of contamination is normally restricted to several tens of meters, or a few hundred meters, depending upon the type of aquifer system and the properties of the organism (Table 3.6). Where the groundwater flow rate is low through unconsolidated sediments the dispersal of pathogens will naturally be limited and, in addition, this type of system offers greater opportunity for the pathogen to interact with the aquifer matrix. Adsorption and physical filtration may then be the major factors controlling pathogen transport.

Despite acting to limit the dispersal of pathogens in the aquifer, interaction with the aquifer matrix may also enhance the survival of the pathogens in the environment. In several cases, adsorption to surfaces in the aquifer (sediment particles and colloids, as well as the aquifer matrix) has been shown to reduce the inactivation rate of both viruses and bacteria. Consequently, although the risk of contamination is contained close to the source, the persistence of pathogens within the zone of contamination may be increased beyond what is predicted from measurements of inactivation in the groundwater.

Schijven and Hassanizadeh (2000) showed that removal of virus in the subsurface often appears to be higher near the source than further away from the source, e.g. within the first 8 m of aquifer passage spores of *Clostridium bifermentans* R5 and bacteriophage MS2 were reduced by 5 $\log_{10}$ and 6 $\log_{10}$ respectively, while in the following 30 m MS2 concentrations were reduced only by 2 $\log_{10}$ and reduction of spore concentrations was negligible. This may be explained by favourable attachment sites that are present in the first meters of transport but rapidly decrease with travel distance or travel time in an exponential fashion, like sites formed by ferric oxyhydroxides. Obviously, predictions of virus removal over larger travel times or distances can be severely overestimated if they are based on removal data from column or field experiments where transport was studied over short times and distances.

Inactivation rates of bacteria and viruses in groundwater vary considerably, not only between the bacteria and virus groups, but also between different strains within each group and between the results of different investigations. Table 3.7 lists inactivation rate coefficients of pathogenic viruses, bacteriophages and bacteria in groundwater. These data are ordered according to microorganism and then according to temperature. Usually inactivation proceeds faster at higher temperatures, although this is highly dependent on the type of microorganism.

Often, inactivation of microorganisms can be described well as a first order rate process, especially under relatively mild conditions like temperatures from 5-20 °C and pH values from 6-8. Under more extreme conditions, the rate of inactivation of, for example viruses is often found to proceed initially at a higher rate followed by a lower rate as if two or more sub-populations exist that differ in stability (see e.g. Hurst *et al.*, 1992). The data given in Table 3.7 are based on the observation, or in some cases assumption, that inactivation or die-off proceeded as a first order process:

$$C_t = C_0 e^{-\mu t} \quad \text{or} \quad \ln\left(\frac{C_t}{C_0}\right) = -\mu t \quad \text{or} \quad \log_{10}\left(\frac{C_t}{C_0}\right) = -\frac{\mu}{2.3} t \qquad \text{(Eqn. 3.1)}$$

where C_t is the remaining concentration of microorganisms after time t, C_0 is the initial concentration at t=0 and μ is the inactivation rate coefficient (T^{-1}). As a means of interpretation, μ is often divided by a factor of 2.3 (equal to the natural logarithm of 10). The inactivation rate coefficient then reflects the number of $\log_{10}$ units per time unit; e.g. a virus decreases in number by 2 $\log_{10}$ (equal to a factor of 100) every 10 days.

From Table 3.7 it can be seen that at common groundwater temperatures of 10-12 °C inactivation rate coefficients for coxsackieviruses B, echoviruses 7, poliovirus 1, hepatitis A virus, but also of bacteriophages ϕX174, MS2 and PRD1 are in the range from 0.01 to 0.04 day^{-1}. This corresponds to a decline in number or concentration of 1 $\log_{10}$ (equal to a factor of 10) every 57 to 230 days. Some studies report an inactivation rate coefficient of zero (e.g. Nasser *et al.*, 1993). This is to be interpreted as no significant inactivation within the time-scale and accuracy of the experiment and is therefore not included in Table 3.7. Given the variation in inactivation rate between microorganisms, inactivation rate coefficients of the more stable microorganisms need to be considered for estimating adequate protection of groundwater wells or removal efficiency of passing microorganisms through soil as a means of treatment.

The data in Table 3.7 make clear that bacterial die-off is both highly dependent on the type of microorganism as well as on temperature. In many cases bacterial inactivation proceeds faster than that of viruses, implying therefore that viruses are more critical for groundwater protection than bacteria.

Table 3.7. Inactivation rate coefficients of pathogenic viruses, bacteriophages and bacteria in groundwater

Microorganism	Temp. (°C)	Other conditions	Inactivation rate coefficient µ (1/day)	Reference
Coxsackievirus A9	10	Sterile	0.019	Matthess *et al.* (1988)
	10		0.027	
	10	Deionized	0.031	
Coxsackievirus B1	10	Sterile	0.012	Matthess *et al.* (1988)
	10		0.019	
	10	Deionized	0.040	
Coxsackievirus B3	3-15		0.49	Keswick *et al.* (1982)
Coxsackievirus B4	5		0.079	Schijven *et al.* (2003)
Coxsackievirus B5	16	1.2 mg/l O2	0.12	Jansons *et al.* (1989a)
	19.4		0.12	Jansons *et al.* (1989b)
Echovirus 1	12		0.24	Yates *et al.* (1985)
	13		0.25	
	17		0.28	
	18		0.35	
	23		0.94	
Echovirus 6	22	0.2 mg/l O2	0.25	Jansons *et al.* (1989a)
Echovirus 7	10	Sterile	0.032	Matthess *et al.* (1988)
	10		0.019	
	10	Deionized	0.038	
Echovirus 11	16	2.3 mg/l O2	0.23	Jansons *et al.* (1989a)
Echovirus 24	16	1.6 mg/l O2	0.12	Jansons *et al.* (1989a)
Hepatitis A virus	10		0.10	Nasser *et al.* (1993)
	20		0.41	
	23	Filtered bottled mineral water	0.038	Biziagos *et al.* (1988)
	25	Sterile	0.082	Sobsey *et al.* (1986)
	25		0.33	
	30		0.054	Nasser *et al.* (1993)
Poliovirus 1	3-15		0.48	Keswick *et al.* (1982)
	4		0.016	Meschke (2001)
	5		0.16	Schijven *et al.* (2003)
	10	Sterile	0.010	Matthess *et al.* (1988)
	10		0.013	
	10	Deionized	0.032	
	10		0.025	Nasser and Oman (1999)
	12		0.18	Yates *et al.* (1985)
	13		0.20	
	14	70 weeks	0.16	Meschke (2001)
	16	5.4 mg/l O2	0.21	Jansons *et al.* (1989a)
	16	0.2 mg/l O2	0.069	
	17		0.19	Yates *et al.* (1985)
	18		0.43	
	20		0.038	Nasser *et al.* (1993)
	22	0.06 mg/l O2	0.16	Jansons *et al.* (1989a)
	22		0.10	Bitton *et al.* (1983)
	23		0.17	Blanc and Nasser (1996)
	23		1.2	Yates *et al.* (1985)
	23	Filtered bottled mineral water	0.044	Biziagos *et al.* (1988)
	24		0.046	Bitton *et al.* (1983)
	25	4 weeks	0.11	Meschke (2001)
	30		0.12	Nasser *et al.* (1993)
Rotavirus	20		0.36	Pancorbo *et al.* (1987)

Microorganism	**Temp. (°C)**	**Other conditions**	**Inactivation rate coefficient μ (1/day)**	**Reference**
Simian Rotavirus	3-15		0.83	Keswick *et al.*(1982)
	23		0.28	Gerba *et al.* (Undated)
ϕX174	5		0.012	Schijven *et al.* (2002b)
F-specific RNA bacteriophages	10		0.025	Nasser and Oman (1999)
	20		0.0077	Nasser *et al.* (1993)
	30		0.031	Nasser *et al.* (1993)
MS2	2-5		0.030	Schijven *et al.* (1999)
	4		0.037	Meschke (2001)
	4		0.063	Yates *et al.* (1985)
	5		0.064	Schijven *et al.* (1999)
	5		0.082	Schijven *et al.* (2002b)
	7		0.0058-0.10	Yahya *et al.* (1993)
	12	Oxic	0.10	Schijven *et al.* (2000)
	12	Anoxic	0.024	
	12		0.16	Yates *et al.* (1985)
	12		0.065	Yates (1992, unpublished observations)
	13		0.22	Yates *et al.* (1985)
	14	70 weeks	0.45	Meschke (2001)
	17		0.17	Yates *et al.* (1985)
	18		0.19	
	23		0.36	Blanc and Nasser (1996)
	23		0.58-1.3	Yahya *et al.* (1993)
	23		0.73	Yates *et al.* (1985)
	25	4 weeks	0.41	Meschke (2001)
PRD1	5		0.0094	Schijven *et al.* (1999)
	5		0.044	Schijven *et al.* (2002b)
	7		0.010-0.10	Yahya *et al.* (1993)
	12	Oxic	0.054	Schijven *et al.* (2000)
	23		0.035	Blanc and Nasser (1996)
	23		0.12-0.30	Yahya *et al.* (1993)
Bacillus subtilis spores	14	70 weeks	0.1382	Meschke *et al.* (2001)
Cl. perfingens spores	14	70 weeks	0.0714	Meschke *et al.* (2001)
E. coli	12		0.083	Schijven *et al.* (2000)
	14	70 weeks	0.51	Meschke *et al.* (2001)
	20		0.044	Nasser and Oman (1999)
	22		0.36	Bitton *et al.* (1983)
	3-15		0.74	Keswick *et al.* (1982)
	9-13		0.84	McFeters *et al.* (1974)
E. coli O157:H7	20		0.32	Rice (1992)
Faecal coliforms	12-20		0.83	Keswick *et al.* (1982)
Faecal streptococci	22		0.066	Bitton *et al.* (1983)
	3-15		0.53	Keswick *et al.* (1982)
Klebsiella spp.	?		0.031	Dowd and Pillai (1997)
Salmonella spp.	?		0.19	Dowd and Pillai (1997)
Salmonella typhimurium	22		0.30	Bitton *et al.* (1983)
Salmonella typhimurium	9-13		0.50	McFeters *et al.* (1974)
Shigella dysentariae	9-13		1.7	McFeters *et al.* (1974)
Shigella flexeri	9-13		1.4	McFeters *et al.* (1974)
Shigella sonnei	9-13		1.6	McFeters *et al.* (1974)
Vibrio cholerae	9-13		5.3	McFeters *et al.* (1974)

The low inactivation rate of *Klebsiella* spp. in groundwater provides an interesting contrast to the other genera of enteric bacteria. *Klebsiella* is an important member of the Enterobacteriaceae, which are commonly, though inaccurately, referred to as ‘coliform bacteria’. Some species of *Klebsiella* are able to grow at 44 ºC, which further defines them as thermotolerant (formerly faecal) coliforms, the group that contains *E. coli*. Although *Klebsiella* are found in the bowel and respiratory tract of humans and animals, they can be isolated also from environmental samples. The persistence of *Klebsiella* in the survival experiments may therefore reflect the ability of these organisms to exist in two very distinct environments.

One problem associated with the detection of pathogenic bacteria is that they may become dormant in the environment (Schijven *et al.,* 2002a). In this state, they are viable but non-culturable, which means that the organisms show metabolizing activity even though they cannot be grown on traditional media (Olson, 1993). As an important example, in water the pathogen *E. coli* O157:H7 appears to be able to enter a viable but non-culturable state (Wang and Doyle, 1998). The dormant state prolongs the pathogen survival, and if its pathogenicity is unaltered, this increases the likelihood of a host infection and illness

Some bacteria like Clostridium and Bacillus species can survive for extended periods of time by producing spores. Clostridium spores are especially robust in that their inactivation rate may be considered to be negligible. This property makes it difficult to interpret their removal, e.g. in sand filters or river bank filtration. In column studies by Schijven *et al.* (2003) it was shown that most of the spores of *Cl. perfringens* attach to the grains of sand, however followed by slow detachment, i.e. adsorption was apparently reversible for a large fraction of spores. It was shown that the removal is dependant on the number of spores that accumulate in the porous medium.

At the time of writing, no data are available on inactivation of oocysts of *Cryptosporidium* in groundwater. *Cryptosporidium* oocyst in vitro viability has been measured repeatedly using a surface water matrix and in vitro excystation and/or dye exclusion assay. For example, Heisz *et al.* (1997) report 0.12 day^{-1} (30 °C), and Medema *et al.* (1997) found inactivation rates of 0.023-0.056 day^{-1} (5-15 °C) in river water and no differences in inactivation rates between 5 °C and 15 °C. From the data of Robertson *et al.* (1992) and Chauret *et al.* (1995), inactivation rates of 0.0051 to 0.0062 day^{-1} can be calculated. Chauret *et al.* (1995) further found that inactivation rate was independent of water temperature up to 20 °C.

Based on their small size and longevity in the environment viruses have the highest potential to be transported to, and within, groundwater, and thus they have been the focus of the majority of studies. As a consequence, the discussion in the following chapter has a greater emphasis toward the factors that influence the transport and survival of viruses in the subsurface. From the data that is available, the same factors appear to affect the survival of bacteria; however, some bacteria are able to utilize specific physiological responses to resist environmental stress that are not available to viruses. These responses will be discussed separately at the end of the chapter.

3.3.3 Summary of major factors influencing pathogen transport and attenuation mechanisms in the underground

The mechanisms by which microbial contaminants may undergo transport and attenuation in the saturated and unsaturated zones have been described in Sections 3.3.1 and 3.3.2. There now follows a description of the factors that control the degree of the impact of these mechanisms. The potential for pathogens in manures, faeces and wastewater to contaminate the underlying groundwater is dependent on a number of factors including the physical characteristics of the site (e.g. soil texture), the hydraulic conditions (e.g. wastewater or manure application rates, wetting/drying cycles), the environmental conditions (e.g. rainfall, temperature) at the site and the characteristics of the specific pathogens present in the water. The factors that influence the transport and attenuation of pathogens in the subsurface have been the subject of a number of reviews summarized in Table 3.8 (Vaughn *et al.*, 1983; Yates *et al.*, 1985; Yates and Yates, 1988; Bitton and Harvey, 1992; Robertson and Edberg, 1997; Schijven and Hassanizadeh, 2000). Some of the major factors influencing pathogen transport and attenuation are described in more detail below.

Temperature

Temperature is probably the most important factor influencing the inactivation of bacteria and viruses in the environment. Laboratory studies have demonstrated a negative correlation between water temperature and the survival of coliform bacteria and enteric viruses, although the magnitude of the effect varies between different strains. Roughly, the inactivation rate of viruses may be one order in magnitude higher at 25 °C than at 5 °C (Table 3.7). Similarly this may be the case for enteric bacteria, such as *E. coli*. The influence of temperature on the migration of bacteria and viruses is currently unknown.

Microbial activity

There are several conflicting reports regarding the influence of indigenous populations of microorganisms on the survival of enteric bacteria and viruses, ranging from increasing the rate of inactivation through to having no effect to decreasing the rate of inactivation. Overall, however, the main finding of laboratory studies is that microbial activity in the soil and groundwater increases the inactivation rate of enteric bacteria and viruses. Evaluating the role of microbial activity normally involves a comparison of inactivation rates in sterile and non-sterile environments. Depending on the environmental conditions and the experimental design, virus inactivation is either unaffected, or accelerated in the presence of indigenous bacteria. Hurst *et al.* (1980a) showed that the inactivation rate of two strains of enterovirus was more rapid in non-sterile, aerobic environments than in sterile environments. By contrast, Matthess *et al.* (1988) found no significant difference between the inactivation rates of several viruses in sterile and non-sterile groundwater. Studies with thermotolerant coliforms as a whole, and *E. coli* in particular, have shown that the concentration of the test organism can increase rapidly in sterile environments, but remains static, or is reduced in non-sterile environments (Gerba and McLeod, 1976).

Table 3.8. Influence of major factors on the survival and migration of microorganisms in the subsurface (Vaughn *et al.*, 1983; Yates *et al.*, 1985; Yates and Yates, 1988; Bitton and Harvey, 1992; Robertson and Edberg, 1997; Schijven and Hassanizadeh, 2000)

Factor	**Viruses**		**Bacteria**	
	Influence on survival	Influence on migration	Influence on survival	Influence on migration
Temperature	Persistence is longer at low temperatures	nknown	Persistence is longer at low temperatures	Unknown
Microbial activity	Varies: some viruses are inactivated more readily in the presence of certain microorganisms, the opposite may also be true, or there may be no effect	Unknown	The presence of indigenous microorganisms appears to increase the inactivation rate of enteric bacteria; possible synergism with some protozoa may reduce inactivation rates	Unknown
Moisture content	Most viruses survive longer in moist soils and even longer under saturated conditions; unsaturated soil may inactivate viruses at the air-water interface	Virus migration usually increases under saturated flow conditions	Most bacteria survive longer in moist soils than in dry soils	Bacterial migration usually increases under saturated flow conditions
pH	Most enteric viruses are stable over pH range of 3 to 9; however, survival may be prolonged by near neutral pH values	Low pH typically increases virus sorption to soils; high pH causes desorption thereby facilitating greater migration	Most enteric bacteria will survive longer at near neutral pH	Low pH encourages adsorption to soils and the aquifer matrix; the tendency of bacteria to bind to surfaces may reduce detachment at high pH
Salt species and concentration	Certain cations may prolong survival depending upon the type of virus	Increasing ionic strength of the surrounding medium generally increases sorption	Unknown	Increasing ionic strength of the surrounding medium generally increases sorption
Association with soil	Association with soil generally increases survival, although attachment to certain mineral surfaces may cause inactivation	Viruses interacting with the soil particles are inhibited from migration through the soil matrix	Adsorption onto solid surfaces reduce inactivation rates; the concentration of bacteria on surfaces may be several orders of magnitude higher than the concentration in the aqueous phase	Bacteria interacting with the soil particles are inhibited from migration through the soil matrix
Soil properties	Probably related to the degree of virus sorption	Greater migration in coarse textured soils; soils with charged surfaces, such as clays, adsorb viruses	Probably related to the degree of bacterial adsorption	Greater migration in coarse textured soils; soils with charged surfaces, such as clays, adsorb bacteria

Factor	Viruses		Bacteria	
	Influence on survival	Influence on migration	Influence on survival	Influence on migration
Bacteria/ virus type	Different virus types vary in their susceptibility to inactivation by physical, chemical and biological factors	Sorption to soils is related to physico-chemical difference in secondary and tertiary capsid surface structure and amino acid sequence	Different species of bacteria vary in their susceptibility to inactivation by physical, chemical and biological factors	Some species of bacteria are more capable of binding to surfaces; variation may also occur between strains of the same bacterial species
Organic matter	Organic matter may prolong survival by competitively binding at air-water interfaces where inactivation can occur	Soluble organic matter competes with viruses for adsorption on soil particles which may result in increased virus migration	The presence of organic matter may act as a source of nutrients for bacteria, promoting growth and extended survival	Organic matter may condition solid surfaces and promote bacterial adsorption
Hydraulic conditions	Unknown	Virus migration generally increased at higher hydraulic loads and flow rates	Unknown	Bacterial migration generally increased at higher hydraulic loads and flow rates

Soil moisture content

Although some investigators have observed no difference between the inactivation rates of viruses in dried and saturated soils (Lefler and Kott, 1974) the majority of reports have shown that soil moisture content influences the survival of viruses in the subsurface. For example, Hurst *et al.* (1980a) found that moisture content affected the survival of poliovirus in loamy sand. The inactivation rate of poliovirus decreased as the moisture content increased from 5 to 15 per cent. However, further increases in soil moisture content increased the inactivation rate of the virus. It was noted that the inactivation rate peaked near the saturation moisture content of the soil (15-25 per cent), and was slowest at the lowest moisture contents (5-15 per cent). Soil moisture has been reported to influence the fate of bacterial contaminants (Robertson and Edberg, 1997), but the magnitude of the effect, and the value of any correlation has not been described.

pH

The effect of pH on the survival of pathogens in the environment has not been studied extensively and the impact can only be inferred from laboratory investigations of the physiological characteristics of the bacteria and the effect on the structural integrity of viruses. In general, every species of bacteria has a narrow pH range that is optimum for growth. Depending on the normal environment of the organism, the pH requirements can range from highly acidic to highly alkaline: for many human pathogenic bacteria the optimum pH is close to neutral. Despite having a preference for a narrow pH range, most species of bacteria can tolerate a short exposure to a much broader range of pH. Outside these limits, the organisms are rapidly killed. It is likely that pH affects the survival of viruses by altering the structure of the capsid proteins and viral nucleic acid.

Some authors have suggested that pH indirectly influences pathogen survival by controlling adsorption to soil particles and the aquifer matrix. It is the adsorption to surfaces that ultimately reduces the inactivation rate of the pathogens. Generally, bacteria and viruses have negative surface charges generated by the level of ionization of the carboxyl and amine groups that are a major component of surface proteins. As the pH of the medium changes, the ionization of the two groups will change, causing a shift in the net strength and polarity of the surface charge. At a specific pH, which is determined by the molecular structure of the protein, the net charge will be zero; this is termed the isoelectric point of the molecule. The isoelectric point has been determined for many different proteins and for a number of virus strains. At pH values below the isoelectric point a virus will have a net positive charge, whereas the charge will be negative at pH values above the isoelectric point.

Within the pH range of most unpolluted groundwater both the matrix surfaces and the surfaces of the microorganisms carry a net negative charge. Under these conditions the microorganisms will be repelled by most mineral grain surfaces. At low pH values the surface charge on the microorganisms will shift to being net positive, which will favour their adsorption to soils and the aquifer matrix by electrostatic attraction. This hypothesis has been confirmed by several groups of workers for both bacteria and viruses (Sobsey, 1983; Gerba and Bitton, 1984; Bales *et al.,* 1991, 1993; Bitton and Harvey, 1992; Grant *et al.*, 1993; Loveland *et al.,* 1996; Penrod *et al.*, 1996; Redman *et al.*, 1997; Ryan *et al.*, 1999).

There are many complicating factors that can interfere with the mechanism discussed above. One is that a given virus may have more than one isoelectric point and the factors responsible for passage from one form to another are unknown at this time. Other factors, such as cations and humic and fulvic acids, may also influence the net surface charge of the organism.

Whilst changes in pH may affect the mobility of microorganisms in the subsurface, the significance of this factor in any particular aquifer is uncertain. Robertson and Edberg (1997) have noted that the pH of most unpolluted groundwater is generally very stable, and in their experience falls within the near-neutral range of 6.5 to 8.5. There are exceptions, and in those African countries underlain by acidic basement gneisses and granites the pH is likely to be much lower, frequently in the range 5.5 to 6.5. In addition, geological materials comprising most aquifers have a significant buffering capacity that helps to maintain a relatively constant pH. Robertson and Edberg conclude that it is unlikely that significant changes in microbe mobility will occur due to these minor pH changes. This assumption may be valid for many stable groundwater systems but in groundwater that is exposed to contamination from a variety of sources, which may be of unknown and variable quality, for example sewage, pH may emerge as a dominant factor in the mobility of pathogens.

Salt species

The adsorption of microorganisms onto surfaces in the groundwater system has been shown to have two counteracting effects: It reduces the dispersal of the organism in the subsurface, but reduces the inactivation rate of the organism in the affected area. If the prevailing geochemical conditions in the groundwater system create opposing charges on the surface of the organism and the aquifer matrix, adsorption will occur by electrostatic attraction. Frequently, however, these conditions do not exist and the organism and the aquifer matrix each have a negative charge.

The types and concentrations of salts in the environment can have a profound influence on the extent of pathogen transport in the subsurface. Cations (positively charged inorganic species), in particular multivalent cations such as Magnesium (Mg^{2+}) and Calcium (Ca^{2+}), can form a bridge between the solid surface and the organism and significantly enhance adsorption. Clearly, the concentration of the salt is also important, as this will influence the number of sites that are available for binding as well as the number of bridges that can be formed between the two surfaces. Thus the capacity for binding and the strength of the bonds will be affected by the salt concentration. Several studies of virus and bacterial transport through simulated groundwater systems have confirmed this hypothesis (Taylor *et al.,* 1981; Sobsey, 1983; Bitton and Harvey, 1992; Simoni *et al.*, 2000).

A decrease in the salt concentration or ionic strength of the soil water, such as would occur during a rainfall event, can cause desorption of viruses and bacteria from soil particles (Gerba and Bitton, 1984). This phenomenon has been observed in both laboratory and field experiments (Landry *et al.*, 1980; Wellings *et al.,* 1980). Furthermore, there is evidence to suggest that only small changes in the salt concentration can dramatically affect the mobilization of some organisms in groundwater systems (Redman *et al.*, 1999). The implication of this discussion is that salt concentration in the groundwater system may be of greater significance to pathogen transport than pH, although it is important to consider that neither factor will act in isolation.

Organic matter

There are conflicting reports about the influence of organic matter on the survival and transport of microorganisms in the subsurface, with different responses being noted for bacteria and viruses, and for different species and strains within each group. The influence of organic matter on virus survival has not been firmly defined. In some studies it has been found that proteinaceous material present in wastewater may have a protective effect on viruses; however, in other studies no effect has been observed. Whilst similar observations have been made of bacterial survival in the presence of organic matter, there remains an additional concern that enteric bacteria, in particular the major pathogens and faecal indicator organisms, may be able to undergo a certain level of growth in the environment if the conditions are suitable. There is some support for this hypothesis, a few reports have been published demonstrating regrowth of faecal indicator bacteria in organically rich tropical surface waters, but the evidence is still insufficient to confirm that regrowth is a significant issue for most enteric bacteria in groundwater.

Dissolved organic matter has generally been found to decrease virus adsorption by competing for binding sites on soil particles and the aquifer matrix. The consequence of this observation is that organic matter will increase the mobility of viruses in the subsurface (Powelson *et al.*, 1991). However, at relatively low concentrations of organic matter the effect may be reversed, causing increased virus adsorption and significantly reduced mobility in the subsurface (Robertson and Edberg, 1997).

Overall, bacteria may respond differently. Binding to surfaces is a characteristic of the growth cycle of most, if not all species of bacteria. Unlike the passive processes that characterize the attachment of viruses to surfaces, bacterial attachment involves active processes, including the synthesis of extracellular appendages specifically required to stabilize the bacteria-surface interaction. The initiation of this binding is favoured by the formation of a conditioning film of organic molecules deposited on the solid surface (Bitton and Harvey, 1992; Wimpenny, 1996). Thus the presence of organic matter may restrict the dispersal of bacteria in the subsurface but reduce the inactivation rate at the site of attachment.

3.4 REFERENCES

Abbaszadegan, M., Stewart, P., Le Chevallier, M., Rosen, J.S. and Gerba, C.P. (1998) *Occurrence of Viruses in Groundwater in the United States*, American Water Works Service Company, Voorhees, New Jersey, Interim Report.

Anderson, A.D., Heryford, A.G., Sarisky, J.P., Higgins, C., Monroe, S.S., Beard, R.S., Newport, C.M., Cashdollar, C.L., Fout, G.S., Robbins, D.E., Seys, S.A., Musgrave, K.J., Medus, C., Vinjé, J., Bresee, J.S., Mainzer, H.M. and Glass, R.I. (2003) A waterborne outbreak of Norwalk like virus among snowmobilers - Wyoming, 2001. *J Infectious Diseases*, **187**, 303-306.

ARGOSS (2001) *Assessing the risk to groundwater from on-site sanitation*, BGS Commissioned Research Report, Wallingford.

Bagdasaryan, G. (1964) Survival of viruses of the Enterovirus group (Poliomyelitis, Echo, Coxsackie) in soil and on vegetables. *J. Hyg. Epidemiol. Microbiol. and Immunol.*, **8**, 497.

Bales, R.C., Hinkle, S.R., Kroeger, T.W. and Stocking, K. (1991) Bacteriophage adsorption during transport through porous media: Chemical perturbations and reversibility. *Environ. Sci. Technol.*, **25**, 2088-2095.

Bales, R.C., Li, S., Maguire, K.M., Yahya, M.T. and Gerba, C.P. (1993) MS-2 and poliovirus transport in porous media: hydrophobic effects and chemical perturbations. *Water Resour. Res.*, **2**, 957-963.

Banks, W.S.L. and Battigelli, D.A. (2002) *Occurrence and Distribution of Microbiological Contamination and Enteric Viruses in Shallow Ground Water in Baltimore and Harford Counties, Maryland.* Water-Resources Investigations Report 01-4216, Reston, Virginia.

Banks, W.S.L., Klohe, C.A. and Battigelli, D.A. (2001) *Occurrence and Distribution of Enteric Viruses in Shallow Ground Water and Factors Affecting Well Vulnerability to Microbiological Contamination in Worcester and Wicomico Counties, Maryland.* USGS, Water-Resources Investigations Report 01-4147, Reston, Virginia.

Barrett, M.H., Johal, K., Howard, G., Pedley, S. and Nalubega, M. (2000) Sources of faecal contamination of shallow groundwater in Kampala. In *Groundwater: Past achievements and future challenges* (eds. O.T.M. Sililo, S. Appleyard, M. Barrett) pp. 691-696, Balkema, Rotterdam.

Bauder, J.W., White, B.A. and Inskeep, W.P. (1991) Montana extension initiative focuses on private well quality. *J. Soil and Water Conservation*, **46**, 69-74.

Bitton, G. and Harvey, R.W. (1992) Transport of pathogens through soils and aquifers. In *Environmental Microbiology*, (ed. R. Mitchell), pp. 103-124, Wiley-Liss, Inc.

Bitton, G., Farrah, S.R., Ruskin, R.H., Butner, J. and Chou, Y.J. (1983) Survival of pathogenic and indicator organisms in groundwater. *Ground Water*, **21**, 405-410.

Biziagos, E., Passagot, J., Crance, J. and Deloince, R. (1988) Long-term survival of Hepatitis A virus and Poliovirus Type 1 in mineral water. *Appl. Environ. Microbiol.*, **54**, 2705-2710.

Blanc, R. and Nasser, A. (1996) Effect of effluent quality and temperature on the persistence of viruses in soil. *Water Sci. Technol.*, **33**, 237-242.

Borchardt, M.A., Bertz, P.D., Spencer, S.K. and Batigelli, D.A. (2003) Incidence of enteric viruses in groundwater from household wells in Wisconsin. *Appl. Environ. Microbiol.*, **69**, 1172-1180.

