SEEING the INVISIBLE

A Strategic Report on Groundwater Quality

Peter Ravenscroft and Lucy Lytton

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Preface

Groundwater is vital to human welfare and development and in many countries is the principal source of drinking, irrigation, and industrial water. It is a core component of the hydrological cycle and critical to sustaining many sensitive aquatic and terrestrial ecosystems.

Because of the prominent role groundwater plays in supporting climate change adaptation strategies, groundwater depletion has grabbed global attention and garnered support for greater attention to its management, including enhanced replenishment through managed aquifer recharge. This report "Seeing the Invisible: A Strategic Report on Groundwater Quality" provides evidence for giving equal focus to groundwater quality as the capacity of the resource to satisfy current use, as well as any future use, is increasingly compromised in the absence of attention to this aspect of groundwater management.

The chemical and microbiological quality of groundwater is central to its utility, yet the resource remains vulnerable to contamination from both natural and anthropogenic sources. This report, and its companion volume "A Practical Manual on Groundwater Quality Monitoring," not only provide a rich description of the types and nature of contaminants in groundwater but also the tools, techniques and resources to approach their measurement and long-term monitoring, and how to protect the resource from getting contaminated in the first place.

This report describes why, and how, groundwater quality is vital to human health, agriculture, industry and the environment. In turn, this explains why it is so important to World Bank staff and clients, as well as diverse managers and administrators in countries and economies at all stages of development.

The theme of World Water Day 2022 is "Groundwater: Making the Invisible Visible." This report contributes to this initiative by highlighting the importance of groundwater quality and its role in water resource management. Together with the companion manual, it will assist budget planners, project managers, and water resource managers to embed groundwater quality monitoring in government plans and project designs, and support on-the-ground implementation of its measurement and practical steps for its protection.

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Executive Summary

Groundwater quality determines whether and how the water can be used for drinking, cooking, washing, irrigation, and industrial purposes. Globally, groundwater is the principal source for each of these uses and it is hard to overstate the importance of groundwater quality or the enormous cost of ignoring it. Securing the quantity and quality of our groundwater resources is key to resilience in a changing world.

Groundwater Contamination—An Evolving Challenge

Natural and anthropogenic contamination of groundwater poses hazards to humans and the environment. The best way to limit damage from natural contaminants is to identify them before they can cause harm, to monitor them, and to instigate mitigation where necessary. The best way to limit damage from anthropogenic pollution is to prevent it from happening in the first place, and where it has already happened, to act quickly. Regulators should adopt policies that encourage polluters to respond quickly and discourage them from ignoring groundwater pollution, or even trying to cover it up. Whether natural or anthropogenic, the longer contamination is ignored, the worse the problems are and the more costly and time-consuming the solutions.

The consequences of contaminated groundwater for health, agriculture, the environment and the economy can be massive. Natural contamination cannot be prevented from occurring, but it can be prevented from causing harm to humans and the environment. Anthropogenic pollution can be prevented and should be remediated at the cost of the polluter. Furthermore, because groundwater, as baseflow, is a major contributor to the dry season flow of most rivers, its quality and quantity greatly influence their ecological states. When unaffected by human activity, most groundwater is of good quality, nevertheless investigations since the 1980’s have revealed that natural groundwater contamination is more extensive, and serious, than previously thought. Further, ever-increasing detections of anthropogenic pollutants, including chemicals that were barely recognized as contaminants a few years ago, pose problems on a scale that is often not appreciated. On top of this is the growing realization that, once polluted, the restoration of aquifers to a state fit for use is difficult, expensive and very slow.

Naturally Occurring Contaminants

The greatest natural (geogenic) hazards in groundwater are arsenic and fluoride (see box ES.1). Both are currently poisoning more than a hundred million people through drinking water across the globe, and both are colorless, odorless, and tasteless. The magnitude of this chronic exposure was first recognized in the 1980s, essentially because the water supplies had not been previously tested. Other widespread

BOX ES.1. The World's Worst Natural Contaminants

Arsenic

Long-term exposure to arsenic in drinking water and foods produced with contaminated irrigation water causes a wide range of ailments ranging from lethargy to characteristically painful skin diseases (photo BES.1.1), liver and kidney disease, and fatalities from heart and lung disease and multiple cancers. Globally, about 150 million people have been exposed to dangerous levels of arsenic in drinking water since the 1970s. In Bangladesh, the worst affected country, the MICS survey of 2009 concluded that over 40 million of the estimated population of 164 million were drinking water contaminated by arsenic in excess of the 10ppb WHO guideline (Flanagan et al 2012). MICS water quality surveys periodically update estimates of arsenic exposure and the progress of mitigation in Bangladesh, the latest being for 2019 (BBS/UNICEF 2019) which suggests there have been modest improvements in mitigating the impacts of arsenic over the preceding decade. The health effects are characterized by strong latency: Skin conditions typically take two to five years to develop, whereas arsenic-induced cancers may not peak until decades after exposure stops; similarly, the severe effects of prenatal exposure are expressed in young adults—hence action on mitigation is all the more urgent. The cost of lost labor alone has been estimated at US$13 billion over twenty years, many times more than the estimated cost of mitigation, which is only a few hundred million dollars (Flanagan et al. 2012; Ravenscroft, Brammer, and Richards 2009).

PHOTO BES.1.1. Arsenic-Induced Keratosis on Hands and Feet in West Bengal

Source: Photo courtesy of the late Dr. Dipankar Chakraborti.

box continues next page

BOX ES.1. continued

Fluoride

Long-term exposure to fluoride in drinking water puts an estimated 200 million people worldwide at risk of developing crippling skeletal fluorosis (photo BES.1.2) and children at risk of developing dental fluorosis, especially in India, China, and some semiarid parts of Africa.

PHOTO BES.1.2. Examples of Skeletal Fluorosis

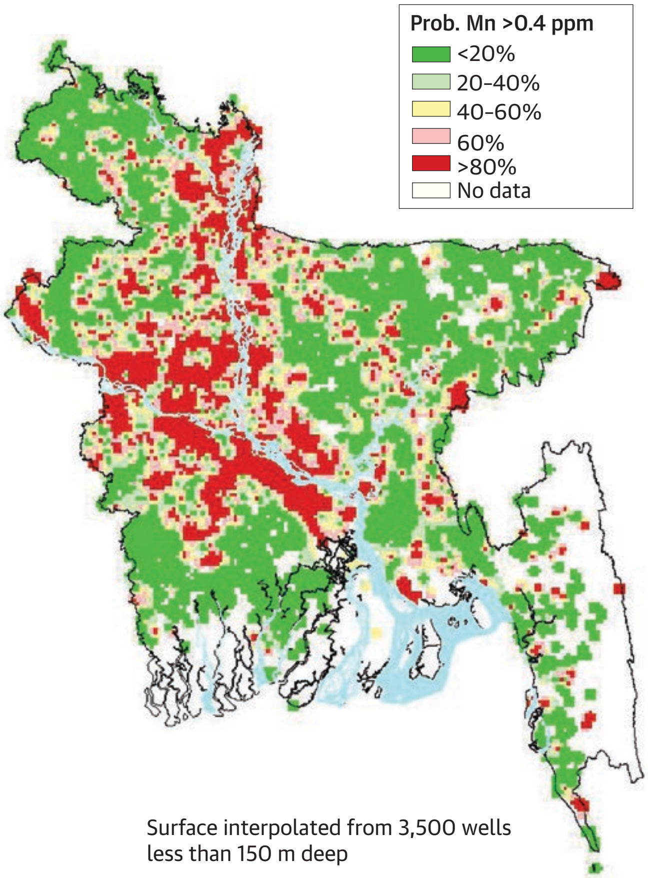
Source: Kesar HWP via Flickr.

natural contaminants include uranium, selenium, and manganese. The latter is a remarkably common component of groundwater (see example in map ES.1). Long recognized as a nuisance, over the past fifteen years, manganese has been recognized to impair the intellectual development of tens, perhaps hundreds, of millions of children, yet some countries still do not test for it or are practically unaware of the consequences. Probably the most widespread groundwater quality problem is salinity, either as seawater intruding into aquifers supplying coastal towns and cities worldwide or in semiarid irrigated lowlands threatening the productivity and sustainability of agriculture. Climate change is exacerbating both processes.

Anthropogenic Contaminants

The range of anthropogenic contaminants stretches from fecal pathogens and fertilizers to toxic and carcinogenic industrial chemicals, of which the best known are petroleum hydrocarbons, pesticides, chlorinated solvents, and hexavalent chromium.[1] These have caused tens of thousands of pollution incidents over the past fifty to one hundred years. In addition, so-called emerging contaminants—which include pharmaceuticals, personal care products, and novel industrial compounds, such as per- and poly- fluoroalkyl substances (PFAS)—are increasingly being detected in groundwater and regarding which the health risks are poorly understood. PFAS exemplify persistent organic pollutants

MAP ES.1. Illustrating the Manganese Risk in Bangladesh, Indicating the Probability of a Shallow Well Exceeding the WHO Guideline



Surface interpolated from 3,500 wells less than 150 m deep

Data source: Ravenscroft et al. 2014.
Note: WHO = World Health Organization.

(POPs), or *forever chemicals* as they are sometimes known, that are bioaccumulative, persistent, and highly toxic. PFAS pose a significant threat to health and will likely result in huge economic costs worldwide. In Michigan in the United States, PFAS exposure of more than a million people has been declared a “groundwater emergency,” and the Minnesota State Court has ordered chemical companies to pay out US$850 million. However, outside North America and Europe, the extent of PFAS pollution is poorly known.

Pathogens

The contamination of well water and groundwater by bacteria, viruses, and protozoa is a major cause of water-related morbidity and mortality, and one of the major challenges in achieving Sustainable Development Goal (SDG) 6. Shallow groundwater may become extensively contaminated beneath human settlements, especially where the soil cover is thin or absent, in fissured aquifers, and where surface water and groundwater are directly connected. Generally, however, the microbes that actually cause disease are closely associated with sanitation and hygiene practices rather than contamination of aquifers, and the remedies lie in better well construction, sanitary protection, and behavior change. Where there is a healthy soil cover, microbial contamination of most aquifers is limited to a shallow depth and proximity to waste sources, so it is less of a concern for water resource managers than for water supply and public health practitioners.

Agricultural Pollutants

The relationships between groundwater quality and agriculture are complex. First, nitrate fertilizers and pesticides can pollute the underlying aquifers. Both are hazardous to health, and nitrate impacts can be extensive in regions of intensive fertilizer application. Diffuse agricultural pollution, primarily nitrate, is the principal driver of poor chemical status in groundwater in the European Union, affecting about 20 percent of all groundwater bodies in the twenty-seven countries. Second, contaminants like salinity and boron are phytotoxic, and others like selenium and cadmium can enter the food chain. Arsenic is both phytotoxic to rice and accumulates in its edible parts, simultaneously threatening both those who consume the rice (adding to their exposure from drinking water) and the sustainability of agriculture. The arsenic in water pumped onto paddy fields accumulates in the soil, from where it is increasingly transferred to the crop, gradually transferring exposure from drinking water to the food chain. In some areas of South Asia that have received the highest arsenic loads on soil, irrigated rice production has been abandoned, a situation that, without changes in farming practice, is expected to be repeated in other areas (Duxbury and Panaullah 2007; Ravenscroft, Brammer, and Richards 2009).[2] Third, the chemistry of groundwater can affect the properties of soil, such as by precipitating salt or impairing drainage.

Pollutants of the Industrial Age

The term *industrial* refers here to contamination directly from both industries and the use of modern industrial products. The most common contaminants are probably petroleum hydrocarbons and chlorinated solvents, such as well-known products like perchloroethylene or tetrachloroethene (PCE) and trichloroethene (TCE), which are used as degreasing agents and in dry cleaning. Because they are used in many small facilities, they are particularly widespread and likely to occur in mixed residential-commercial areas. Petroleum hydrocarbons and chlorinated solvents also represent two different classes of contaminants: the light and dense nonaqueous phase liquids (LNAPL and DNAPL). Both are volatile and both are only slightly soluble in water, but petroleum is lighter than water, so it floats on the water table and needs to be skimmed or "sucked" away. Chlorinated solvents, by contrast, are denser than water, so they sink rapidly to accumulate at the bottom of the aquifer or perched on low permeability horizons within it. These pools of DNAPL are difficult to locate, persistent, and challenging to remediate.

Peculiar Challenges

The variable, heterogenous and unseen nature of groundwater environments lead to challenges in their management which are analogous to those of climate change.

A Historical Legacy

Groundwater quality management must deal not only with ongoing pollution but also the legacy of undocumented pollution from waste disposal and old and abandoned facilities such as factories, warehouses and stores, gasworks, and railway yards. Often there is no "responsible person," so governments must intervene in the public interest. Plumes of polluted groundwater vary enormously in scale and persistence. Although most are probably no more than a few hundred meters long, they can extend for tens of kilometers. Contaminant plumes also vary in their thickness and how deep they penetrate below the ground. Depending on the local hydrogeology, some dissolved plumes are drawn laterally to discharge into streams, whereas others are drawn deep into the aquifer under the influence of pumping. This emphasizes the need for prior conceptualization and rapid investigation to limit further damage.

Persistent Problems

What most distinguishes groundwater from other branches of hydrology is the long timescale over which change occurs. Unlike a river, the intakes cannot be closed down for a few days or weeks to the allow the system to clean itself. Perhaps the most underestimated aspect of groundwater pollution is its persistence, which depends on the properties of the contaminant and the hydrogeochemical conditions in the receiving aquifer, particularly whether they are oxidizing or reducing.[3] For example, petroleum compounds are readily degraded under oxidizing conditions but can persist for many years under reducing conditions, whereas chlorinated solvents show the opposite behavior. Even relatively benign and degradable contaminants, such as nitrate, can persist for decades in oxygen-rich aquifers; yet under reducing conditions, they disappear rather quickly.[4] At the other extreme, POPs may resist degradation under almost all conditions. Whatever the chemicals, there is a general tendency for contaminants to diffuse into low-permeability layers during the early stages of a pollution event and slowly diffuse back out later, adding to the persistence of contamination.