Chauret, C., Chen, P., Springthorpe, S. and Sattar, S. (1995) Effect of environmental stressors on the survival of Cryptosporidium oocysts. In *Proc. Water Quality Technology Conference, New Orleans, Louisiana*, pp. 1567-1585. AWWA, Denver, Colorado.

Dahling, D. (2002) An improved filter elution and cell culture as a procedure for evaluating public groundwater systems for culturable enteroviruses. *Water Environ. Res*., **74**, 654-568.

Davis, J. and Witt, E.C. (2000) *Microbiological and Chemical Quality of Ground Water used as a Source of Public Supply in Southern Missouri- Phase I, May 1997-March 1998.* USGS Water-Resources Investigations Report 00-4038, Reston, Virginia.

Doherty, K. (1998) Status of the New England ground water viral study. In *Proc. AWWA Annual Meeting Dallas Texas, June 23, 1998*, AWWA, Denver.

Dowd, S.E. and Pillai, S.D. (1997) Survival and transport of selected bacterial pathogens and indicator viruses under sandy aquifer conditions. *J Environ. Sci. & Health Part A*, **32**, 2245-2258.

Femmer, S.R. (2000) *Microbiological and Chemical Quality of Ground Water Used as a Source of Public Supply in Southern Missouri-Phase II, April-July, 1998.* USGS Water-Resources Investigations Report 00-4260, USGS, Denver, Colorado.

Gerba, C.P. and Bitton, G. (1984) Microbial pollutants: Their survival and transport pattern to groundwater. In *Groundwater Pollution Microbiology*, (eds. G. Bitton and C.P. Gerba), pp. 65-88, Wiley, New York.

Gerba, C.P. and McLeod, J.S. (1976) Effects of sediments on the survival of *Escherichia coli* in marine waters. *Appl. Environ. Microbiol*., **32**(1), 114-120.

Gerba, C.P., Kutz, S.M., Bradford, A.W. and DeLeon, R. (Undated) *Rotavirus Survival and Transport in the Subsurface*. Cooperative Agreement Final Report to Steve Hutchson, US EPA, Ada, Oklahoma, CR-813566-0101.

Gleeson, C. and Gray, N. (1997) *The Coliform Index and Waterborne Disease*, 1st edn, E&FN Spon, London.

Goss, M.J., Barry, D.A.J. and Rudolph, D.L. (1998) Contamination of Ontario farmstead domestic wells and its association with agriculture: 1. Results from drinking water wells. *J. Contam. Hydrol*., **32**, 267-293.

Grant, S.B., List, E.J. and Lidstrom, M.E. (1993) Kinetic analysis of virus adsorption and inactivation in batch experiments. *Water Resour. Res*., **29**, 2067-2085.

Hancock, C.M., Rose, J.B. and Callahan, M. (1998) Crypto and Giardia in US groundwater. *JAWWA*, **90**(3), 58-61.

Havelaar, A.H., van Olphen, M. and Drost, Y.C. (1993) F-specific RNA bacteriophages are adequate model organisms for enteric viruses in fresh water. *Appl. Environ. Microbiol*., **59**, 2956-2962.

Heisz, M., Chauret, C., Chen, P., Springthorpe, S. and Sattar, S.A. (1997) In vitro survival of Cryptosporidium oocysts in natural waters. In *Proc. International Symposium on Waterborne Cryptosporidium, March 2-5, 1997, Newport Beach, California*, (eds. C. Fricker, J.L. Clancy and P.A. Rochelle), pp. 71-175, AWWA, Denver, Colorado,.

Howard, K.W.F. (2001) Polluted groundwater - deadly lessons from Walkerton, Ontario, Canada. In *New Approaches to Characterising Groundwater Flow*, (eds. K.P. Seiler and S. Wohnlich), pp. 521-525, Swets and Zeitlinger, Balkema, Rotterdam.

Howard, G., Bogh, C., Goldstein, G., Morgan, J., Prüss, A., Shaw, R. and Teuton, J. (2002). *Healthy villages: A guide for communities and community health workers.* WHO, Geneva.

Hurst, C.J., Gerba, C.P. and Cech, I. (1980a) Effects of environmental variables and soil characteristics on virus survival in soil. *Appl. Environ. Microbiol*., **40**, 1067-1079.

Hurst, C.J., Gerba, C.P. Lance, J.C. and Rice, R.C. (1980b) Survival of enteroviruses in rapid-infiltration basins during the land application of wastewater. *Appl. Environ. Microbiol.*, **40**,192.

Hurst, C.J., Wild, D.K. and Clark, R.M. (1992) Comparing the accuracy of equation formats for modelling microbial population decay rates. In *Modelling the Metabolic and Physiologic*

Activities of Micro-organisms, (ed. C.J. Hurst), pp. 149-175, John Wiley & Sons. Inc., New York.

Jansons, J., Edmonds, L.W., Speight, B. and Bucens, M.R. (1989a) Movement of viruses after artificial recharge. *Water Res.*, **23**, 293-299.

Jansons, J., Edmonds, L.W., Speight, B. and Bucens, M.R.(1989b) Survival of viruses in groundwater. *Water Res.*, **23**, 301-306.

Keswick, B.H., Gerba, C.P., Secor, S.L., Cech, I. (1982) Survival of enteric viruses and indicator bacteria in groundwater. *J. Environ. Sci. Health*, **A17**, 903-812.

Korhonen, L.K., Niskanen, M., HeinonenTanski, H., Martikainen, P.J., Salonen, L. and Taipalinen, I. (1996) Groundwater quality in wells in central rural Finland: A microbiological and radiochemical survey. *Ambio*, **25**, 343-349.

Landry, E.F., Vaughn, J.M. and Penello, W.P. (1980) Poliovirus retention in 75-cm soil cores after sewage and rainwater application. *Appl. Environ. Microbiol.*, **40**, 1032.

Lawrence, A.R., Williams, A.T., Brewerton, L.T., Barker, J.A., Bird, M. and Ward, R.S. (1996) *Pathogen transport in the Chalk aquifer: An assessment of the risk to chalk groundwater resources*. BGS Technical Report No. WD/96/48, Wallingford.

Lee, J.V. (1993) Contamination of a well by the direct influence of surface water. In *Proc. of the Annual Conference of the American Waterworks Association, San Antonio, Texas*, AWWA, pp. 215-231.

Lefler, E. and Kott, Y. (1974) *Virus Retention and Survival in Sand*, Centre for Research in Water Resources, Austin, Texas.

Lerner, D.N. and Barrett, M.H. (1996) Urban groundwater issues in the United Kingdom. *Hydrogeology J.*, **4**, 80-89.

Lewis, W.J., Foster, S.S.D. and Drasar, B.S. (1982) The risk of groundwater pollution by on-site sanitation in developing countries: A literature review. *Internat. Ref. Centre for Wastes Disposal,* **01**, 82.

Lieberman, R., Shadiz, L.C., Newport, B.S., Frebis, C.P., Safferman, R.S., Stetler, R.E., Lye, D., Fout, G.S. and Dahling, D. (2002) *Microbial Monitoring of Vulnerable Public Ground Water Supplies*. AWWARF, Denver, Colorado.

Lieberman, R.J., Shadix, L.C., Newport, B.S., Crout, S.R., Buescher, S.E., Safferman, R.S., Stetler, R.E., Lye, D., Fout, G.S. and Dahling, D.R. (1994) *Source Water Microbial Quality of Some Vulnerable Public Groundwater Supplies*. AWWA, Denver, Colorado.

Lindsey, B.D., Rasberry, J.S. and Zimmerman, T.M. (2002) *Microbiological Quality of Water from Noncommunity Supply Wells in Carbonate and Crystalline Aquifers of Pennsylvania.* USGS, Water-Resources Investigations Report 01-4268, Reston, Virginia.

Loveland, J.P., Ryan, J.N., Amy, G.L. and Harvey, R.W. (1996) The reversibility of virus attachment to mineral surfaces. *Colloids and Surfaces. A: Physicochemical and Engineering Aspects*, **107**, 205-221.

Macler, B.A. and Merkle, J.C. (2000) Current knowledge on groundwater microbial pathogens and their control. *Hydrogeology J.,* **8,** 29-40.

Mahler, B.J., Personne, J.C., Lods, G.F. and Drogue, C. (2000) Transport of free and particulate-associated bacteria in karst. *J. Hydrology*, **238**, 179-193.

Matthess, G.A., Pekdeger, A. and Schroeter, J. (1988) Persistence and transport of bacteria and viruses in groundwater - a conceptual evaluation. *J. Contam. Hydrol.*, **2**, 171-188.

McFeters, G.A., Bissonnette, G.K., Jezeski, J., Thomson, C.A. and Stuart, D.G. (1974) Comparative survival of indicator bacteria and enteric pathones in well water. *Appl. Microbiol.*, **27**, 823-829.

Medema, G.J., Bahar, M. and Schets, F.M. (1997) Survival of Cryptosporidium parvum, Escherichia coli, faecal enterococci and Clostridium perfringens in river water: Influence of temperature and autochthonous microorganisms. *Water Sci. Technol.*, **35**(11-12), 249-252.

Melian, R., Myrlian, N., Gouriev, A., Moraru, C., and Radstake, F. (1999) Groundwater quality and rural drinking-water supplies in the Republic of Moldova. *Hydrogeology J.*, **7**, 188-196.

Meschke, J.S. (2001) Comparative Adsorption, Persistence, and Mobility of Norwalk virus, Poliovirus type 1, and F+RNA Coliphages in Soil and Groundwater. Ph.D. thesis, School of Public Health, University of North Carolina, Chapel Hill, North Carolina.

Nasser, A., Tchorch, Y. and Fattal, B. (1993) Comparative survival of E. coli, F+bacteriophages, HAV and poliovirus 1 in wastewater and groundwater. *Water Sci. Technol.,* **27**, 401-407.

Nasser, A.M. and Oman, S.D. (1999) Quantitative assessment of the inactivation of pathogenic and indicator viruses in natural water sources. *Water Res.*, **33**, 1748-1752.

Olson, B.H. (1993) Pathogen occurrence in source waters: factors affecting survival and growth. In *Safety of Water Disinfection: Balancing Chemical and Microbial Risks*, (ed. G.F. Craun), ILSI Press, Washington DC.

Pancorbo, O.C., Evanshen, B.G., Campbell, W.F., Lambert, S., Curtis, S.K. and Woolley, T.W. (1987) Infectivity and antigenicity reduction rates of human Rotavirus strain Wa in Fresh Waters. *Appl. Environ. Microbiol.*, **13**, 1803-1811.

Parshionikar, S.U., Willian-True, S., Fout, G.S., Robbins, D.E., Syes, S.A., Cassady, J.D. and Harris, R. (2003) Waterborne outbreak of gastroenteritis associated with a Norovirus. *Appl. Environ. Microbiol.,* **69**(9), 5263-5268.

Penrod, S.L., Olson, T.M. and Grant, S.B. (1996) Deposition kinetics of two viruses in packed beds of quartz granular media. *Langmuir*, **12**, 5576-5587.

Powell, K.L., Barrett, M.H., Pedley, S., Tellam, J.H., Stagg, K.A., Greswell, R.B. and Rivett, M.O., (2000) Enteric virus detection in groundwater using a glasswool trap. In *Groundwater: Past Achievements and Future Challenges*, (ed. O.T.M. Sililo), pp. 813-816, Balkema, Rotterdam.

Powell, K.L., Cronin, A.A., Barrett, M.H., Sellwood, J. and Pedley, S. (2001a) *Distribution of Microbiological Contaminants in Triassic Sandstone Urban Aquifers*. Environment Agency R&D Technical Report P2-255/TR, Bristol.

Powell, K.L., Cronin, A.A., Pedley, S., Barrett, M.H. (2001) Microbiological quality of groundwater in UK urban aquifers: do we know enough? In *Proc. 3rd International conference on Groundwater Quality, 'Groundwater Quality 2001'*, (eds. S. Thornton and S. Oswald), University of Sheffield, June 2001, pp. 236-238.

Powelson, D.K., Simpson, J.R. and Gerba, C.P. (1991) Effects of organic matter on virus transport in unsaturated flow. *Appl. Environ. Microbiol.*, **57**, 2192-2196.

Redman, J.A., Grant, S.B., Olson, T.M., Amkins, J.M., Jackson, L., Castillo, M.S. and Yanko, W.A. (1999) Physiochemical mechanisms responsible for the filtration and mobilisation of filamentous bacteriophage in quartz sand. *Water Res.*, **33**(1), 43-52.

Redman, J.A., Grant, S.B., Olson, T.M., Hardy, M.E. and Estes, M.K. (1997) Filtration of recombinant Norwalk virus particles and bacteriophage MS2 in quartz sand: Importance of electrostatic interactions. *Environ. Sci. Technol.,* **31**, 3378-3383.

Rice, E.W., Johnson, C.H., Wild, D.K. and Reasoner, D.J. (1992) Survival of *Escherichia coli* O157:H7 in drinking-water associated with a waterborne disease outbreak of hemorrhagic colitis. *Letters in Appl. Microbiol.*, **13**, 38-40.

Robertson, J.B. and Edberg, S.C. (1997) Natural protection of spring and well drinking water against surface microbial contamination. I. Hydrogeological Parameters. *Crit. Rev. in Microbiol.*, **23**, 143-178.

Robertson, L.J., Campbell, A.T. and Smith, H.V. (1992) Survival of *Cryptosporidium parvum* oocysts under various environmental pressures. *Appl. Environ. Microbiol.*, **58**, 3494-3500.

Romero, J.C. (1972) The movement of bacteria and viruses through porous media. In *Water Quality in a Stressed Environment*, (ed. W.A. Pettyjohn), pp. 200-224, Burgess Publishing Company, Minnesota.

Ryan, J.N., Elimelech, M., Ard, R.A., Harvey, R.W. and Johnson, P.R. (1999) Bacteriophage PRD1 and silica colloid transport and recovery in an iron oxide-coated sand aquifer. *Environ. Sci. Technol.,* **33**, 63-73.

Schijven, J.F. and Hassanizadeh, S.M. (2000) Removal of viruses by soil passage: Overview of modelling, processes and parameters. *Crit. Rev. Environ. Sci. Technol.*, **30**(1), 49-127.

Schijven, J.F., Hoogenboezem, W., Hassanizadeh, S.M. and Peters, J.H. (1999) Modelling removal of bacteriophages MS2 and PRD1 by dune infiltration at Castricum, the Netherlands. *Water Resour. Res.*, **35**, 1101-1111.

Schijven, J.F., Medema, G., Vogelaar, A.J. and Hassanizadeh, S.M. (2000) Removal of microorganisms by deep well injection. *J Contam. Hydrol.*, **44**, 301-327.

Schijven JF, Berger P, Miettinen I. (2002a) Removal of pathogens, surrogates, indicators and toxins using bank filtration. In *Riverbank Filtration: Improving source water quality*, (eds. R. Chittaranjan, G. Mlin and R.B. Linsky), Kluwer Academic, University of Hawaii.

Schijven, J.F., Hassanizadeh, S.M., de Bruin, H.A.M. (2002b) Two-site kinetic modeling of bacteriophages transport through columns of saturated dune sand. *J Contam. Hydrol.*, **57**, 259-279.

Schijven, J.F., de Bruin, H.A.M., Hassanizadeh, S.M., de Roda Husman, A.M. (2003) Bacteriophages and clostridium spores as indicator organisms for removal of pathogens by passage through saturated dune sand. *Water Res.*, **37**, 2186-2194.

Simoni, S.F., Bosma, T.N.P., Harms, H. and Zehnder, A.J.B. (2000) Bivalent cations increase both the subpopulation of adhering bacteria and their adhesion efficiency in sand columns. *Environ. Sci. Technol.*, **34**(6), 1011-1017.

Singleton, P. and Sainsbury, D. (1999) *Dictionary of Microbiology and Molecular Biology*, 2nd edn, John Wiley & Sons Ltd, New York.

Skilton, H. and Wheeler, D. (1988) Bacteriophage tracer experiments in groundwater. *J. Appl. Bacteriol.*, **65**(5), 387-395.

Skilton, H. and Wheeler, D. (1989) The application of bacteriophage as tracers in chalk aquifer systems. *J. Appl. Bacteriol.*, **66**, 549-557.

Sobsey, M.D. (1983) Transport and fate of viruses in soils. In *Microbial Health Considerations of Soil Disposal of Domestic Wastewaters*, US EPA, Cincinnati, Ohio.

Sobsey, M.D., Shields, P.A., Hauchman, F.H., Hazard, R.L., and Canton, L.W. (1986) Survival and transport of hepatitis A virus in soils, groundwater and wastewater. *Water Sci. Technol.*, **18**, 97-106.

Taylor, D.H., Moore, R.S. and Sturman, L.S. (1981) Influence of pH and electrolyte composition on adsorption of poliovirus by soils and minerals. *Appl. Environ. Microbiol.*, **42**, 976.

US EPA (2000) National Primary Drinking Water Regulations: Ground Water Rule. Proposed Rule. *Federal Register*, **10**, 30194-30274.

US Government (1996) Safe Drinking Water Act, Public Law 104-182.

USGS (1998) *Microbiological Quality of Public Water Supplies in the Ozark Plateaus Aquifer System, Missouri.* Washington DC, USGS, Ref Type: Pamphlet.

Vaughn, J.M., Landry, E.F. and Thomas, M.Z. (1983) Entrainment of viruses from septic tank leach fields through a shallow, sandy soil aquifer. *Appl. Environ. Microbiol.*, **45**, 1474-1480.

Wang, G. and Doyle, M.P. (1998) Survival of enterhemorrhagic *Escherichia coli* O157:H7 in water. *J. Food Protection*, **61**, 662-667.

Wellings, M., Lewis, A.C., Mountain, C.W. and Pierce, L.V. (1975) Demonstration of viruses in groundwater after effluent discharge onto soil. *Appl. Microbiol.*, **29**, 751.

West, J.M., Pedley, S., Baker, S.J., Barrott, L., Morris, B., Storey, A., Ward, R.S. and Barrett, M. (1998) *A Review of the Impact of Microbiological Contaminants in Groundwater*, UK Environment Agency, R and D Technical Report P139, Bristol.

Wimpenny, J.W.T. (1996) Ecological determinants of biofilm formation. *Biofouling*, **10**(1-3), 43-64.

Yahya, M.T., Galsomies, L., Gerba, C.P. and Bales, R.C. (1993) Survival of bacteriophages MS2 and PRD1 in groundwater. *Water Sci. Tech.*, **27**, 409-412.

Yates, M.V. and Yates, S.R. (1988) Modelling microbial fate in the subsurface environment. *Crit. Rev. Environ. Control*, **17**, 307-344.

Yates, M.V., Gerba, C.P. and Kelley, L.M. (1985) Virus persistence in groundwater. *Appl. Environ. Microbiol.*, **49**(4), 778-781.

4

Chemicals: Health relevance, transport and attenuation

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The presence of substances in groundwater may be affected by naturally occurring processes as well as by actions directly associated with human activities. Naturally occurring processes such as decomposition of organic material in soils or leaching of mineral deposits can result in increased concentrations of several substances. Those of health concern include fluoride, arsenic, nitrate, selenium, uranium, metals, and radionuclides such as radon. Problems of aesthetic quality and acceptance may be caused by iron, manganese, sulphate, chloride and organic matter.

Sources of groundwater contamination associated with human activities are widespread and include diffuse as well as point source pollution like land application of animal wastes and agrochemicals in agriculture; disposal practices of human excreta and wastes such as leaking sewers or sanitation systems, leakage of waste disposal sites, landfills, underground storage tanks and pipelines; and pollution due to both poor practices and accidental spills in mining, industry, traffic, health care facilities and military sites.

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The exploitation of petroleum products and the development of industrial chemistry has given rise to a large number of organic chemicals, many of which can be found in the environment. Many organic chemicals are known to have potential human health impacts, and some of these may occur in drinking-water in health-relevant concentrations. In consequence, the list of those for which guideline values and national quality standards have been developed has been continually added to and revised as data on the occurrence of chemicals in water and new toxicological data emerge. Organic chemicals commonly used by industry with known or suspected human health impacts that are often encountered in groundwaters include, for example, aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylenes (BTEX) as well as volatile chlorinated hydrocarbons such as tetrachloroethene (PCE) and trichloroethene (TCE). A diverse range of pesticides is also found in groundwaters. These are primarily, but not exclusively, ascribed to agricultural activities. Typically pesticide concentrations encountered are low. In some cases they have exceeded regulatory limits for drinking-water supplies, although often the regulatory levels exceeded were often much lower than those based on public health considerations.

This chapter concentrates on the groups of chemical substances that are toxic to humans and have reasonable potential to contaminate drinking-water abstracted from groundwater. It provides foundational knowledge of natural groundwater constituents and anthropogenic groundwater contaminants and discusses their relevance to human health, origin, and transport and attenuation in groundwater systems. The chapter is sub-divided as follows: Section 4.1 provides introductory theory on the transport and attenuation of chemicals in the subsurface; Sections 4.2 to 4.4 focus upon inorganic chemicals – natural inorganic constituents, nitrogen species and metals respectively; Sections 4.5 to 4.8 focus upon organic chemicals including an introductory section on conceptual contaminant models and transport and attenuation theory specific to organic contaminants followed by sections on some organic chemical groups of key concern – aromatic hydrocarbons, chlorinated hydrocarbons and pesticides respectively; finally, the chapter closes with a brief consideration of currently emerging issues (Section 4.9). Further information on the individual chemicals discussed in this chapter is available in the WHO *Guidelines for Drinking-water Quality*, Volume 1 (WHO, 2004a), as well as in detailed background documents on WHO's Water, Sanitation and Health website (http://www.who.int/water_sanitation_health/dwq/chemicals/en/index.html).

4.1 SUBSURFACE TRANSPORT AND ATTENUATION OF CHEMICALS

Understanding of the transport and attenuation of chemicals in the subsurface is fundamental to effective management of risks posed by chemicals and their possible impact on groundwater resources. A risk assessment approach to groundwater protection incorporates the three-stage combination of source, pathway and receptor. All three must be considered and understood to arrive at a balanced view of the risks to health of groundwater users. Informed consideration of the pathway, which in the context of this monograph means transport through the groundwater system, is vital. This not only includes consideration of the general and local hydrogeologic characteristics covered in

Chapters 2 and 8, but also the transport and attenuation of chemicals within that pathway. The latter depend upon the properties of the chemical itself, particularly those properties that control interactions of the chemical with the subsurface regime, a regime that includes not only the host rock and groundwater, but other natural and anthropogenic chemical constituents present as well as microbial life.

Within the overall transport process, attenuation processes may cause movement of the chemical to differ from that of the bulk flowing groundwater, for example dispersion, sorption and chemical or biological degradation of the chemical. Such attenuation processes potentially act to mitigate the impact of chemicals and are a function of both the specific chemical and geologic domain. Indeed, attenuation may vary significantly between individual chemicals and within different geological settings. In recent years natural attenuation of organic contaminants has been increasingly recognized to play an important role in many aquifer systems leading to monitored natural attenuation becoming a recognized remedial strategy to manage risks to groundwater at some contaminated sites (EA, 2000).

This section provides an overview of the key processes that control the transport and attenuation of chemicals in groundwater. Elaboration of some of the more specific attenuation processes is also included in later sections. Further details may be found in the following texts and references therein: Freeze and Cherry (1979), Appelo and Postma (1993), Stumm and Morgan (1996), Domenico and Schwartz (1998), Bedient *et al.* (1999), Fetter (1999) and Schwartz and Zhang (2003).

4.1.1 Natural hydrochemical conditions

It is important to understand at the outset the natural hydrochemical conditions that exist in a given aquifer system, as these provide the baseline from which quality changes caused by human impacts can be determined. The natural hydrochemical conditions may also affect the behaviour of some pollutants. Because groundwater movement is typically slow and residence times long, there is potential for interaction between the water and the rock material through which it passes. The properties of both the water and the material are therefore important, and natural groundwater quality will vary from one rock type to another and within aquifers along groundwater flow paths. Water is essentially a highly polar liquid solvent that will readily dissolve ionic chemical species. Rock material is predominantly inorganic in nature and contact of flowing groundwater with the rock may dissolve inorganic ions into that water, i.e. dissolution of the rock occurs. ‘Major ions’ present are the anions nitrate, sulphate, chloride and bicarbonate and the cations sodium, potassium, magnesium and calcium. Ions typically present at lower concentration, ‘minor ions’, include anions such as fluoride and bromide and a wide variety of metal ions that are predominantly cations. Combined, the total inorganic concentration within the water is referred to as the total dissolved solids (TDS).

Natural groundwater quality changes start in the soil, where infiltrating rainfall dissolves carbon dioxide from biological activity in the soil to produce weak carbonic acid that may assist removal of soluble minerals from the underlying rocks, e.g. calcite cements. At the same time, soil organisms consume some of the oxygen that was dissolved in the rainfall. In temperate and humid climates with significant recharge, groundwater moves relatively quickly through the aquifer. Contact time with the rock matrix is short and only readily soluble minerals will be involved in reactions. Groundwater in the outcrop areas of aquifers is likely to be low in overall chemical content, i.e. have low major ion contents and low TDS, with igneous rocks usually having less dissolved constituents than sedimentary rocks (Hem, 1989). In coastal regions, sodium and chloride may exceed calcium, magnesium and bicarbonate and the presence of soluble cement between the grains may allow major ion concentrations to be increased. Groundwaters in carbonate rocks have pH above 7, and mineral contents usually dominated by bicarbonate and calcium.

In many small and shallow aquifers the hydrochemistry does not evolve further. However, the baseline natural quality of groundwater may vary spatially within the same aquifer if the mineral assemblages vary, and also evolves with time as the water moves along groundwater flow lines. If an aquifer dips below a confining layer (Figure 2.5), a sequence of hydrochemical processes occurs with progressive distance downgradient away from the outcrop, including precipitation of some solids when relevant ion concentrations reach saturation levels for a solid mineral phase. These processes have been clearly observed in the United Kingdom, where the geological history is such that all three of the major aquifers exhibit the sequence shown in Figure 4.1, which has been characterized by sampling transects of abstraction boreholes across the aquifers (Edmunds *et al.*, 1987).

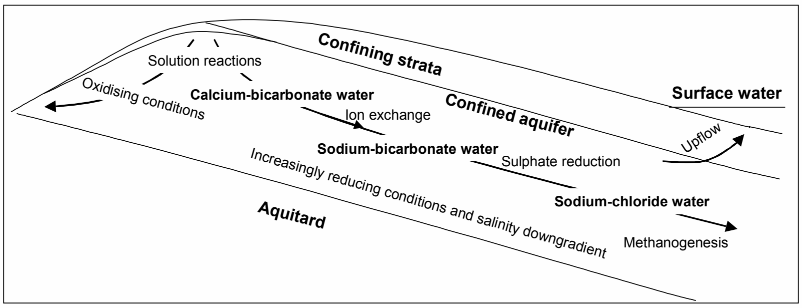

Figure 4.1. Schematic representation of downgradient hydrochemical changes

In the recharge area, oxidizing conditions occur and dissolution of calcium and bicarbonate dominates. As the water continues to move downgradient, further modifications are at first limited. By observing the redox potential (E_h) of abstracted groundwater, a sharp redox barrier is detected beyond the edge of the confining layer, corresponding to the complete exhaustion of dissolved oxygen. Bicarbonate increases and the pH rises until buffering occurs at about 8.3. Sulphate concentrations remain stable in the oxidizing water, but decrease suddenly just beyond the redox boundary due to sulphate reduction. Groundwater becomes steadily more reducing as it flows downgradient, as demonstrated by the presence of sulphide, increase in the solubility of iron and manganese and denitrification of nitrate. After some further kilometres, sodium begins to increase by ion exchange at the expense of calcium, producing a natural softening of the water. Eventually, the available calcium in the water is exhausted, but sodium continues to increase to a level greater than could be achieved purely by cation exchange. As chloride also begins to increase, this marks the point at which recharging water moving slowly down through the aquifer mixes with much older saline water present in the sediments (Figure 4.1). The observed hydrochemical changes can thus be interpreted in terms of oxidation/reduction, ion exchange and mixing processes.

In arid and semi-arid regions, evapotranspiration rates are much higher, recharge is less, flow paths longer and residence times much greater and hence much higher levels of natural mineralization, often dominated by sodium and chloride, can be encountered. Thus the major ion contents and TDS are often high. In some desert regions, even if groundwater can be found it may be so salty (extremely high TDS) as to be undrinkable, and the difficulty of meeting even the most basic domestic requirements can have serious impacts on health and livelihood.

Natural variations in pH and oxygen status are also important and are not restricted to deep environments. Many groundwaters in tropical regions in weathered basement aquifers and alluvial sequences have low pH, and the reducing conditions which prevail can promote the mobilization of metals and other parameters of health significance such as arsenic. Thus prevailing hydrochemical conditions of the groundwater that are naturally present and develop need to be taken into account when: (i) developing schemes for groundwater abstraction for various uses and in protecting groundwater; and (ii) considering the transport and attenuation of additional chemicals entering groundwaters due to human activity.

4.1.2 Conceptual models and attenuation processes

Effective prediction of transport of chemical pollutants through a subsurface groundwater system and associated assessments of risk requires a valid conceptual model of the contaminant migration scenario. The classical contaminant conceptual model is one of a near-surface leachable source zone where chemical contaminant is leached, i.e. dissolved/solubilized, into water infiltrating through the source (Figure 4.2). A dissolved-phase chemical solute plume subsequently emerges in water draining from the base of the contaminant source zone and moves vertically downward through any unsaturated zone present. The dissolved solute plume ultimately penetrates below the water table to subsequently migrate laterally in the flowing groundwater. Many sources, e.g. a landfill, chemical waste lagoon, contaminated industrial site soils, pesticide residues in field soils, may have sufficient chemical mass to enable them to act as long-term generators of dissolved-phase contaminant plumes; potentially such sources can last decades. This will lead to continuous dissolved-phase plumes extending from these sources through the groundwater pathway that grow with time and may ultimately reach distant receptors unless attenuation processes operate. This near-surface leachable source – dissolved-plume conceptual model is the model most frequently invoked and the one to which groundwater vulnerability and protection concepts and groundwater risk-assessment models are most easily applied. It is important to note, however, that the above conceptualization may be too simplified and alternative conceptual models need to be invoked in some cases, most notably for non aqueous phase liquids (NAPLs) as discussed in Section 4.5.