The Costs of Contamination

Once the obligation to identify and remediate anthropogenic pollution has been recognized, the costs are likely to be high, and the greater the delay in taking action, the greater the cost. An indication of this comes from the costs of treating water supplies and remediating contaminated sites in the United States and Europe. In the United Kingdom, by 2003, almost half of groundwater used for public supply was affected by deteriorating quality with a cost of more than US$1.2 billion for treatment, blending, and replacing water sources. In the United States, the famous 1980 "Superfund" created to clean up severely contaminated sites contained, at its peak, US$9 billion, yet at the turn of the millennium, 126,000 sites did not meet clean-up standards, leaving a predicted "bill" of US$100 billion to $500 billion. Even by 2016, only 20 percent of 1,743 sites had been removed from the National Priorities List (USEPA 2001; Suthersan, Horst, et al. 2016).

Considering all of the above, how much of a concern is groundwater contamination (box ES.2)?

BOX ES.2. How Big Is the Problem of Groundwater Contamination?

Although almost always less polluted than nearby streams, the pervasive nature of groundwater contamination is often underappreciated.

It is difficult to convey, accurately and effectively, the magnitude and community-, regional-, and national-scale, or even aquifer-scale, severity of groundwater contamination from natural and anthropogenic sources. In a few areas, such as within some of the most severely arsenic-affected regions of South Asia, most groundwater may be affected, but generally most groundwater is not contaminated; and even here lateral and vertical variations mean that good groundwater can be accessed. On the other hand, unless the aquifer is covered by a thick confining layer, most aquifers considered to contain good-quality groundwater also contain some contamination; and unlike in streams, an isolated anthropogenic pollution event does not immediately or inevitably endanger the entire aquifer.

Estimating the extent of anthropogenic contamination is difficult because of the legacy of pollution already in the ground. An idea of the scale can be obtained by considering the number of current and historical hazards, such as landfills, poorly maintained sewers and septic tanks, underground fuel storage tanks, factories using degreasing agents, dry cleaners, and so on. For example, anecdotal evidence suggests that as many as half of older petrol stations in the United Kingdom have experienced leaks at some time. Of course, not at all leaks contaminate groundwater and protection measures have greatly improved. Nevertheless, it is a warning of the legacy waiting to be discovered elsewhere. The precautionary principle suggests that contamination should be expected in shallow groundwater in all urban-industrial areas.

Reporting under the European Union's Water Framework Directive (WFD) provides a near-continental scale picture of the chemical status and trends of all groundwater bodies (GWB) in 27 countries. A 2021 report revealed that 23 percent of groundwater bodies (by area) are of poor chemical status. The most significant driver of poor chemical status was agriculture, with 20 percent of the area affected by diffuse pollution. Other significant pressures included discharges from dwellings not connected to sewerage networks (5 percent), point source pollution from abandoned industrial or contaminated sites (4 percent), and point source pollution from regulated industrial plants (4 percent). Many of the GWBs were affected by multiple pressures. Overall, saline intrusion was a minor contributor to poor status but was severe along parts of the Mediterranean coast and predicted to get worse with climate change. Where the GWBs were divided by depth (horizon), it was not surprising that only 13 percent of deeper horizons had poor chemical status, compared to 32 percent where only a single horizon was defined.

It is notable that the area failing on qualitative (chemical) status (23 percent) is much larger than that failing on quantitative status (12 percent).

Source: Psomas et al. 2021.

Responding to the Challenge

Just as groundwater quality is evolving through the addition of an increasingly complex cocktail of contaminants, so also is the suite of tools and techniques to address the problem. However, even the most sophisticated approach demands simple steps at the outset.

Characterizing and Managing the Risks

Plans to deal with actual or potential groundwater contamination should follow four steps:

- Conceptualizing the aquifer and the pollution
- Characterizing the risks to understand what harm might occur and when
- Monitoring—collecting the information that is key to management
- Remediation and mitigation—taking action to ensure safe water

In addition, there must be institutional and financial support so that these steps can be implemented.

Understand the System

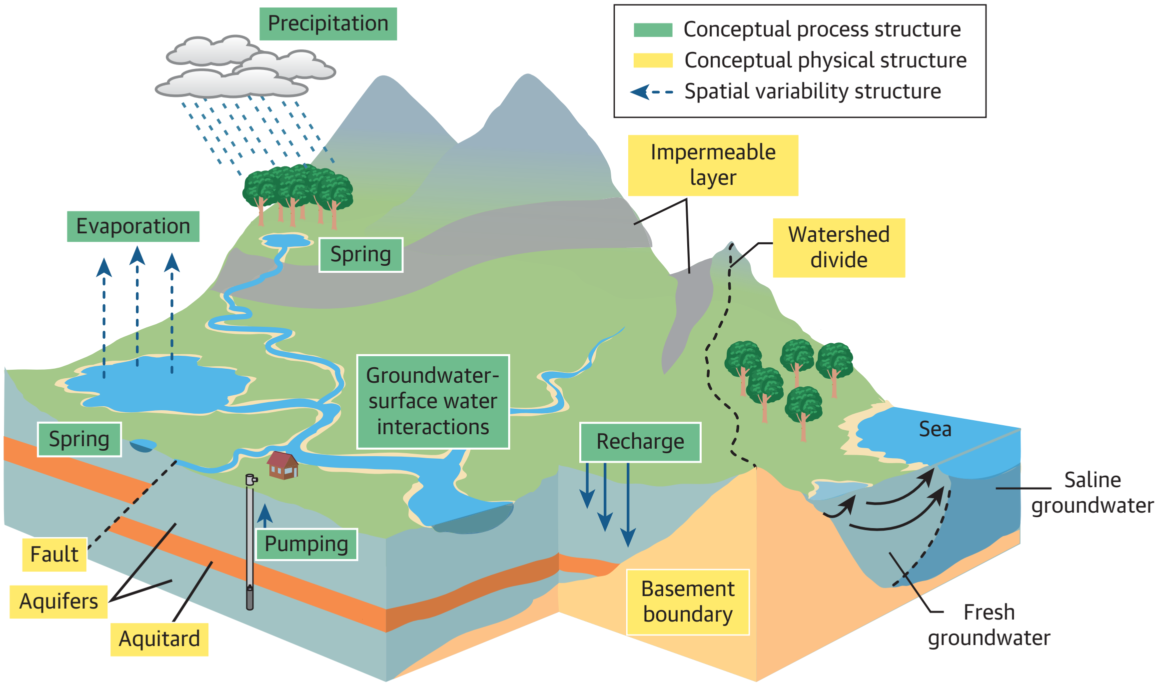
Conceptualization underpins investigating, monitoring, and managing groundwater quality problems. The understanding of the processes that control the movement of pollutants through an aquifer should be summarized in a conceptual hydrogeological model (figure ES.1). There is no rigid specification, but good models will graphically represent the geology, the connections between surface water and groundwater, and pathways connecting sources and receptors of contaminants, supported by a narrative description, tables of data, and graphs. A core element of conceptualization is to assess uncertainty so the model is progressively refined, starting with however little data are available. An agreed conceptual model should be a precondition for any numerical or statistical modeling and for a monitoring strategy. Where resources are lacking, a good conceptual model backed up by even basic monitoring can be highly cost-effective and much less demanding on resources than numerical modelling

Know the Starting Point

A vital, and often overlooked, part of managing groundwater is establishing a baseline before serious development takes place. Aquifers are complex, and it should be seen as imperative to define the initial state of the aquifer, against which human impacts can be measured and whereby the presence of any harmful geogenic contaminants identified and mitigated before harm occurs.

Uncertainty is the enemy of remediation and requires systematic characterization—at the regional scale to understand natural contamination and at site-scale or smaller for anthropogenic pollution events using so-called "smart characterization" techniques.

FIGURE ES.1. Example of a Conceptual Hydrogeological Model



Source: Adapted from Enemark et al. 2019.

Risk Assessment

Except when groundwater contamination causes a major municipal or commercial supply to be shut down, resources for groundwater quality management are always limited so that actions must be justified and prioritized. The bridge between characterization and mitigation or remediation lies in risk assessment. While this can involve sophisticated laboratory, epidemiological and modelling studies, often a great deal can be done quickly and cheaply using geographic information system (GIS) techniques and techniques and calculations by hand. GIS is particularly effective in locating the sensitive receptors that might be affected and in communicating this information to administrators and budget holders. GIS-based risk assessments also support the cost-effective design of monitoring programs.

Groundwater Quality Monitoring

Monitoring is the key to management, the measure of plans, the means by which status is determined, trends identified and the health of humans and the environment is protected. Groundwater quality monitoring is deceptively complicated, with opportunities for error at each step along the chain from identifying suitable wells through sampling to laboratory analysis and data processing. Despite these complications, senior managers do not need to know all the technicalities provided they exercise enough “interested skepticism” to know what hazardous chemicals are used in an area and are willing to ask the open-ended “how do you know?” questions like “is this is a representative sample?” and “is this well the right depth to intercept a plume?”. Many agencies follow now invalidated practices of which they may not even be aware. A few of the many issues are listed here:

- Many networks were created by adopting existing wells that may no longer represent the current groundwater environment. Networks require periodic review and upgrading.
- A monitoring well should measure water quality and level at a specific depth in an aquifer. Wells that mix water from different layers are not fit-for-purpose and should be replaced with multilevel piezometers.
- Obtaining a representative groundwater sample requires flushing (purging) of the water inside a well, so wells should be designed to minimize the time, cost and effort for this task.
- Sampling procedures must ensure appropriate filtration, preservation, and storage.
- Some parameters (for example, pH, temperature, and dissolved oxygen) are unstable and need to be measured in the field.
- With ever more complex and expensive analytical requirements, agencies should
  - Work closely with laboratories in the design of monitoring programs;
  - Consider outsourcing analysis, which can both save cost and resolve liability concerns over reliability; and
  - Provide better support and award higher status to staff who conduct monitoring.

To achieve the reforms needed, independent reviews of the adequacy of established practices should be commissioned periodically. The cost of such a review is negligible compared with a single misguided water management decision.

Remediation and Mitigation

For natural contamination, because there is no responsible person to be held accountable, public agencies will follow a mitigation approach to limit damage to health and the environment in the most cost-effective way. By contrast, for anthropogenic pollution, the responsible person should be required to restore the aquifer to its natural condition or at least a level of no significant risk.[5]

Mitigating natural contamination. For contaminants such as fluoride or arsenic, the absolute priority is to reduce human exposure. This is done through rapid surveys[6] and emergency water supply interventions, such as sharing safe water sources, domestic water treatment, and providing bottled water or water tanks with standpipes, and backed up by awareness raising and health education programs. Following closely behind should be programs of applied research, and monitoring of water sources and aquifers, leading to development of a long-term water supply plan and investment program.

Remediating anthropogenic pollution. Apart from agrochemicals and fecal pathogens, such pollution may be severe but usually much less extensive. The objectives will be to prevent contamination of drinking water sources and to restore the aquifer to a natural or “safe” state. Since around 1980, strict regulation in North America has driven the development of innovative investigation and remediation techniques. Two key lessons of these developments are that remediation should be (a) preceded by detailed (“smart”) characterization of the source area and (b) guided by quantitative risk assessment. Early remediation programs focused on “pump-and-treat” operations using conventional wells and industrial treatment systems. Often, this achieved encouraging early progress but was followed by rapidly diminishing returns on effort and investment. Consequently, new methods have been developed, such as in-situ treatment, where powerful reactants are injected into the source zone or where the contaminant plume is guided to flow through a permeable reactive barrier (figure ES.2). Such techniques are often combined with monitored natural attenuation (MNA) to complete the clean-up of low-level residual pollution.

Supporting Activities

Cost-effective groundwater quality management is facilitated by a proactive approach to curating data, establishing simple protection measures, and aligning institutional capacity.

Managing the Data

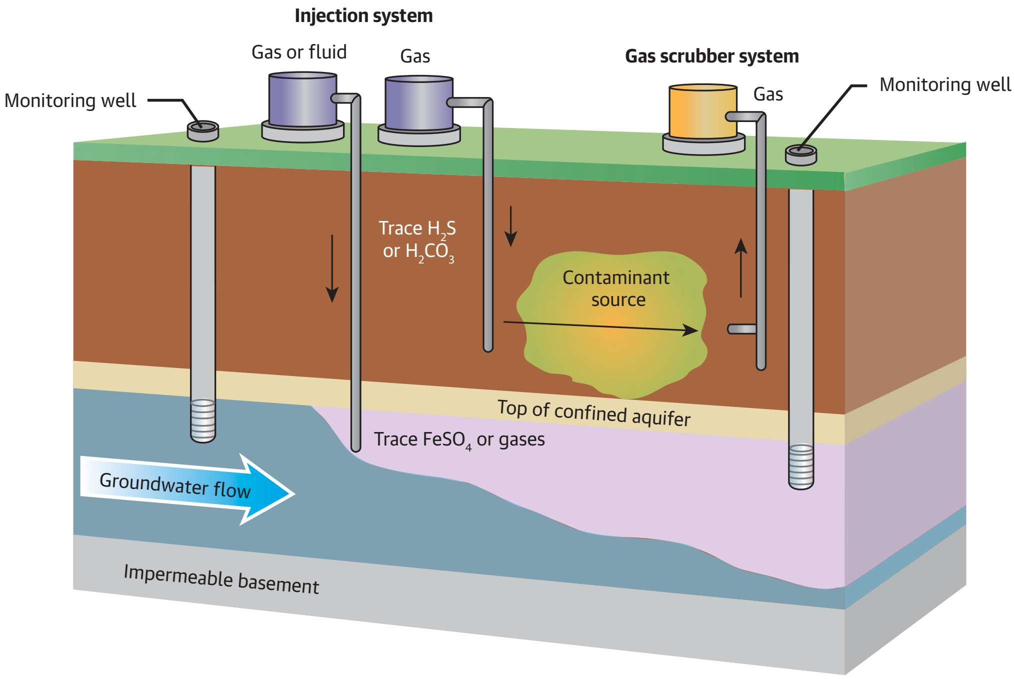
The study of groundwater quality is data intensive and requires high-quality information systems and processing and cross-cutting skills, including the forensic skills to identify “fake data,” which is much harder than with surface water. Good systems are required for each of four stages: (a) importing and collating the data, (b) verifying data, (c) analysing data, and (d) presenting and communicating. In the data analysis phase, both graphical-statistical and GIS tools are almost essential. Interest has been given to applying artificial intelligence (AI) and machine learning (ML) to water quality considering their influence in other sectors. This is to be welcomed but also treated with caution. These techniques cannot make up for fundamental deficiencies in the data, so the first step is to use these techniques to help clean up the data sets before proceeding to more ‘interesting’ and ambitious analyses.

Groundwater Protection—A “No-Brainer” Call to Action

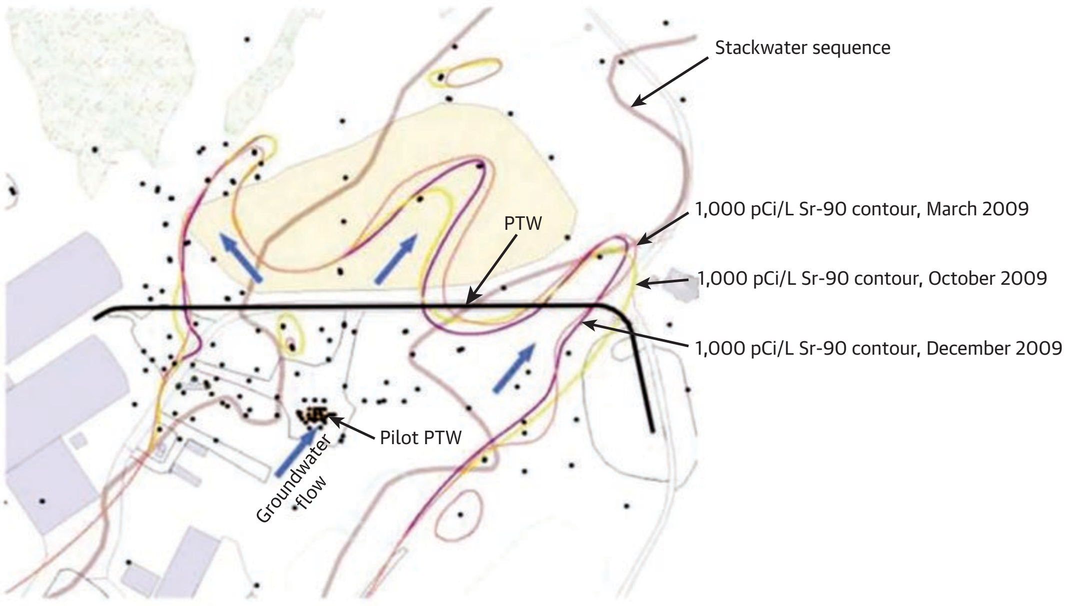
The best way to limit the damage from pollution is to stop it happening in the first place. The basic approach is to delineate source protection zones (SPZs) around abstraction points and link them to the planning process so that planners can identify where hazardous activities are prohibited or permitted only with special precautions. The cost of such measures is negligible compared with, say, having to replace a single public water source. Saving one major water source would probably pay for an entire protection program.

FIGURE ES.2. **Examples of Modern Remediation Systems**

a. In-situ injection



b. Permeable reactive barrier



Sources: (a) Adapted from Hashim et al. 2011; (b) adapted from Vandermeulen 2012.

Note: Panel b depicts the permeable treatment wall (PTW) location in relation to the site topography and groundwater plume location. $FeSO_4$ = iron sulphate; H_2CO_3 = carbonic acid; H_2S = hydrogen sulfide; pCi/L = picocuries per liter (a measure of radioactivity); Sr-90 = strontium-90.

Appropriate Institutions

Preventing and solving the problems of groundwater contamination can only happen when the right institutional and financing structure is in place. Many of the problems described are the result of systemic institutional failures, and reform of these institutions and their professional cultures will be required to solve them. The mandates and structures of responsible departments are often not aligned with the real state of groundwater quality issues, trapping agencies in a stasis in which necessary functions are either not performed or performed badly. Breaking out of this cycle requires parallel updating of legislation and departmental mandates, which will, in turn, define a program of formal institutional strengthening with regard to staffing, logistics, and finance and a commitment to accountability through public reporting and information sharing.

Notes

1. As featured in the 2000 movie *Erin Brockovich*.
2. This repeats a phenomenon observed in the southern United States in the 1930s where the arsenic resulted from excessive pesticide application and produced the same Straighthead Disease in the grains that do not ripen, and virtually all yield is lost.
3. Oxidizing conditions exist when dissolved oxygen or nitrate are present; reducing conditions exist when there is no dissolved oxygen, when there is solid organic matter, or when there are other indications of reducing conditions, such as dissolved manganese or iron.
4. This difference is apparent by comparing nitrate in the groundwater of eastern and western parts of the Indo-Gangetic Basin.
5. In practice, contamination from fertilizers and pathogens from domestic waste are so widespread, and the transaction costs too high, to apply the polluter pays principle, so a publicly financed mitigation approach is likely to be followed.
6. These surveys can be massive undertakings. In Bangladesh, for example, five million tests were conducted in three years—roughly three a minute 24/7.

Abbreviations

AI	artificial intelligence
ASR	aquifer storage and recovery
BTEX	benzene, toluene, ethylbenzene, and xylene
CEC	chemical of emerging concern
CHM	conceptual hydrogeological model
DDT	dichlorodiphenyltrichloroethane
DEET	N,N-diethyl-meta-toluamide
DNAPL	dense nonaqueous phase liquid
DRASTIC	depth-recharge-aquifer-soil-topography-impact-conductivity
DWSS	Department of Drinking Water Supply and Sanitation
EC	electrical conductivity (a proxy for salinity)
EM	electromagnetic
EU	European Union
FIB	fecal indicator bacterium
GAA	Guarani Aquifer Agreement
GAC	granulated activated carbon
GAS	Guarani Aquifer System
GEMS	Global Environmental Monitoring System
GFH	granular ferric hydroxide
GIS	geographic information system
GRACE	Gravity Recovery and Climate Environment
GWB	groundwater body
GWMU	groundwater management unit
LNAPL	light nonaqueous phase liquid
MAR	managed aquifer recharge
MCL	maximum concentration level, a legal definition used by the USEPA
MDG	Millennium Development Goal
ML	machine learning
MNA	monitored natural attenuation
MSP	multistakeholder partnership
NAPL	nonaqueous phase liquid
NGO	nongovernmental organization
O&M	operation and maintenance
PAH	polyaromatic hydrocarbon
PCE	per- or tetrachloroethene
PCP	personal care products
PFAS	perfluoroalkyl and polyfluoroalkyl substances

PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
pmC	percentage modern carbon
POP	persistent organic pollutant
PRB	permeable reactive barrier
P&T	pump and treat
PVC	polyvinyl chloride
QA	quality assurance
QRA	quantitative risk assessment
QHRA	quantitative health risk assessment
RBCA	risk based corrective action
RO	reverse osmosis
SDG	Sustainable Development Goal
SPR	source-pathway-receptor
SPZ	source protection zone
SVOC	semivolatile organic compound
TCE	trichloroethene
TDS	total dissolved solids
USEPA	United States Environmental Protection Agency
VOC	volatile organic compound
WASH	water supply, sanitation, and hygiene
WFD	Water Framework Directive
WHO	World Health Organization

Definitions

Groundwater. All water below the surface of the Earth.

Aquifer. We apply a loose definition, referring to saturated geological strata (rocks or sediments) of sufficient permeability to allow significant quantities of groundwater abstraction.

Basement aquifer. Known as bedrock in the United States, this term applies to aquifers formed of ancient rocks, typically of Precambrian age and granitic composition, that develop significant porosity and permeability, where they have been intensely weathered for tens of thousands or hundreds of thousands, even millions, of years. They are particularly common and important in Sub-Saharan Africa, South America, and Peninsular India.

Groundwater body. We use this term for distinct or delineated volumes or zones of groundwater within recognized aquifers, equivalent to the European Union's Water Framework Directive (WFD) definition of "a distinct volume of groundwater within an aquifer or system of aquifers, which is hydraulically isolated from nearby groundwater bodies." A groundwater body can also be considered as a groundwater management unit (GWMU).

Contamination and pollution. These terms are often, but wrongly, used synonymously. All pollutants are contaminants, but not all contaminants are pollutants. Contamination is simply the presence of a substance where it should not be or at concentrations above background. Pollution is contamination that can result in adverse biological effects (Chapman 2007).

Chemical Concentration Units

g/L = ppt	grams per liter or parts per thousand. This unit is only rarely used for groundwater and almost always for highly saline water.
mg/L = ppm	milligrams per liter or parts per million. These abbreviations are practically synonymous, except very saline waters, and the most commonly encountered units for the major ions (calcium (Ca), magnesium (Mg), chloride (Cl), sulphate (SO_4), and so on) encountered in groundwater.
µg/L = ppb	micrograms per liter or parts per billion. These units are commonly used for trace elements and synthetic organic compounds.
ng/L = ppt	nanograms per liter or parts per trillion. These are used for some synthetic organic compounds that are significant at very low concentrations like pesticides and per- and poly-fluoroalkyl substances (PFAS). Note the abbreviation ppt is used for parts per trillion and parts per thousand; however, the context should make the meaning obvious because salinity would never be measured at nanogram level, and g/L of, say, a pesticide would represent pure product.
µS/cm	microsiemens per centimeter. These are units of electrical conductivity (EC), which is a common measurement and a proxy for salinity and total dissolved solids (TDS). When EC exceeds about 1,000 to 2,000 µS/cm, it has an approximately linear relation to TDS.

Chapter 1
Introduction

In many countries, groundwater is the principal source of water for drinking, irrigation, and industry.[1] In addition to the autonomy it grants users, one of the great attractions of groundwater as a source of supply is its perceived superior quality. Although most groundwater in its natural state is of excellent quality, this is not universally true, and it is increasingly affected or threatened by pollution from human activities (box 1.1). In many parts of the world, groundwater resources are being depleted and degraded, threatening society's ability to provide the water needed for drinking, agriculture, industry, and the environment, and highlighting the importance of protecting the quality of what remains. This report explains why groundwater quality is so important and what, at a strategic level, needs to be done to manage it. This chapter provides a context for what follows.

BOX 1.1. Some Major Groundwater Quality Issues

- The combination of self-supply from shallow wells and onsite sanitation risks fecal pathogens contaminating the drinking water of many hundreds of millions of poor people worldwide.
- Saline intrusion threatens the sustainability of water supplies of coastal communities globally, especially in the densely populated Asian mega-deltas.
- Naturally occurring arsenic has affected the drinking water of the order of 150 million people in more than seventy countries, including a quarter of the population of Bangladesh, and is also a threat to the sustainability of irrigated rice production.
- Naturally occurring fluoride puts about 200 million people worldwide at risk of developing crippling fluorosis.
- The drive to increase food production has polluted many shallow aquifers with nitrate from fertilizers and pesticides. In dry areas, these impacts have been aggravated by naturally present salinity and that induced by poor land and water management practices.
- Many urban aquifers in industrialized countries have been blighted by a century or more of mismanagement of petroleum hydrocarbons, chlorinated solvents, pesticides, and improper waste disposal. This pattern is being repeated in low- and middle-income countries.
- The legacy of industrial and agricultural pollution is resulting in enormous economic costs in groundwater remediation and in water treatment at municipal and private supplies.
- Within the past two decades, new classes of emerging contaminants, toxic at nanogram levels and resistant to remediation, are being discovered to have contaminated groundwater widely, the global extent of which is largely unknown.

Background

The quality of groundwater is important for many reasons, most notably because of its effects on human health and agriculture, its huge economic impact, and its role in water resilience and resisting the effects of climate change (see chapter 2).

Detecting and managing groundwater contaminants requires a different approach to that for surface water. In surface waters, pollution is tangible—offending the eyes, nose, and sense of touch—and immediately affecting our aesthetic and recreational appreciation of it. Surface water pollution can occur rather quickly and be extreme, but it is largely reversible once the contaminant source is removed. Groundwater pollution has almost opposite characteristics. Groundwater is unseen and mysterious; it is intrinsically protected (for example, by soil); its pollution happens slowly but with no less serious consequences; and once damaged, it takes far, far longer to recover. This report deliberately focuses on groundwater contamination—why it deserves attention (see example in box 1.2), how and where to measure it, approaches to managing it, and how to prioritize that effort.