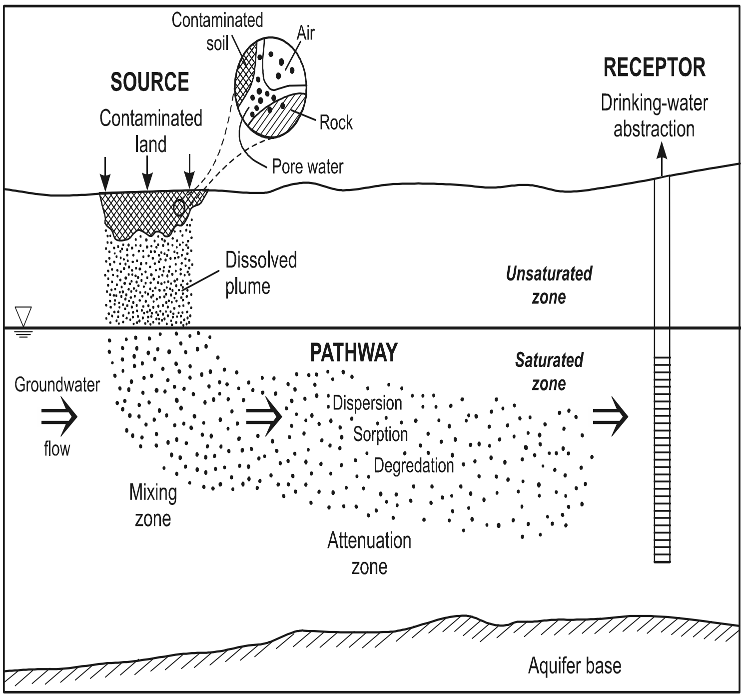

Figure 4.2. Classical contaminant conceptual model

Attenuation processes operative in the groundwater pathway, both for unsaturated and saturated zones, are summarized below and briefly described in the text that follows. Further details may be found in the texts referenced in other sections of this chapter.

DEF ▶

Advection and dispersion

Advection *is the transport of dissolved solute mass present in groundwater due to the bulk flow (movement) of that groundwater. Advection alone (with no dispersion or reactive processes occuring) would cause a non-reactive solute to advect (move) at the mean groundwater pore velocity. All solutes undergo advection, however, reactive solutes are subject to influences by other processes detailed below.*

Molecular diffusion *is the movement of solute ions in the direction of the concentration gradient from high towards low concentrations. It affects all solutes.*

Mechanical dispersion *causes spreading of solute and hence dilution of concentrations, it arises from the tortuosity of the pore channels in a granular aquifer and of the fractures in a consolidated aquifer and the different speeds of groundwater within flow channels of varying width. It affects all solutes.*

Retardation

Sorption *is a process by which chemicals or organisms become attached to soils and/or the geologic rock material (aquifer solids) and removed from the water. Often the sorption process is reversible and solutes desorb and hence dissolved-solute plumes are retarded, rather than solutes being permanently retained by the solids.*

Cation exchange *is the interchange between cations in solution and cations on the surfaces of clay particles or organic colloids.*

Filtration *is a process that affects particulate contaminants (e.g. organic/inorganic colloids or microbes) rather than dissolved solutes. Particles larger than pore throat diameters or fracture apertures are prevented from moving by advection and are therefore attenuated within the soil or rock.*

Reactions and transformations of chemicals

Chemical reactions (abiotic reactions) *are classical chemical reactions that are not mediated by bacteria. They may include reaction processes such as precipitation, hydrolysis, complexation, elimination, substitution, etc., that transform chemicals into other chemicals and potentially alter their phase/state (solid, liquid, gas, dissolved).*

Precipitation *is the removal of ions from solution by the formation of insoluble compounds, i.e. a solid-phase precipitate.*

Hydrolysis *is a process of chemical reaction by the addition of water.*

Complexation *is the reaction process by which compounds are formed in which molecules or ions form coordinate bonds to a metal atom or ion.*

Biodegradation (biotic reactions) *is a reaction process that is facilitated by microbial activity, e.g. by bacteria present in the subsurface. Typically molecules are degraded (broken down) to molecules of a simpler structure that often have lower toxicity.*

Advection

As described in Chapter 2, groundwater moves due to the presence of a hydraulic gradient and may be characterized by the Darcy velocity q (alternatively named the specific discharge). The Darcy velocity may be calculated via Darcy's law and is the product of the geologic media hydraulic conductivity K and the groundwater hydraulic gradient i. The actual mean groundwater pore (linear) velocity of groundwater, henceforth referred to as the 'groundwater velocity' v differs from the Darcy velocity as flow can only occur through the effective porosity n_e of the formation. The groundwater velocity may be quantified by modifying the Darcy equation:

$$v = -Ki / n_e \qquad \text{(Eqn. 4.1)}$$

Advection is the transport of dissolved solutes in groundwater due to the bulk movement of groundwater. The mean advective velocity of non-reactive solutes is equal to the groundwater velocity, v (Eqn. 4.1) and is normally estimated by knowledge of the Equation 4.1 hydrogeological parameters. Occasionally v may be estimated from the mean position of a solute plume, typically within a groundwater tracer test (Mackay *et al*., 1986). Reactive solutes also advect with the flowing groundwater, however, their velocities are modified due to co-occurrence of attenuation processes.

Dispersion

All reactive and non-reactive solutes will undergo spreading due to dispersion, causing dissolved-phase plumes to broaden both along and perpendicular to the groundwater flow direction (Figure 4.3). Dispersion is most easily observed for ‘conservative’ non-reactive solutes, such as chloride, as these only undergo advection and dispersion. Dispersion causes mixing of the dissolved-solute plume with uncontaminated water and hence concentration dilution as well as plume spreading. Longitudinal dispersion, spreading in the direction of predominant groundwater flow, is greatest causing solutes to move at greater or less than the mean advective velocity v. Solute spreading is due to mechanical dispersion that can arise at the pore-scale due to (Fetter, 1999): (i) fluids moving faster at pore centres due to less friction; (ii) larger pores allowing faster fluid movement; (iii) routes of varying tortuosity around grains. At a larger scale, macro-dispersion is controlled by the distribution of hydraulic conductivities in the geologic domain; greater geological heterogeneity resulting in greater plume spreading. The above processes cause increasing dispersion with plume travel distance, i.e. dispersion is scale dependent (Gelhar, 1986; Fetter, 1999).

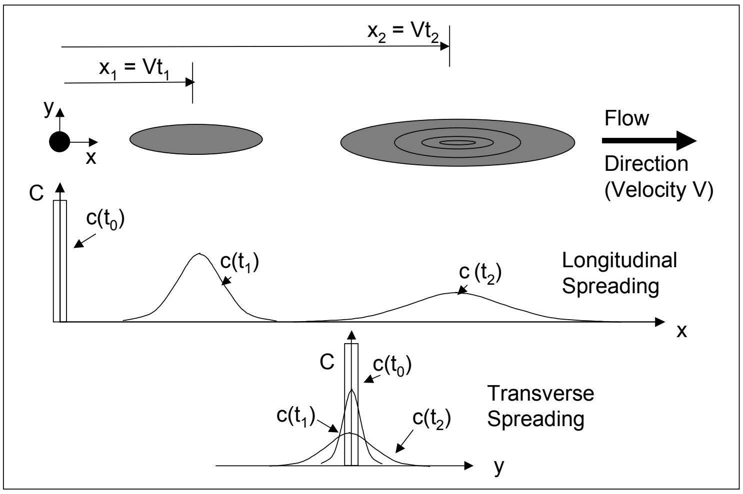

Figure 4.3. Dispersion of a pulse release of dissolved-solute plume

Plume dispersion in other directions is much reduced. Transverse horizontal spreading may arise from flowpath tortuosity and molecular diffusion due to plume chemical-concentration gradients. Transverse vertical spreading occurs for similar reasons, but is generally more restricted due to predominantly near-horizontal layering of geologic strata. Overall, a hydrodynamic dispersion coefficient D is defined for each direction (longitudinal, transverse horizontal, transverse vertical):

$$D = \alpha v + D^* \qquad \text{(Eqn. 4.2)}$$

which is seen to depend upon D*, the solute's effective diffusion coefficient and α the geologic media dispersivity. Dispersion parameters are most reliably obtained from tracer tests or, less reliably, at the larger (>250 m) scale, by model fitting to existing plumes. Collated values have yielded simple empirical relationships to estimate dispersion, e.g. the longitudinal dispersivity is often approximated to be 0.1 (10 per cent) of the mean plume travel distance (Gelhar, 1986). However, such relationships are very approximate.

Retardation

The processes that cause retardation (slowing down) of dissolved-solute plume migration include filtration, sorption and cation exchange. Filtration is a process that affects particulate contaminants (e.g. organic/inorganic colloids or microbes) rather than dissolved solutes, the key focus here. Sorption is a process by which chemicals or organisms become attached to soils and/or the geologic rock material (aquifer solids) and are removed from the water. Often the sorption process is reversible and solutes desorb back into the water phase and hence dissolved-solute plumes are retarded, rather than solutes being permanently retained by the solids. Preferred sorption sites depend upon the chemical solute properties, in general clay strata or organic matter within the geologic solid media are key sorption sites. Such sites may, however, be limited and sorption to other mineral phases, e.g. iron oxyhydroxides, may become important in some cases. Sorption processes normally lead to a Retardation Factor, R_i, being defined that is the ratio of the mean advective velocity (conservative solute velocity) (v) to the mean velocity of the retarded sorbing solute plume (v_i):

$$R_i = v / v_i \qquad \text{(Eqn. 4.3)}$$

Typically R_i is not estimated from Equation 4.3, rather various methods may be used to estimate R_i relating to the specific chemical nature of the sorption interaction and a relevant sorption coefficient (e.g. see Section 4.5.2). Sorption-related processes can be sensitive to the environmental conditions. For example, relatively small pH changes may cause significant changes to the mobilization of metals or perhaps organic contaminants that are themselves acids or bases, e.g. phenols or amines.

Reactions and transformations of chemicals

Many chemicals undergo reaction or transformation in the subsurface environment. In contrast to retardation, contaminants may be removed rather than simply slowed down. Reactions of harmful chemicals to yield benign products prior to arrival at a receptor are the ideal, e.g. many toxic hydrocarbons have potential to biodegrade to simple organic acids (of low health concern and themselves potentially degradable), carbon dioxide (bicarbonate) and water. Transformation often causes a deactivation (lowering) of toxicity. Reactions and/or transformations incorporate processes such as chemical precipitation, complexation, hydrolysis, biodegradation (biotic reactions) and chemical reactions (abiotic reactions).

Chemical *precipitation* and *complexation* are primarily important for the inorganic species. The formation of coordination complexes is typical behaviour of transition metals, which provide the cation or central atom. Ligands include common inorganic anions such as Cl^-, F^-, Br^-, SO_4^{2-}, PO_4^{3-} and CO_3^{2-} as well as organic molecules such as amino acids. Such complexation may facilitate the transport of metals.

Biodegradation is a reaction process mediated by microbial activity (a biotic reaction). Naturally present bacteria may transform the organic molecule to a simpler product, e.g. another organic molecule or even CO_2. Biodegradation has wide applicability to many organic chemicals in a diverse range of subsurface environments. Rates of biodegradation vary widely, some compounds may only degrade very slowly, e.g. high molecular weight polynuclear aromatic hydrocarbons (PAHs) that are relatively recalcitrant (unreactive). Rates are also very dependent upon environmental conditions, including redox, microbial populations present and their activity towards contaminants present.

Abiotic reactions, classic chemical reactions not mediated by bacteria, have been found to be of fairly limited importance in groundwater relative to biodegradation. For example, a few organics, e.g. 1,1,1-trichloroethane (1,1,1-TCA) and some pesticides, may readily undergo reaction with water (hydrolysis), others such as the aromatic hydrocarbon benzene are essentially unreactive to water and a range of other potential chemical reactions.

Potential for attenuation

Potential for attenuation processes to occur varies within the various subsurface zones, i.e. soil, unsaturated and saturated zone. Attenuation processes can be more effective in the soil rather than aquifers due to higher clay contents, organic carbon, microbial populations and replenishable oxygen. This makes the soil a very important first line of defence against groundwater pollution, often termed ‘protective layer’. Consideration of the soil and its attenuation properties is a key factor in assessing the vulnerability of groundwater to pollution (Chapter 8). This also means that where the soil is thin or absent the risk of groundwater pollution may be greatly increased. Many human activities that give rise to pollution by-pass the soil completely and introduce pollutants directly into the unsaturated or even saturated zones of aquifers. Examples include landfills, leaking sewers, pit latrines, transportation routes in excavated areas and highway drainage.

4.2 NATURAL INORGANIC CONSTITUENTS

The occurrence of natural constituents in groundwater varies greatly depending on the nature of the aquifer. In general, aquifers in magmatites and metamorphic rocks show lower dissolved contents than in carbonate or sedimentary rocks. The mobility and thus the concentration of nearly all natural groundwater constituents can be significantly influenced by changes of physical and chemical conditions in groundwater through human activities.

Fluoride and arsenic are now recognized as the most serious inorganic contaminants in drinking-water on a worldwide basis. Further natural constituents that can cause a public health risk addressed in this chapter (in alphabetical order) are selenium, radon and uranium. Although nitrate has occasionally been found naturally in health-relevant concentrations, in most cases these are caused anthropogenically, and therefore nitrate is addressed in Section 4.3.

NOTE ▶ *Arsenic, fluoride, selenium, radon and uranium are examples of health-relevant naturally occurring groundwater constituents. Their concentrations in groundwater are strongly dependant on hydrogeological conditions. In some settings, nitrate may naturally occur in health-relevant concentrations.*

4.2.1 Arsenic

Health aspects

The International Agency for Research on Cancer (IARC) has classified arsenic (As) as a Group 1 human carcinogen (IARC, 2001). The health effects of arsenic in drinking-water include skin cancer, internal cancers (lung, bladder, kidney) and peripheral vascular disease (blackfoot disease). Evidence of chronic arsenic poisoning includes melanosis (abnormal black-brown pigmentation of the skin), hyperkeratosis (thickening of the soles of the feet), gangrene and skin and bladder cancer (WHO, 2003a). Arsenic toxicity may not be apparent for some time but the time to appearance of symptoms and the severity of effects will depend on the concentration in the drinking-water, other sources of exposure, dietary habits that may increase arsenic concentrations in staple dishes and a variety of other possible nutritional factors.

While earlier maximum allowable concentrations recommended by WHO for arsenic in drinking-water were higher, in 1993 the provisional WHO guideline value for arsenic in drinking-water was reduced to 10 µg/l based on concerns regarding its carcinogenicity in humans (WHO, 2004a). Regulations in some countries, e.g. the European Union (EU), Japan and the USA follow this guideline value and Australia has established a drinking-water standard for arsenic of 7 µg/l. A number of countries operate at present at a 50 µg/l standard, which corresponds to the provisional WHO guideline value before 1993. Some national authorities are currently seeking to reduce their own limits in line with the WHO guideline value. It is important to realize that the WHO Guidelines emphasize the need for adaptation of national standards to local health priorities, social, cultural, environmental and economic conditions and also advocate progressive improvement that may include interim standards. Furthermore, the WHO Guidelines emphasises the scientific uncertainty of the dose-response curves at low intakes and thus in deriving the guideline value of 10 µg/l. For improving public health benefits, other issues may therefore take priority over upgrading the sensitivity of analytical facilities for detecting lower concentrations or investing in upgrading drinking-water supplies to reduce arsenic concentrations to levels below 50 µg/l.

In recent years both the WHO guideline value and current national standards for arsenic have been found to be frequently exceeded in drinking-water sources. The scale of the arsenic problem in terms of population exposed to high arsenic concentrations is greatest in Bangladesh with between 35 and 77 million people at risk (Smith *et al.*, 2000). However, many other countries are also faced with elevated arsenic concentrations in groundwater, such as Hungary, Chile, Mexico, northeast Canada, the western USA and many countries in South Asia. More detailed information on occurrence and health significance of arsenic can be found in '*Arsenic in Drinking-water*' (WHO, In Press).

Occurrence

Arsenic is an ubiquitous element found in soils and rocks, natural waters and organisms. It occurs naturally in a number of geological environments, but is particularly common in regions of active volcanism where it is present in geothermal fluids and also occurs in sulphide minerals (principally arsenopyrite) precipitated from hydrothermal fluids in metamorphic environments (Hem, 1989). Arsenic may also accumulate in sedimentary environments by being co-precipitated with hydrous iron oxides or as sulphide minerals in anaerobic environments. It is mobilized in the environment through a combination of natural processes such as weathering reactions, biological activity and igneous activity as well as through a range of anthropogenic activities. Of the various routes of exposure to arsenic in the environment, drinking-water probably poses the greatest threat to human health.

Background concentrations of arsenic in groundwater in most countries are less than 10 µg/l. However, surveys performed in arsenic-rich areas showed a very large range, from <0.5 to 5000 µg/l (Smedley and Kinniburgh, 2001). Cases of large scale naturally occurring arsenic in groundwater are mainly restricted to hydrogeological environments characterized by young sediment deposits (often alluvium), and low-lying flat conditions with slow-moving groundwater such as the deltaic areas forming much of Bangladesh. Investigations by WHO in Bangladesh indicate that 20 per cent of 25 000 boreholes tested in that country have arsenic concentrations that exceed 50 µg/l. High concentrations of arsenic in groundwater also occur in regions where oxidation of sulphide minerals (such as arsenopyrite) has occurred (Alaerts *et al.*, 2001).

Arsenic concentration in German groundwater downstream of abandoned waste disposal sites was found to have a mean concentration of 61 µg/l (n = 253 sites) due to arsenic leaching from domestic coal ashes deposited with household wastes. In contrast, the mean arsenic concentration in uncontaminated aquifers is 0.5 µg/l (n = 472 sites) (Kerndorff *et al.*, 1992).

Transport and attenuation

The concentration of arsenic in natural waters is normally controlled by solid-solution interactions, particularly in groundwater where the solid/solution ratio is large. In most soils and aquifers, mineral arsenic interactions are likely to dominate over organic matter-arsenic interactions, although organic matter may interact to some extent through its reactions with the surfaces of minerals (Smedley and Kinniburgh, 2001). One of the best correlations between the concentration of arsenic in sediments and other elements is with iron. These interactions have also been the basis for the use of iron, aluminium and manganese salts in water treatment for arsenic removal.

Arsenic shows a high sensitivity to mobilization at the pH values typically found in groundwater (pH 6.5-8.5) and under both oxidizing and reducing conditions. Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5) but in natural waters is mostly found in inorganic oxyanion forms as trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Redox potential (E_h) and pH are the most important factors controlling arsenic speciation. Relative to the other oxyanion-forming elements, arsenic is among the most problematic in the environment because of its mobility over a wide range of redox conditions (Smedley and Kinniburgh, 2001). Under oxidizing conditions, $H_2AsO_4^-$ is dominant at low pH (less than ~pH 6.9), while at higher pH, $HAsO_4^{2-}$ becomes dominant (H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions, respectively). Under reducing conditions at less than ~pH 9.2, the uncharged arsenate(III)-species (H_3AsO_3) will predominate.

Transport is largely controlled by the aquifer conditions, particularly by adsorption on ferric oxohydroxides, humic substances and clays. Arsenic adsorption is most likely to be non-linear, with the rate of adsorption disproportionally decreasing with increasing concentrations in groundwater. This leads to reduced retardation at high concentrations. Since different arsenic species exhibit different retardation behaviour, arsenate (V) and arsenate (III) should travel through an aquifer with different amounts of interactions resulting in different velocities and increased separation along a flow path. This was demonstrated by Gulens *et al.* (in Smedley and Kinniburgh, 2001) using controlled soil-column experiments and various groundwaters. They showed that: (i) As(III) moved five to six times faster than As(V) under oxidizing conditions (at pH 5.7); (ii) with a 'neutral' groundwater (pH 6.9) under oxidizing conditions, As(V) moved much faster than under (i) but was still slower than As(III); (iii) under reducing conditions (at pH 8.3), both As(III) and As(V) moved rapidly through the column; (iv) when the amount of arsenic injected was substantially reduced, the mobility of the As(III) and As(V) was greatly reduced.

There is no process in the subsurface that alters arsenic species beside precipitation and adsorption. If groundwater with elevated arsenic levels is used for drinking-water supply, then treatment should be applied. There has been increasing research into this area and a number of low-cost household treatment technologies are available. Data from studies in Bangladesh suggest that low-cost technologies can remove arsenic to below 0.05 mg/l and sometimes lower (Ahmed *et al.,* 2001). Technologies are also available for system treatment including activated alumina, chemical precipitation and reverse osmosis (for arsenate). However, in some situations, source substitution or mixing is preferable to arsenic removal (Alaerts *et al.*, 2001).

4.2.2 Fluoride

Health aspects

Because fluoride is widely dispersed in the environment, all living organisms are widely exposed to it and tolerate modest amounts. In humans, fluoride has an affinity for accumulating in mineralizing tissues in the body, in young people in bone and teeth, in older people in bone, and incorporation of fluoride into the matrix of teeth during their formation is protective against dental caries.

Health problems associated with the condition known as fluorosis may occur when fluoride concentrations in groundwater exceed 1.5 mg/l: staining of the tooth enamel may become apparent (dental fluorosis) and, with continued exposure, teeth may become extremely brittle. The incidence and severity of dental fluorosis, and the much more serious skeletal fluorosis, depend on a range of factors including the quantity of water drunk and exposure to fluoride from other sources, such as from high fluoride coal in China. Nutritional status may also be important. Estimates based on studies from China and India indicate that for a total intake of 14 mg/day there is a clear excess risk of skeletal adverse effects, and there is suggestive evidence of an increased risk of effects on the skeleton at total fluoride intakes above about 6 mg/day (WHO, 2004b). In its most severe form, this disease is characterized by irregular bone deposits that may cause arthritis and crippling when occurring at joints.

The WHO guideline value for fluoride is 1.5 mg/l since 1984 (WHO, 2004a). The EU maximum admissible concentration for fluoride in drinking-water is 1.5 mg/l. The US Environmental Protection Agency (US EPA) set an enforceable primary maximum contaminant level of 4 mg/l in water systems to prevent crippling skeletal fluorosis. A secondary contaminant level of 2 mg/l was recommended by US EPA to protect against objectionable dental fluorosis. In setting national standards for fluoride, it is particularly important to consider volumes of water intake (which are affected by climatic conditions) and intake of fluoride from other sources (e.g. food, air). Where higher fluoride concentrations occur in groundwater used as drinking-water source, treatment and/or change or mixing with other waste sources containing lower fluoride levels is necessary in order to meet drinking-water standards. In areas with high natural fluoride levels, the public health benefits of investments in the treatment necessary to meet the WHO guideline value may need to be balanced against other priorities for optimising public health benefits.

More detailed information on occurrence and health significance of fluoride can be found in ‘Fluorides in Drinking Water’ (Bailey *et al.*, In Press).

Occurrence

Fluoride (F^-) naturally occurs in rocks in many geological environments (Hem, 1989) but fluoride concentrations in groundwater are particularly high in groundwater associated with acid volcanic rocks, e.g. in Sudan, Ethiopia, Uganda, Kenya and Tanzania (Bailey *et al.*, In Press). High concentrations of fluoride also occur in some metamorphic and sedimentary rocks that contain significant amounts of fluoride-bearing minerals such as fluorite and apatite. Fluoride in water supply based on groundwater is a problem in a number of countries and over 70 million people worldwide are believed to be at risk of adverse health effects from consumption of water containing high levels of fluoride. India and China have particular problems and estimates suggest up to 60 million are affected in these two countries alone.

Exposure to fluoride from drinking-water depends greatly on natural circumstances. Levels in raw water are normally below 1.5 mg/l, but groundwater has been found to contain >50 mg/l in some areas rich in fluoride-containing minerals. For example, in Kenya, 61 per cent of groundwater samples collected nationally from drinking-water wells exceeded 1 mg/l (Bailey *et al.*, In Press). In general high fluoride concentrations in groundwater show a strong positive correlation with dissolved solids, sodium, and alkalinity, and a strong negative correlation with hardness.

Transport and attenuation

The concentration of fluoride ions in groundwater is driven by the presence of calcium ions and the solubility product of fluorite (CaF_2). In equilibrium, a calcium concentration of 40 mg/l equates to a concentration of 3.2 mg/l fluoride. In groundwater with a high concentration of calcium ions, fluoride concentrations rarely exceed 1 mg/l. Substantially higher fluoride concentrations in groundwater are usually caused by a lack of calcium. During high percolation rates, Flühler *et al.* (1985) observed increased fluoride concentration in the leachate of fluoride-enriched soils due to a limited additional delivery of calcium.

In groundwater with a high pH (>8) and dominated by sodium ions and carbonate species, fluoride concentrations commonly exceed 1 mg/l, and concentrations in excess of 50 mg/l have been recorded in groundwater in South Africa, and in Arizona in the USA (Hem, 1989). Moreover, the fluoride-ion (F^-) can interact with mineral surfaces, but is substituted by hydroxyl-ions at high pH values. Hem (1989) observed a fluoride concentration of 22 mg/l in a caustic thermal groundwater (pH 9.2, 50 °C) in Owyhee County, Idaho. Fluoride ions form strong complexes especially with aluminium, beryllium and iron (III).

4.2.3 Selenium

Health aspects

Selenium is an essential trace element with a physiologically required intake of about 1 µg per kg body weight and day for adults. Deficiencies of selenium in diets may cause a number of health effects, although few reports of clinical signs of deficiency are available. However, the range of concentrations of this element in food and water that provide health benefits appears to be very narrow. When ingested in excess of nutritional requirements in food and drinking-water, selenium can cause a number of acute and chronic health effects including damage to or loss of hair and fingernails, finger deformities, skin lesions, tooth decay and neurological disorders (WHO, 2003b).

Although drinking-water generally accounts for less than 1 per cent of the typical dietary intake of selenium, in some circumstances naturally-occurring concentrations of selenium in groundwater may be sufficiently high to cause health problems. The WHO guideline value for selenium in drinking-water is 0.01 mg/l (WHO, 2004a).

Occurrence

Selenium has similar chemical properties and behaviour to sulphur (Hem, 1989), and is commonly associated with metal sulphide minerals in mineral deposits in a wide range of igneous rocks and with sulphur-rich coal. Sedimentary rocks and overlying soil in some regions may have high background concentrations of selenium. In the western part of the USA, these are associated with uranium and vanadium mineralization in shales and sandstones. In some semi-arid areas in China and India, selenium reaches high concentrations in soil and accumulates in plant tissue. Runoff from irrigated agriculture on seleniferous soil may contain dissolved selenium concentrations of up to 1 mg/l (Hem, 1989), and groundwater in these areas also typically contains high concentrations of leached selenium (Barceloux, 1999). Groundwater concentrations of selenium rarely exceed 1 µg/l (Hem, 1989), but up to 6000 µg/l have been reported (WHO, 2003b), and high concentrations (tens to hundreds of micrograms per litre) may occur in surface water and groundwater near metal-sulphide mine sites.

Selenium concentrations are often particularly high in surface waters and groundwater in coal mining areas where solid wastes and wastewater from coal power stations are disposed to the environment (Barceloux, 1999; US EPA, 2000).

Transport and attenuation

Selenium can exist in nature in four oxidation states: 0 (elemental selenium), -2 (selenide), +4 (selenite) and +6 (selenate). Under oxidizing conditions, the selenium occurs predominantly as selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) ions in natural waters. These ions have a very high solubility, and can reach very high concentrations in conditions when water is being subjected to high rates of evapotranspiration such as in regions with semi-arid or arid climates. Selenate and selenite minerals can accumulate with sulphates in soils in regions with semi-arid or arid climates.

High concentrations of selenium may also occur in groundwater beneath areas where intense irrigated agriculture flushes selenium compounds through the soil profile, and if groundwater pumping rates are high, the concentration of selenium may be progressively increased by the recycling of salts by the process of pumping, evaporation and recharge of pumped effluent. Consequently, selenium concentrations in shallow groundwater and in drainage from irrigated agriculture on seleniferous soils are often highly toxic to wildlife that ingests the water, as in the widely studied case of the Kesterson National Wildlife Refuge in the San Joaquin Valley of California (NRC, 1989). This water is also potentially toxic to humans who might use shallow groundwater as a drinking-water source, although water contaminated with high selenium concentrations is often too saline for potable use.

Under reducing conditions in groundwater or in marshes, selenium can also be removed from water through co-precipitation with sulphide minerals such as pyrite (FeS_2) or the precipitation of ferroselite ($FeSe_2$); through volatilization as dimethyl selenide or hydrogen selenide, or through the uptake of organo-selenium compounds by plants. Consequently, anaerobic bioreactors or artificial wetlands are being used for selenium removal from water, predominantly to protect receiving environments from the discharge of wastewater contaminated by selenium.

Selenium can be removed from water by adsorption onto iron oxyhydroxide minerals (especially ferrihydrite) and this is one of the preferred water treatment methods. Selenium can also be removed from drinking-water by reverse osmosis and through the use of anion-exchange resins.

4.2.4 Radon

Health aspects

Radon is a radioactive gas emitted from radium, a daughter product of uranium that occurs naturally in rocks and soil. The main health effect of radon is to cause lung cancer. Radon, together with its decay products, emits alpha particles that can damage lung tissue. Although most radon is exhaled before it can do significant damage, its decay products can remain trapped in the respiratory system attached to dust, smoke and other fine particles from the air.

The global average human exposure to radiation from natural sources is 2.4 mSv per year with an average dose from inhalation of radon of 1.2 mSv per year. There are large local variations in this exposure depending on a number of factors, such as height above sea level, the amount and type of radionuclides in the soil, and the amount taken into the body in air, food, and water (WHO, 2004a). Unlike most other naturally occurring groundwater contaminants, most of the health effects of radon in groundwater are considered to be due to its contribution to indoor air quality rather than due to effects caused by direct ingestion of water. UNSCEAR has calculated the average doses from radon in drinking-water as low as 0.025 mSv/year via inhalation and 0.002 mSv/year from ingestion as compared to the inhalation dose from radon in the air of 1.1 mSv/year (UNSCEAR, 2000). The WHO has recommended a reference level of committed effective dose of 0.1 mSv from 1 year's consumption of drinking-water (WHO, 2004a).