In a world where hundreds of millions of wells service basic needs for drinking water, food production, and industry, it is a near universal experience that top-down management of groundwater does not work (for example, Alley and Alley 2017). This is because most wells are privately owned, which confers a sense of ownership in the resource and the infrastructure that is guarded so passionately. Groundwater management demands the active participation of stakeholders and takes patience, persistence, and good will to build a consensus for collective action. Too often when plans are handed down, they fail to connect with the interests of water users—this is where groundwater monitoring data show their value, placing water resources managers at the center of a dialogue to construct a coherent explanation of the

BOX 1.2. Groundwater Quality More Important Than Depletion in the Indo-Gangetic Basin

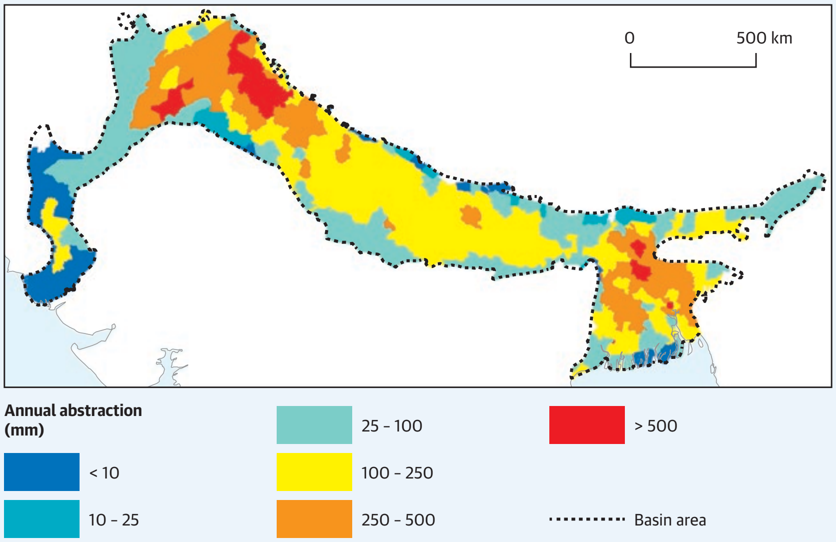
India, Pakistan, and Bangladesh are among the world's largest groundwater abstractors. Together with Nepal they abstract groundwater from the Indo-Gangetic Basin (IGB) which is drained by the Indus, Ganges, and Brahmaputra rivers and supports a population of about 900 million. Much attention has rightly been given to groundwater depletion in the IGB, especially in northwest India and adjoining areas of Pakistan, based on observations from the Gravity Recovery and Climate Environment (GRACE) satellite (Rodel, Velicogna, and Famigletti 2009). The IGB aquifer system is also affected by widespread occurrences of groundwater salinity and natural arsenic (map B1.2.1). Hence, the conclusions of a major review of the entire IGB alluvial system by MacDonald et al. (2016) are particularly relevant. They state, "we report new evidence from high-resolution in situ records of groundwater levels, abstraction and groundwater quality, which reveal that sustainable groundwater supplies are constrained more by extensive contamination than depletion."

box continues next page

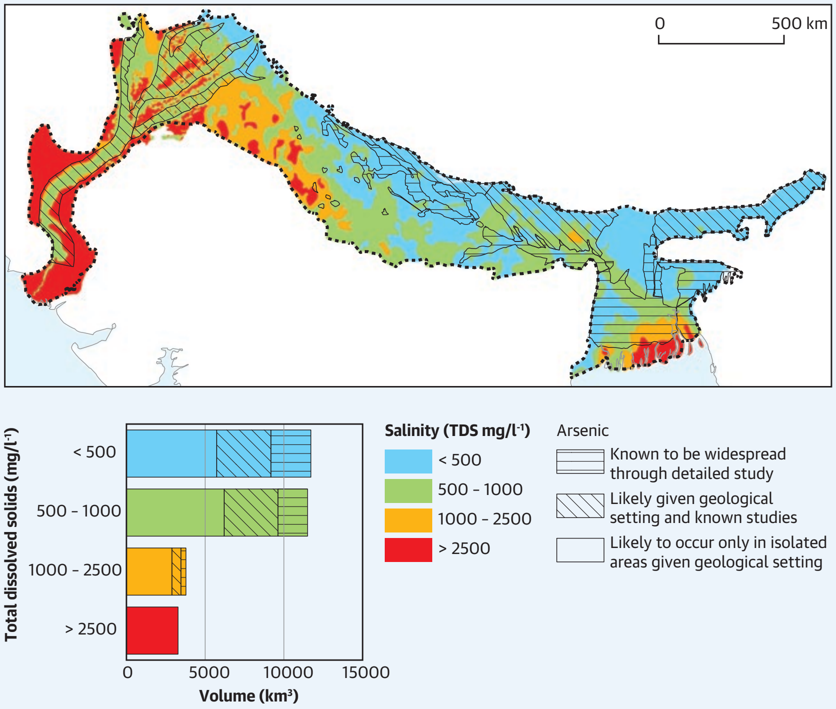
BOX 1.2. continued

MAP B1.2.1. Groundwater Abstraction and Quality in the Indo-Gangetic Basin

a. Abstraction from the IGB Aquifer System



b. Groundwater quality in the IGB Aquifer System



Source: Adapted with permission from Springer Nature: *Nature Geoscience* "Groundwater Quality and Depletion in the Indo-Gangetic Basin Mapped from In Situ Observations," MacDonald et al. © 2016.
Note: TDS = total dissolved solids.

problems experienced by different stakeholders—and to respond to their questions until there is a consensus on the causes and consequences of current actions and proposals. When agreement is reached and a plan agreed and funded, monitoring data can chart the way out of the crisis.

Purpose and Readership

The World Bank publication *Quality Unknown* (Damania et al. 2019) broadened awareness of the importance of water quality, especially economically, focusing on a small but representative range of contaminants: arsenic, nitrate, salinity, microplastics, and pharmaceuticals. This document builds on *Quality Unknown* to meet a widely felt need for an accessible but strategic guide to groundwater quality that explains why it matters and provides nonspecialists sufficient understanding to plan and coordinate cross-cutting water programs, to anticipate the "unexpected" and to engage effectively in developing integrated solutions to water problems. A companion manual expands on how to put such programs into practice.

This report is aimed primarily at managers and budget holders and more generally to enable World Bank staff to understand key groundwater quality topics and the practices required in the operational departments of borrowing institutions, as well as to guide them and their counterpart agencies in understanding essentials of groundwater quality monitoring as the key to management and to support them in making sound investment decisions. The reader should be able to manage programs that include groundwater quality investigations or the design and operation of a monitoring program without knowing all the technicalities by asking the right questions. Because it is in the nature of groundwater quality to change over months to decades, it is ideally suited to adaptive management based on verified and intelligently presented monitoring data to facilitate a consensus for action among stakeholders.

Although it will serve managers in the broadest sense, this report is specifically aimed at team leaders in the World Bank, heads of resource agencies who have responsibility for groundwater quality, and program managers in development agencies, nongovernmental organizations (NGOs), and water utilities. It may also help groundwater scientists to explain their work to nonspecialist managers.

Although this guide cannot cover all the possible contamination scenarios, it attempts to cover the major categories of groundwater quality issues and aims to equip the reader to ask the right questions even when faced with problems that go beyond its direct scope.

The Importance of Groundwater Quality

There are many reasons why groundwater quality matters. Quality determines suitability for drinking and other purposes. The persistent myth that groundwater can be used everywhere without treatment is central to many countries' aspirations for achieving SDG 6.1[2] yet is not a sound assumption (see box 1.3) because natural contamination is more prevalent than commonly believed, as is increasing anthropogenic pollution. In China and Bangladesh, for instance, surveys found that more than half of groundwater samples were chemically unfit for most uses without treatment, albeit that safe groundwater was

BOX 1.3. Downplaying Groundwater Quality in the MDGs and SDGs

The Millennium Development Goal (MDG) target to "halve the proportion of people without access to safe drinking water" was met in 2010, five years ahead of schedule. Although a remarkable achievement, it was recognized as a likely overestimate since the definition of "safe" was "improved sources of water" such as a piped source or a "protected well" and did not include specific objectives relating to water quality.

Groundwater quality features prominently in two SDG targets: 6.1 (drinking water) and 6.3 (ambient water quality). Target 6.1— "achieve universal and equitable access to safe and affordable drinking water for all" — appeared to address the earlier (MDG) shortcoming. However, indicator 6.1.1 — "the proportion of population using safely managed drinking water services"—focuses on the management, not safety, of water. Even though the supporting notes require the source to be "free of fecal and priority chemical contamination," this is defined as an absence of *E. coli* (in a 100-mL sample) and arsenic and fluoride below drinking water standards. Hence, achieving SDG 6.1 will be further progress, but it will not mean "safe water for all."

Target 6.3 sets out to improve ambient water quality, without regard to its use, by reducing pollution and has an indicator 6.3.2— "the proportion of water bodies with good ambient water quality." This is discussed further in chapter 4 (box 4.2).

available at many locations, even if users were unaware or unable to access it (BBS/UNICEF 2011; Zheng and Liu 2013).[3]

Why Is Groundwater Quality Neglected?

Despite its self-evident importance as a source of supply, groundwater is routinely neglected by many water resources professionals, which is an obvious obstacle to good water resources management (see box 1.4). There are several explanations. First, without an education in geology, people tend to distrust what they cannot see. They find it difficult to sense how much water is available, let alone how its quality varies with location and depth. For many, aquifers and aquitards are challenging to conceptualize. Second, water resources management is too often compartmentalized with engineers managing rivers, canals, dikes, and dams; geologists managing groundwater; and chemists and microbiologists analyzing water in laboratories. Third, most water resources managers and administrators tend to lack expertise in groundwater and have limited connection with the private sector and utility stakeholders who are the main groundwater users and have little representation in planning and decision making.

Addressing these structural biases requires building a new professional culture through academic and in-service training, job rotation, and recognition of breadth of experience as a criterion for promotion. The skill sets of water resource managers should mirror the water economy they work in and the voices of water users, many or most of whom are outside the public sector.

BOX 1.4. Groundwater Quality and Resource Estimation

The widespread practice of assessing groundwater availability purely in terms of volumes and flows is virtually meaningless without reference to its quality. To be useful, available groundwater quantities must be classified in terms of water quality that can be evaluated against treatment costs or lower value uses, which may or may not be economically viable. When remediation or treatment is not feasible, it can result in what has been called pollution-induced water stress.

Although not always shown in standard diagrams, the evolution of groundwater quality is a vital part of the hydrological cycle and a source for present and future supplies; its study helps to quantify recharge and understand the resilience and sustainability of the resource. For example, it can answer questions such as, "Will artificial recharge react with the aquifer and mobilize contaminants?" "What will happen if groundwater is mixed with other waters at the surface?" or "Will pollutants be attenuated as they migrate through the subsurface?" Also, groundwater chemistry contains a memory of climate history, and the great groundwater reservoirs provide a buffer against climate change. In all these situations, understanding natural groundwater quality is key to understanding how it will respond to human influence.

For historical reasons, with the exception of mineral waters, the expansion of groundwater exploitation was driven by the search for quantity, responding to shortages of surface water, waterlogging, falling groundwater levels, and advances in pumping and irrigation[4] technologies. Although this oversight is slowly becoming apparent, with the exception of the unmissable effects of salinity, groundwater quality issues were largely neglected. Consequently, many major groundwater-extracting countries have a high awareness of overabstraction but much less of quality issues. Even less is there an attempt to see a connection between the two.

Economics of Groundwater Pollution and Its Irreversibility

During the early stages in the economic development of an area and given a suitable geology, groundwater is typically quick, cheap, and easy to develop with low treatment requirements. It solves many of the immediate problems with onsite surface water; however, with continued growth, the pollution that ruined local surface water sources finds its way into groundwater. Early industrializers may attribute these to the ignorance of previous generations, whereas some rapidly industrializing countries appeal to a form of historical injustice to claim the right to "pollute and grow now and clean up later." This is a false dichotomy because the economic costs of polluted groundwater are staggering (chapter 2). The critical message from history is that economic growth and the avoidance of pollution are not mutually exclusive. Groundwater quality protection is technically simple and cheap but takes political will and contributes to sustainable and lower-cost development. Even when the political will exists and the regulations are in place, these cannot guarantee the clean-up of an aquifer. Lessons should be learned from what Siegel (2014) calls "the dismal history of clean-up success" in the United States, where the National Research Council (NAP 2013) has documented decades of failed attempts to clean up Superfund sites, urging "caution and humility in the face of subsurface heterogeneity." Siegel's review recognizes that contamination, such as petroleum fuels in water table aquifers, can be cleaned up but others, such as solvents, some other organic pollutants, and radioactive waste, are "profoundly difficult" and can be practically impossible to restore such that the resource is permanently blighted.

Organization of the Report

The report begins (chapter 2) with an overview of the importance of groundwater quality and why it requires to be managed differently from surface water quality. Notwithstanding its normally excellent quality, this report focuses on where groundwater is, or could be, contaminated, and chapter 3 summarizes the most important types of natural and anthropogenic contaminants. Chapter 4 then describes the procedures used to understand, evaluate, and develop solutions for a groundwater quality problem and is followed (chapter 5) by an overview of monitoring as the key to managing groundwater quality problems.

The final part of the report introduces the methods for mitigating and remediating polluted groundwater (chapter 6) and institutional aspects of groundwater quality management, both its legal and much underappreciated personnel dimensions (chapter 7). Few resources better exemplify the adage that prevention is better than cure, so the report concludes with a brief account of the policies and practices for groundwater protection (chapter 8).

This report is accompanied by a practical manual, which builds on the present account of why groundwater quality is so important. It emphasizes the essential role of monitoring in managing groundwater quality. Changes in technology and advances in understanding are transforming monitoring, and managers need to be aware of these changes and their implications, which will require reforming many long-established practices. The manual will help managers in collaborating with diverse experts to conserve resources and release the potential of groundwater to deliver sustainable economic growth and protect the health of humans and the environment.

Notes

1. See, for example, the São Paulo-Brussels Groundwater Declaration at https://iah.org/news/make-a-difference-in-groundwater (accessed February 8, 2021).
2. A reference to the United Nations Secretary General. For example, see https://www.theguardian.com/global-development/2012/mar/06/water-millennium-development-goals (accessed February 8, 2021).
3. For more about pollution-induced water stress, see https://www.circleofblue.org/ (accessed January 27, 2021).
4. Such as the center-pivot system in the 1950s.

Chapter 2

Why Groundwater Quality Matters

Key Points

- The quality of groundwater determines whether it is useful.
- Groundwater quality massively affects health, food production, and the economy.
- The more you look, the more you find. More testing is finding more natural and anthropogenic pollution.
- Today's limits are tomorrow's toxic concentrations. More knowledge often leads to more stringent drinking water and environmental guidelines, so water classified as safe today may not be in the future.
- The challenge and cost of cleaning up polluted groundwater is far greater than protecting it in the first place.