Stirring and transferring water from one container to another will liberate dissolved radon. Water that has been left to stand will have reduced radon activity, and boiling will remove radon completely. As a result, it is important that the form of water consumed is taken into account in assessing the dose from ingestion. Moreover, the use of water supplies for other domestic purposes will increase the levels of radon in the air, thus increasing the dose from inhalation. This dose depends markedly on the form of domestic usage and housing construction (NCRP, 1989). The form of water intake, the domestic use of water and the construction of houses vary widely throughout the world. It is therefore not possible to derive an activity concentration for radon in drinking-water that is universally applicable.

WHO recommends implementing controls if the radon concentration of drinking-water exceeds 100 Bq/litre (WHO, 2004a), and the EU likewise recommends assessing the need for protective measures at concentrations above this level (Euratom 2001/928; CEC, 2001).

Occurrence

Radon (Rn) is a naturally occurring, colourless, odourless gaseous element that is soluble in water. It occurs naturally only as a product of the radioactive decay of radium, itself a radioactive decay product of uranium. As is the case for uranium, concentrations of radon are directly related to the local geology, and are particularly high in granitic rocks and pegmatites and sediments with phosphate nodules or heavy mineral sand deposits.

Radon-222 is a frequently encountered radioactive constituent in natural waters and typically exceeds the concentration of other radionuclides, including uranium, thorium and radium, by orders of magnitude. High radon emanation, especially along fracture surfaces, contributes significantly to radon concentrations in groundwater. Data from sampling campaigns indicate that there is a great degree of variability in the radon-222 concentration of samples drawn from any given rock type. The United States Geological Survery (USGS) conducted a study on occurrence of dissolved radon in groundwater in Pennsylvania (Senior, 1998). Findings of this study indicated that rock types with the highest median radon concentrations in groundwater include schist and phyllite (2400 pCi/l) as well as quartzite (2150 pCi/l). The geohydrologic groups with lowest median radon concentrations in ground water include carbonate rocks (540 pCi/l) and other rocks (360 pCi/l). Water from wells in gneiss had a median radon concentration of 1000 pCi/l, and water from wells in Triassic-age sedimentary rocks had a median radon concentration of 1300 pCi/l. Radon concentrations generally do not correlate with well characteristics, the pH of water or concentrations of dissolved major ions and other chemical constituents in the water samples.

Transport and attenuation

The rate of radon's radioactive decay is defined by its half-life, which is the time required for one half of the amount of radon present to break down to form other elements. The half-life of radon is 3.8 days. Several factors probably control the concentration of radon-222 in a water supply. The flux of radon-222 within the ground may be controlled by the radium-226 concentration in the surrounding rocks, the emanation fraction for the radon-222 from the rock matrix and the permeability of the rock to radon-222 movement. For a given flux, the concentration of radon-222 in a water supply would then also be controlled by the ratio of aquifer surface area to volume.

4.2.5 Uranium

Health aspects

Uranium is a heavy metal of toxicological rather than radiological relevance in drinking-water. In particular, it is of concern because of its impact on kidney function following long-term exposure. Because of uncertainties regarding the toxicity of uranium for human beings the WHO has proposed a provisional drinking-water guideline value of 15 μg/l (WHO, 2004a; 2005a). The US EPA maximum contaminant level for uranium in drinking-water is 30 μg/l.

Occurrence

Uranium (U) is widely distributed in the geological environment, but concentrations in groundwater are particularly high in granitic rocks and pegmatites, and locally in some sedimentary rocks like sandstones. Uranium often occurs in oxidizing and sulphate-rich groundwater. There are three naturally occurring isotopes of uranium: ^{234}U (<0.01 per cent), ^{235}U (0.72 per cent), and ^{238}U (99.27 per cent). All three isotopes are equally toxic.

Concentrations of uranium in natural waters usually range between 0.1 and 10 μg/l (Hem, 1989), but are often up to 100 μg/l in groundwater in areas underlain by granitic rocks, and may exceed 1 mg/l near uranium mineral deposits.

Transport and attenuation

The transport of uranium in groundwater varies widely according to the aquifer conditions. In anoxic conditions, uranium is reduced to U(IV) which is relatively insoluble and precipitates. In oxidizing environments, uranium exists mainly as UO_2X_2-(= uranyl)-compounds with U(VI) which is considerably more soluble. Even with the higher solubility of U(VI), transport of U(VI) can be limited as it sorbs strongly to solid surfaces at circum-neutral pH. Very low and very high pH conditions limit sorption as does the presence of certain complexing ligands such as natural organic matter, organic chelating agents and carbonate, all of which can significantly enhance the transport of uranium.

4.3 NITROGEN SPECIES

Ammonia, nitrate and nitrogen containing organic compounds of humic type are the dominating nitrogen compounds in groundwater. Though nitrite is highly toxic, it usually occurs only in very low concentrations in groundwater and these are not relevant to human health. However, nitrite can become relevant from conversion of ammonia or nitrogen in the drinking-water supply system or human body.

NOTE ▶ *Though nitrogen may occur naturally in groundwater, the main sources of groundwater pollution are human activities such as agriculture and sanitation (see Chapters 9 and 10).*

Health aspects

Ammonia in drinking-water is not of direct health relevance, and therefore WHO have not set a health-based guideline value. However, ammonia can compromise disinfection efficiency, can cause the failure of filters for the removal of manganese, and can cause taste and odour problems. Also in distribution systems it can lead to nitrite formation which is of health relevance.

The toxicity of nitrate to humans is mainly attributable to its reduction to nitrite. Nitrite, or nitrate converted to nitrite in the body, causes a chemical reaction that can lead to the induction of methaemoglobinaemia, especially in bottle-fed infants. Methaemoglobin (metHb), normally present at 1-3 per cent in the blood, is the oxidized form of haemoglobin (Hb) and cannot act as an oxygen carrier in the blood. The reduced oxygen transport becomes clinically manifest when the proportion of metHb concentration reaches 5-10 per cent or more of normal Hb values (WHO, 1996a). Nitrate is enzymatically reduced in saliva forming nitrite. Additionally, in infants under one year of age the relatively low acidity in the stomach allows bacteria to form nitrite. Up to 100 per cent of nitrate is reduced to nitrite in infants, as compared to 10 per cent in adults and children over one year of age. When the proportion of metHb reaches 5-10 per cent, the symptoms can include lethargy, shortness of breath and a bluish skin colour (‘blue baby syndrome’). Anoxia and death can occur at very high uptakes of nitrite and nitrate from drinking-water.

Methaemoglobinaemia is observed in populations where food for infant formula in prepared with water containing nitrate in excess of around 50 mg/l, but other factors are also involved in disease causation. The risk is enhanced by sewage contamination. This contributes nitrate and renders chemical conditions in the water to be reducing, thus supporting the presence of nitrate reducing bacteria. Moreover, ingestion of microbially contaminated water causes gastroenteritis infection which would also predispose the infant to a nitrate reducing conditions and thereby more nitrite exposure (WHO, 2004a). A review of numerous case studies of water-related infant methaemoglobinaemia in the 1980s indicated high correlation with microbial contamination of the water (US EPA, 1990; WHO, 2005b).

The weight of evidence is strongly against an association between nitrite and nitrate exposure in humans and the risk of cancer (WHO, 2004a). Studies in laboratory animals demonstrate increased tumour incidence only after exposure to extremely high levels of nitrite in the order of 1000 mg/l in drinking-water and simultaneously high levels of nitrosatable precursors (WHO, 1996b). At lower nitrite levels, tumour incidence resembled those of control groups treated with the nitrosatable compound only. On the basis of adequately performed and reported studies, it may be concluded that nitrite itself is not carcinogenic to animals (WHO, 1996a).

Based on methaemoglobinaemia in infants (an acute effect), the WHO has established a guideline value for nitrate ion of 50 mg/l as NO_3^- and a provisional guideline value for nitrite of 3 mg/l as NO_2^- (WHO, 2004a). Because of the possibility of simultaneous occurrence of nitrite and nitrate in drinking-water, the sum of the ratios of the concentrations ($C_{nitrate}$ or $C_{nitrite}$) of each to its guideline value ($GV_{nitrate}$ or $GV_{nitrite}$) should not to exceed one.

Sources and occurrence

Nitrogen is present in human and animal waste in organic form, which may then subsequently be mineralized to inorganic forms. Ammonia (ionized as NH_4^+, non-ionized as NH_3) as well as urea $(NH_2)_2CO$ is a major component of the metabolism of mammals. Ammonia in the environment mainly results from animal feed lots and the use of manures in agriculture (Chapter 9), or from on-site sanitation or leaking sewers (Chapter 10). Thus ammonia in water is often an indicator of sewage pollution. The nitrite ion (NO^-_2) contains nitrogen in a relatively unstable oxidation state. Nitrite does not typically occur in natural waters at significant levels, except temporarily under reducing conditions. Chemical and biological processes can further reduce nitrite to various compounds or oxidize it to nitrate. The nitrate ion (NO^-_3) is the stable form of combined nitrogen for oxygenated systems. Nitrate is one of the major anions in natural waters, but as for ammonia, concentrations can be greatly elevated due to agricultural activities (Chapter 9), and sanitation practices (Chapter 10).

Natural levels of ammonia in ground and surface waters are usually below 0.2 mg/l, and nitrate concentrations in groundwater and surface water typically range between 0-18 mg/l as NO_3^-. Although elevated concentrations of nitrate in groundwater are mostly caused by agricultural activity or sanitation practices, natural nitrate concentrations can also exceed 100 mg/l as NO_3^- as observed in some arid parts of the world such as the Sahel and north Africa (Edmunds and Gaye, 1994) and the arid interior of Australia (Box 4.1).

Box 4.1. Naturally-occurring high nitrate in Australia

High groundwater nitrate concentrations have been observed in the arid interior of Australia, commonly exceeding 45 mg/l, and often exceeding 100 mg/l in groundwater which otherwise meets national and international drinking-water guidelines (Lawrence, 1983; Barnes *et al*., 1992). The nitrate in this region is partially derived from nitrogen fixing by native vegetation, and by cyanobacteria crusts on soils. Termite mounds appear to be a significant contributory source of the nitrate (Barnes *et al*., 1992), possibly due to the presence of nitrogen fixing bacteria in many termite species, and the nitrogen-rich secretions used to build the walls of the mounds. Nitrate is leached to the water table in arid Australia after periodic heavy rainfall events, particularly after bush fires that allow soluble nitrate salts to accumulate in soils. Denitrification in these soils appears to be inhibited by low carbon levels.

Transport and attenuation

Ammonium (NH_4^+) shows a high tendency for adsorption to clay minerals, which limits its mobility in the subsurface (saturated and unsaturated zones). In contrast, interactions between minerals and nitrate or nitrite are usually negligible and both ions are mobile in the subsurface.

Under aerobic conditions in the subsurface oxidation of ammonium through nitrite to nitrate by microorganisms is the only process where nitrate is formed in natural systems.

DEF ▶ ***Nitrification*** *is the biological conversion of ammonium through nitrite to nitrate.* ***Denitrification*** *is the biological process of reducing nitrate to ammonia and nitrogen gas.*

Despite the natural high concentrations of nitrate in groundwater in much of inland Australia, there have been no verified cases of MetHb in Aboriginal people (Hearn *et al*., 1993), who are the main users of groundwater in this part of the country. Because potable quality groundwater is scarce in the interior of Australia, and because the use of water is vital for maintaining hygiene in the region, the National Health and Medical Research Council revised the national water quality guidelines in 1990. The revised guidelines allow the use of groundwater with concentrations of nitrate exceeding 100 mg/l for all non-potable needs, up to 100 mg/l for potable use except for infants under 3 months old, and up to 50 mg/l for infants under 3 months old. Although technologies exist to remove nitrate from drinking-water using microbial denitrification, the equipment is difficult to maintain in remote aboriginal settlements, and it was considered in this case that changing guideline concentrations would produce better health outcomes. These changes were incorporated into the Australian drinking-water guidelines in 1996. The autotrophic conversion of ammonia to nitrite and nitrate (nitrification) requires oxygen. The discharge of ammonia nitrogen into groundwater and its subsequent oxidation can thus seriously reduce the dissolved oxygen content in shallow groundwater, especially where high ammonia loads are applied and re-aeration of the soil is limited.

In the absence of dissolved oxygen (such as in some deep or confined groundwaters), denitrification can occur, driven by denitrifying bacteria. Under fully anaerobic conditions, in an aquifer where predominantly sulphides serve as reduction agents, the microbial oxidation of sulphides into sulphate and simultaneous reduction of nitrate to nitrogen gas can occur which also reduces the nitrate content.

As microbial processes, both nitrification and denitrification are affected by many factors that are of importance to microbial activity. Nitrification and denitrification are optimal at about 25°C and are inhibited at 10°C or less. Other regulating factors are pH and all factors affecting the diffusion of oxygen such as soil density, grain structure, porosity and soil moisture. Warm, moist and well aerated soils provide ideal conditions for nitrification. Denitrification occurs only under anoxic or almost anoxic conditions. Beside the presence of nitrate, the denitrifying bacteria require a carbon source. A soil moisture of more than 80 per cent has been found to be essential for denitrification. Thus in many settings natural attenuation can substantially reduce nitrate concentrations in groundwater over time, but rates of attenuation strongly depend on conditions in the aquifer.

4.4 METALS

The following focuses on those metals which are toxic to humans and which have frequently been observed as groundwater contaminants in connection with human activities and/or have physical and chemical properties which make them potential groundwater contaminants, i.e. cadmium (Cd), lead (Pb), nickel (Ni), chromium (Cr), and copper (Cu).

Health aspects

Cadmium has a high renal toxicity, which is not only due to its mode of action but also to its irreversible accumulation in the kidney. The health based guideline value for cadmium in drinking-water is 3 µg/l (WHO, 2004a).

Lead is a strong neurotoxin in the unborn, newborn and young children. It crosses the placenta easily and is toxic to both the central and the peripheral nervous system, thus causing cognitive and behavioural effects (WHO, 2004a). The threshold of neurotoxicological concern, defined as a group based mean blood lead level, has decreased continually during the last 10 to 20 years, and epidemiological evidence indicates lead levels above 30 µg of lead per litre of blood to be associated with intelligence quotient deficits in children (WHO, 2004a). The use of lead in antiknock and lubricating agents in petrol is being phased out in many countries, thus decreasing this source of contamination. However, a major main source of exposure to lead through water is household plumbing systems, i.e. pipes, fittings, solder and connections from the mains to homes. Dissolution from such materials strongly depends on chemical properties of the drinking-water, with soft, acidic water dissolving the largest amount. The WHO guideline value for lead in drinking-water is 10 µg/l (WHO, 2003c; 2004a).

The significance of Nickel from the health point of view is mainly due to its high allergenic potential. The WHO drinking-water guideline value for the protection of sensitive persons is 20 µg/l (WHO, 2004a).

Chromium can be found in the environment in two valency states, Cr(III) and Cr(VI). The former predominates in soils, whereas the latter occurs exclusively as chromate (CrO_4^{2-}) from anthropogenic sources. Cr(VI) is the form which is of toxicological significance because of its easy uptake into cells together with SO_4^{2-} and PO_4^{2-}. Within cells and during its reduction to Cr(III), the chromate ion represents a considerable genotoxic and clastogenic potential (Costa, 2002). However, since even very high doses of Cr(VI) are subjected to rapid chemical reduction in the upper gastrointestinal tract (Kerger *et al.*, 1997), only negligible amounts of Cr(VI) should reach the blood compartment and other body fluids and organs. The health based guideline value for chromium in drinking-water is 50 µg/l (WHO, 2004a), and while higher concentrations have been reported from some drinking-water supplies, most studies indicate the concentration of chromium in groundwater to be low (WHO, 2003d). Cr(III) in drinking-water may eventually be oxidized to Cr(VI) during its ozonation.

Copper is an essential trace element with an optimal daily oral intake of 1-2 mg per person. Naturally occurring copper concentrations in groundwater are without any health significance and scatter mostly around 20 µg/l. If drinking-water drawn from groundwater contains elevated levels, in most situations corrosion of copper pipes is the primary source. Mean concentrations of more than 2 mg/l could lead to liver cirrhosis in babies if their formula is repeatedly prepared using such water (Zietz *et al.*, 2003). The prevalent endpoint of acute copper toxicity by time, concentration and dose is nausea (Araya *et al.*, 2003). The health based guideline value for copper in drinking-water is 2 mg/l (WHO, 2004a; 2004c).

Sources and occurrence

Metals from activities such as mining, manufacturing industries, metal finishing, wastewater, waste disposal, agriculture and the burning of fossil fuels can reach concentrations in groundwater which are hazardous to human health. Chapter 11 lists industry types together with the metals they commonly emit (see Table 11.2.) Metals are natural constituents in groundwaters, having their origin in weathering and solution of numerous minerals. However, natural concentrations of metals in groundwaters are generally low. Typical concentrations in natural groundwaters are <10 µg/l (copper, nickel), <5 µg/l (lead) or <1 µg/l (cadmium, chromium). Even so, the concentrations can locally increase naturally up to levels which are of toxicological relevance and can exceed drinking-water guidelines, e.g. in aquifers containing high amounts of heavy metal bearing minerals (ore). Metal concentrations in groundwater may be of particular concern where it is directly affected by manufacturing and mining as well as downstream of abandoned waste disposal sites. Another anthropogenic cause of elevated metal concentrations in groundwaters is the acidification of rain and soils by air pollution and the mobilization of metals at lower pH values. This problem predominantly appears in forested areas, because the deposition rates of the acidifying anions sulphur and nitrate from the atmosphere are evidently higher in forests due to the large surface of needles and leafs, and because soils in forests are generally poor in nutrients and have a low neutralization capacity against acids.

Transport and attenuation

Most of the metals of concern occur in groundwater mainly as cations (e.g. Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}) which generally become more insoluble as pH increases. At a nearly neutral pH typical for most groundwaters, the solubility of most metal cations is severely limited by precipitation as an oxide, hydroxide, carbonate or phosphate mineral, or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter in the aquifer matrix. The adsorption decreases with decreasing pH. As a consequence, in naturally or anthropogenically acidified groundwaters metals are mobile and can travel long distances. Furthermore, as simple cations there is no microbial or other degradation.

In a soil solution containing a variety of heavy metal cations that tend to adsorb to particle surfaces, there is competition between metals for the available sites. Of several factors that determine this selectivity, ionic potential, which is equal to the charge of an ion over its ionic radius, has a significant effect. Cations with a lower ionic potential tend to release their solvating water molecules more readily so that inner sphere surface complexes can be formed. Selectivity sequences are arranged in order of decreasing ionic radius, which results in increasing ionic potential and decreasing affinity or selectivity for adsorption. As an example the following selectivity sequence of transition elements belonging to group IIb has been determined (Sposito, 1989):

$$Hg^{2+} > Cd^{2+} > Zn^{2+}$$

As a consequence, mercury is the most strongly adsorbed; this being the probable reason for its generally very low concentration occurrence in groundwater.

Metals within the transition group differ in that electron configuration becomes more important than ionic radius in determining selectivity. The relative affinity of some metals belonging to different transition groups is given by:

$$Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$$

However, this sequence can be more or less changed in groundwater by naturally occurring complexing agents like fulvic acids which is especially true for copper (Schnitzer and Khan, 1972).

In addition, most oxyanions tend to become less strongly sorbed as the pH increases (Sposito, 1989). Therefore, the oxyanion-forming metals such as chromium are some of the more common trace contaminants in groundwater. Chromium is mobile as stable Cr(VI) oxyanion species under oxidizing conditions, but forms cationic Cr(III) species in reducing environments and hence behaves relatively immobile under these conditions. For example, in contaminated groundwater at industrial and waste disposal sites Chromium occurs as Cr^{3+} and CrO_4^{2-} species, with CrO_4^{2-} being much more toxic but less common than Cr^{3+}. In most aquifers chromium is not very mobile because of precipitation of hydrous chromium(III)oxide. In sulphur-rich, reducing environments, many of the trace metals also form insoluble sulphides (Smedley and Kinniburgh, 2001).

4.5 ORGANIC COMPOUNDS

Organic compounds in groundwater commonly derive from breakdown and leaching of naturally occurring organic material, e.g. from organic-rich soil horizons and organic matter associated with other geologic strata, or human activity, e.g. domestic, agricultural, commercial and industrial activities.

Natural sources will always contribute some organic compounds to groundwater, often at low levels. Natural organic matter comprises water-soluble compounds of a rather complex nature having a broad range of chemical and physical properties. Typically, natural organic matter in groundwater is composed of humic substances (mostly fulvic acids) and non-humic materials, e.g. proteins, carbohydrates, and hydrocarbons (Thurman, 1985; Stevenson, 1994). While natural organic matter is a complex, heterogeneous mixture, it can be characterized according to size, structure, functionality, and reactivity. Natural organic matter can originate from terrestrial sources (allochthonous natural organic matter) and/or algal and bacterial sources within the water (autochthonous natural organic matter). Dissolved organic carbon (DOC) is considered to be a suitable parameter for quantifying organic matter present in groundwater; however, DOC is a bulk organic quality parameter and does not provide specific identification data and may also incorporate organic compounds arising from human activity. Natural organic matter, although considered benign, may still indirectly influence groundwater quality. For example, contaminants may bind to organic-matter colloids allowing their facilitated transport within groundwater, a process proposed (but not proven) to be of most significance for the more highly sorbing organic compounds. Also, routine chlorination of water supplies containing natural organic matter may form disinfection by-products such as trihalomethanes. However, because of their low direct health relevance, natural organic substances are not addressed further herein.

Human activity has released a vast range of anthropogenic organic chemicals, commonly termed ‘micro-pollutants’, to the environment, some of which may detrimentally impact groundwater quality. This chapter focuses on commercially and industrially derived chemicals which (i) have a high toxicity, (ii) have physical and chemical properties facilitating their occurrence in groundwater and (iii) have been observed to occur frequently as groundwater contaminants. Chapter 11 lists industry types together with substances that may potentially be released to the subsurface from their respective industrial activities. The occurrence of organic pollutants in groundwater is controlled not only by their use intensity and release potential, but also by their physical and chemical properties which influence subsurface transport and attenuation. Discussion of this aspect specific to organic chemicals follows and extends the general concepts covered in Section 4.1.

4.5.1 Conceptual transport models for non aqueous phase liquids

A correct conceptual model of contaminant behaviour is essential for assessing subsurface organic contaminant migration. The classical near-surface leachable source zone – dissolved plume model presented earlier (Section 4.1.2, Figure 4.2) is not applicable for all organic substances. Of key importance is the recognition that organic chemicals have very different affinities for water, ranging from organic compounds that are hydrophilic (“love” water) to organics that are hydrophobic (“fear” water). Such concepts are used below to develop appropriate contaminant conceptual models followed by discussion of specific transport processes applicable within the models developed.

Water is a highly polar solvent, so polar in fact that it develops a hydrogen-bonded structure and will easily dissolve and solvate ionic species. The vast majority of organic compounds are covalent molecules, rather than ionic species, and most have a limited tendency to partition or dissolve into water. Further, many organic compounds found in groundwater are used as liquids, e.g. hydrocarbon fuels or industry solvents. A focus upon organic liquids is hence relevant. Organic compounds that most easily partition or dissolve into water tend to be small molecules, have a polar structure and may hydrogen-bond with water. Typically they have only a few carbon atoms and often contain oxygen. Examples include methanol (CH_3OH) and other short-chain alcohols, e.g. ethanol and propanols that may be used as de-icers, and ketones such as methyl-ethyl-ketone and ethers such as dioxane that are used as industrial solvents. Some compounds are so hydrophilic that they form a single fluid phase with the water and are said to be miscible with the water, e.g. methanol, acetone, dioxane.

Most organic compounds are, however, relatively hydrophobic as they are comparatively large molecules of limited polarity with low hydrogen-bonding potential. Most organic liquids are so hydrophobic that they form a separate organic phase to the water (aqueous) phase. They are immiscible with water and a phase boundary exists between the organic phase and the aqueous phase, with the organic phase generally being referred to as the non aqueous phase liquid (NAPL). When a separate organic NAPL exists it is important to consider the density of the NAPL relative to water as this controls whether the NAPL will be upper or lower phase relative to the water phase. Most hydrocarbon-based organic liquids have a density <1 (g/ml), e.g. benzene is 0.88 and pentane is 0.63 and when in contact with water will be the upper phase and “float” upon the water phase of density 1. Such “light” organic compounds are generally referred to as being LNAPLs .

In contrast, other hydrophobic organics have a relatively high density due to incorporation of dense chlorine (or other halogen) atoms in their structure and for example chlorinated solvents such as trichloroethene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA) and polychlorinated biphenyl (PCB) mixtures have densities in the 1.1 to 1.7 range. Due to their density such organic phases will be the lower phase and ‘sink’ below the water phase. Such “dense” organic compounds are generally referred to as DNAPLs.

Although hydrophobic, LNAPL and DNAPL organics still have potential for some of their organic molecules to dissolve into the adjacent aqueous phase. The organics are ‘sparingly soluble’ and will have a finite solubility value in water leading to dissolved concentrations in the water phase. Solubility values achieved by individual organic compounds in water are highly variable between organics and controlled by their relative hydrophobicity. For example, small and/or polar organics have the greatest solubility with for example dichloromethane (DCM) (CH_2Cl_2) being one of the most soluble with a solubility of ca. ~20,000 mg/l, which contrasts with e.g. DDT, a large pesticide molecule that is not easily accommodated in the polar water structure and has a solubility of just about 0.1 mg/l. Similarly benzene, as single aromatic ring hydrocarbon, has a solubility ca. 1,800 mg/l that is much greater than benzo[a]pyrene, a PAH of solubility ca. 0.004 mg/l that is composed of five adjacent aromatic rings.

The above provides fundamental understanding for conceptual models of organic contaminant transport in the subsurface and why specific organic compounds have a tendency to occur or not occur in groundwater. Hydrophilic miscible organics behave similarly to the classical leachable source model (Figure 4.2). In essence, a spill of e.g. a de-icer fluid at surface would migrate as a concentrated organic-aqueous fluid through the unsaturated zone and then migrate laterally in the groundwater as a concentrated dissolved-phase plume. Importantly, hydrophobic immiscible organics, i.e. NAPLs, exhibit very different behaviour. Conceptual models for LNAPL releases and DNAPL releases (Mackay and Cherry, 1989) are shown in Figures 4.4 and 4.5.

NAPLs may migrate as a separate NAPL phase and displace air and water from the pores they invade if they have sufficient head (pressure) to overcome the entry pressure to the pores or fractures. This head is controlled by aspects such as the spill volume and rate and the vertical column of continuous NAPL developed in the subsurface. NAPL migration is also controlled by its density and viscosity. Petrol fuel and chlorinated solvents have viscosities lower than water and more easily migrate in the subsurface; in contrast, PCB oils or coal tar (PAH-based) hydrocarbons may be very viscous and perhaps take years for the NAPL to come to a resting position in the subsurface. Chlorinated solvents such as PCE have high densities and may penetrate to significant depths through aquifer systems in very short time periods. Whereas dissolved pesticides may take years to decades to migrate through a 30 m unsaturated zone, DNAPL may migrate through such a zone in the order of hours to days (Pankow and Cherry, 1996). DNAPLs may penetrate discrete sand horizons and hairline fractures in clays and compromise clay units that are normally an effective barrier to dissolved plume migration.

At the water table, LNAPLs, being less dense than water, will form a floating layer of LNAPL on the water table often slightly elongated in the direction of the water table hydraulic gradient. DNAPL, in contrast may penetrate as a separate immiscible DNAPL below the water table. Predominant movement will be vertically downward due to its density, but some lateral spreading will occur as it encounters lower permeability strata. If spilt in sufficient volume and with sufficient driving head, the DNAPL may penetrate the full aquifer depth to the underlying aquitard/bedrock (Kueper *et al.*, 1993). This should not be assumed to occur in all cases. Migrating NAPL leaves a trail of immobile residual NAPL droplets behind its migration pathway held by capillary forces causing NAPL to spread across an aquifer thickness. DNAPL accumulating on low permeability features, often referred to as pools, is potentially mobile. It may ultimately penetrate that formation due to changes in pressure arising from continued DNAPL spillage, pumping or remediation attempts or via drilling (for boreholes, piling etc) through that layer.