This chapter provides a high-level summary of why groundwater quality is so important in terms of its impact on human health, agriculture, and the environment and the economic impact of neglecting to protect this vital resource.

Groundwater Quality and Health

Most groundwater sources supply water that is inherently[1] safe compared with surface water sources when consumed without treatment and so has a positive impact on health. Nevertheless, because of natural and anthropogenic contamination, hundreds of millions of people drink water that is contaminated by toxic chemicals. In addition, many more—mostly the rural poor—consume untreated groundwater, which, by the time it is consumed, is contaminated by fecal pathogens. Groundwater also influences health through its use in cooking and food processing and by consumption of irrigated crops. The following sections illustrate how some of the most important contaminants affect health.

Natural Contaminants

As Paracelsus (photo 2.1) stated in the sixteenth century, it is the dose that makes the poison; hence any constituent in excess can be harmful. In practice, there is a relatively short list of naturally occurring elements that cause widespread concern for public health or give rise to objections from users (box 2.1). A historical irony that partially explains the delayed discovery of geogenic pollution worldwide is that much of public health practice developed in Western Europe, where geogenic pollution is relatively rare, so colonial-legacy institutions did not look for what they did not expect.

In terms of effects on global health, two contaminants—arsenic and fluoride—outweigh all others. The most common, however, are iron and manganese, which give rise to nuisances and, in the case of manganese, health issues. Occasionally natural groundwaters contain significant concentrations of barium, cadmium, chromium, lead, nickel, selenium, and uranium, all of which are hazardous to health. As more testing is done, these are proving to be more common than previously thought, and not all countries and regions have conducted adequate baseline surveys.

Health Effects of Arsenic in Groundwater

Arsenic, a favorite poison of historical murderers, is also the world's most important natural groundwater contaminant, yet until the 1990s, it was given little attention outside a few disparate locations like western Argentina, Chile, Hungary, and Taiwan, China. It is now recognized that arsenic poisoning from groundwater has affected more than 150 million people in more than seventy countries, with a huge toll of mortality and morbidity (Ravenscroft, Brammer, and Richards 2009). The World Health Organization (WHO), European Union (EU), and United States Environmental Protection Agency (USEPA) guidelines for arsenic are all 10 ppb, but some affected countries still apply a drinking water standard of 50 ppb, which is no longer considered to be protective of health.

Long-term exposure to arsenic has a bewildering array of adverse health effects. Most characteristic are the painful and disfiguring skin conditions melanosis, keratosis, and hyperkeratosis, typically found on the palms of the hands and soles of the feet. These semidiagnostic conditions are sometimes wrongly thought to be synonymous with the effects of arsenic poisoning, but epidemiological studies have identified even more serious effects, such as liver and kidney disease, gangrene, potentially fatal heart and lung disease, and cancers of the skin, lung, bladder, kidney, and liver. The majority of cancer deaths are not preceded by classic skin conditions (Ahsan and Steinmaus 2013; Hassan, Atkins, and Dunn 2005; Smith et al. 2006; Wasserman et al. 2004).

PHOTO 2.1. Portrait of Paracelsus, the Sixteenth-Century Swiss Physician Born Theophrastus von Hohenheim

Source: https://commons.wikimedia.org/wiki/File:Paracelsus.jpg.

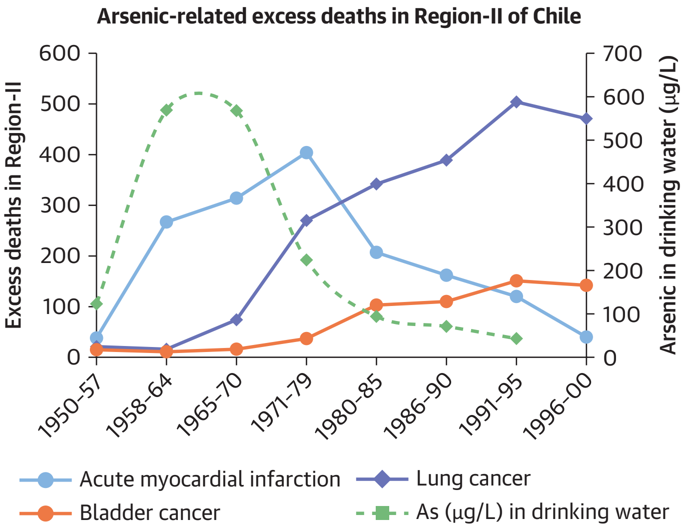
BOX 2.1. Aesthetics Affect Health

Aesthetic (or organoleptic) aspects, such as taste, odor, and color, are routinely treated as secondary. However, health and aesthetics are closely connected because, as has been shown many times, if the aesthetic aspects are ignored, people are liable to revert to drinking from unsafe sources, such as a microbially polluted surface water source.

Attributing an individual death to arsenic ingestion is difficult. Epidemiologists draw such conclusions at the population level, and based on global data, arsenic is likely to have caused millions of deaths since the 1980s.[2] Arsenic exposure affects neonatal health, impairs the intellectual development of children, and even causes fatalities in young adults from exposure in utero. Arsenic poisoning also has serious socioeconomic effects. Parents who are sick and without other support may withdraw children from school to work. People with skin lesions—even whole families with a single affected member—may be ostracized; women become unmarriageable or forcibly divorced; and children may be withdrawn from school to conceal their condition.

A characteristic feature of chronic arsenic poisoning is its latency. Skin conditions typically take two to five years to develop. Mortality from cancers and heart disease can peak years or decades after exposure has stopped, as shown in landmark studies in northern Chile (figure 2.1), which demonstrate the future health burdens facing countries that are currently struggling to control exposure. From 1958, the rapidly growing city of Antofagasta, located in a coastal desert, commissioned a conventional treatment plant on a river fed by a hot spring in the Andes. This plant supplied almost the whole city with drinking water, but unknown to the residents, it contained about 800 ppb of arsenic. During the 1960s, visible symptoms of arsenic poisoning became apparent and the cause identified; in 1971, an arsenic removal plant was commissioned, which reduced the arsenic concentration in the city supply initially to less than 100 ppb and later to less than 10 ppb. Unfortunately, this was not the end of the city's health woes. Although the incidence of visible symptoms like skin conditions reduced, a long-term retrospective analysis showed that the numbers of excess deaths from heart attacks and lung and bladder cancer, in

FIGURE 2.1. Latency of Arsenic-Induced Fatal Disease at Antofagasta, Chile



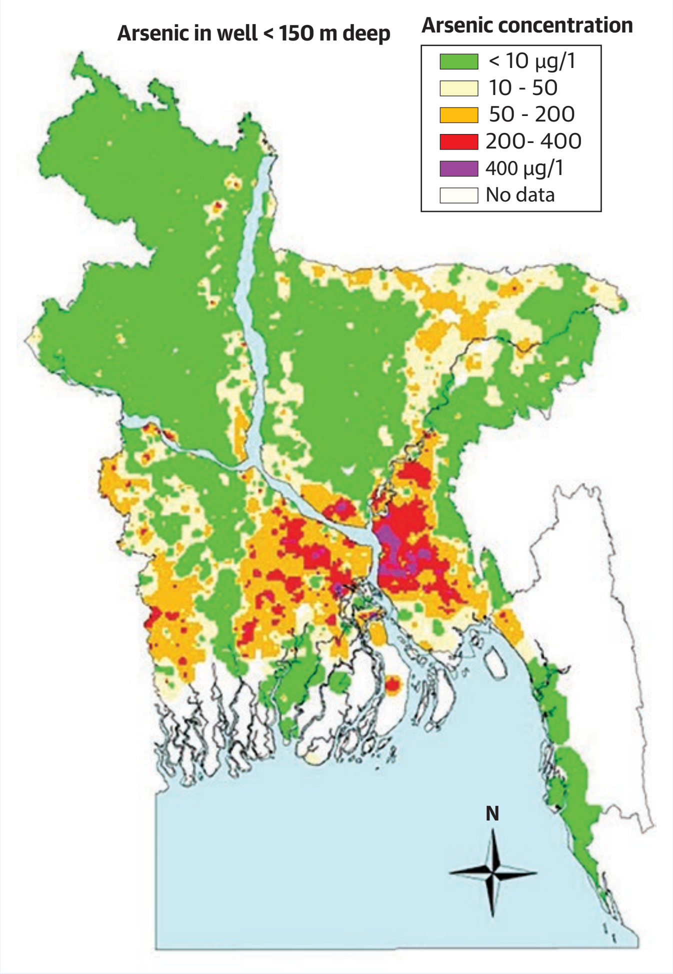
Source: After Yuan et al. 2007.

Note: From 1958 to 1970, the entire town consumed drinking water containing around 800 ppb of arsenic until an arsenic removal plant was installed in 1971. However, excess deaths increased for decades after exposure ceased.

BOX 2.2. Arsenic in Bangladesh

The most extreme case of arsenic poisoning is in Bangladesh. Although unknown until 1995, it was declared the "world's worst case of mass chemical poisoning" by the World Health Organization (WHO) in 2000 (Smith et al. 2000). The first national survey completed in 1999 estimated that 35 million people were exposed to drinking water exceeding the national standard of 50 ppb and about 40 percent of the population were consuming water with more than the 10 ppb WHO guideline. The additional exposure from consumption of groundwater-irrigated rice remains unknown. Maps like map B2.2.1 give general impressions of safety and danger but also demonstrate the limitations of two-dimensional representations of groundwater quality; even where the probability of a shallow well being severely contaminated is more than 90 percent, manually drilled wells, costing less than US$1,000, can be installed in aquifers below 200 meters with more than 95 percent probability of extracting safe water.

MAP B2.2.1. **Most Probable Concentration of Arsenic in Wells Less Than 150 Meters Deep in Bangladesh**



Source: Authors, using data from British Geological Survey (BGS) and Department of Public Health Engineering (DPHE) National Hydrochemical Survey, available at https://www2.bgs.ac.uk/groundwater/health/arsenic/Bangladesh/data.html(accessed March 8, 2021).

men and women, attributable to earlier arsenic poisoning continued to increase for three decades after exposure ceased (Yuan et al. 2007). A summary of the arsenic situation in Bangladesh is provided in box 2.2.

Health Effects of Fluoride in Groundwater

Fluoride is second only to arsenic in its global extent and the severity of its health effects, and it is estimated that about 200 million people are at risk of fluorosis. The maximum acceptable concentration for fluoride in most countries is 1.5 mg/L. Unlike arsenic, which has no known beneficial level of intake, at low concentrations (optimally between 0.7 and 1.2 mg/L) fluoride is beneficial to teeth. Yet higher levels of flouride exposure result in skeletal fluorosis, resulting in painful and crippling swelling and distortion of bones and joints, leaving adults unable to work. Fluoride exposure in children under the age of about 8 years may lead to dental fluorosis but not from exposure at a greater age (EAWAG 2015).

Manganese and the Impaired Intellectual Development of Children

Manganese is a common constituent of groundwater, gives rise to taste and odor issues, and adversely affects health. The WHO long ago defined health-related and aesthetic guidelines of 0.4 and 0.1 mg/L, respectively. Because the aesthetic guideline is lower than the health guideline, water utilities have long acted to avoid complaints and in the process ensured safety. However, in private supplies and resource monitoring, manganese has been widely overlooked, and it is present at high concentrations in domestic well water consumed by many tens of millions of people. The consequences of this neglect have become tragically apparent. In 2006, it was discovered that manganese significantly impairs the intellectual development of children. However, awareness remains low, and some countries still do not routinely test for it (for example, Bouchard et al. 2011; Khan et al. 2012; Wasserman et al. 2006). In 2011, the WHO removed manganese from its drinking water guidelines on the basis that high concentrations are rare and would not be consumed. The economic impact of impaired intellectual development on tens of millions of poor rural children is enormous.

Uranium and Radon in Groundwater

Uranium may be the most significant emerging natural contaminant, affecting large areas of India and China, among others, and is also associated with industrial and mining operations (Sahoo et al. 2021; Guo et al. 2018). Uranium is radiologically and chemically toxic, and notwithstanding considerable uncertainty, the WHO, EU, and USEPA have set guideline values of 30 ppb. There is an association with a small increase in bone cancer risk, but the main effect is chemical damage to the kidneys. In many countries, uranium is not routinely tested for, so the full extent of the problem is yet to be determined. Radon gas is formed by the decay of uranium, so the same areas are liable to have high radon dissolved in water and possibly also household air, with a consequent risk of lung cancer (Yang et al. 2014).

Anthropogenic Contaminants

The range of contaminants that may enter groundwater as a result of human action is almost incredibly diverse, and this is illustrated here by reference to just a few of the many possible categories.

Nitrate and Pesticides

Nitrate fertilizers and pesticides lay at the center of increased global food production in the Green Revolution, but this comes with environmental costs. In addition to a modest natural background, huge quantities of nitrate enter groundwater worldwide from fertilizer, human and animal waste, and ploughing up grassland. Nitrate in drinking water has long been recognized as harmful, being associated with blue baby syndrome (methemoglobinemia), which is the basis of the WHO health-related guideline for nitrate of 50 mg/L (measured as NO_3).[3] Studies since 2005 have reported that there is good evidence of increased risks of colorectal cancer, thyroid disease, and neural tube defects, possibly at below the current regulatory limit (Ward et al. 2018). In addition, *Quality Unknown* (Damania et al. 2019) used indirect evidence from large data sets to identify an association with stunting in children and reduced economic output in adults. Often used together with fertilizers, pesticides are by their nature toxic—many are known or suspected carcinogens and endocrine-disrupting chemicals, and some are highly persistent.

The Emerging Threat of PFAS Compounds

Perhaps the most significant group of emerging groundwater pollutants are the per- and poly-fluoroalkyl substances (PFAS), of which the most important are perfluoro-octane sulfonate (PFOS) and perfluorooctanoate (PFOA). PFAS comprise a group of 3,500 industrial chemicals used as flame retardants, stain protectors, water repellents for nonstick surfaces like Teflon, and in tannery wastes. They are highly toxic, persistent, mobile, and bioaccumulating and nicknamed the “forever chemicals.” Epidemiological studies[4] have linked exposure to PFAS to developmental effects in fetuses and breastfed infants, testicular and kidney cancer, liver damage, immune and thyroid effects, and other cholesterol changes. Awareness of their significance has mushroomed in the past decade to the point that they are claimed to be a “groundwater emergency” in the U.S. state of Michigan (map 2.1), where it was reported that 1.8 million people consume measurable levels of PFAS in municipal supplies. The financial cost of such contamination is also proving to be massive. For example, in 2018, the state of Minnesota reached a court settlement of US$850 million with the 3M Corporation after originally seeking US$5 billion in punitive damages (Bjorhus 2021). In many areas of the world, groundwater has not been tested for PFAS.

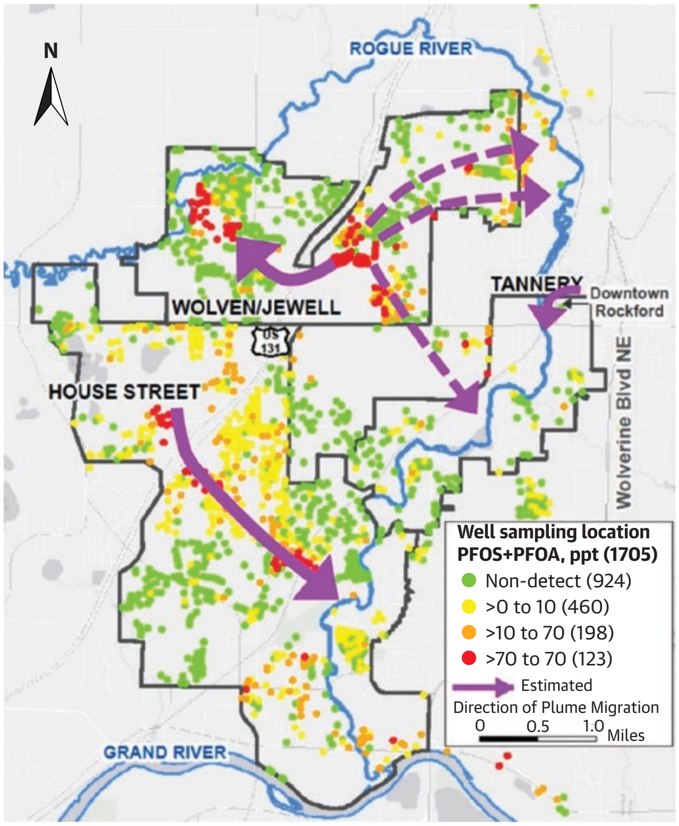
Other Emerging Threats: 1,4-Dioxane

The volatile compound 1,4-Dioxane is widely used as a stabilizer for solvents and in personal care products, detergents, electronics, fibers, and pharmaceuticals. It is a suspected carcinogen and damages the liver and kidney. In countries where it has been monitored, such as the United States (map 2.2), 1,4-Dioxane is emerging as a major issue with exceedances of the 0.35 μg/L health advisory level across much of the country. Many areas of the world have not been tested for 1,4-Dioxane.

Fecal Pathogens and Groundwater Supplies

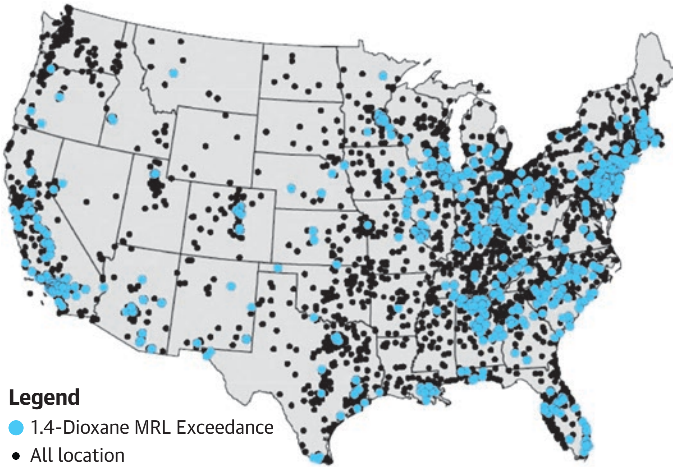
A huge proportion of the world’s rural and periurban poor obtain their drinking water from shallow handpumped wells, and many of these populations rely on onsite sanitation. Although the mechanism of contamination remains a matter of contention (see chapter 3), it is a fact that a high percentage, typically 30 to 50 percent, of water collected from these wells contain fecal indicator bacteria, such as *E. coli* or fecal coliforms, and that these communities experience a high prevalence of diarrheal disease.

MAP 2.1. PFAS Contamination Sites in Michigan



Source: USEPA 2018.

MAP 2.2. Occurrences of 1,4-Dioxane in Groundwater in the United States



Source: USEPA 2015.
Note: 1,4-Dioxane public water supply sampling results from USEPA unregulated contaminant monitoring rule 3. MRL = minimal risk level.

Indicator bacteria are the working tool of water managers because they are abundant and measurement techniques are well established, but they are generally not what causes disease. Viruses are particularly likely to cause illness and are more mobile and persistent than bacteria. According to a review of 649 groundwater-related outbreaks between 1948 and 2013, the most important pathogens are Norovirus, Campylobacter, Shigella, Hepatitis A, and Giardia (Murphy et al. 2017). Although most attention is given to human waste, animal wastes can also be sources of pathogens, such as Cryptosporidium.

Groundwater Quality and Agriculture

The interactions between groundwater quality and agriculture are complex. Some aspects of groundwater quality can harm agriculture, and some agricultural practices can harm groundwater quality. The former occurs through groundwater irrigation and depends on the specific crops and water quality parameters. Two effects are important: phytotoxicity (for example, salinity, arsenic, boron, and selenium) and bioaccumulation (for example, arsenic, selenium, and heavy metals). The first affects farmer's productivity and the second affects health. The impacts of agriculture on groundwater quality fall into three main categories: fertilizer (for example, nitrate and phosphate), pesticides, and livestock (for example, nitrate and pathogens).

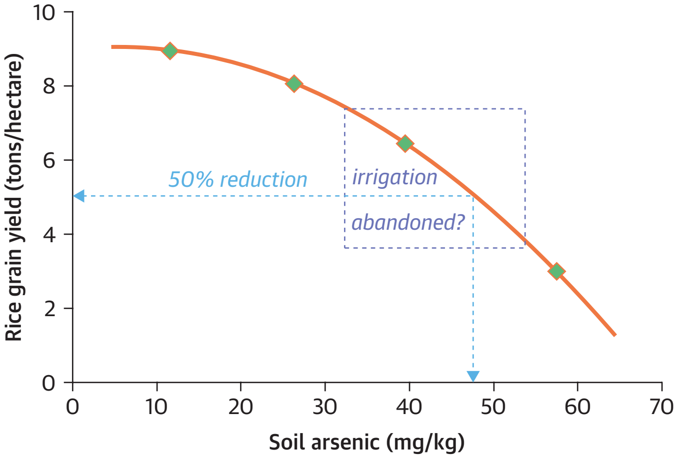
Groundwater Salinity and Agriculture

Salinity is an issue for agriculture in two main settings. First, groundwater may be naturally saline in coastal areas, which is a constraint that must be mitigated at the local scale through crop selection and good drainage and at the regional scale by preventing overpumping that leads to salinization of irrigation wells. Second, in many low-lying arid and semiarid areas, the combination of irrigation and inadequate drainage has raised the water table to within a few meters of the ground surface, where capillary rise and evapotranspiration act to both concentrate the shallow groundwater and deposit salts in the soil zone, with sometimes devasting economic impacts as witnessed in the rise and fall of civilizations over millennia (for example, chapter 2 in Zaman, Shahid, and Lee 2018). Because of the connection between salinization and high water tables, groundwater quality and soil salinity are two sides of the same coin and affect many parts of the world, including the Aral Sea Basin, the Indo-Gangetic Basin in India and Pakistan, the Yellow River Basin in China, the Tigris and Euphrates Basins in Syria and Iraq, the Murray-Darling Basin in Australia, and the San Joaquin Valley in the United States. Although less extensive, groundwater salinity problems also arise from ancient seawater trapped deep below ground and from dissolution of rock salt deposits.

Arsenic and Groundwater Irrigation

Arsenic in groundwater poses a major problem when used to irrigate rice because it is phytotoxic and accumulates in rice more than any other major crop (Heikens, Panaullah, and Meharg 2007; Sambu and Wilson 2008). Vast swaths of paddy rice in Asia are irrigated with iron- and arsenic-rich tubewell water, in which the arsenic accumulates in the soil year on year, gradually transferring more and more arsenic to the rice plant. This enters the edible grain, and its phytotoxicity eventually leads to total loss of yield (Duxbury and Panaullah 2007; Huhmann et al. 2017; see figure 2.2), both threatening the sustainability of agriculture and poisoning whole populations through the food chain (for example, Brammer and Ravenscroft 2009).

FIGURE 2.2. Effect of Soil Arsenic Accumulated from Tubewell Irrigation on Rice Yield



Source: After Duxbury and Panaullah 2007.

Although drinking water is usually considered the principal source of exposure, studies in India provide examples of victims of arsenicosis receiving more than half their exposure from food (Rahman et al. 2006). Such exposure is additive, and if the same contaminated water is used for cooking contaminated rice by traditional means, this can lead to extreme exposure of as much as ten times the maximum recommended daily intake. In one area of Bangladesh, drinking water had been successfully mitigated but still failed to reduce urinary arsenic to acceptable levels because of the continuing intake from food (Kippler et al. 2016). Generally, farmer and bureaucrat awareness of the consequences of arsenic in irrigation water is much less than that in drinking water. Thus, although drinking water mitigation progresses, flood irrigation with contaminated groundwater remains the norm, transferring arsenic from the aquifer to the soil and hence progressively transferring exposure from drinking water to the food chain. If soil arsenic reaches critical levels or stricter food standards imposed before the aquifer is depleted of arsenic, then the aquifer may be abandoned and food production will drop dramatically.

Fluoride and Groundwater Irrigation

Human exposure to fluoride comes from both water and food, and although there is significant uncertainty in detail, there is evidence that fluoride accummultates in rice and some vegetables irrigated with contaminated groundwater and some plants are subject to phytotoxic effects (Gupta and Banerjee 2009, 2011).

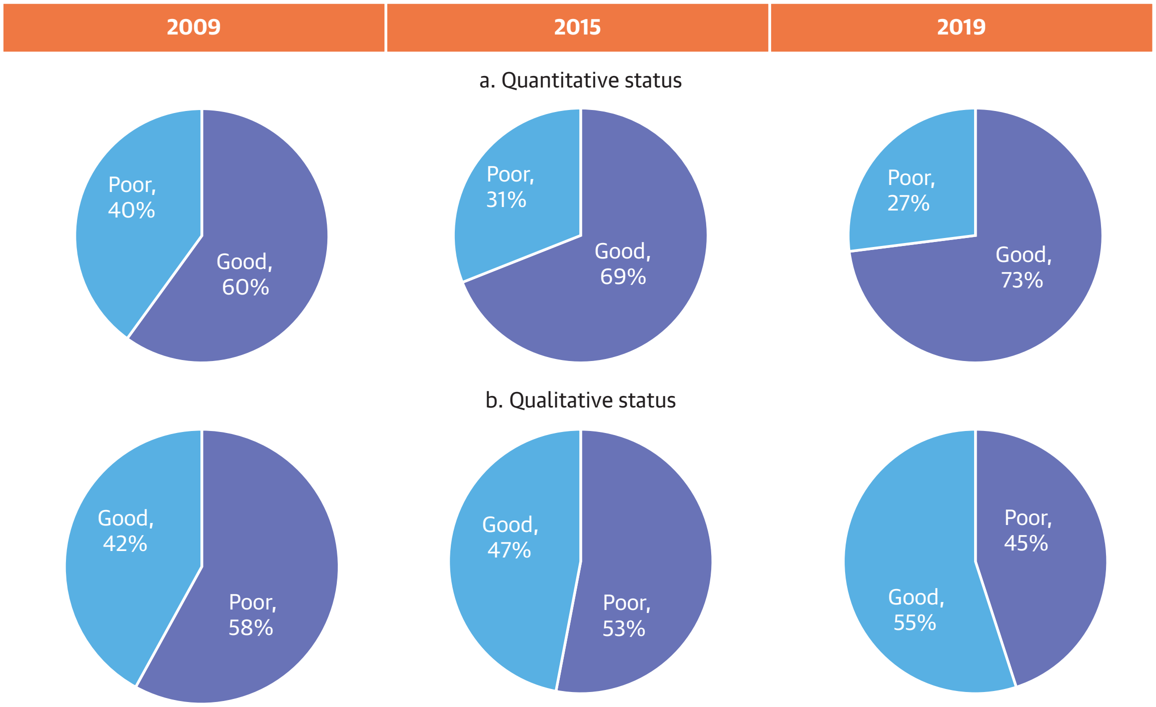
Long-Term Impact of Fertilizer Application

Most anthropogenic pollution is highly localized. The big exception to this is the diffuse application of nitrate fertilizer, which accumulated over decades. The sheer volume of contaminated water may be so enormous it would take many years to pump out even if fertilizer applications stopped completely.

In practice, it is managed by reducing fertilizer inputs in sensitive areas, modifying abstractions, and treating water at the point of abstraction.