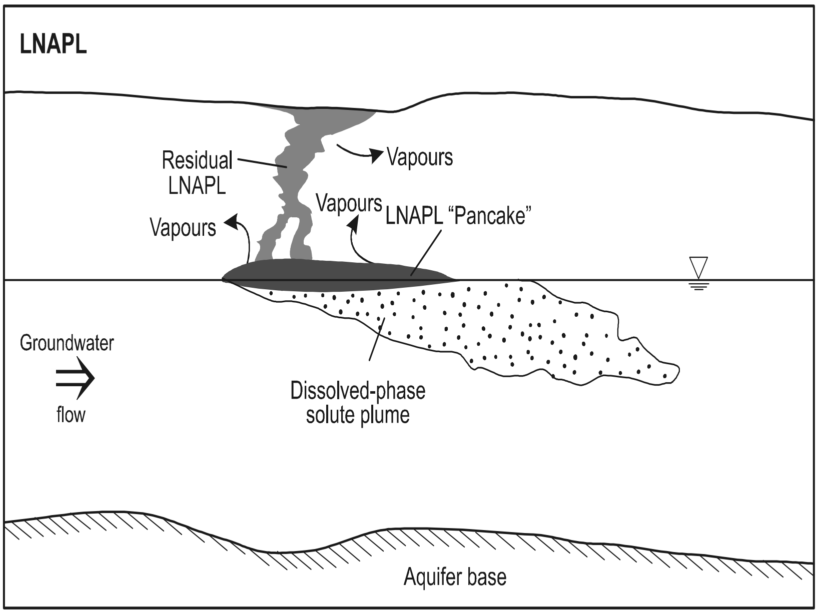

Figure 4.4. Conceptual model of a light non aqueous phase liquid (LNAPL) release

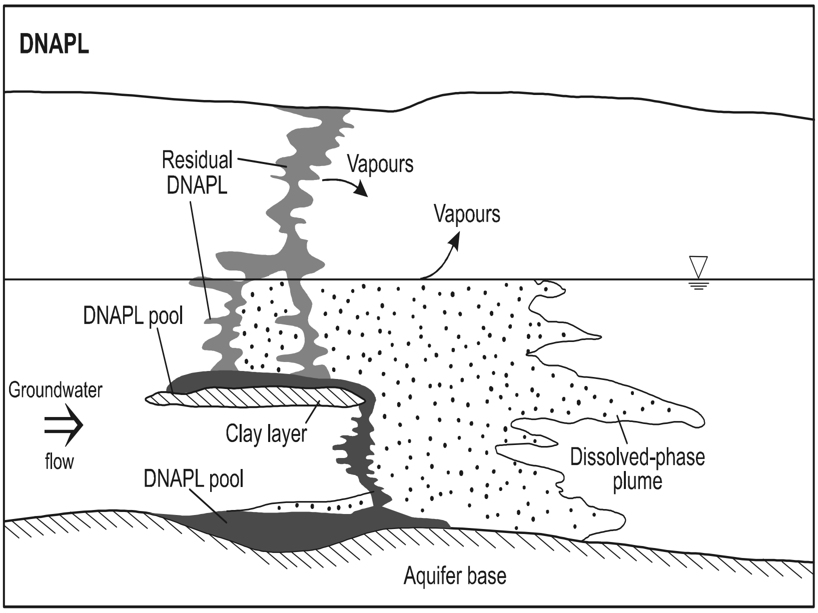

Figure 4.5. Conceptual model of a dense non aqueous phase liquid (DNAPL) release

Often NAPL will remain relatively local to a site, possible exceptions being the migration of LNAPL to a local surface water and perhaps huge NAPL spills, e.g. at a poorly operated oil refinery/distribution facility. Risks posed to groundwater resources and supplies are most often concerned with the migration of the dissolved-phase plume formed by the contact of flowing groundwater with the spilt NAPL. Although the presence of NAPL may impede the flow of groundwater, e.g. in DNAPL pools and central LNAPL body, areas where NAPL residual saturations are lower will still be permeable to water and NAPL dissolution will occur. Often the mass of NAPL is so large and the dissolution (solubilization) of NAPL into water so slow that the entire NAPL body post spill should be regarded as a largely immobile source zone able to continuously generate a dissolved-phase solute plume of organics downgradient for years to decades, even centuries for low-solubility NAPLs. Thus historic spill sites may still constitute major sources of NAPL in the deep subsurface and cause very large dissolved-phase plumes, particularly where dissolved-phase plume attenuation is limited. In general, DNAPLs tend to pose the greatest groundwater threat as they reside deep in groundwater systems and many, being chlorinated, are less susceptible to attenuation. In contrast, LNAPLs are restricted to shallower groundwater-table depths, and are more susceptible to attenuation via biodegradation.

The above provides a basic introduction to NAPLs in groundwater. Much research and field experience has been gained since the pioneering NAPLs research of Schwille (1988) and the reader is referred to Mercer and Cohen (1990) and Pankow and Cherry (1996) and references therein for further details.

4.5.2 General aspects of transport and attenuation of organics

Some of the transport and attenuation processes introduced earlier require specific discussion for organic contaminants. Several physiochemical properties/parameters exert a key control over subsurface organic contaminant migration. A selection of parameters is listed in Table 4.1 for a range of organic chemicals of groundwater-health concern. Values for a specific parameter generally vary over orders of magnitude across the listed chemicals and infer substantial variations in transport and attenuation between organic contaminants. Table 4.1 is not exhaustive: there are many more organic chemicals; values of individual chemical parameters may show significant variability across the literature; and other parameters exist, most notably half-life, that due to their dependency on site conditions display significant variability (see Section 4.5.4 for references to some half-life literature). For more detailed databases and their supporting literature see e.g. US EPA (1996; 1999) and Montgomery (1996).

Table 4.1. Selected physiochemical parameter values for important organic groundwater contaminants at 20-25°C (Mercer and Cohen, 1990; US EPA, 1996; 1999) (see Section 4.5.3 for an explanation of the abbreviations)

Chemical	**Density (g/ml)**	**Absolute viscosity (cP)**	**Aqueous solubility (mg/l)**	**Vapour pressure (atm.)**	**Henry's constant (atm. m^3/mol)**	K_{OC} **(ml/g)**	K_{OW}
Aromatic Hydrocarbons (single aromatic ring)							
Benzene	0.87	0.60	1750	0.13	0.0056	62	130
Toluene	0.86	0.55	535	0.037	0.0064	140	540
Ethylbenzene	0.87	0.68	152	0.0092	0.0064	200	1400
o-Xylene	0.88	0.81	175	0.0087	0.0051	240	890
Chlorinated Hydrocarbons							
DCM	1.34	0.45	20 000	0.48	0.0020	8.8	20
TCM	1.50	0.60	8200	0.20	0.0029	53	93
CTC	1.58	0.97	757	0.12	0.024	152	440
TCE	1.47	0.57	1100	0.076	0.0091	94	240
PCE	1.63	1.93	150	0.024	0.026	265	400
VC	Gas	Gas	2760	3.7	0.027	18	14
1,2-DCA	1.26	0.89	8520	0.084	0.00098	38	30
1,1-DCE	1.22	0.36	2250	0.79	0.034	65	69
cDCE	1.27	0.44	3500	0.27	0.0076	49	5.0
tDCE	1.26	0.40	6300	0.43	0.0066	38	3.0
1,2-DCB	1.30	1.32	100	0.0018	0.0021	379	2790
1,4- DCB	1.28	1.04	73	0.0014	0.0028	616	2580
Others							
Naphthalene	1.16	solid	31	0.00012	0.00048	1190	2290
Anthracene	1.24	solid	0.043	$3.6x10^{-8}$	0.00007	23 500	35 500
Benzo(a) pyrene	1.35	solid	0.0016	$6.4x10^{-12}$	0.000001	969 000	1 260 000
PCB-1248	1.44	212	0.054	$6.6x10^{-7}$	0.0035	437 000	562 000

Volatilization

Although other processes may be enhanced in the unsaturated zone relative to the saturated zone, e.g. biodegradation through the ready availability of oxygen, volatilization is a key process that only occurs in the unsaturated zone. Organic compounds with high vapour pressures (P) (>0.008 atm., i.e. xylene in Table 4.1) are termed (volatile organic compounds (VOCs). The vapour concentration adjacent to a NAPL or organic solid is dictated by its vapour pressure. Although volatilization of subsurface organic contaminants, e.g. NAPL sources, may occur and organic vapours potentially lost to the above ground atmosphere, VOCs are nevertheless very widely encountered in groundwaters; possible reasons include many VOCs are NAPLs of relatively high solubility (S) and low sorbing potential (K_{oc}). Vapours migrate due to diffusion and advection within the air phase and may migrate due to pressure (barometric) and temperature fluctuations, water infiltration and preferential conduit routes (Mendoza *et al.*, 1996). In relation to vapour-phase diffusion, it is emphasized diffusion coefficients in the air phase are ~4 orders of magnitude greater that the water phase. This allows much greater opportunity for lateral (radial) migration of vapour plumes and, due to vapour contact, contamination of underlying groundwaters over a wide area (Rivett, 1995).

Partitioning of dissolved organic solutes between a contaminated water phase and an adjacent air-phase is controlled by the Henry's Law partition coefficient:

$$H=C_A / C_W \qquad \text{(Eqn. 4.4)}$$

where H is the Henry's Law constant, C_W is the concentration of an organic compound in water and C_A is its vapour concentration in the gaseous phase. It should be noted that similar concentration units will yield a dimensionless (i.e. unitless) H value, however, the air concentration is often expressed in terms of pressure and hence H values may be quoted with units of the type atmos $m^3\ mol^{-1}$, e.g. for benzene H (dimensionless) is 0.24 and with units H is 5.5×10^{-3} atmos $m^3\ mol^{-1}$ (Table 4.1).

Solubilization

As indicated in Section 4.5.1, the differing hydrophobic nature of organic compounds means their solubility in water varies over orders of magnitude (Table 4.1). Solubility values represent maximum concentrations that may be achieved in a dissolved-phase plume. VOC contaminants, e.g. benzene and TCE tend to be small molecules that are moderately soluble, amenable to analysis and hence often detected in groundwater. Although solubilities are relatively low compared to inorganic ions, they may nevertheless achieve concentrations 4-5 orders of magnitude greater than drinking-water standards or guideline values. Larger molecular weight organics will have lower solubilities, hence concentrations e.g. of DDT in groundwater may only reach about 0.1 mg/l (its solubility).Thus DDT at solubility only exceeds the WHO guideline value of 1 µg/l by a factor of approx. 50, hence allowing for dilution and some attenuation, the prospects of exceeding the DDT standard in groundwater are low except in close proximity to a DDT source. DDT's high hydrophobicity and hence high sorption (see below) tends to cause DDT (and other organic chemicals of similar properties, e.g. high molecular weight PCBs and PAHs) to perhaps be more of a soil rather than a groundwater problem.

Sorption

Sorption exerts a key control over the transport of anthropogenic organic contaminants. Organic sorption is a complex topic, a detailed review is provided by Allen-King *et al.* (2002). Sorption is a function of the properties of both the organic solute and aquifer solid. Hydrophobic non-ionic organic contaminants preferentially sorb to the low-polarity components of geosolids, e.g. any organic material present. Sorption is inversely related to organic compound solubility; the more hydrophobic and less soluble an organic solute, the greater its intrinsic potential for sorption to any organic material present in the aquifer solids. Hence hydrophilic organics have negligible sorption, and mild to moderately hydrophobic organics such as the VOCs show limited sorption. In contrast, hydrophobic, high molecular weight, large organics such as PAHs and PCBs of low solubility exhibit high sorption (Table 4.1).

An additional measure of organic compound hydrophobicity often used in sorption research is the octanol-water partition coefficient (K_{ow}) (Table 4.1), that is simply an equilibrium partitioning of the organic solute between the organic octanol phase and water phase. The higher the K_{ow} value, the more hydrophobic, less soluble and more sorptive the organic compound.

The degree of sorption is also controlled by the sorption potential of the sorbate, i.e. the aquifer material that dissolved concentrations in groundwater contact. Frequently sorption is assumed to be at equilibrium and linear with organic solute concentrations, the magnitude of sorption being expressed by the sorption partition coefficient K_d:

$$K_d = C_S / C_W \qquad \text{(Eqn. 4.5)}$$

where C_S is the sorbed concentration. The main sorbing phase for organic solutes is any organic material present in the rock phase originating for example from organic detritus, e.g. humic material, deposited at the time of rock deposition. This organic material is referred to as the fraction of organic carbon (f_{oc}) within the geologic or soil matrix. Although f_{oc} values may be on the order of one per cent or more in organic-rich soil horizons, many aquifers comprise geologic strata with low f_{oc} values, e.g. an f_{oc}~0.02 per cent is recorded for the Borden glaciolacustrine sands, Canada (Rivett and Allen-King, 2003). The f_{oc}, even at such low concentrations, may still be the dominant sorption phase rather than poorly sorbing mineral surfaces. Simultaneous laboratory measurements of f_{oc} and K_d have shown that they are approximately linearly related, with the constant of proportionality being termed the organic-carbon partition coefficient (K_{oc}) of the specific organic solute (Table 4.1). Typically practitioners assessing sorption controls now obtain K_{oc} values from databases (e.g. US EPA, 1996), measure the aquifer f_{oc} (Heron *et al*., 1997) and estimate the sorption K_d from the relationship:

$$K_d = f_{oc} K_{oc} \qquad \text{(Eqn. 4.6)}$$

where f_{oc} is in mass fraction dimensionless units, e.g. expressed as 0.0002 rather than as 0.02 per cent. Hence the greater the f_{oc} of the aquifer deposits (e.g. higher values are often found in shallow soils or recent sub-river, i.e. hyporheic zone), and greater the K_{oc} (Table 4.1), which will increase with solute hydrophobicity, the greater the K_d value, i.e. sorption. Assuming ideal linear equilibrium sorption and calculation of K_d from the above, the retardation factor R_i of organic solute i may be estimated from:

$$R_i=1+(\rho/\eta)K_d \qquad \text{(Eqn. 4.7)}$$

where ρ and η are the bulk density and porosity of the porous media respectively.

The above hydrophobic partitioning ideal sorption approach is an approximation of reality; it provides a reasonable first estimate. It should be recognized, however, that non-ideal sorption processes may be significant (Allen-King *et al*., 2002); these include slow equilibration of sorbed and dissolved phases, dependence of the degree of sorption on dissolved concentration magnitude and the presence of any competing, also sorbing, solutes within multi-contaminant plumes. Further, the nature of the f_{oc}, i.e. ratio of the carbon-hydrogen-oxygen contents, has an important control on the sorption that occurs.

It is often useful to combine some of the above parameters visually to assess how organic contaminants may comparatively behave. Figure 4.6 plots K_{ow}, a measure of compound hydrophobicity that will indicate solubility and sorptive retardation trends against vapour pressure, a measure of volatilization tendency. The figure indicates PAHs are unlikely to volatilize and will undergo high sorption, and this would infer that soil/unsaturated zone solids concentrations of PAHs could often be high (frequently the case) and perhaps there is relatively limited development of PAH plumes to groundwater (often relatively small plumes are encountered). The chlorinated hydrocarbons, in contrast, are volatile but of low sorption potential. It is likely they would vaporize (and potentially be a vapour hazard to receptors at the soil surface) and also leach to groundwater leaving low concentrations in soils and unsaturated samples (quite often the case).

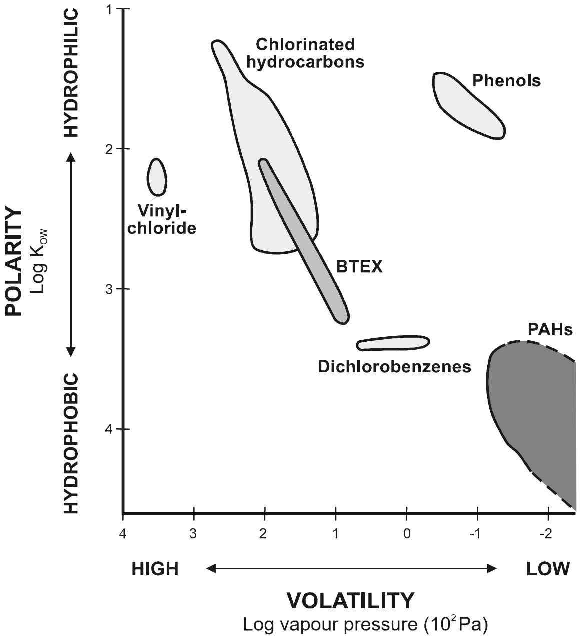

Figure 4.6. Polarity-volatility diagram for selected organic contaminants

Chemical reactions

Although there are a multitude of possible chemical reactions (abiotic reactions, i.e. not mediated by bacteria), reactions of low-concentration organics in a water-based environment tend to be fairly limited. Perhaps the most common reaction is that of slightly positively charged organic compounds ($C^{\delta+}$) with negatively charged (nucleophilic) species, such as HS^-, OH^- or water. The latter is a hydrolysis reaction. Reactive organic solutes tend to be organic halides, particularly brominated compounds and to a lesser extent chlorinated compounds. An example of a chemical reaction is that of the chlorinated solvent 1,1,1-TCA which was commonly used to degrease metals and circuit boards (as a less toxic replacement to TCE, before concerns were raised about its ozone-depletion potential). TCA in water will either undergo an elimination reaction to yield 1,1-DCE, or alternatively a sequential hydrolysis reaction replacing all the chlorine atoms as chloride to yield ethanoic acid. Interestingly it may also biodegrade to predominantly form a different product, 1,1,-DCA (Klecka *et al.*, 1990). Further information on chemical reactions in water may be found in Schwarzenbach *et al.* (1993).

Biodegradation

Bacteria degrade organic contaminants to simpler, often less toxic, products. Biodegradation is perceived to be the primary attenuation process that may mitigate dissolved-plume impacts to receptors by organic chemicals. monitored natural attenuation (MNA) remedial strategies generally have their main focus upon demonstration of occurrence of biodegradation (Wiedemeier *et al*., 1999). This not only entails monitoring the disappearance of the organic contaminant, but also the appearance of intermediate organic contaminants that may themselves persist or be further biodegraded, ideally to benign inorganic products, e.g. water, carbon dioxide, chloride.

Monitoring of the inorganic hydrochemistry is also a key requirement to assessing biodegradation occurrence. Sites may be initially aerobic/oxic (containing oxygen), and under these conditions biodegradation of many contaminants is often the most rapid. Dissolved oxygen concentrations in groundwater are usually low, maximally ~10 mg/l. Such levels can easily be depleted by even low to moderate levels of organic contamination present and are not easily renewed as dispersive mixing in groundwaters to allow oxygen re-entry is typically low. Other electron acceptors, for example sulphate, nitrate, iron and manganese, are then used to allow biodegradation to continue under anaerobic conditions. Finally site conditions may become so reducing that biodegradation occurs under methanogenic conditions.

Specific examples of biodegradation are included in the sections that follow. In general, most hydrocarbon-based compounds and most oxygenated-organics are relatively biodegradable under a wide range of conditions, and natural attenuation of such plumes often significant. Chlorinated (halogenated) compounds are generally less biodegradable but evidence has increasingly shown that they do biodegrade under appropriate redox-bacterial conditions. A sequence of reactions under varying redox conditions may be required to allow complete biodegradation to benign products. This means that for some contaminants and sites full biodegradation to benign products is difficult and there may be persistence of both the original contaminants and their intermediate degradation products, both of which may have toxicity.

4.5.3 Organic chemicals of major concern in groundwater

Consideration of the above transport and attenuation processes, together with data on organic chemical toxicity, use of chemicals and associated potential for release to the subsurface, and actual chemical occurrence in groundwater data, enables identification of groups of organic chemicals, as well as individual chemicals, thought to be of major concern in groundwater. Two organic chemical groups of key concern include:

- aromatic hydrocarbons: benzene, toluene, ethylbenzene and xylenes (BTEX);
- chlorinated hydrocarbons (aliphatic and aromatic): dichloromethane (DCM), trichloromethane (TCM, also known as chloroform), tetrachloromethane (also known as carbon tetrachloride, CTC), trichloroethene (TCE), tetrachloroethene (PCE, also known as perchloroethylene), vinyl chloride (VC), 1,2-dichloroethane (1,2-DCA), 1,1-dichloroethene (1,1-DCE), 1,2-dichloroethene (cis and trans isomers, cDCE and tDCE respectively), 1,2 dichlorobenzene (1,2-DCB) and 1,4 dichlorobenzene (1,4-DCB).

Properties of the above compounds are included in Table 4.1.

Figure 4.7 presents data based upon 250 sites in Germany and 500 sites in the USA (Kerndorff *et al*., 1992) and indicates the prevalence of the above compounds in groundwater. A third (predominantly) organic chemical group of key concern in groundwater is pesticides.

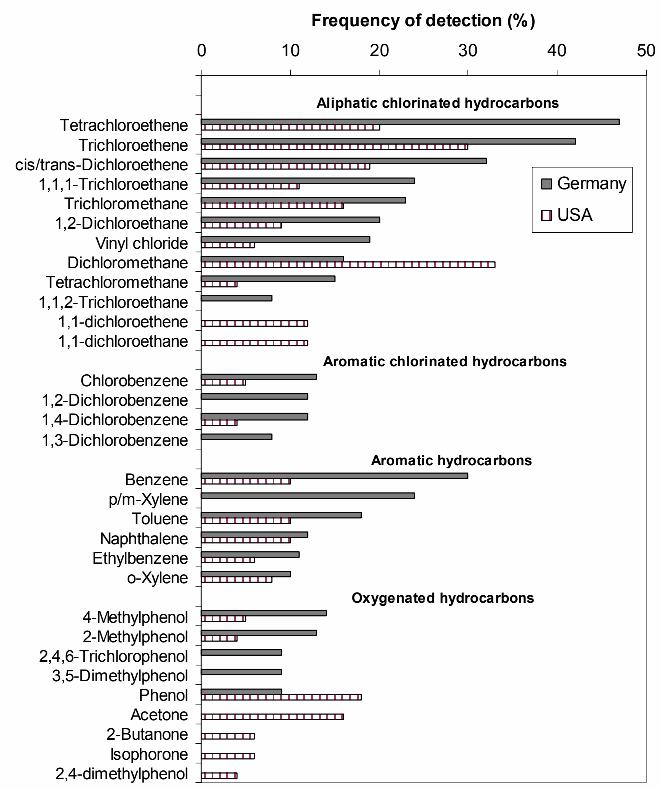

Figure 4.7. The 25 most frequently detected organic groundwater contaminants at hazardous waste sites in Germany (250 sites) and the USA (500 sites) (based on concentrations ≥ 1μg/l) (adapted from Kerndorff *et al*., 1992)

Of the many organic chemicals that may potentially contaminate groundwater, these three groups have perhaps received the most attention from both the groundwater practitioner and research communities during the 1980s and 1990s. The following Sections 4.5.4, 4.5.5 and 4.6 are hence devoted to these three groups.

The focus upon the above three groups does not preclude the potential importance of other organic contaminants in groundwater. Although compounds may perhaps not occur frequently due to restricted use within specialized industries, some compounds may have low natural attenuation (NA) properties and potentially develop extensive plumes. Other chemical groups may, in contrast, have received widespread industrial use, but were perhaps thought (sometimes mistakenly) to pose a much lower risk to groundwater due to high NA properties. Examples of the latter may include PAHs and PCBs that are both briefly discussed below.

PAHs are a component of creosotes and coal tars frequently associated with former gasworks and coal carbonization (coking) works (Johansen *et al.*, 1997). They are a diverse class of compounds of natural and anthropogenic origin, some of which show carcinogenic properties. WHO has derived a guideline value of 0.7 μg/l for benzo(a)pyrene because it may be released from coal tar coatings of drinking-water distribution pipes. Most PAHs have extremely low solubilities in water and have a high tendency to adsorb to the organic matrix of soils and sediments, particularly the higher molecular mass, higher-ring PAHs, e.g. the 5-ring benzo(a)pyrene. Thus, they are generally not found in water in notable concentrations, and human exposure is mostly through food prepared at high temperatures and air (particularly from open fires) (WHO, 2004a). Countering the processes that may serve to attenuate groundwater impacts, however, are: (i) creosote and coal tars may occur as a DNAPL (density is composition dependent, but may be around 1.05) and slowly migrate as a DNAPL deep into the subsurface potentially penetrating the water table; and (ii) higher molecular mass, higher ring-member PAHs are much more resistant to biodegradation and hence dissolved plumes, although slow to develop, may persist and grow over decades (King and Barker, 1999).

PCBs are a class of stable compounds, each containing a biphenyl nucleus (two linked benzene rings) with two or more substituent chlorine atoms. PCBs are produced industrially as complex mixtures that often contain between 40 and 60 different chlorinated biphenyls. Similar to PAHs, most PCBs are of low solubility in water and sorptive and hence dissolved-phase plumes in groundwater tend not to be large. However, PCB oils, historically used in electrical transformer facilities, are DNAPLs and may potentially penetrate deep into aquifer systems. Dissolved PCBs are generally slow to biodegrade and hence PCBs, like PAHs, may serve as long-term sources of groundwater contamination.

An emergent groundwater issue in the 1990s relating to hydrocarbon fuels has been the use of oxygenates, particularly methyl tertiary-butyl ether (MTBE) and methanol or ethanol within fuels (Squillace *et al.*, 1996). Use of MTBE has been most significant in the USA with MTBE first used in gasoline at greater than 10 per cent by volume in 1992. MTBE has a strong taste and odour and is likely to impair drinking-water quality at concentrations in the 0.01-0.1 mg/l range. However, because of its low relevance to human health, MTBE is not further discussed in this chapter; see WHO (2005c) for further information on MTBE.

4.5.4 Aromatic hydrocarbons (BTEX)

Health aspects

Mononuclear (single-ring) aromatic hydrocarbons such as BTEX are amongst the most common groundwater contaminants (Figure 4.7) and the main aromatic faction of many hydrocarbon fuels. The key compound of health relevance within the BTEX group is benzene, a proven carcinogen in humans. The mechanism or metabolic form by which it exerts its action (haematological changes, including leukaemia) is not clear. WHO (2004a) has established a guideline value for benzene in drinking-water of 10 μg/l, corresponding to a lifespan risk of 10^{-5} to contract cancer by exposure to benzene via drinking-water. Alkylated benzenes are much less toxic than benzene, and correspondingly their WHO guideline values are 700 μg/l for toluene, 300 μg/L for ethylbenzene and 500 µg/l for xylene (WHO, 2004a), whereas no health-based guideline values are given for trimethylbenzenes and butylbenzene. However, some of them may be perceived by odour and/or taste at only a few micrograms per litre.

Sources and occurrence

The aromatic hydrocarbons BTEX are the primary contaminants of concern associated with point-sources of fuels and fuel-related contamination originating from petroleum production, refining and wholesale and retail distribution (service stations) of petroleum products (Newell *et al.*, 1995). They are also used as solvents and raw materials in chemical production. Spills and accidental releases of gasoline (petrol), kerosene and diesel are common sources of their occurrence in the environment. The German-USA groundwater survey data in Figure 4.7 indicate BTEX was relatively common, benzene being the most prominent.

Transport and attenuation

Most petroleum products are LNAPLs and hence the Figure 4.4 conceptual model applies. BTEX components typically comprise just a few per cent of the LNAPL fuel. BTEX concentrations dissolving in groundwater near fuel sources are reduced from their pure-phase solubility values (as individual component solubilized concentrations form NAPL mixtures depend upon the mass (strictly mole) faction of that component in the NAPL). BTEX-aromatics, being the most soluble hydrocarbons, are still the main risk driver for groundwater at hydrocarbon-contaminated sites, as solubilized concentrations and mobility of other alkane (branched and straight-chain) and PAH hydrocarbons are much lower. Since the early 1990s, it has been recognized that natural attenuation (NA) of BTEX is highly significant at most sites due to the high biodegradability of BTEX under a range of conditions. Monitored natural attenuation, i.e. monitoring of the growth, stability and eventual decline of dissolved-phase BTEX plumes, has indeed become a viable and cost-effective remediation option at many sites rather than active remedial measures such as pump-and-treat (McAllister and Chiang, 1994).

Studies that have examined dissolved-phase hydrocarbon plume lengths from over 600 hydrocarbon-release sites in the USA are particularly instructive on the potential for NA applicability (Newell and Connor, 1998; Wiedemeier *et al.*, 1999 and references therein). Of the 604 plumes evaluated, 86 per cent were less than 300 feet (~100 m) long with only 2 per cent of plumes greater than 900 feet. One of the studies that examined 271 plumes indicated only 8 per cent of these plumes were still growing, 59 per cent of plumes were approximately stable as mass being dissolved from the source was balanced by mass being depleted by attenuation (biodegradation), and 33 per cent of plumes were shrinking as source mass inputs declined or biodegradation of contaminants perhaps became increasingly efficient with time. These studies hence provide a strong rationale for occurrence of NA across a variety of site conditions. Under the vast majority of circumstances the potential for impacts of hydrocarbon plumes is limited to distances of a few hundred meters from source zones. Thus although hydrocarbon sources can be numerous, hydrocarbon and BTEX impacts are likely to remain local to those sources zones. However, although dissolved-phase plume may extend to relatively short distances from source areas, LNAPL source zones (i.e. pancake-like of hydrocarbon) themselves can on occasion be very extensive, for example Albu *et al.* (2002) depict zones of LNAPL extending over 5 km around oil refinery sites near Ploiesti, Romania.

Much insight into the importance of biodegradation and associated controlling factors has been obtained in plume studies. A controlled injection of dissolved-phase benzene, toluene and xylene at the Borden site, Canada (Barker *et al.*, 1987) showed complete benzene, toluene and xylene biodegradation by just over 400 days with only benzene persisting beyond 270 days. This study, and many real spill sites indicate BTEX are readily degraded when dissolved oxygen is present in groundwater. Under anaerobic conditions, rates of biodegradation of remaining hydrocarbon was governed by both the rate of oxygen re-entry across the contaminant plume fringe and rates of alternative anaerobic biodegradation pathways using less efficient electron acceptors such as nitrate, sulphate, and iron(III). Many other field sites have demonstrated the importance of anaerobic processes, primarily through changes in the groundwater geochemistry. For example, the Plattsburgh, Hill and Patrick Air Force Bases in the USA (Wiedemeier *et al.*, 1999) indicate development of depleted dissolved oxygen, nitrate and sulphate coincident with the BTEX plumes as these electron acceptors are consumed in the oxidation of the BTEX. pH declines as well as production of Fe(II) and methane arising from methanogenic activity were also evident where the most reducing conditions prevailed.

A myriad of aerobic and anaerobic BTEX biodegradation rates are available from the literature, e.g. data and references within Wiedemeier *et al.* (1999) and Noble and Morgan (2002). Rates are typically expressed as a first order rate constant or an equivalent half-life. Table 4.2 summarizes half-life data provided in the review by Noble and Morgan (2002) for BTEX, naphthalene and some chlorinated hydrocarbons. These chemicals represent the most studied groundwater contaminants in relation to biodegradation. The table subdivides rate data between laboratory and field studies that are in turn subdivided to aerobic and anaerobic conditions. Although the work of Noble and Morgan is reasonably comprehensive and based upon many citations, it should be noted that Table 4.2 aims to be illustrative rather than comprehensive of all literature available on biodegradation rates for the chemicals listed; biodegradation is an active area of study worldwide and half-life data continue to be published.

Rates selected for risk assessment modelling at other sites (where field data are insufficient to determine rates) need to be used with care as modelling results, and hence plume attenuation predicted and any site risk-based remediation standards computed, are very sensitive to degradation mass-loss parameters selected. Rates may vary significantly for individual compounds that may be a reflection of rates being lab-based or field based and the particular aerobic-anaerobic site conditions. This is apparent from examination of Table 4.2. Also, field biodegradation rates may be derived from a localized point measurement, or more often a rate predicted from whole plume behaviour that will average varying rates and different biodegradation processes and aerobic/anaerobic conditions occurring throughout the plume.