The impact of fertilizer has long been a major concern for the EU, which established its Nitrates Directive in 1991. Following implementation of the Water Framework Directive (WFD) two decades ago, EU member states are legally obliged to achieve time-bound targets called "good quantitative status" and "good qualitative status" in all groundwater bodies. The difficulty of improving the qualitative status of groundwater bodies is illustrated by the past ten years of progress in the United Kingdom (figure 2.3), which made significant progress in increasing the number of groundwater bodies that attained good quantitative status, from 60 to 73 percent. However, the number of groundwater bodies that attained good qualitative status dropped from 58 to 45 percent over the same period. This deterioration is attributed principally to agricultural nitrate that has accumulated in soil and groundwater over decades, illustrating the enormous challenge of reversing downward groundwater quality trends. When reversing overabstraction, groundwater levels may rise rapidly in response to reductions of abstraction or artificial recharge, but there is no short cut to restoring large volumes of contaminated groundwater. Nevertheless, there are a few good news stories: Denmark, which is almost completely dependent on

FIGURE 2.3. **Evolution of the Status of Groundwater Bodies in the United Kingdom, 2009-19**



Source: Courtesy of Tim Besien, Environment Agency, United Kingdom.
Note: There is a net increase in the number of groundwater bodies meeting good quantitative status and a net decrease in the number of groundwater bodies meeting good chemical status.

groundwater for its drinking water, reports that no groundwater bodies are significantly affected by diffuse pollution from agriculture even though intensive livestock and crop farming are widespread (Psomas et al. 2021). The lesson is clear: Prevention is better than cure.

Economic Consequences of Groundwater Pollution

Groundwater is the classic out-of-sight-out-of-mind forgotten resource. Polluted rivers are palpable, but polluted groundwater can remain hidden long after contaminant concentrations have reached critical levels, even after the contaminating activity has ceased.[5] The consequences of polluted groundwater can play out in many ways:

- Mitigating natural pollution through paying for water treatment, developing alternative supplies, mortality and health care costs, lost labor, and monitoring. These are mostly public costs.
- Remediating anthropogenic pollution, which ought to be predominantly private cost (that is, polluter pays), but in practice, especially regarding agrochemicals, carries substantial public costs.
- Loss of agricultural production, especially as a result of salinity and arsenic.
- The opportunity cost of a blighted resource.
- Loss of buffering against climate change.

Economic studies have highlighted not only the high costs of remediating contaminated aquifers and treating affected water supplies but also the comparably low costs of protection. In real-world cases, all three costs may follow—that is, an affected water supply has to be treated at the point of supply, clean-up of the pollution source is required, and protection measures are applied to prevent a recurrence.

The costs and benefits of developing uncontaminated groundwater may be assessed with conventional cost-benefit analysis, but valuing groundwater quality is less straightforward and warrants a distinction between natural and anthropogenic contamination. If the presence of a natural contaminant, such as arsenic or fluoride, was not appreciated and humans were already exposed, the economic impact may be assessed either in terms of health impacts (box 2.3) or through the cost of providing an alternative supply. Anthropogenic pollution is normally more localized and appears well suited to application of the polluter pays principle and cases in which the cost has three components: (a) the cost of remediation, (b) damages to others, and (c) indirect costs. There are at least five mechanisms by which these costs are imposed:

- Punitive fines for criminal activity
- Civil action for private damages
- The costs of investigation, assessment, and remediation

BOX 2.3. Costs of Natural Arsenic Pollution of Drinking Water in Bangladesh

In the world's most arsenic-affected country, Flanagan et al. (2012) combined exposure data from national well surveys—which showed that forty-five million people were drinking water containing more than the 10 μg/L WHO guideline—with all-cause mortality dose-response curves to estimate the numbers of people exposed to different levels of risk and hence estimated that this would result in 43,000 adult deaths a year, or one in eighteen of all adult deaths. They also estimated the cost of lost productivity (that is, labor) to be US$13 billion over twenty years. By contrast, the estimated cost of scaling up water supply mitigation to end exposure was only a few hundred million dollars.

- Indirect market costs, such as reputational damage[6]
- Increased overheads, such as insurance premiums and pollution prevention

Many countries have legal requirements to remediate anthropogenic pollution that, in theory, ensures that remediation costs are met by the polluter. Although this is not rigorously enforced everywhere, it will become the norm in the foreseeable future, and because there is no obvious reason to believe that industrial pollution will be more or less likely in other parts of the world, the experiences of the United States and the EU (boxes 2.4 and 2.5) offer salutary lessons of possible future costs or, better, of costs to be avoided. As (a) the size of these costs become apparent; (b) the legal obligation to remediate is seen as inevitable; and (c) the benefits of early—that is, voluntary—action is understood, these costs alone could be sufficient to change behavior.

The costs of groundwater pollution (damages to others and indirect costs) also involve issues of environmental and intergenerational justice. If the regulatory regime is weak or, in the case of legacy pollution, if there is no responsible person, the financial costs of pollution are transferred—as treatment costs—to individual abstractors or to the general public via higher utility charges or clean-up by public bodies. If there is widespread and ongoing pollution but abstractions have not yet been compromised, the costs of remediation or treatment may be transferred to future generations. Furthermore, for contaminants with long latency, the health and associated economic costs may be transferred to future generations.

In a world concerned with international commerce and news reporting, the risk of reputational damage encourages corporations to act as advocates for pollution prevention. Any reporting of pollution, even in another country, is damaging to brand image and, in the case of the food and drink industries, can be business critical.[7]

Insurance companies are increasingly conscious of the implications of polluting activities, fearing, for example, bearing the cost of a major pollution incident that has caused a business to go into bankruptcy.

BOX 2.4. Cost of Groundwater Clean-Up in the United States

In response to a legacy of industrial pollution, in 1980 the United States passed the world's most famous piece of environmental clean-up legislation, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or "Superfund" as it is commonly known. This created a fund for cleaning up severely contaminated sites that, at its peak, contained US$9 billion. However, there were reported to be some 126,000 groundwater sites in the United States that had not met clean-up standards, and the national clean-up "bill" was estimated by the USEPA (2001) to be of the order of US$100 billion to US$500 billion. Note for present-day costs, these values may be increased by about 48 percent. A 2016 update (Suthersan, Horst et al. 2016) gives a measure of the continuing scale of the clean-up task in the United States, noting that only 20 percent of 1,743 sites had been removed from the National Priorities List on the grounds of acceptable risk.

BOX 2.5. Costs of Contaminated Groundwater in Europe

A 2004 study of the U.K. Water Industry (UKWIR Report 04/WR/09/8) found that almost half the groundwater used for public supply—27 percent of total supply—was affected by deteriorating quality and had cost the industry £754 million (US$1.3 billion in 2003 prices) between 1975 and 2003, of which £436 million (US$0.7 billion) was spent on treatment, £134 million (US$0.2 billion) on blending, and £184 million (US$0.3 billion) on replacing water sources. They predicted that ongoing problems would require further capital investments of £73 million to £180 million (US$0.1 billion - 0.3 billion) for each five-year Asset Management Period and probably more depending anticipated regulatory changes.

BRGM/Ecologic (2003) reported costs from elsewhere in the EU:

- In Belgium, the average remedial cost at contaminated sites was €600,000 (US$678,000), where 60 percent of sites cost less than €100,000 (US$113,000) but 3.5 percent of sites cost more than €12 million (US$13.6 million).
- In Austria, treatment at contaminated sources was estimated to average €210M (US$237 million) in capital costs and €30M (US$34 million) in annual operating costs.
- In France, the cost of nitrate removal plants averaged €870,000 (US$983,000), with an equivalent totalized annual cost of €0.26 (US$0.29) per cubic meter or €20 (US$23) per person per year.
- Studies of willingness to pay for groundwater protection produced estimates of €94 to €559 (US$106 to US$632) per household per year in various EU countries, not greatly dissimilar to estimates in the United States (US$72 to US$1,860).

This applies not only to factories and the like but also farming, where there have already been attempts by utilities to recover the cost of water treatment rather than simply passing it on to the consumer (Dybdahl 2018).

Groundwater Quality, Climate Change, and Sustainability

This topic is complex, but a few principles will serve as a guide for groundwater managers. Groundwater quality changes slowly. Depending on the size of the aquifer, this may take anywhere from decades to thousands of years. In addition to what is renewed annually, many large aquifers contain water that was recharged tens of thousands of years ago, which is an advantage because it provides resilience in the face of rapid climate change impacts that may affect surface water and atmospheric systems. Climate-induced changes in groundwater quality will occur at the boundaries, such as saline intrusion at the coast or at the water table because of changes in the recharge process. These complex feedbacks are difficult to predict; however, with good monitoring, an adaptive management process can be employed.

Groundwater quality and sustainability are interrelated in many ways, the most obvious being saline intrusion (see chapter 3, Salinity and Saline Intrusion). Aquifers have a certain capacity to attenuate pollution, but in rapidly urbanizing and industrializing areas, this capacity may be exceeded, rendering some shallow aquifers effectively unusable and posing a threat to deeper aquifers. A similar condition applies when users of arsenic-contaminated aquifers have switched to deeper aquifers. In both scenarios, the questions arise as to whether, after how long, and at what concentration contaminants might break though into the lower aquifer.[8]

Why Is It So Difficult to Remediate Polluted Groundwater?

The greatest difference between surface water and groundwater pollution is the time required to recover. Rivers can recover from a single incident in weeks to months and in more extreme cases a few years. Even rivers systematically abused for centuries, such as the Thames and the Rhine, restored within fifty years. Single incidents of groundwater pollution typically take years to decades to recover, and systematic abuse may be practically irrecoverable. Water professionals and land managers have a duty to learn from experience and bequeath these resources to future generations in good condition.

The difficulty and time taken to remediate aquifers is the main reason groundwater protection is so important, and it is made worse when there are long gaps between the start of pollution, its discovery, and the start of remediation. Whether pollution originates from a point source (such as a leaking storage tank) or a more diffuse source (such as application of fertilizer to fields), contaminants may travel slowly through the ground for months or years until intercepted by a pumping well. By this time, the stores of contaminants in the soil and aquifer are significant and can continue to pollute abstraction wells for years after the source of pollution has stopped.

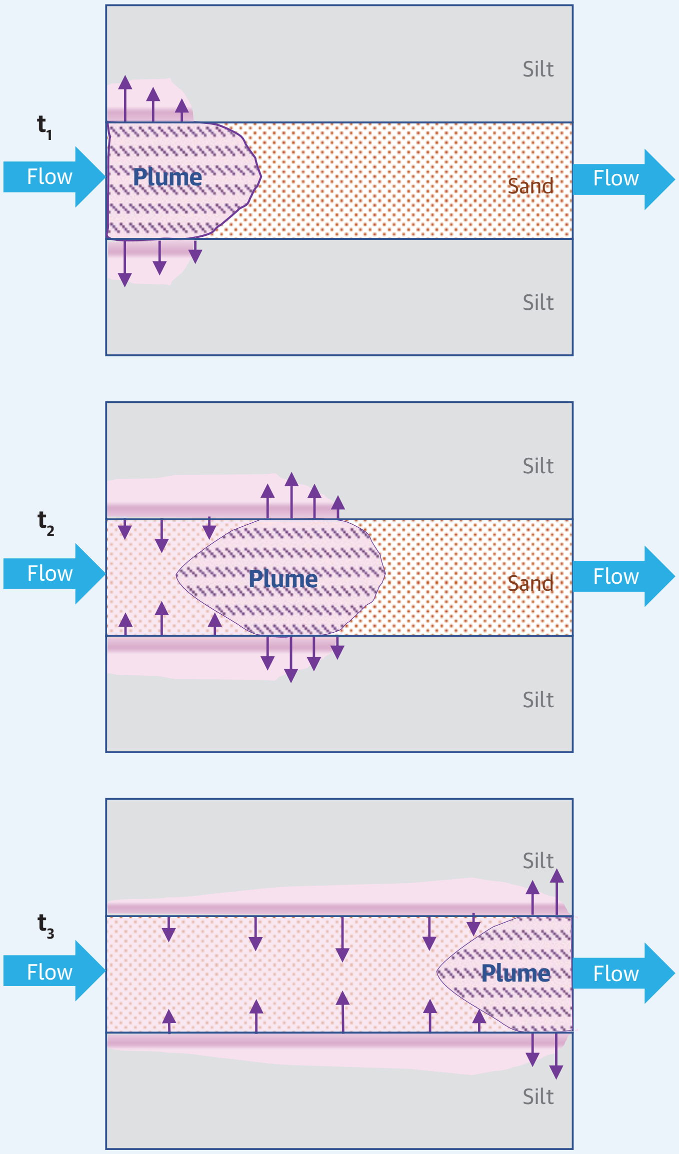
A characteristic feature of aquifers that makes restoration so troublesome is that as a contaminant plume flows through it, the initially very high pollution concentrations diffuse into the layers above and below.

BOX 2.6. Back-Diffusion: Why Clean-Ups Take So Long

It is often assumed that the simplest way to clean up an aquifer is to pump out the polluted water and treat it. Unfortunately, the real world is not so simple. Real aquifers are interbedded with bands of silt and clay, or they comprise fissures separated by porous but low permeability blocks of rock.

Consider a plume of pollution flowing through a sand layer (or fissures in rock), which is the main aquifer (figure B2.6.1). Contaminants diffuse into adjacent silt or clay layers (or the porous blocks that separate the fissures). Although this initially removes some of the pollutants from fast-moving groundwater, after the main plume has passed, the chemicals will slowly diffuse back out into the aquifer, forming a long-term source of low-level contamination.

FIGURE B2.6.1. Sequential Progress of Pollution in a Groundwater Aquifer at Times t_1, t_2 and t_3.



Later, after the main plume has passed by, these pollutants diffuse back out at ever slower rates (box 2.6). As a general rule, the longer pollution has been going on, the longer it will take to clean up, especially if regulations require pristine standards. Many industrial sites in the United States have required remediation and monitoring to continue for decades, costing tens of millions of dollars—without achieving the end goal. Back-diffusion explains why expensive, aggressive remediation has only temporary success: the fast-moving groundwater is removed, creating an illusion of clean-up, only for the contaminants to return at the next monitoring event, requiring remediation to resume.