The laboratory half-lives in Table 4.2 are generally shorter than the equivalent field-based values, i.e. plumes are apparently more persistent in the field presumably as a reflection of field conditions, e.g. supply of electron acceptors being less optimal than can be achieved in a laboratory. In general, BTEX degradation rates will be lower under anaerobic conditions and plume may be persistent and indeed attain significant lengths where groundwater is naturally anaerobic, e.g. confined aquifer conditions. This is reasonably demonstrated by the Table 4.2 field data, but less so by the laboratory-based data; the latter is in part from the limited studies undertaken (at least reported) for some of the chemicals. A cautionary approach is warranted to the application to sites of the half-life data provided in Table 4.2 (and elsewhere); clearly the range in half-life values for a specific contaminant is large and for some contaminants and conditions insufficient data exist to yield a reliable average and range. Some Table 4.2 entries are based on a single study, in some cases no data are provided. The latter may be a reflection of a genuine lack of data or else biodegradation not being effective under the specific conditions (e.g. aerobic biodegradation of PCE).

Table 4.2. Summary of biodegradation half-life data (at 10^{o}C) for important organic groundwater contaminants (adapted from Noble and Morgan, 2002)

Chemical	**Aerobic - laboratory data**			**Aerobic - field study data**			**Anaerobic - laboratory data**			**Anaerobic - field study data**		
	No. of studies (n)	Mean half-life (days)	Range in half-life (days)	No. of studies (n)	Mean half-life (days)	Range in half-life (days)	No. of studies (n)	Mean half-life (days)	Range in half-life (days)	No. of studies (n)	Mean half-life (days)	Range in half-life (days)
Aromatic Hydrocarbons												
Benzene	18	34	3-200	6	220	15-490	11	79	20-200	13	502	85-2000
Toluene	5	120	5-320	3	120	15-178	15	64	5-320	9	257	10-660
Ethylbenzene	No data provided			No data provided			4	239	53-548	4	519	238-693
Xylenes	1	11	11-11	3	58	1-123	5	63	30-155	8	489	72-800
Naphthalene	11	138	10-400	No data provided			No data provided			No data provided		
Chlorinated Hydrocarbons												
PCE	No data provided			No data provided			6	23	4-62	4	1600	4-3600
TCE	No data provided			No data provided			8	43	3-99	12	1460	3-6600
DCE	5	2	0.5-3	3	39	12-56	1	280	280-280	9	4060	42-16860
VC	7	14	84	1	10	10-10	5	81	24-124	5	948	506-1265
DCA	No data provided			No data provided			5	157	16-340	2	1430	460-2400

4.5.5 Chlorinated hydrocarbons

Health aspects

A number of aliphatic and aromatic chlorinated hydrocarbons are of health significance because of their toxicity and occurrence in drinking-water, particularly as in groundwater, their concentrations do not decrease rapidly through volatilisation, anaerobic degradation is slow, and in consequence contaminants may persist for some time.

WHO (2004) gives guideline values for dichloromethane (DCM), trihalomethanes chloromethane (e.g. chloroform which may be generated as by-products of disinfection), tetrachloromethane (also known as carbon tetrachloride, CTC), trichloroethene (TCE), tetrachloroethene (PCE, also known as perchloroethylene), vinyl chloride (VC), 1,2-dichloroethane (1,2-DCA), 1,1-dichloroethene (1,1-DCE), 1,2-dichloroethene (cis and trans isomers, cDCE and tDCE respectively), 1,2 dichlorobenzene (1,2-DCB) and 1,4 dichlorobenzene (1,4-DCB) (see Table 4.1 for selected physiochemical parameter values). Generally, among the saturated chlorinated compounds, the 1,1- halogenated ones (e.g. 1,1-dichloroethane) are of less health concern than the 1,2-halogenated ones (e.g. 1,2-DCA), since they are metabolized differently. This is also true for higher halogenated compounds (e.g. trichloroethanes).

Dichloromethane (DCM, also known as methylene chloride) is of low acute toxicity, and current evidence suggests that it is not a genotoxic carcinogen. The WHO drinking-water guideline value for DCM is 20 µg/l, based on hepatotoxic effects observed in rats (WHO, 2004a). Carbon tetrachloride (CTC) has a WHO guideline value of 4 µg/l based on its liver toxicity, and from carcinogenic effects observed in laboratory animals it is classified as possibly carcinogenic to humans. 1,2-dichloroethane (1,2-DCA) is potentially genotoxic and a proven carcinogen in experimental animals with a WHO guideline value of 30 µg/L (WHO, 2003d; 2004a).

Trichloroethene (TCE) and tetrachloroethene (PCE) may degrade to the more toxic vinyl chloride. The provisional WHO guideline value for TCE is 70 µg/l based on liver effects in mice (WHO, 2004a; 2005d). PCE causes nervous disorders at high dose, whereas at lower doses kidney and liver damage have been reported. It is classified as possible human carcinogen with overall evidence indicating that it is not genotoxic (WHO, 2003e), and its WHO guideline value for drinking-water is 40 µg/l (WHO, 2004a). Vinyl chloride (VC) is genotoxic and carcinogenic in experimental animals as well as in humans. Administered orally to experimental animals, it produced cancer at a variety of sites (WHO, 2004d). Its WHO drinking-water guideline value is 0.3 µg/l (WHO, 2004a).

1,1-Dichloroethene (1.1-DCE) is a weak in vitro-mutagen and not classifiable as to its carcinogenicity to humans. It is a central nervous system depressant and may cause liver and kidney toxicity. The WHO guideline value is 30 µg/l (WHO, 2004a; 2005e). Among the two isomers of 1,2-dichloroethene, the cis-form is detected more frequently and at higher concentrations than the trans-form as a water contaminant, since the former is the main anaerobic metabolite of TCE and PCE. As such it may indicate as well the presence of vinyl chloride, the next anaerobic breakdown product, which is not only much more toxic than all higher chlorinated ethenes but also a genotoxic human carcinogen (see above). In contrast, both 1,2-DCEs do not seem to be genotoxic and there is no information on their carcinogenic potential. The WHO drinking-water guideline value for each of the 2 isomers is 50 µg/l (WHO, 2003f; 2004a).

Dichlorobenzenes are the least toxic of this group of contaminants. Their health based guideline values in drinking-water are 300 and 1000 µg/l for 1,2- and 1,4-DCB, respectively. These exceed their odour threshold range of 0.3-30 µg/l by far (WHO, 2003g; 2004a).

Sources and occurrence

Chlorinated hydrocarbons are employed in a variety of industrial activities, including almost any facility where degreasing, e.g. of metals, circuit boards, textiles (dry cleaning) and animal/leather hides, metal stripping, chemical manufacturing, pesticide production or other activities where chlorinated solvents, cleaners, dry cleaning fluids, paint removers are used (Chapter 11).

In many industrialized countries, chlorinated hydrocarbons are the most frequently detected groundwater contaminants at hazardous waste sites (Kerndorff *et al*., 1992; Plumb, 1992; NRC, 1994). This is highlighted by the German-USA survey data in Figure 4.7. TCE and PCE together with their principal metabolites cDCE and VC have been the most frequently detected chlorinated hydrocarbons at the investigated sites. Point source release of chlorinated hydrocarbons to groundwater is anticipated to be the main source of groundwater contamination. Complex mixtures of chlorinated hydrocarbons may arise from leakages at hazardous waste disposal sites where many solvent types may have been disposed. In contrast, spills at industrial manufacturing/processing sites may well comprise liquid chlorinated hydrocarbon as a DNAPL with a high proportion of a single chlorinated hydrocarbon component. A multitude of point sources exist in many urban areas due to the diversity and frequency of chlorinated hydrocarbon users.

Examples of regional chlorinated hydrocarbon contamination within aquifers underlying urban towns and cities emerged during the 1980s. Many groundwater supplies or monitoring wells were contaminated in some instances, particularly by TCE and to a lesser extent PCE. Examples include Milan, Italy (Cavallero *et al*., 1985); the New Jersey coastal plain aquifer, USA (Fusillo, 1985) and Birmingham, United Kingdom (Rivett *et al.*, 1990); the latter example is described in Box 4.2.

Transport and attenuation

Many of the chlorinated hydrocarbons will have entered the subsurface in the DNAPL form and may reside to significant depths within aquifers (Pankow and Cherry, 1996). They typically have low to medium water solubility (in the range of 0.2-20 g/l; Table 4.1). Dissolution of DNAPL sources is expected to be slow taking years to decades, particularly from long lengths of residual DNAPL pools that have invaded or diffused into low-permeability strata. Dissolved-phase plumes of chlorinated hydrocarbons can be very extensive, for example Mackay and Cherry (1989) depict several plumes in the km-scale and Jackson (1998) several plumes in the alluvial aquifers of the southwestern USA that are around 10 km in length. Some plumes have lead to high profile court cases and set legal precedents on apportioning liability for historic contamination events, e.g. the near 2-km PCE plume that caused contamination of the

Sawston public water supply borehole in Cambridgeshire, United Kingdom (Ashley, 1998).

Box 4.2. Chlorinated-hydrocarbon contamination of groundwater in Birmingham, United Kingdom (based on Rivett *et al.*, 1990; Rivett *et al.*, 2005)

Birmingham is the second largest city in the United Kingdom and has a long history of manufacturing, particularly in metal-related industries. Groundwater samples were taken during the late 1980s from 59 abstraction boreholes typically screened over 100 m in the Triassic Sandstone aquifer underlying the city. Chlorinated solvents were found to be widespread, particularly TCE detected in 78 per cent of abstraction boreholes with over 40 per cent of the sampled boreholes showing concentrations over 30 μg/l to a maximum of 5500 μg/l. The majority of highly contaminated abstractions were located in solvent-user sites, predominantly metals-related industry. The predominance of TCE was ascribed to its main United Kingdom use within metal cleaning applications since the 1930s. PCE was less evident as it has generally only been used for dry cleaning in the United Kingdom since 1950s. Lower TCA occurrence was ascribed to its much later introduction in the United Kingdom starting about 1965 as a less toxic replacement to TCE. Greatest groundwater contamination occurred in the Tame valley area that was hydrogeologically vulnerable due to low depths to groundwater and limited aquifer protection by low permeability drift. Moderate contamination was present in other less vulnerable areas of the unconfined aquifer with least contamination evident in the Mercia Mudstone confined aquifer.

The aquifer was re-visited a decade later during the late 1990s. Declines in industrial use of groundwater meant only 36 abstractions were active and available for sampling, of these 26 were from the 1980s survey. Overall contamination detected was less and attributed to most of the new boreholes being located in industry areas where solvent use appeared limited. Also, many of the former highly contaminated abstractions had ceased operation due to industry closure. The latter was of some concern as contamination previously inadvertently captured by such abstractions was now able to more freely migrate into the wider aquifer. Comparison of the 26 abstractions common to both surveys indicated contamination at individual boreholes was at similar or greater concentrations in the more recent survey compared to the decade-earlier survey. These levels are unlikely to be due to major ongoing contamination, rather, it is reasonably assumed that incidences of new contamination will have declined over the decade as industry has become much more environmentally aware. The sustained level of contamination was hence ascribed to persistent sources of chlorinated solvents, likely DNAPL sources at depth. These will have remained unaffected by remedial works implemented at many sites to date because under a land redevelopment focused agenda these predominantly focused upon shallow soil and groundwater problems.

Under aerobic conditions, biodegradation of solvents such as TCE and PCE can be limited to non-existent and may account for the extensive plume examples noted above. Sorption is often limited too, particularly for the less hydrophobic compounds where compound solubility exceeds 1g/l (Table 4.1). A controlled emplacement of a DNAPL chlorinated solvent source in the Borden aquifer research site, Canada, resulted in TCM and TCE plumes exhibiting near conservative behaviour with retardation factors in the range of 1.0-1.2 and no evidence of biodegradation for these solvents and also PCE that was more retarded at about 1.6 (Rivett *et al*., 2001; Rivett and Allen-King, 2003). Dispersion of these plumes, although moderate in this relatively homogeneous sand aquifer, nevertheless produced leading plume contours at concentrations in the range of drinking-water standards that had travelled toward 100 per cent further than the mean advection (groundwater) velocity.

In contrast, other sites have shown significant natural attenuation of chlorinated hydrocarbons due to biodegradation activity. The most well known biodegradation pathways are those involving the sequential reductive dechlorination of chlorinated hydrocarbons where lesser chlorinated organics, chloride and ultimately hydrocarbons such as ethane or ethane, are formed (Vogel *et al*., 1987), e.g. PCE is transformed to TCE to cDCE (usually the predominant isomer) to VC to ethene. On average chlorinated hydrocarbon plumes are significantly longer than the aforementioned BTEX plumes. For example, Newell *et al.* (1990) reported a median length of 1000 feet (about 300 m) for chlorinated ethene (PCE, TCE, DCE, VC) plumes (88 sites sampled).

Biodegradation of chlorinated hydrocarbons has proven to be relatively complicated with five possible degradation processes (Wiedemeier *et al*., 1999). Most chlorinated compounds have been observed to biodegrade by three or four of these processes, only DCE and VC may biodegrade via all five processes. Under anaerobic or low oxygen conditions degradation processes include (i) dehalorespiration, in which the chlorinated hydrocarbon is used as the electron acceptor and effectively respired, (ii) direct anaerobic oxidation and (iii) anaerobic co-metabolism. Under aerobic conditions, further processes are (iv) direct aerobic oxidation and (v) aerobic co-metabolism. Direct processes involve the chlorinated hydrocarbon being used as the primary growth substrate. Dehalorespiration and co-metabolism both require an alternative primary growth substrate to be present. That primary substrate is normally a relatively biodegradable substrate and may include anthropogenic carbon such as BTEX contamination. Alternatively, anaerobic conditions may be driven by high levels of naturally occurring carbon acting as the substrate, a primary example being wetland sediments and sub riverbed deposits, e.g. Lorah and Olsen (1999) observed TCE and 1,1,2,2-PCE dechlorinations in the former.

Due to the complexity of biodegradation processes outlined, there is a wide divergence in reported biodegradation rates of chlorinated hydrocarbons (Wiedemeier *et al*., 1999; Noble and Morgan, 2002; Table 4.2). This is clearly illustrated by the Table 4.2 half-life data for the more common chlorinated hydrocarbon groundwater contaminants, e.g. DCE field-based half life data vary from just 42 days to nearly 17 000 days. Also, Table 4.2 indicates laboratory half-life data are generally much shorter (by 1-2 orders of magnitude) than equivalent field data, e.g. TCE data under anaerobic conditions indicate a laboratory half life mean of 43 days compared to a field mean of

1460 days. This is perhaps ascribed to the fact that optimal anaerobic reducing conditions can be achieved in the laboratory for the whole sample, whereas in the field such anaerobic conditions may in fact only occur in localized portions of a plume. Table 4.2 emphasizes the sensitivity of half life to aerobic and anaerobic conditions and that much longer half life values may occur for chlorinated hydrocarbons relative to the aromatics. The above strongly endorses the need to recognize that literature half-life data have very significant uncertainty when applied in a predictive manner to sites elsewhere. The unfortunate reality is that most sites require individual case-by-case assessment to allow effective prediction of natural attenuation rates.

4.6 PESTICIDES

Pesticides represent a wide range of compounds used mostly as insecticides, herbicides, and fungicides. Formerly a small number of classes of chemicals included most pesticides, i.e. organochlorines, organophosphates, carbamates, phenoxyacetic acids and triazine herbicides. However, modern pesticides include other types of chemicals, and therefore such a classification is of more limited use for descriptive purposes. Many of the historically used pesticides, such as the organochlorines, are however environmentally persistent and may pose a long-term groundwater problem.

Health aspects

In general, health effects associated with pesticides are specific for each chemical. This is reflected in their different WHO guideline values for drinking-water quality (see WHO, 2004a) and in the wide range of acceptable daily intake values derived by the Food and Agricultural Organization (FAO) for exposure through food (resulting from pesticide uses on crops; FAO, 2004). Most health effect studies are conducted using single compounds, little is known about effects associated with pesticide mixtures. Health effects from acute (short-term and high level) or chronic (long-term and low-level) exposure include liver and kidney damage, major interference with nervous, immune and reproductive system functions, birth defects and cancer. In most cases the risk from food contaminated by unduly high levels of pesticides is likely to be more significant than that posed by pesticide levels in drinking-water.

Chronic exposure associated with pesticides has declined in Europe and North America as many of the more persistent herbicides (such as chlordane, DDT, dieldrin, endrin, heptachlor, γ-HCH and toxaphene) have been restricted or phased out (Barnard *et al.*, 1997). They have been replaced with less persistent and more species-specific toxicants. While acute toxicities have often increased, some important new biologically-derived insecticides have very low mammalian toxicity.

Sources and occurrence

Pesticides are intentionally applied to protect crops in agriculture (Chapter 9) as well as to control pests and unwanted vegetation in gardens, buildings, railway tracks, forests and roadsides (Chapter 13). They may be accidentally released from production sites (Chapter 11) or, more often, transported away from their site of application in water, air or dust. Pesticides can reach groundwater after accidental spills or excessive application in geologically sensitive settings, from contamination of poorly sealed wells by surface runoff after intensive rains following field application and from storage or production sites. Though some organochlorine insecticides have been banned or are subject to severe restrictions in many countries, in several developing countries production and use of, for example, DDT has continued because of its relatively inexpensive production and its high efficacy against mosquitoes in malaria control. Generally the dilemma of the low cost and high efficacy of persistent pesticides versus their long term health and environmental effects remains a contentious global issue which has been addressed by a global convention (see Box 9.5).

As sampling has become more extensive and monitoring programmes developed, increasing numbers of pesticide compounds are being detected in groundwater. A major study, the National Pesticide Survey, conducted by the US EPA in the late 1980s detected 46 pesticides in groundwater in 26 states originating from normal agricultural practice (Williams *et al.*, 1988) but with low frequency and usually below health-based standards. Pesticides detected in more than five states were alachlor, aldicarb, atrazine, cyanazine, metolachlor and simazine. More recently, extensive sampling within the USGS National Water Quality Assessment programme has confirmed the widespread occurrence of pesticides in both surface water resources and groundwater, but generally at concentrations below their respective allowable maximum contaminant levels (Kolpin *et al.*, 2000). The newer work has, however, shown that pesticides, especially insecticides, are also reaching water resources in urban and suburban areas, including residential sources. This work has also demonstrated widespread detection of pesticide metabolites, often at concentrations exceeding the parent compound, and for which there may not be adequate toxicity data to establish their health significance.

This picture is largely confirmed by monitoring efforts in Europe. Herbicides which are widely used in cereal cultivation, such as MCPP and isoproturon are detected in the countries of northern Europe (Spliid and Køppen, 1998) with carbamates perhaps more common further south. Most detected groundwater pesticide concentrations were in the range 0.1 to 10 µg/l. Concentrations significantly above this range can probably be attributed to local point source contamination from poor disposal practices, or from non-agricultural usage such as on railways.

Because of high analysis costs, much less monitoring has been undertaken in low-income countries and data from tropical regions are scarce. However, atrazine residues from its use in sugar cane cultivation were widely observed in groundwater in Barbados and carbofuran was detected in shallow groundwater beneath irrigated vegetable cultivation in Sri Lanka (Chilton *et al.*, 1998). Elsewhere, presence of organochlorines in groundwater reflects their highly persistent nature and perhaps continuing usage even when banned (Matin *et al.*, 1996).

Transport and attenuation

The mobility and persistence of pesticides in the environment are well understood because admission of a new pesticide for the market requires a series of standardized laboratory and field experiments.

The overall likelihood of a pesticide to be a groundwater pollutant is dependent both on its persistence and its soil sorption. Table 4.3 lists pesticides used in agriculture for which WHO has derived health-based drinking-water guideline values. It provides a classification of their leaching and runoff potential based on their physical-chemical characteristics, i.e. their persistence (characterized by soil half-lives) and soil organic carbon sorption (K_{OC}). Other pesticides used for public health purposes (e.g. DDT, chlorpyrifos and pyriproxyfen in malaria control) and wood conservation (e.g. pentachlorophenol or PCP) are not listed in Table 4.3.

As for the organic contaminants discussed in Sections 4.1.2 and 4.5.2, soil organic matter content, clay content and permeability all affect the potential for pesticides to leach through soils. In general, soils with moderate-to-high organic matter and clay content will absorb pesticides onto soil particles, making them less available for leaching, and moderate or low permeability soils allow less water infiltration.

A wide range of pesticide soil sorption K_d values (as defined earlier in Section 4.5.2) exist. DDT, for example, has a K_d value roughly 20 000 times as high as that for aldicarb and 1500 times as high as that for atrazine. This explains why aldicarb and atrazine have been found in groundwater in agricultural areas while DDT has not.

There are several processes by which pesticide may be degraded. Exposure to sunlight may cause photolysis before they leach into soils. Hydrolysis, the degradation of a chemical in reaction with water that may occur at surface, in the soil zone and underlying groundwater; the longer the hydrolysis half-life the more probable it will enter groundwater. Biodegradation, i.e. enzymatic reactions driven by microorganisms, will occur at greatest rates in microbially active soil. Chlorinated pesticides and triazine herbicides are the most resistant to biodegradation and may persist for years following application. Although the mobility of some organochlorine insecticides is limited by their high hydrophobicity (Table 4.3), their persistence is mirrored in the accumulation in fatty tissues in animals, including fish and humans, mostly from pesticides in surface-water food chains. Organic phosphorus pesticides tend to hydrolyse rather quickly at pH values above neutral, thus losing their toxic properties. However, under dry conditions some have been observed to persist for many months (Graham-Bryce, 1981). Carbamates are noted for their high susceptibility to degradation (Williams *et al.*, 1988).

Higher water solubility does not necessarily correlate with a lower degree of persistence, but highly sorbed pesticides tend to be more persistent. The biodegradability of pesticides depends on their molecular structure and soil half-lives can vary between a couple of days to years (Table 4.3). Quite long half lives can occur once pesticides leave the soil and reach the less biologically active zones of aquifers (Lavu *et al.,* 1996; Chilton *et al.*, 2000). It should be noted that although many pesticide half-lives, have been determined for soils (Table 4.3); use of such half-lives to predict aquifer behaviour may cause misleadingly optimistic attenuation estimates.

Several other pesticide concerns remain. Little is known about the fate of pesticides in tropical environments, most published data are from registration trials in temperate regions. For all pesticides there is potential for incomplete transformation of the parent compound into metabolites which may also be more or less toxic (Sawyer *et al.*, 1994) and may themselves be persistent enough to be detected in groundwater. When pesticides do get into groundwater, cleanup of the contamination is usually prohibitively costly and often may not be practically feasible. The contamination can last many years and spread over a large area before dilution and degradation eventually reduce the pesticide concentrations.

Table 4.3. Classification of leaching potential for agricultural pesticides for which WHO has derived guideline values (data from the US Department of Agriculture Natural Resources Conservation Service and Agricultural Research Service)

Common name	**CAS-No.**	**WHO GV (mg/l)**	**Water solubility at 20-25 °C**	**Soil half-life (days)**	**K_{OC} (ml/g)**	**Leaching potential**	**Solution runoff potential**	**Adsorbed runoff potential**
Alachlor	15972-60-8	20	240	15	170	Medium	Medium	Low
Aldicarb	116-06-3	10	6000	30	30	High	Medium	Low
Aldrin	309-00-2	0.03	0.027	365	5000	Low	Medium	High
Dieldrin	60-57-1	0.03	0.200	1000*	12000	Very low	Medium	High
Atrazine	1912-24-9	2	33	60	100	High	High	Medium
Carbofuran	1563-66-2	7	351	50	22	High	High	Medium
Chlordane	57-74-9	0.2	0.060	350*	20000	Very low	Medium	High
Chlorotoluron	15545-48-9	30	74	35	350	Medium	High	Low
Cyanazine	21725-46-2	0.6	170	14	190	Medium	Medium	Low
2,4-D	94-75-7	30	890	10	20	Medium	Medium	Low
2,4-DB	94-82-6	90	46	5	440	Low	High	Low
1,2-Dibromo-3-chloro-propane	96-12-8	1	1000	180	70	High	High	Medium
1,2-Dibromoethane (ethylene dibromide)	106-93-4	0.4 (P)	4300	100*	34	High	High	Medium
1,2-Dichloropropane	78-87-5	40 (P)	2700	700*	50	High	High	Medium
1,3-Dichloropropene	542-75-6	20	2250	10	32	Medium	Medium	Low
Dimethoate	60-51-5	6	39800	7	20	Medium	Medium	Low
Endrin	72-20-8	0.6	0.230	4300	10000	Low	Medium	High
2,4,5-TP	93-72-1	0.09	140	21	300	Medium	Medium	Low
HCB	118-74-1	None[1]	0.005	1000*	50000	Very low	Medium	High
Isoproturon	34123-59-6	9	700	21	130	Medium	Medium	Low
γ-HCH	58-89-9	None[2]	7	400	1100	Medium	High	High
MCPA	2039-46-5	2	866000*	25	20	High	Medium	Low
MCPP	708-51-90	None[2]	660000*	21	20	High	Medium	Low
Methoxychlor	72-43-5	20	0.100	120	80000	Very low	Medium	High
Metolachlor	51218-45-2	10	530	90	200	High	High	Medium
Molinate	2212-67-1	6	970	21	190	Medium	Medium	Low
Pendimethalin	40487-42-1	20	0.275	90	5000	Low	Medium	High
Simazine	122-34-9	2	6	60	130	High	High	Medium
2,4,5-T	93-76-5	9	278	30	80	High	Medium	Low
Terbuthylazine	5915-41-3	7	9	45	200	High	High	Medium
Trifluralin	1582-09-8	20	0.300	60	8000	Low	Medium	High

* Estimated value; [1] occurs in drinking-water at concentrations well below those causing toxic effects; [2] unlikely to occur in drinking-water

4.7 EMERGING ISSUES

4.7.1 Pharmaceuticals

There is increasing concern about micropollutants originating from pharmaceuticals and active ingredients in personal care products excreted by people as complex mixtures into wastewater systems (Kümmerer, 2004). There are a number of routes through which pharmaceuticals can impact groundwater, but primarily the sources are both untreated and treated sewage. There is also evidence that substances of pharmaceutical origin are not completely eliminated during wastewater treatment or biodegraded in the environment (Daughton and Ternes, 1999; Drewes and Shore, 2001).

Health aspects

Current knowledge on the health effects of pharmaceutically active compounds at concentration levels found in groundwater samples, which are several orders of magnitude lower than concentrations which would be therapeutically active, indicates that there are no effects on human health reasonably to be expected from this source of exposure (Ternes, 2001). However, there is an ongoing debate on how comprehensive health effect data from short-term high dose exposure during diagnosis and treatment should be extrapolated to long-term low dose exposure during drinking-water consumption. Moreover, the problem of correctly assessing the risk from unexpected environmental (underground) and technical metabolites (from oxidative drinking-water treatment) is not resolved. Investigation on the fate of pharmaceutically active substances in drinking-water unit operations and processes is in progress in numerous research studies e.g. in Europe, Australia, Japan, and North America. Additionally, proposals for risk assessment procedures have been suggested (Montforts, 2001).

Transport and attenuation

A lack of knowledge still persists regarding the fate of pharmaceuticals during travel through the subsurface. Findings of recent studies indicate that travel through the subsurface can substantially attenuate the majority of pharmaceutically active compounds where surface water or domestic wastewater is used for groundwater recharge. However, where groundwater is influenced by surface water, such as artificial recharge, polar pharmaceutically active compounds such as clofibric acid (blood-lipid regulating agent), carbamazepine and primidone (antiepileptic drugs) and iodinated X-ray contrast agent can migrate through the subsurface and have been detected in groundwater samples in Germany and the USA (Heberer *et al.*, 1998; Kuehn and Mueller, 2000; Drewes *et al.*, 2001).

4.7.2 Endocrine disrupting compounds

There has been increasing public concern about various environmental contaminants which mimic estrogens and other sex-hormones and hence interfere with endogenous endocrine systems, with potential adverse effects on human health. A global assessment of the state of knowledge on endocrine disrupters was published by the International Programme on Chemical Safety (Damstra *et al.*, 2002).

More than 70 000 chemicals are discussed with respect to endocrine disruptive potential (Bradley and Zacharewski, 1998). These compounds represent both synthetic chemicals produced industrially (such as cleaners, pesticides, food additives, birth control pills, cosmetics) and naturally occurring compounds (such as steroidal hormones, plant-produced estrogens, herbal supplements and metals). Whilst endocrine disrupting compounds (EDCs) are largely organic compounds, it should be noted that some inorganic substances such as metals are also suspected of endocrine disrupting effects. Although their potential occurrence in drinking-water has been the subject of public attention and discussion in some countries, it is important to note that human exposure is chiefly through food.

The steroidal sex hormones estradiol, estrone and testosterone are a class of hormonally active agents of particular interest because they are naturally excreted into the environment from human and animal sources as well as extensively used as pharmaceuticals (e.g. birth control pills). Of the numerous synthetic chemicals that have been implicated as endocrine disrupters, many are no longer used in commerce in many countries, such as some organochlorine pesticides (e.g. DDT, endosulphan, dieldrin, and toxaphene), and PCBs. Other hormonally active compounds, such as various phenolics and phthalates, continue to be used in a variety of industrial applications worldwide (NRC, 1999). Alkylphenol is a biological metabolite of alkylphenol polyethoxylates commonly used in a variety of industrial, agricultural and household applications as non-ionic surfactants. Alkylphenol and compounds are both believed to be endocrine disrupters (Lye *et al.*, 1999). Another synthetic chemical that has measurable hormonal activity is Bisphenol A used as a chemical intermediate for numerous industrial products including polymers, resins, dyes and flame retardants.

Health effects of hormonally active compounds are based on binding of these compounds on steroid hormone receptors which control fundamental mechanisms of gene regulation. The disruption of this process can result mainly in reproductive changes. Developmental defects, neurobehavioral abnormalities, immunological deficits, carcinogenesis and ecologic effects can also be induced (NRC, 1999).

Determining the risk of EDCs to humans is difficult because exposure to these agents has not been routinely monitored, and effects that might be attributed to background concentrations could be complicated by endogenous hormones, pharmacological estrogens (e.g. hormonal contraceptives), and naturally occurring hormonally active agents (e.g. phytoestrogens) that are ubiquitous in the environment (NRC, 1999). Although it is clear that exposures to EDCs at high concentrations can affect human health, the extent of harm caused by exposure to these compounds in concentrations that are commonly found in groundwater is debated (NRC, 1999). Generally, natural and synthetic steroidal hormones are several thousand times more potent than industrial chemicals, pesticides and metals (Khan and Ongerth, 2000).

The WHO has not yet specifically proposed any guidelines for the occurrence of EDCs in drinking-water. However, some of the organochlorine compounds are regulated as pesticides.

The relevance to human health of EDCs occurring in water is currently uncertain. Their occurrence in groundwater is linked to the release of sewage, manure, or spill of specific synthetic chemicals into the environment. The specific processes used in wastewater treatment facilities play a key role in the introduction of EDCs into surface water and groundwater (Drewes and Shore, 2001). The transport of EDCs to groundwater depends on their hydrophobicity and degradability. The majority of highly potent compounds such as steroids are hydrophobic and degradable. Degradation rates of EDC compounds depend on temperature, soil characteristics and their molecular weights (IUPAC, 2003).

The potential risk related to an uptake of individual EDCs present in wastewater affected groundwater by humans does not appear to be very significant. The small data set about the fate of EDCs (such as natural and synthetic hormones, surfactants and pesticides) during percolation through the soil and aquifer and the lack of toxicity data on long-term exposure of low concentrations makes it at present impossible to finally assess the impact of EDCs in groundwater on human health. However, contaminated groundwater may be impacted by a mix of different compounds, which could additively impose endocrine disrupting effects.

4.8 REFERENCES

Ahmed, F.M., Ali, M.A. and Adeel, Z. (2001) *Technologies for Arsenic Removal From Drinking Water*, BUET, Dhaka.

Alaerts, G.J., Khouri, N. and Kabir, B. (2001) Strategies to mitigate arsenic contamination in water supply. In *United Nations Synthesis Report on Arsenic in Drinking Water*, www.who.int/water_sanitation_health/dwq/en/arsenicun8.pdf (accessed April 29. 2005).

Albu, M.A., Morris, L.M., Nash. H. and Rivett, M.O. (2002) Hydrocarbon contamination of groundwater at Ploiesti, Romania. In: *Sustainable Groundwater Development* (eds. K.M. Hiscock, M.O. Rivett and R.M. Davison), pp. 293-301, Geological Society Special Publication No. 193, London.

Allen-King, R.M., Ball, W.P. and Grathwohl, P. (2002) New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. *Advances in Water Resour.*, **25**, 985-1016.

Appelo, C.A.J. and Postma, D. (1993) *Geochemistry, Groundwater and Pollution*, Balkema, Rotterdam.

Araya, M., Chen, B., Klevay, L.M., Strain, J.J., Johnson, L., Robson, P., Shi, W., Nielsen, F., Zhu, H., Olivares, M., Pizarro, F., Haber, L.T. (2003) Confirmation of an acute no-observed-adverse-effect and low-observed-adverse-effect level for copper in bottled drinking water in a multi-site international study. *Regul. Toxicol. Pharmacol.* **38**, 389-399.

Ashley, R.P. (1998) Foreseeability of environmental hazards: the implications of the Cambridge Water Company case. In: *Groundwater Contaminants and their Migration*, (ed. J. Mather), pp. 23-26, Special Publication 128, Geological Society, London.

Bailey, K., Chilton, J., Dahi, E, Lennon, M. and Jackson, P (In Press) *Fluoride in Drinking Water.* WHO Drinking-water Series. IWA Publishing, London.

Barceloux, D.G. (1999) Selenium. *J. Toxicol. Clin. Toxicol.,* **37**(2), 145-172.

Barker, J.F., Patrick, G.C. and Major, D. (1987) Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. *Ground Water Monitor Review* **7**(4), 64-71.

Barnard, C., Daberkow, S., Padgitt, M., Smith, M.E. and Uri, N.D. (1997) Alternative measures of pesticide use. *Sci. Total Environ.*, **203**, 229-244.

Barnes, C.J. Jacobson, G. and Smith, G.D. (1992) The origin of high-nitrate groundwaters in the Australian arid zone. *J. Hydrology*, **137**, 181-197.

Bedient, P.B., Rifai, H.S. and Newell, C. (1999) *Ground Water Contamination: Transport and Remediation*, 2nd edn, Prentice-Hall, New Jersey.

Bradley, E.G. and Zacharewski, T.R. (1998) Exoestrogens: mechanisms of action and strategies for identification and assessment. *Environ. Toxicol. Contam.*, **17**, 49-57.

Cavallero, A., Corradi, C., De Felice, G. and Grassi, P. (1985) Underground water pollution in Milan by industrial chlorinated organic compounds. In *Effects of Landuse Upon Freshwaters*, (ed. J.F. de L.G. Solbe), pp. 68-84, Ellis Harwood, Chichester.

CEC (2001) Commission Recommendation on the protection of the public against exposure to radon in drinking water supplies. Document number C (2001) 4580. *Official Journal of the European Communities,* L 344/85.

Chilton, P.J., Lawrence, A.R. and Stuart, M.E. (1998) Pesticides in groundwater: some preliminary results from recent research in temperate and tropical environments. In *Groundwater Contaminants and Their Migration,* (ed. J. Mather), pp. 333-345, Special Publication 128, Geological Society, London.

Chilton, P.J., Stuart, M.E., Lawrence, A.R., Gooddy, D.C., Williams, R.J. and Johnson, A.C. (2000) Assessing pesticide pollution of groundwater: current knowledge and remaining gaps. In *Groundwater: Past Achievements and Future Challenges,* (ed. O.T.N. Sililo), pp. 17-26, Balkema, Rotterdam.

Costa, M. (2002) Potential hazards of hexavalent chromate in our drinking water. *Toxicol. Appl. Pharmacol.*, **188**, 1-5.

Damstra, T., Barlow, S., Bergman, A., Kavlock, R. and van der Kraak, G. (2002) *Global Assessment of the State-of-the-Science of Endocrine Disruptors*. International Programme on Chemical Safety. http://www.who.int/ipcs/publications/new_issues/endocrine_disruptors/en/index.html

Daughton, C. and Ternes, T. (1999) Pharmaceuticals and personal care products in the environment: agents of subtle change? *EHP,* **107**, suppl. 6, 907-938.

Domenico, P.A. and Schwartz, R.W. (1998) *Physical and Chemical Hydrogeology*, 2nd edn, John Wiley & Sons, New York.

Drewes, J.E. and Shore, L.S. (2001) Concerns about pharmaceuticals in water reuse, groundwater recharge, and animal waste. In *Pharmaceuticals and Personal Care Products in the Environment*, (eds. Ch. Daughton and T.L. Jones-Lepp), pp. 206-228, American Chemical Society Symposium Series No. 791, Washington, DC.

Drewes, J.E., Fox, P. and Jekel, M. (2001) Occurrence of iodinated X-ray contrast media in domestic effluents and their fate during indirect potable reuse. *J. Environ. Sci. Health Part A,* **36A**(9), 1633-1645.

EA (2000) *Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater*. R&D Publication 95, Environment Agency, Bristol.

Edmunds, W.M. and Gaye, C.B. (1994) Estimating the spatial variability of groundwater recharge in the Sahel using chloride. *J. Hydrology*, **156**, 47-59.

Edmunds, W.M., Cook, J.M., Darling, W.G., Kinniburgh, D.G., Miles, D.L., Bath, A.H., Morgan-Jones, M. and Andrews, J.N. (1987) Baseline geochemical conditions in the Chalk aquifer, Berkshire UK: a basis for groundwater quality management. *Appl. Geochem*., **2**(2), 252-274.

FAO (2004) Pesticide residues in food - 2004. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group on Pesticide Residues. FAO Plant Production and Protection Paper 178, Food and Agricultural Organization, Rome, Italy.

Fetter, C.W. (1999) *Contaminant Hydrogeology*, 2nd edn, Macmillan, New York.

Flühler, H.P., Ferlin, P., Selim, H.M., and Schulin R. (1985) Transport von Fluorid, Bromid und Chlorid in Bodensäulen und in einem natürlich gelagertem Boden. *Z. Dtsch. Geol. Gesellschaft*, **136**, 375-383.

Freeze, R.A. and Cherry, J.A. (1979) *Groundwater*, Prentice-Hall, Englewood Cliffs, New Jersey.

Fusillo, T.V., Hochreiter J.J. and Lord, D.G. (1985) Distribution of volatile organic compounds in a New Jersey coastal plain aquifer. *Ground Water,* **23**(3), 354-360.

Gelhar, L.W. (1986) Stochastic subsurface hydrology from theory to applications. *Water Resour. Res*., **22**(9), 135S-145S.

Graham-Bryce, I.J. (1981) The behaviour of pesticides in soil. In *The Chemistry of Soil Processes*, (eds. D.J. Greenland and M.H.B. Hayes), pp. 621-671, John Wiley & Sons Ltd., Sussex.

Hearn, W., Henderson, G., Houston, S., Wadw, A. and Walker, B. (1993) Water supply and Aboriginal and Torres Strait Ilsander health: an overview. *AGSO J. Austral. Geology and Geophysics*, **14**(2/3), 135-146.

Heberer, T., Schmidt-Bäumler K. and Stan H–J. (1998) Occurrence and distribution of organic contaminants in the aquatic system in Berlin. Part I: Drug residues and other polar contaminants in Berlin surface and groundwater. *Acta Hydrochim. Hydrobiol.* **26**, 272-278.

Hem, J.D. (1989) *Study and Interpretation of the Chemical Characteristics of Natural Water*, 3rd ed, USGS, Water Supply Paper 2254.

Heron, G., Barcelona, M.J., Anderson, M.L. and Christensen, T.H. (1997) Determination of nonvolatile organic carbon in aquifer solids after carbonate removal by sulphurous acid. *Ground Water*, **35**, 6-11.

IARC (2001) *Overall Evaluations of Carcinogenicity to Humans*, http://www-cie.iarc.fr/monoeval/crthall.html (accessed April 29. 2005).

IUPAC (2003) Endocrine Disrupters in the Environment. IUPAC Technical Report, *Pure and Applied Chemistry*, **75**(5), 631-681.

Jackson, R.E. (1998) The migration, dissolution and fate of chlorinated solvents in the urbanized alluvial valleys of the southwestern USA. *Hydrogeology J.*, **6**(1), 144-155.

Johansen, S.S., Hansen, A.B., Mosbaek, H. and Arvin, E. (1997) Characterization of heteroaromatic and other organic compounds in groundwater at creosote-contaminated sites in Denmark. *Groundwater Mon. Remediation*, **17**(2), 106-115.

Kerger, B.D., Finley, B.L., Corbett, G.E., Dodge, D.G. and Paustenbach, D.J. (1997) Ingestion of chromium(VI) in drinking water by human volunteers: absorption, distribution, and excretion of single and repeated doses. *J. Toxicol. Environ. Health*, **50**, 67-95.

Kerndorff, H., Schleyer, R., Milde, G. and Plumb, R. H. (1992) Geochemistry of groundwater pollutants at German waste disposal sites. In *Groundwater Contamination and Analysis at Hazardous Waste Sites*, (eds. S. Lesage and R.E. Jackson), Marcel Dekker, Inc. New York, Basel, Hong Kong.

Khan, S. and Ongerth, J. (2000) *Hormonally Active Agents in Domestic Wastewater Treatment – A Literature Review*. Report prepared for CGE Australia.

King, M.W.G. and Barker, J.F. (1999) Migration and natural fate of a coal tar creosote plume 1. Overview and plume development. *J. Contam. Hydrol.*, **39**, 249-279.

Klecka, G.M., Gonsior, S.J. and Markham, D.A. (1990) Biological transformations of 1,1,1-trichloroethane in subsurface soils and groundwater. *Environ. Sci. Technol.*, **9**, 1437-1451.

Kolpin, D.W., Barbash, J.E. and Gilliom, R.J. (2000) Pesticides in groundwater of the United States, 1992-96. *Ground Water*, **38**(6), 858-863.

Kuehn, W. and Mueller, U. (2000) Riverbank filtration – an overview. *JAWA*, **92**(12), 60-69.

Kueper, B.H., Redman, D., Starr, R.C., Reitsma, S. and Mah, M. (1993) A field experiment to study the behavior of tetrachloroethylene below the water table: spatial distribution of residual and pooled DNAPL. *Ground Water*, **31**(5), 756-766.

Kümmerer, K. (2004) Ecotoxicological evaluation of pharmaceuticals. In *Pharmaceuticals in the Environment: Sources, occurrence, fate and effects*, 2nd ed, Springer, Heidelberg, New York.

Lavy, T.L., Mattice, J.D., Massey, J.H., Skulman, B.W. and Senseman, S.A. (1996) Long-term in situ leaching and degradation of six herbicides aged in subsoils. *J. Environ. Qual.*, **25**, 1268-1279.

Lawrence, C.R. (1983) *Nitrate-rich groundwaters in Australia*. Australian Water Resources Council Technical Paper No. 79, Australian Government Publishing Service, Canberra.

Lorah, M.M. and Olsen, L.D. (1999) Natural attenuation of chlorinated volatile organic compounds in a freshwater tidal wetland: field evidence of anaerobic biodegradation. *Water Resour. Res.*, **35**, 3811-3827.

Lye, C.M., Frid, C.L.J., Gill, M.E., Cooper, D.W. and Jones, D.M. (1999) Estrogenic alkylphenols in fish tissues, sediments, and waters from the UK Tyne and Tees Estuaries. *Environ. Sci. Technol.*, **33**(7), 1009-1014.

Mackay, D.M. and Cherry, J.A. (1989) Groundwater contamination: pump-and-treat remediation. *Environ. Sci. Technol.*, **23**(6), 630-636.

Mackay, D.M., Freyberg, D.L., Roberts, P.V. and Cherry, J.A. (1986) A natural gradient experiment on solute transport in a sand aquifer, 1. Approach and overview of plume movement. *Water Resour. Res.,* **22**(13), 2017-2029.

Matin, M.A., Malek, M.A., Amin, M.R., Rahman, S., Khatoon, J., Rahman, M., Aminuddin, M.. McLachlan, M.S., Horstmann, M. and Hinkel, M. (1996) Polychlorinated dibenso-p-dioxins and dibenzofurans in sewage sludge: sources and fate following sludge application to land. *Sci. Total Environ.,* **185**, 109-123.

McAllister, P.M. and Chiang, C.Y. (1994) A practical approach to evaluating natural attenuation of contaminants in ground water. *Ground Water Monitoring & Remediation*, **14**(2), 161-173.

Mendoza, C.A., Johnson, R.L. and Gillham, R.W. (1996) Vapor migration in the vadose zone. In *Dense Chlorinated Solvents and Other DNAPLs in Groundwater*, (eds. J.F. Pankow and J.A. Cherry), pp. 179-201, Waterloo Press, Portland, Oregon.

Mercer, J.W. and Cohen, R.M. (1990) A review of immiscible fluids in the subsurface: Properties, models, characterization and remediation. *J. Contam. Hydrol.*, **6**, 107-163.

Montforts, M. (2001) Regulatory and methodological aspects concerning the risk assessment for medicinal products; need for research. In *Pharmaceuticals in the Environment: Sources, Occurrence, Fate and Effects*, (ed. K. Kümmerer), pp. 159-174, Springer, Heidelberg, New York.

Montgomery, J.H. (1996) *Groundwater Chemicals Desk Reference*, 2nd edn, CRC Press, Inc., Florida.

NCRP (1989) *Control of Radon in Houses: Recommendations of the NCRP*. National Council on Radiation Protection Report No. 103, Bethesda, Maryland.

Newell, C.J. and Connor, J.A. (1998) *Characteristics of Dissolved Hydrocarbon Plumes: Results from four studies*, API technical transfer bulletin, American Petroleum Institute, Washington DC.

Newell, C.J., Hopkins, L.P. and Bedient, P.B. (1990) A hydrogeologic database for ground-water modelling. *Ground Water*, **28**(5), 703-714.

Newell, C.J., Acree, S.D., Ross, R.R. and Huling, S.G. (1995) *Light Non Aqueous Phase Liquids*, US EPA, Ada, Oklahoma.

Noble, P. and Morgan, P. (2002) *The Effects of Contaminant Concentration on the Potential For Natural Attenuation*. EA (for England & Wales) R&D Technical Report P2-228/TR. Bristol.

NRC (1989) *Irrigation-induced water quality problems*, National Academy Press, National Research Council, Washington, DC.

NRC (1994) *Alternatives of Ground Water Cleanup*, National Academy Press, National Research Council, Washington, DC.

NRC (1999) *Hormonally Active Agents in the Environment*, National Academy Press, National Research Council, Washington, DC.

Pankow, J.F. and Cherry, J.A. (1996) *Dense Chlorinated Solvents and Other DNAPLs in Groundwater*, Waterloo Press, Portland, Oregon.

Plumb, R.H. (1992) The importance of volatile organic compounds as a disposal site monitoring parameter. In *Groundwater Contamination and Analysis at Hazardous Waste Sites*, (eds. S. Lesage and R.E. Jackson), pp. 173-197, Marcel Dekker, Inc. New York, Basel, Hong Kong.

Rivett, M.O. (1995) Soil-gas signatures from volatile chlorinated solvents: Borden field experiments. *Ground Water*, **33**(1), 84-98.

Rivett, M.O. and Allen-King, R.M. (2003) A controlled field experiment on groundwater contamination by a multicomponent DNAPL: dissolved-plume retardation. *J. Contam. Hydrol.*, **66**, 117-146

Rivett, M.O., Lerner, D.N., Lloyd, J.W. and Clark, L. (1990) Organic contamination of the Birmingham aquifer. *UK J. Hydrology*, **113**, 307-323.

Rivett, M.O., Feenstra, S. and Cherry J.A. (2001) A controlled field experiment on groundwater contamination by a multicomponent DNAPL: creation of the emplaced-source and overview of dissolved plume development. *J. Contam. Hydrol.*, **49**, 111-149.

Rivett, M.O., Shepherd, K.A., Keeys, L. and Brennan, A.E., (2005) Chlorinated Solvents in the Birmingham Aquifer, UK: 1986 – 2001. *Quarterly Journal of Engineering Geology & Hydrogeology*, 38(4), 337-350.

Sawyer, C.N., McCarty, P.L. and Parkin, G.F. (1994) *Chemistry for Environmental Engineering*, 4th edn, McGraw-Hill, New York.

Schnitzer, M. and Khan, S.U. (1972) *Humic Substances in the Environment*, Marcel Dekker, Inc., New York.

Schwartz, F.W. and Zhang, H. (2003) *Fundamentals of Groundwater*, John Wiley & Sons, Inc., New York.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. (1993) *Environmental Organic Chemistry*, John Wiley & Sons, Inc, New Jersey.

Schwille, F. (1988) *Dense Chlorinated Solvents in Porous and Fractured Media*, (ed. J.F. Pankow), Lewis Publishers, Chelsea, Michigan.

Senior, L.A. (1998) *Radon-222 in the Ground Water of Chester County, Pennsylvania:* USGS Water-Resources Investigations Report 98-4169.

Smedley, P.L. and Kinniburgh, D.G. (2001) Source and behaviour of arsenic in natural waters. In *United Nations Synthesis Report on Arsenic in Drinking Water*, www.who.int/water_sanitation_health/dwq/en/arsenicun1.pdf (accessed April 29, 2005).

Smith, A.H., Lingas, E.O. and Rahman, M. (2000) Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bulletin of the WHO*, **78**, 1093-1103.

Spliid, N.H. and Køppen, B. (1998) Occurrence of pesticides in Danish shallow groundwater. *Chemosphere*, **37**(7), 1307-1316.

Sposito, G. (1989) *The Chemistry of Soils*, OUP, New York.

Squillace, P.J., Zogorski, J.S., Wilber, W.G. and Price, C.V. (1996) Preliminary assessment of the occurrences and possible sources of MTBE in groundwater in the United States, 1993-1994. *Environ. Sci. Technol.*, **30**(5), 1721-1730.

Stevenson, F.J. (1994) Structural basis of humic substances. In *Humus Chemistry: Genesis, Composition, Reactions*, (ed. P.J. Stevenson), 2nd edn, pp. 285-302, John Wiley & Sons, New York.

Stumm, W. and Morgan, J.J. (1996) *Aquatic Chemistry*, 3rd edn, John Wiley & Sons, New York.

Ternes, T. (2001) Pharmaceuticals as New Emerging Environmental Contaminants: A Survey. In *Proc. Second International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water, Minneapolis, Minnesota,* pp. 1-9.

Thurman, E.M. (1985) *Organic Geochemistry of Natural Waters: Developments in Biogeochemistry*, Martinus Nijhoff/Dr. W. Junk Publishers, Dordrecht.

UNSCEAR (2000) *Sources, Effects and Risks of Ionizing Radiation*, UN, New York.

US EPA (1996) *Soil Screening Guidance*, Office of Emergency and Remedial Response, EPA/540/R95/128. http://www.epa.gov/superfund/resources/soil/index.htm (accessed August 11, 2005).

US EPA (1999) *Screening Level Ecological Risk Assessment Protocol for Hazardous Waste Combustion Facilities*, vol. 2, Appendix A, EPA530-D-99-001B. http://www.epa.gov/combustion/eco-risk/volume2/appx-a.pdf (accessed August 11, 2005).

US EPA (2000) *Summary of EPA Coal Combustion Waste Damage Cases Involving Sand and Gravel Mines/Pits/Operations*, http://www.epa.gov/epaoswer/other/fossil/ sandgrav.pdf (accessed April 29, 2005).

Vogel, T.M., Criddle, C.S. and McCarty, P.L. (1987) Transformations of halogenated aliphatic compounds. *Environ. Sci. Technol.*, **21**, 722-736.

Wiedemeier, T.H., Rifai, H.S., Newell, C.J. and Wilson, J.T. (1999) *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*, John Wiley & Sons, New York.

Williams, W.M., Holden, P. W., Parsons, D.W. and Lorber, M.W. (1988) *Pesticides in Ground Water Data Base*, Interim Report, US EPA, Office of Pesticide Programs, Washington, DC.

WHO (1993) *Guidelines for Drinking-water Quality: Recommendations*, 2nd edn, vol. 1, World Health Organization, Geneva.

WHO (1996a) *Guidelines for Drinking-water Quality: Health criteria and other supporting information*, 2nd edn, vol 2, World Health Organization, Geneva.

WHO (1996b) *Toxicological Evaluation of Certain Food Additives and Contaminants*. Prepared by the 44th Meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA), Geneva.

WHO (2003a) *Arsenic in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/arsenic.pdf (accessed September 8, 2005).

WHO (2003b) *Selenium in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/selenium.pdf (accessed September 8, 2005).

WHO (2003c) *Lead in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/lead.pdf (accessed September 8, 2005).

WHO (2003d) *Chromium in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/chromium.pdf (accessed September 8, 2005).

WHO (2003e) *Vinyl Chloride in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/vinylchloride.pdf (accessed September 8, 2005).

WHO (2003f) *1,2-Dichloroethene in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality*. World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/1,2-Dichloroethene.pdf (accessed September 8, 2005).

WHO (2003g) *Dichlorobenzenes in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva http://www.who.int/water_sanitation_health/dwq/chemicals/dichlorobenzenes.pdf (accessed September 8, 2005).

WHO (2004a) *Guidelines for Drinking-water Quality: Recommendations*. 3rd edn, vol. 1, Geneva.

WHO (2004b) *Fluoride in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/fluoride.pdf (accessed September 8, 2005)..

WHO (2004c) *Copper in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/copper.pdf (accessed September 8, 2005).

WHO (2004d) *Vinyl Chloride in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality.* World Health Organization, Geneva http://www.who.int/water_sanitation_health/dwq/chemicals/vinylchloride.pdf (accessed September 8, 2005).

WHO (2005a) *Uranium Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality*. World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/uranium290605.pdf (accessed September 8, 2005).

WHO (2005b) *Nitrate in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality*. World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/en/index.html (accessed September 8, 2005).

WHO (2005c) *Methyl tertiary-butyl ether (MTBE) in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality*. World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/MTBE200605.pdf (accessed September 8, 2005).

WHO (2005d) *Trichloroethene in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality*. World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/trichloroethenemay05.doc (accessed September 8, 2005).

WHO (2005e) *Dichloroethene in Drinking-water: Background Document for development of WHO Guidelines for Drinking-water Quality*. World Health Organization, Geneva, http://www.who.int/water_sanitation_health/dwq/chemicals/11dichloroethenefinal.pdf (accessed September 8, 2005).

WHO (In Press) *Arsenic in Drinking-water*, WHO Drinking-water Quality Series. IWA Publishing, London.

Zietz, B., Dieter, H.H., Lakomek, M., Schneider, H., Kessler-Gaedtke, B. and Dunkelberg, H. (2003) Epidemiological Investigation on chronic copper toxicity to children exposed via the public drinking water supply. *Sci. Tot. Environ.*, **302**, 127-144.

5

Socioeconomic, institutional and legal aspects in groundwater assessment and protection

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The socioeconomic conditions in areas where groundwater is used or recharge occurs are critical to the development of groundwater protection measures. The protection of groundwater may be expensive and disruptive to the inhabitants of the land above the aquifers. Socioeconomic conditions play an important role in determining the likely contaminant loads and types of contaminant that affect the groundwater. It is also critical in determining what types of intervention are possible, how such interventions will be implemented and what resources (including human) will be required and are available.

Institutional and legal issues are also critical in determining the success or failure of groundwater protection policies and strategies. Weak institutions and poor institutional frameworks are commonly identified with poor implementation of water policy (World Bank, 1993; WELL, 1998). The development of groundwater policies and strategies must therefore provide adequate consideration of the appropriate institutional arrangements and consider how the needs of all stakeholders can be incorporated into the policy. The latter demands that there are effective processes of public consultation and participation in policy and strategy development. Legislation is also vital to support

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effective groundwater protection. Not only should the law be supportive of groundwater protection, effective implementation of the law is required to ensure groundwater protection objectives are met (Caponera, 1992; Foster *et al.*, 1992).

The purpose of this chapter is to discuss some of the key socioeconomic, institutional and legal issues that are important to consider in groundwater protection. In Chapter 7, the types of information and methods of data collection will be discussed; Chapter 20 outlines how socioeconomic issues and the institutional and legal frameworks can be addressed in developing groundwater protection.

5.1 SOCIOECONOMIC STATUS: ISSUES OF POVERTY AND WEALTH

Socioeconomic status is a measure of the wealth of individuals, households and communities and reflects their assets as well as the ability of households to obtain goods and services. Socioeconomic status is of importance when considering the level of investment in groundwater management which individuals, communities and societies are willing and able to make.

Socioeconomic conditions influence the capacity for different groups to protect their environment. For instance, in some communities short-term priorities for resource exploitation override the need for resource protection necessary to secure a long-term livelihood, despite the recognition in the communities of the need for such protection.

The poor are usually at greater risk from the adverse effects of poor resource management and it is essential that their needs be properly addressed when developing groundwater strategies. Critical to this approach is to avoid disadvantage for the poor caused by the implementation of groundwater protection policies and strategies. Such disadvantage may occur, for instance, because agricultural use of land is restricted in order to protect groundwater, which may result in reduced incomes and decreased security for poor farmers. Consideration must be given to compensation, financial support, the creation of alternative employment opportunities or provision of new land when no restrictions apply. However, the latter is often difficult to implement and should only be considered where there is strong evidence from consultations that such an approach is acceptable to the communities affected and that the proposed land for relocation is at least the same quality as the land being left.

The implementation of groundwater protection measures will often have important implications for the livelihoods of the households affected and this applies in all countries. For instance, significant changes in land use regulations in developed countries will also have a profound impact on the users of land, water and other resources. Changes may have positive or negative impacts on some or all of the components of livelihoods. The implications of such impacts in terms of compensation, social services and environmental protection should be taken into account when reaching a decision about what and how land use regulations are applied. The population affected must be fully consulted and be willing to accept any restrictions as part of the process of establishing protection norms. Box 5.1 outlines the problems faced in parts of Germany in relation to controlling groundwater contamination when families facing financial hardship are able to access alternative sources of water.

Box 5.1. Socioeconomic factors and illegal use of private wells in some rural areas of Germany

After the political changes in Germany in 1990, the connection of rural areas in eastern Germany to central water supplies was rapidly developed. This was particularly urgent in some mountainous areas of Erzgebirge, Thuringia, as the supply from individual wells was highly unsatisfactory because aquifers in fractured bedrock fell dry at intervals. They were also vulnerable to short-circuiting with surface water and sewage. Connection to central supplies of high quality and reliable quantity in the 1990s was therefore warmly welcomed by the population. Individual wells were abandoned and sometimes illegally misused as undrained sewage pits. As local aquifers were no longer needed for feeding household wells, their protection was no longer perceived as a priority.

However, the introduction of cost recovery for drinking-water significantly increased prices within a few years. At the same time, unemployment rates were very high and available work often poorly paid. As a result, many households struggled financially. This made individual supplies attractive again, and a large number were re-activated illegally. The German Drinking-water Ordinance requires annual monitoring of private wells, which typically involves partial or total cost coverage for the analyses by the well owner, but numerous households connected to a central supply avoided these costs by not registering their re-activated wells for surveillance. Their use only became known because metering showed large numbers of households that were not using any water from the central supply.

Ensuing public health concerns include the high rate of household wells with microbial contamination (up to 60 per cent in one survey) and a high risk of unintentional cross-connection between self-built piping from the household well and the public supply, potentially contaminating the public supply. Furthermore, because of increasing stagnation in the mains due to reduced flow, the costs of the central supply have further increased as flushing is required more often to prevent microbial re-growth. This further reduces the attractiveness of the central supply and encourages greater use of the re-activated wells.

When actions are required by specific communities to protect groundwater resources, consideration must be given to the incentives that may be required and how these can be provided. It should be noted that in many cases such incentives do not refer to direct monetary compensation packages but could, for example, address improved security of tenure for poor farmers in order to promote reduced pollution loads derived from agriculture.

The socioeconomic status of communities is likely to influence the type of interventions that will be feasible for groundwater protection. For instance, in low-income communities in developing countries with shallow groundwater, the use of pit latrines may not be the preferred technical solution for excreta disposal, as they lead to an increased risk of contamination. However, alternative technologies may be too expensive for the majority of the population to sustain. In this case, some degree of contamination of groundwater may be tolerated in order to reduce a greater health risk caused by the lack of excreta disposal. In urban areas, if contamination is deemed unacceptable, then it is often more cost-effective to provide an alternative (often piped) water supply that uses water from a more distant and protected water source (Franceys *et al.,* 1992). In rural areas it is often more difficult to implement such solutions and the use of an alternative sanitation technology may need to be considered and potentially subsidized.

Similar situations may occur in developed countries where balances need to be made between protection of the groundwater resource and sanitation provision. In rural communities, septic tanks may be used where shallow groundwater is tapped for domestic supply thus representing a risk to the quality of the groundwater source. Off-site methods may not be feasible because of the cost of operation and maintenance. In this case, it is likely to be more cost effective to treat the water or use an alternative source of water rather than attempt to change the sanitation technology.

5.1.1 Livelihood concepts

The concept of livelihoods is now used in many countries when considering the nature of poverty. The basic concept of a livelihoods approach is that the ability of households and communities to sustain and improve their livelihood relies on income, assets, capabilities and their vulnerability. This approach also takes into account gender, environmental sustainability and cultural norms in defining sustainable livelihoods. Chambers and Conway (1991) provided definitions of sustainable livelihoods in relation to both environmental sustainability and social sustainability. DFID (2003) has combined these to define a sustainable livelihood:

> *'A livelihood is sustainable when it can cope with and recover from stresses and shocks and maintain or enhance its capabilities and assets both now and in the future, while not undermining the natural resource base.'*

Stresses and shocks refer to events or changes in assets, income or vulnerability that put pressure on the livelihood. For instance, sudden loss of employment or large increases in price of basic goods result in a shock or stress to the livelihood. Equally, a poor harvest or sudden change in allowed land use may affect the asset base of a community. The onset of a significant health problem may increase vulnerability (infection with human immunodeficiency virus (HIV) being a good example) of an individual such that previous levels of health protection are no longer adequate.

Water and health are both considered as assets within this framework and the degree to which households or communities have access to these assets and their resilience to shocks and stresses are fundamental components of securing a sustainable livelihood. The livelihood approach also encompasses concepts of vulnerability and environmental sustainability when considering poverty.

Vulnerability is composed of risks that are shared by a community (sometimes called exposure), which includes lack of access to a specific water resource, and those risks unique to an individual (often termed susceptibility) such as HIV infection. Vulnerability may be physical, social or political (Nichol, 2000). In the context of groundwater protection, physical vulnerability may refer to the increased risk of contamination from inappropriate land use. Social vulnerability arises from marginalization of parts of a community within the larger community or society and factors such as gender-specific restrictions to assets or decision-making. In relation to groundwater, this may result in marginalization of women in decision-making regarding groundwater development, management and protection. Political vulnerability typically relates to the capability of communities to be engaged in wider decision-making processes in relation to resource access and management.

The livelihood approach ensures that the sustainability of natural resources and the environment is given an important place in the understanding of poverty. This may be given greater priority in rural areas where livelihood may depend on sustainable use of natural resources (Tamuno *et al*., 2003). However, natural resources always remain an important component of livelihoods, as sustainability is defined in terms of a livelihood that does not degrade the asset base. This has implications for both rural and urban dwellers. For instance, the protection and sustainable use of groundwater has important implications for urban households that rely on groundwater for domestic supply, as both deterioration and protection of the resource may increase water costs and affect the livelihood of the users.

5.1.2 Source of livelihoods

Understanding the source of livelihood of communities that utilize and potentially pollute groundwater sources is important. Different means of sustaining a livelihood will result in different types of pollution. Where commercial farming is the principal source of livelihood, groundwater may be vulnerable to pollution derived from agrochemicals such as fertilizers and pesticides (Chapter 9). Where irrigation is practised, contamination is likely to increase because many irrigation systems are inefficient, resulting in significant volumes of water infiltrating the aquifer. The water used for irrigation is frequently under-priced and this tends to reinforce the inefficient use of water (World Bank, 1993). However, where irrigation is essential for growing crops, the development of groundwater protection strategies will have to take this into account and compensation packages and alternative irrigation practices (such as drip irrigation) promoted (Chapter 21).

Small subsistence or near subsistence farming may make relatively little use of agrochemicals or irrigation, but their use may be significant in countries where there are government subsidies on agricultural production. In this case, it may be more appropriate to remove the subsidy on agrochemical use than to try to regulate application in particular areas.

Where agrochemical use derives from private purchase, the groundwater strategy will have to consider the capacity of regulatory bodies to develop and deliver incentives to reduce or change applications and the cost of inspection and monitoring. Where there is widespread small-scale private use of agrochemicals, it will be important to consider targeting those areas where groundwater is at greatest risk from pollution, rather than trying to implement broad measures.

The situation with large commercial farming may be simpler to regulate, as there will be a smaller number of people to deal with. Where direct actions are taken to change land use to an economically less productive use, the land-owner would usually expect compensation and this would have to reflect their overall economic loss. However, in many cases, the restrictions may actually apply more directly to applications of agrochemicals on a seasonal basis, which would not require the same level of economic recompense. It may, however, require systems of monitoring to ensure compliance.

Where the majority of the population derive an income from small-scale agriculture, groundwater protection may be more difficult to regulate as there will be many more farmers whose needs must be addressed. Any compensation packages that are developed in such situations may have a lower per capita outlay than larger farms but it is likely to result in a higher per ha cost. This will increase overall direct costs of the protection strategy. As noted above, alternative incentives may need to be developed in some situations. These may be related to land tenure, but also include aspects such as providing more secure markets for produce or providing improved extension programmes as a way of off-setting economic losses.

5.2 POPULATION AND POPULATION DENSITY

Increasing population and population density can increase the risk to groundwater from pollution and unsustainable abstraction. Balancing the needs for protection of resources against demands from rapidly increasing populations is a key element in groundwater protection. Population growth often provides an impetus for improving protection strategies as the need to secure and conserve high-quality water resources for domestic supply becomes increasingly important. This can provide a strong argument for the need to protect groundwater against pollution.

It should be noted, however, that the protection of particular groundwater resources is also dependent on whether it is considered a key source of domestic water in the long-term. In some cases, other resources (either surface water or more remote groundwater) can satisfy demands for water and the threatened groundwater will not form a key part of the water resources used for supply. This is common in wetter countries where urban groundwater has been abandoned. In other situations, typically much drier counties, alternatives may not exist and groundwater resources will therefore need to be protected.

5.3 COMMUNITY PARTICIPATION AND CONSULTATION

Protection of groundwater resources is a public concern and a public responsibility and therefore requires public participation. Participation can be defined as a process through which all stakeholders influence and share control over development and environmental initiatives and the decisions and resources which affect them. The principle of public participation and consultation is found in developed and developing countries.

The Regional Environmental Centre for Central and Eastern Europe states that: '*The most fundamental interest that must be addressed in the process of public participation is the basic right of individuals to have a say in matters affecting their lives… The basic right to participate in decisions affecting oneself… applies in circumstances where the rights and interests may be less recognizable [such as* *right to have a clean environment]… Taking into account the users' interests should actively involve the users themselves*.' (REC, 1995).

The American Waterworks Association Policy Statement on Public Involvement states that: '*Involving the public in decision making… is… important because many drinking water issues, including adequacy of supply, water quality, rates and conservation, are not only technical issues, they are also social, political, personal health, and economic issues. As such, they are best resolved through a process of meaningful dialogue with concerned parties and the public*.' (Kusel, 1998; AWWA, 1995).

The World Bank Policy Research Working Paper states that: '*Recent evidence from Asia, Latin America and North America suggests that neighbouring communities can have a powerful influence on factories' environmental performance… where formal regulators are present, communities use the political process to influence the tightness of enforcement. Where formal regulators are absent or ineffective, 'informal regulation' is implemented through community groups or NGOs*.' (Afsah and Benoit-Wheeler, 1996).

Community or public participation and consultation are important aspects of resource management as successful implementation is commonly dependent on broad agreement with the objectives and in some cases active public participation in programmes, to ensure these objectives are met. Although the general public in most countries is aware that pollution of surface water is caused by mismanagement of waste and inappropriate land use, awareness is more limited when it comes to groundwater, which is often considered 'pure' and clean. This may present particular challenges to ensuring commitment and participation by the public in protecting groundwater resources.

The role of communities may be critical to promoting improved protection, but the nature of the role that they will play may vary. In many situations, communities are consulted but play limited practical roles in the implementation of groundwater protection strategies. In other cases, communities are expected to play an active role in the design, planning and implementation of groundwater protection.

It is important to be clear about the differences in two of the principal approaches to community involvement: consultation and participation. Consultation is a process of discussion with stakeholders about proposed actions or strategy and is geared towards obtaining the opinion from each stakeholder about these and to review the options that are available. However, it may not mean that the agency undertaking the consultation is bound by the outcome of these discussions and usually does not imply a responsibility for action by the community.

Participation is a set of processes where communities and individuals play an active role in the design, planning and implementation of programmes of water resource development or protection. This often implies that the agency and the community have responsibilities for ensuring agreed actions are performed. It is therefore a more long-term and proactive process than consultation. However, for successful participation there must be effective consultation and therefore the two processes are often combined.

5.3.1 Consultation

It is essential that there is proper consultation with stakeholders in the development of policy and implementation of groundwater protection plans. A key activity in the initial stages of policy development is to ensure that the views and needs of different stakeholders are properly reviewed and incorporated into the policy being developed as far as possible. The stakeholders should also have an opportunity to comment on the policy and strategies developed to ensure that these reflect a position of agreement among key stakeholding groups.

Consultation should bring in the views of Government, affected interest groups and the views of the broader society. Therefore various consultation exercises may need to be undertaken to ensure that the views of all concerned and in particular those groups whose livelihood may be directly affected are collected and concerns addressed. Very often, these groups are those most directly affected by water resource management through lack of access to safe drinking-water supplies, contamination of water sources and limited water for irrigation. In order for policy to be effectively implemented, it is important that there is general support for the overall policy and strategy framework within the country. This is an ongoing process and not something that is engaged in only at the start of policy development. It should be seen as a necessary process which supports the development and implementation of resource management policy and strategy.

Perceptions and cultural values attached to water are also important to understand in the context of groundwater quality management and protection. Many of these concepts provide a foundation upon which to build effective protection strategies as they attach important religious or cultural values on the protection of the groundwater. Examples include some aboriginal beliefs about the origins and sacred nature of water in Australia. In other examples traditional beliefs may hamper the development of groundwater protection strategies. For instance in Uganda beliefs about the use of certain springs by ancestral spirits prevented action being taken to improve water sources.

5.3.2 Participation

In wealthier industrialized countries although public participation occurs, the emphasis tends to be on consultation in the development of the underlying principles, policies and plans that define the development of environmental protection. In most cases, groundwater protection strategies are implemented by local or central government with systems of land use restriction, compensation and appeal processes operating. Specific activities required will often result in specific negotiated agreements with individual land-owners.

By contrast, in developing countries, the development of groundwater protection plans and implementation of protection measures is likely to require the direct involvement of large numbers of people and communities. Many of the tasks that will be required can only be undertaken by local people taking responsibility themselves to enforce protection measures, although this means that communities need support to develop effective capacity. The development of community management committees or users organizations is an important component in promoting effective resource use (Subramanian *et al*., 1997).

By understanding these issues, appropriate strategies and plans can be developed that identify key stakeholders, where responsibilities lie and what role is expected to be undertaken by the community. Such decisions will be arrived at partly through stakeholder consultation. However, during the initial stages of the development of the policies and strategies, it is important to collect information about communities in order to be able to provide direction for subsequent discussions.

5.4 LAND TENURE AND PROPERTY RIGHTS

Land tenure and property rights are an important consideration when planning interventions to protect groundwater resources as they will directly influence the scope and depth of consultation and negotiation regarding land use. They may also influence what type of intervention is possible and the nature of any regulations that will need to be developed.

One aspect of land tenure of particular importance is the degree to which ownership of land confers rights of ownership and use of underlying resources. In many countries, ownership of land may confer automatic rights to exploit, although these are increasingly subject to licensing and permitting procedures, but ownership resides with the Government. In these cases, controls over abstraction and land use may be easier to implement and monitor.

In other countries, resource ownership has historically resided with the land owner, although this is being revised in many countries. In the Sultanate of Oman, for example, private ownership of water was abolished by a Royal decree in 1988 and a centrally regulated system of water management introduced with an associated well permit system (Government of Oman, 1995).

Revisions to land laws may require significant transitional periods. For instance, the Spanish Royal Decree of 1986 (No 849) considers underground waters to be in the public domain and licences to abstract are required. Public ownership is however subject to the right of landowners to carry out activities on their land but these must not interfere with groundwater quality. In order to avoid opposition to the transition from private ownership to public resource, the Act gave extensive protection to existing rights owners, and complete transition will not occur until 75 years have elapsed.

Land tenure is often complicated and there are many different forms of rights including customary rights to land, private freehold ownership and publicly owned land, with many different variants (Payne, 1997). In addition to issues of ownership, the nature of tenancy arrangements varies and there are further groups who lack any form of *de jure* right to abode, but which may have a variety of *de facto* rights (Hardoy and Satterthwaite, 1989). There are also a significant number of people who have no rights and no security of tenure. The sections below review some key forms of tenure and discuss their implications in relation to groundwater management.

5.4.1 Private land ownership

Private land-ownership is common in many parts of the world and refers to situations where individuals own land, for instance through freehold arrangements. This may be complicated where land is subsequently let to third parties, a common arrangement in European agricultural areas.

This form of land ownership has particular consequences for the development of groundwater protection strategies. The large number of land-owners or tenants may make the process of consultation more cumbersome as the numbers of people involved may increase the time it takes to collect and synthesize local opinions and a greater range of views may need to be accommodated. Such patterns of land ownership will also often result in compensation packages being developed to offset loss of earnings resulting from restrictions placed on land use. However, where such tenure is in place, it may be easier to define a legal framework that can be transparent in its operation and where compulsory purchase or mandatory development controls can be enforced.

5.4.2 Customary land rights

This is common throughout much the developing world and reflects a situation where rights to land are held by a community, although ownership is retained by an individual or the Government. An example of such an arrangement is ‘common’ land within a village where all residents have the right to graze their livestock. In some parts of the world, this may be expanded into communal ownership of land.

Customary rights imply that decisions relating to the use of the land require agreement with all those with rights to use the land, which may result in a more difficult decision-making process when establishing protection strategies. However, customary rights may already implicitly or explicitly restrict activities acceptable on the ‘common’ land, for instance by proscribing activities that would restrict the full enjoyment of rights by others.

Communal rights to land can also offer benefits in terms of discussions with communities regarding actions required to protect water resources. Firstly, the impact of poor groundwater management is likely to be felt directly by the community as in many cases they may be using the sources being polluted from land that is used by the community. Secondly, it introduces the broader concept of public goods that may be easier to accept when restrictions apply across a community rather than to specific individuals. Thirdly, management and protection strategies can be designed to respond to the demands of the community. Where communities have been active participants in strategy development, they will be able to provide a degree of self-policing which may ultimately prove more effective than outside inspection.

5.4.3 Publicly owned land

Publicly owned land is land owned by a Government for all its population. Examples of publicly owned land include national parks where the land is held for the nation, even though some of the land may be let to individual farmers. In some European countries, the catchment areas of major sources of water are purchased specifically for the purpose of protecting the quality of the water source, particularly where it is used for domestic purposes.

As most groundwater protection policies and plans are implemented by Government bodies, publicly-owned land is the most amenable to restriction of land use, but will still require a process of public consultation during policy development. Particular issues that are likely to need resolution will be changes in allowable use of land where part of the land is let in long-term tenancy to farmers or where there is a public right of access. In the former case, changes may need to be phased or supported by compensation packages, whilst in the latter case, broad consultation should be undertaken to ensure that there is public acceptance of the need for such restrictions. Where public access rights are maintained within areas where there are restrictions, it is essential that appropriate services (such as public toilets) are provided to reduce the potential for release of contaminants into the groundwater.

5.4.4 Informal settlements

Informal settlements – situations where land tenure is unclear and where rights are limited – represent particular problems for groundwater protection. In many cases the residents of such settlements have little or no resources and are vulnerable both to exploitation and to ill-heath derived from contamination in the environment. At the same time, such settlements may become a major source of pollution for groundwater resources as they typically lack basic sanitation, solid waste disposal or surface water drainage. Where water supplies are also lacking use is likely to be made of shallow groundwater systems, potentially leading to direct impacts on the health of the community.

Enforcement of land use restrictions in informal areas is unlikely to be successful as they are illegal and unlicensed settlements. However, simply trying to remove such settlements is not only highly discriminatory against the poor, but it is unlikely to be effective and will result in simply shifting the problem and not resolving it. In these situations, it is more appropriate to identify ways of working with community groups to make improvements in environmental health that reduces health risks.

5.5 VALUING AND COSTING GROUNDWATER PROTECTION

An important approach to protection of groundwater is to put an economic and social value on groundwater resources. This value should take into account the direct and indirect cost of protecting the resources as a function of the direct compensation costs (if any) and lost opportunity costs from other, potentially more productive, uses of the land. This should be balanced through placing a value on the aquifer in relation to its importance in supporting economic growth. The latter should consider the current value of groundwater to different industries and the value of each industry to the overall economy. It should also include the incremental marginal costs caused by increased treatment costs (either derived from use of alternative sources or due to pollution of groundwater) and increased abstraction costs derived from exploitation of deeper resources due to contamination of shallow groundwater.

Most environmental protection activities will result in some increase in the cost of production and distribution of drinking-water and more generally in terms of overall environmental protection. For instance, there may be a requirement to pay compensation to existing land-users or to purchase land in drinking-water catchment areas. Within this debate it is important to obtain the views of the public (perhaps represented by consumer groups) on their willingness to pay for such improvements and to assess whether this will be sufficient to off-set costs, discounted over an appropriate period where necessary. Unless there is a willingness by the public (or specific water consumers) to pay the costs of protection, it may be very difficult to sustain intervention strategies. This is discussed further in Chapter 20.

In addition to a direct balancing of economic costs, it is important that social aspects such as the access to safe water supply and the burdens placed upon poor families from having to walk long distances to collect poor quality water should also be assigned a value. One way of doing this is to calculate the likely public health burden derived from poor access to water supply. This may also include a factoring in of the numbers of people whose welfare depends on the continued exploitation of groundwater, whether for domestic use or in agriculture or industry. An example of an approach to valuing groundwater protection is shown in Box 5.2.

Box 5.2. Putting a value on groundwater: Managua (based on Scharp *et al.*, 1997)

The city of Managua in Nicaragua is dependent on groundwater for domestic water supplies and therefore groundwater protection is a priority. Work undertaken by the Sustainable Use of Water Resources project developed a methodology to assign a groundwater protection value to groundwater sources as an input to groundwater protection planning. The project used four criteria: available quantity, groundwater quality, present or planned use and sensitivity to changes in groundwater level. These criteria were based on the economic valuation of water resources in relation to current use, option for future use and environmental significance.

A protection value was calculated based on scores calculated for each criteria. The scores for quantity, quality and sensitivity to changes in groundwater level were used to define the protection value, whilst the present or planned use criteria was overlain on a final map to indicate current and planned abstraction. The authors note that the protection value was a relative measure based on five classes. The data was compiled into a map on a Geographical Information System (GIS) platform that allowed abstraction to be overlain on the protection value. The authors concluded that the areas where there was currently greatest use corresponded to the areas where the protection value was highest. They also concluded that the approach provided a simple and effective tool to assist planners to develop groundwater protection plans.

5.6 SETTING GOALS AND OBJECTIVES – HOW MUCH WILL BE PROTECTED?

The goals and objectives of groundwater protection programmes must be determined before appropriate choices can be taken. Where they existed, in the past, water resource management and environmental protection agencies often made decisions on goals and objectives exclusively. More recently, however, it has been increasingly recognized that planning agencies, local government authorities, key industry groups and the general community need to be consulted. If the inherent conflicts in land use controls are to be resolved, then the understanding of the resource should be accompanied by an appreciation of its value to the community and of the potential impacts of specific land uses on groundwater quality. The community as a whole should decide what needs to be protected and how much protection it can afford. The introduction of obligatory environmental impact studies in Chile, for example, has included the whole community of affected interests into the decision-making process for the first time (Garcés, 2000). Of course, there are still many countries where little or no protection is afforded.

Protection can either extend across an entire aquifer or be restricted to important recharge areas, or capture zones, for specific water supply wells. The question of how much protection is needed or desired depends on the characteristics of the resource, the degree to which it is used, as well as other community social and economic goals. Alternative macro-protection land use management policies include:

No degradation. The maintenance of the quality of groundwater at no worse than existing levels. Generally, such a policy would only be applied to vital resources, typically a resource that provides the sole source of drinking-water. For practical reasons it can only be applied to groundwater resources in undeveloped areas, or areas of very low intensity development. Further land development will normally be excluded from the designated area

Limited or controlled degradation. Such a policy acknowledges that existing or proposed land uses will cause a deterioration of groundwater quality, but strives to maintain the quality above certain specified limits. This policy normally involves controlling the density and types of land development, and the prescription of specific management practices for activities that can affect groundwater quality.

Differential protection. Differential protection policies allow for combinations of no-degradation and limited degradation. Land use management practices normally result in a combination of exclusion and restriction. Such differential protection policies allow the development of different protection objectives taking into account factors such as present and potential uses of water resources, the tenure, zoning and uses of land in the locality, and the desires of the communities involved.

Conflicts in land use management for groundwater quality protection. Restrictions on land use for groundwater protection will always have an economic cost, and decisions must be made about how to minimize these costs while maximizing protection. For example, any limitation on the type and amount of industrial or urban development will have a cost. Consequently, the setting of land use controls for groundwater protection can be very controversial. Obviously, landowners have an expectation that their land can be used freely in its economic highest value use. The wider community interest, on the other hand, can require that groundwater should not be put at risk of pollution. Those responsible, therefore, usually have the difficult task of trying to balance the optimum protection of groundwater resources with the economic interests of the owners of the overlying land surface.

There may be many potential complications involved in land use management, for instance in trying to control problems such as the salinization of groundwater due to irrigation return waters. There may be extreme examples of conflicts, as for instance in the Doon Valley in Uttar Pradesh, India where limestone quarrying is physically destroying the aquifer (Shaman, 1996). Many different types of land use may have to be restricted to protect the quality of groundwater. It is not simply a question of limitations on activities involving toxic materials or the disposal of sewage. Run off from urban areas can be a serious contaminant and it and other sources of diffuse contamination, particularly from agriculture, are those that are best controlled through land use management policies. However, it is with controls over diffuse sources that most conflicts will tend to arise. The problem is particularly acute in rapid growing cities and in those cities in poorer countries where there is reliance on water supplies from shallow aquifers and disposal of excreta in situ.

5.7 INSTITUTIONAL ISSUES

The development of groundwater protection strategies and policies requires effective institutions responsible for the planning, implementation and management of groundwater in the country. In a great number of cases, the failure to protect groundwater resources results not from a lack of appropriate legislation, but because of the poor enforcement of existing regulations. This frequently reflects both weaknesses in the overall institutional framework for groundwater protection and weaknesses within key institutions themselves. Part of the weakness often noted is that the institutions dealing with health, water resource or water supply fail to collaborate to define groundwater protection needs.

Where groundwater policies do not exist or are in need of revision, it is important that a lead institution should be identified for policy direction, and the co-operation of other relevant organizations in decision making should be sought. Generally the lead organization is placed at the central government level. Even in countries where local public participation in water management is high, such as parts of the USA, local water management plans must be consistent with national water quality management objectives and plans.

It is essential that the different roles and responsibilities of different agencies working in the water sector are clearly defined and that one agency is charged with the responsibility to develop, implement and enforce a groundwater protection plan. It is important that the institution identified does not have any conflicts of interest that will compromise its ability to work independently. It is usually preferred that a water resources management body is established that is involved in the approval of development of water sources and the control of the quality of the resource, but is not directly involved in water source development.

Institutional mandates must reflect the aims and objectives of each institution with respect to their roles and responsibilities within the sector (Alaerts, 1997). One of the consequences of this is to consider carefully the scale and scope of activities. For instance, water and wastewater service provision is often most effectively performed when decision-making is devolved to decentralized bodies such as municipalities, water companies or water users associations. National central bodies may still retain some responsibility for policy or strategic development, but may have little influence on operational matters. This implies that when considering roles and responsibilities, the level of action (national policy or local implementation) needs to be considered as well as the area over which the institution has a mandate for action.

The regulation and control of groundwater quality requires a somewhat different approach, although the principles of decentralized operation are still valid. However, although implementation of regulatory activities may be decentralized, there is a need for a strong national institution capable of providing the overall policy and strategic guidance for groundwater protection.

5.8 LEGAL FRAMEWORK

The protection of groundwater requires an adequate legal framework (Caponera, 1992; Soulsby *et al.*, 1999). As governments move towards the strategic management of the country's water resources, it is often necessary to replace basic common law and property rights with statutory provisions regulating the use, development and protection of water (Caponera, 1992). Legal issues related to water ownership, the means used to control abstraction and polluting activities, and the enforcement of such legislation become important. The framework must be supported by appropriate institutions that are capable of implementing the policies and enforcing the relevant laws and regulations, and these organizations must also have the necessary legal status and powers. The willingness to enforce compliance with pollution control measures and whether regulatory frameworks create incentives for potential polluters to comply are critical in ensuring effective regulation (Lane *et al.*, 1999). Within the general considerations of the scope of environmental legislation, the legitimate demands of economic development must be considered to ensure that a sensible balance is struck between the two (Lane *et al.*, 1999).

Legal frameworks in place or developed for water protection deal often with many other issues apart from groundwater. It is possible to identify the shortcuts that relate solely to groundwater, but it is not usually possible to change the laws so as to concentrate only on groundwater quality. The use of more general laws must therefore be accepted, and the specific legislative provisions that may be applicable to the groundwater situation should be identified and used as appropriate, working within the framework of all the provisions of the relevant legislation.

Legislative reform may be required in order to achieve the objectives of groundwater protection. This may involve the revision of existing legislation to encompass these policy objectives or the development of new legislation geared towards groundwater. The approach adopted depends in large part on the nature of existing legislation, the ease with which this may be updated (bearing in mind that existing legislation may deal with broader issues and updating may be time consuming) and the importance of groundwater in the national water resources. Furthermore, as noted by Foster *et al.* (1992), legislative reform will only be effective where political will exists to ensure implementation. These issues are discussed further in Chapter 20.

5.9 REFERENCES

Afsah, S-L. and Benoit-Wheeler, D. (1996) *Controlling Industrial Pollution: A new paradigm.* World Bank Policy Research Working Paper WPS1672.

Alaerts, G. (1997) Institutional arrangements. In *Water Pollution Control*, (eds. R. Helmer and I. Hespanhol), pp. 219-244, E&F Spon, London.

AWWA (1995) *AWWA government affairs: public involvement policy.* www.awwa.org (accessed April 29, 2005).

Caponera, D.E. (1992) *Principles of Water Law and Administration*, Balkema, Rotterdam.

Chambers, R. and Conway, G. (1991) *Sustainable Rural Livelihoods: Practical Concepts for the 21st Century*, IDS Discussion Paper 296, Brighton.

DFID (2003) *Sustainable livelihoods guidance sheets.* www.livelihoods.org/info/info-guidancesheets.html (accessed April 29, 2005).

Foster, S., Adams, B., Morales, M. and Tenjo, S. (1992) *Estrategias par la protección de aguas subterráneas*, Centro Panamericano de Ingeniería Sanitaria y Ciencias del Ambiente, Lima.

Franceys, R., Pickford, J. and Reed, R. (1992) *A Guide to the Development of On-site Sanitation.* World Health Organization, Geneva.

Garcés, J.A. (2000) *El Sistema de Evaluación de Impacto Ambental y el Sector Sanitario*, Revista AIDIS, No. 25, Chile.

Government of Oman (1995) *Water Resources of the Sultanate of Oman, Ministry of Water Resources*, Oman.

Hardoy, J.E. and Satterthwaite, D. (1989) *Squatter Citizen: Life in the Urban Third World*, Earthscan Publications, London.

Kusel, M. (1998) Perspective. *American Waterworks Association Mainstream*, **42**(3), 5.

Lane, S.N., Richards, K.S., Sinha, S. and Wy, S. (1999) Screw the lid even tighter? Water pollution and the enforcement of environmental regulation in less developed countries. In *Water Quality: Processes and Policy*, (eds. S.T. Trudgill, D.E. Walling and B.W. Webb), pp. 233-255, John Wiley & Sons, Chichester.

Nichol, A. (2000) *Adopting a Sustainable Livelihoods Approach to Water Projects: Policy and Practical Implications*, Working Paper No. 133, ODI, London.

Payne, G. (1997) *Urban Land Tenure and Property Rights in Developing Countries: A review*, IT publications and ODA, London.

REC (1995) *Status of Public Participation Practices in Environmental Decision making in Central and Eastern Europe Case Studies of Albania, Bulgaria, the Czech Republic, Croatia, Estonia, Hungary, Latvia, Lithuania, FYR Macedonia, Poland, Romania, the Slovak Republic and Slovenia*. Report of the Regional Environmental Centre for Central and Eastern Europe, Budapest, http://www.rec.org/REC/Publications/PPstatus/cover. html (accessed April 29, 2005).

Scharp, C., Alveteg, T., Johansson, P-O. and Caldera, M. (1997) Assigning a groundwater protection value: methodology development. In *Groundwater in the Urban Environment: Problems, Processes and Management*, (ed. J. Chilton), pp. 659-664, Balkema, Rotterdam.

Shaman, D. (1996) *India's Pollution Regulatory Structure and Background*, NIPR Papers, World Bank, Washington.

Soulsby, C., Chen, M. and Malcolm, R. (1999) Towards groundwater protection in the UK: problems of integrating science and policy. In *Water Quality: Processes and policy*, (eds. S.T. Trudgill, D.E. Walling and B.W. Webb), pp. 151-179, John Wiley & Sons, Chichester.

Subramanian, A., Jaggannathan, N.V. and Meinzen-Dick, R. (1997) *User organizations for Sustainable Water Services,* World Bank Technical Paper No. 354, The World Bank, Washington DC.

Tamuno, P.B.L., Howard, G. and Smith, M.D. (2003) Ecological Risk Assessment (ERA): How appropriate for developing countries? *Environmental Infomatics Archives*, **1**, 204-212.

WELL (1998) *Guidance Manual on Water Supply and Sanitation Programmes*, WEDC, Loughborough.

World Bank (1993) *Water Resources Management,* World Bank Policy Paper, World Bank, Washington, DC.