Notes

1. Meaning the quality of the water in the ground before it comes into direct contact with a well or manmade structure.
2. This estimate is based on combining data from Argos et al. (2010); Flanagan et al. (2012); and Ravenscroft, Brammer, and Richards (2009).
3. Or 11.3 mg/L when measured as the equivalent amount of nitrogen (NO_3-N). Measurement as NO_3-N is useful for comparing with the equivalent amounts of nitrogen in ammonium and nitrite. This multiplicity of reporting formats often causes confusion, so wherever only "nitrate" is reported, it is essential to ask what the units are.
4. For information on drinking water health advisories for PFOA and PFOS, see the USEPA website at https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos.
5. This, for example, occurred with an industrial source of bromate in Hertfordshire in Southern England, which was the United Kingdom's largest known groundwater plume, and in its most important aquifer, the Chalk (Wyke et al. 2013).
6. Which can accrue not only to individual businesses but also, if perceived to be systemic, to entire sectors and economies (see box 7.1 regarding the Bangladesh textiles sector).
7. Bottled water, which is almost always groundwater, is a case in point. In rich countries, the norm is to label the bottle with what is in the water, but in low- and middle-income countries, there is a tendency to label bottles with what is not in the water because the primary market demand is safety, not taste.
8. Modeling studies can offer guidance, but robust predictions will require calibration against long-term sentinel monitoring.

Chapter 3
Natural and Anthropogenic Groundwater Contamination

Key Points

- Since the 1980s natural contaminants such as arsenic, fluoride, manganese, and uranium, have been recognized to be more extensive and more significant than previously recognized.
- Most groundwater is naturally of good quality, but anthropogenic contaminants pose increasing threats in urban and rural areas worldwide.
- The thousands of anthropogenic groundwater contaminants are extremely diverse in their origins, characteristics, and effects. They range from well-established risks such as fecal waste and industrial and agrochemicals to poorly understood emerging classes of synthetic chemicals.
- Groundwater salinity poses an increasing threat to water supplies in coastal areas and to agriculture in low-lying semiarid regions, and their effects are exacerbated by climate change.

This chapter surveys the vast range of groundwater contaminants, concentrating on those that have the most widespread impacts, and emphasizing their effects on health, agriculture, and the economy.

Natural Groundwater Quality

When it is not affected by human activity, most groundwater extracted by water wells is of such good quality that it requires only precautionary disinfection. An exception occurs with shallow open wells, but generally the soil and the unsaturated zone[1] filter and degrade harmful microbes and many chemicals, providing protection in a way that cannot be achieved for surface water. Traditionally, the chemical quality of groundwater might have been analyzed only when commissioning a new well and for just a short list of ions[2] that constitute the majority of the dissolved load.

The chemistry of unpolluted groundwater depends largely on the nature of the rock or sediment forming the aquifer and the climate and soil conditions under which it is recharged (box 3.1). The biggest influence of rock type is usually whether it includes calcium carbonate to buffer the effect of slightly acidic rainwater and increase resistance to change, albeit at the cost of limescale and incrustation problems. The main influence of climate is on oxidation and reduction potential. Under hot and humid conditions, organic matter in the soil soaks up atmospheric oxygen, creating conditions that favor dissolving iron and manganese and removing nitrate. Under drier climates, dissolved oxygen persists further into the subsurface, suppressing the release of iron and manganese and allowing nitrate to persist.

BOX 3.1. Natural Groundwater Quality and Understanding Aquifers

In addition to issues of contamination and water use criteria, hydrogeologists study natural groundwater chemistry, including use of isotopes and tracers, because it helps them understand how aquifers work. These techniques provide insight into how and where recharge occurs; the mechanisms of flow, especially long-term flow patterns in sluggish aquifers; and whether groundwater can move through an aquitard on a meaningful timescale. In addition, the distribution of water quality can often be related to hydraulic parameters and to the vulnerability and resilience of aquifers to pollution. This information plays an important part in developing the conceptual model (see chapter 4).

Groundwater Contaminants

The following sections discuss groundwater contaminants in terms of four broad groups:

- *Natural or geogenic contaminants* range from widespread but relatively benign elements, such as iron, to life-threatening substances, such as arsenic and fluoride. Most will change slowly and remain a problem for more than a lifetime.

- *Anthropogenic contaminants* are extremely diverse and can have mild to extreme effects on human health and the environment. Except for agrochemicals, they are mostly localized and amenable to attribution of responsibility and remediation or containment, with the prospect of elimination of certain types of within years or a few decades, though some will last longer.

- *Pathogens*. Harmful bacteria, viruses, and other microorganisms often have an anthropogenic origin and are largely restricted to the near-surface environment.

- *Salinity*. Saline groundwater is most commonly encountered near the coast or in low-lying arid plains, such as the Indus and Tigris-Euphrates rivers, where shallow groundwater is concentrated by evaporation.

Many processes can degrade, slow down the movement, or reduce the concentrations of contaminants in the subsurface. A distinction can be drawn between organic compounds that can be broken down into carbon dioxide, methane and water, and toxic elements, such as arsenic, which cannot be destroyed but can be immobilized. These are the main processes that control the fate of contaminants in the subsurface:

- *Dissolution and weathering*. Flowing groundwater can dissolve or react with aquifer solids.

- *Mineral precipitation*. Flowing groundwater can also evolve by precipitating minerals, such as calcium carbonate, iron oxides, and sulfides.

- *Dilution and dispersion*. As plumes migrate, they expand but also become diluted.

- *Miscibility*. Some contaminants, such as petroleum and solvents, do not mix with water and form a nonaqueous phase liquid (NAPL) that floats or sinks according to its density.
- *Oxidation and reduction (redox)*. Depending on the availability of oxygen, the stability of elements such as iron and many organic chemicals changes—for example, dissolved iron can be converted to a rust-like solid.
- *Biodegradation*. Most organic compounds will degrade in groundwater if the redox conditions are suitable. For instance, petroleum compounds, such as benzene, are easily degraded if there is a good supply of oxygen, but others, such as chlorinated solvents, are degraded only under reducing conditions.
- *Adsorption and ion-exchange*. Clays and iron oxides have charged surfaces that can bind (adsorb) heavy metals and arsenic, and organic matter can adsorb organic contaminants.
- *Matrix diffusion*. Contaminants moving though high permeability (aquifer) layers can diffuse in and (later) out of adjacent low permeability zones.
- *Volatilization*. Organic chemicals, such as solvents and components of petroleum, are more volatile than water and so may be lost by evaporation.

Natural Groundwater Contamination—Learning to Live with What's There

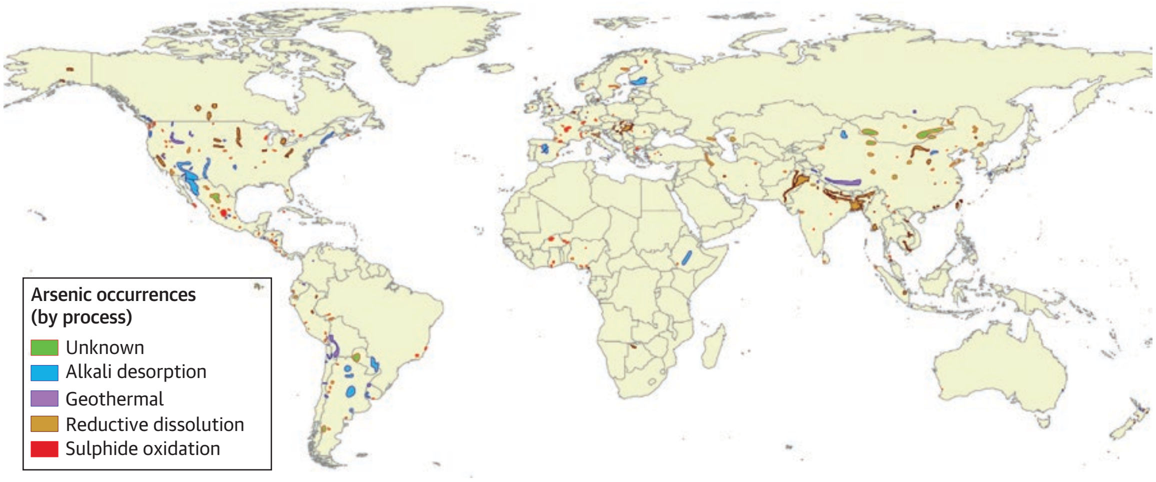
The following sections present accounts of the most serious and/or widespread natural contaminants in groundwater: arsenic, fluoride, iron, manganese, and radioactive elements. Groundwater salinity is something of a special case and is dealt with separately later in the chapter. Other natural contaminants are important locally but not described here.

Arsenic

Arsenic is the world's most important natural groundwater contaminant and until the 1990s was given little attention, but it is now recognized to have affected more than 150 million people. Arsenic pollution is global (map 3.1) but strongly concentrated along river valleys that drain young mountain ranges, which are the primary source of arsenic that eventually finds its way into groundwater in the lower reaches of the basins. These include some of the most densely populated areas on Earth.

Arsenic can be mobilized into groundwater by four different mechanisms (box 3.2). Reductive dissolution mechanism is the most important and is responsible for the vast majority of human exposure and disease across the densely populated river basins draining the Himalayas in South and Southeast Asia. This process produces a distinctive arsenic-depth profile with low concentrations close to the water table that increase rapidly to a peak within the first few tens of meters and then gradually tail away. By contrast, sulfide oxidation produces a peak at the water table, where water and air mix. Failure to appreciate this difference has led to severe pollution—which was poisoning people—being overlooked. Arsenic pollution is also associated with mining wastes and mineral processing, as well as industries such as pesticide and semiconductor manufacture.[3]

MAP. 3.1. Global Distribution of Mapped Arsenic Pollution of Groundwater



Source: Authors compilation of public data sets and updated after UNICEF 2008.

BOX 3.2. Arsenic Mobilization Mechanisms

Reductive dissolution occurs when decaying organic matter causes iron oxide particles to dissolve, releasing the arsenic bound to them.

Alkali desorption releases arsenic attached to iron oxides under highly alkaline (pH ≥ 8.5) conditions.

Sulfide oxidation releases arsenic from minerals, such as pyrite and various ores, under oxidizing conditions.

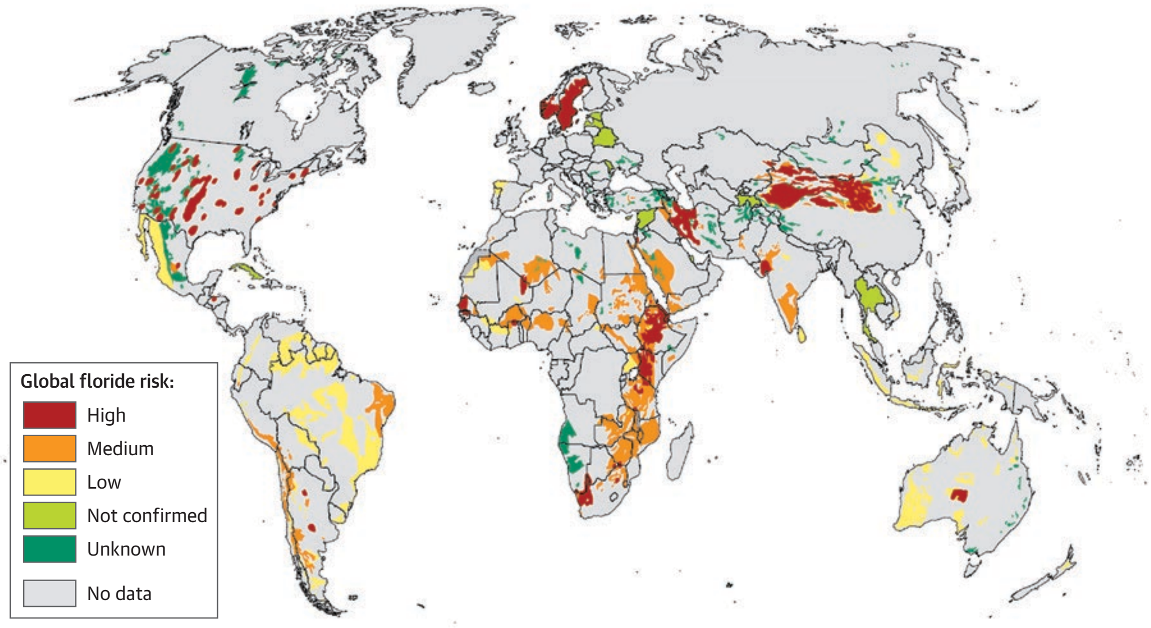
Geothermal areas can produce extreme pollution, and all such areas should be considered suspect.

Arsenic concentrations vary over time, both increasing and decreasing depending on local circumstances. Seasonal changes may be significant in the zone of water table fluctuation. At greater depths, changes occur more slowly but can increase from below detection limits to more than 100 ppb over periods of months to a few years and so must be monitored regularly (for example, McArthur et al. 2010). Maps of arsenic should be viewed with caution because areas that appear to be thoroughly contaminated may still have safe water available at specific depths, and vice versa.

The options for mitigating arsenic pollution are either treatment, which can be effective though expensive in urban settings but unreliable in rural areas, or avoidance, either by switching to a treated surface water source or to a different aquifer. The latter solution is usually the quickest and most cost effective but may leave a residual risk of arsenic being drawn from one aquifer to another under the influence of pumping.

Despite the well-publicised examples, until now (2021) some areas of the world have not been tested for arsenic, including some where arsenic contamination is suspected (UNICEF and WHO 2018).

MAP 3.2. **Areas of Mapped Groundwater Fluoride Contamination**



Source: Map created by the authors using IGRAC data: https://ggis.un-igrac.org/view/groundwater-quality.

Fluoride

Fluoride is second only to arsenic in its global extent (map 3.2) and health effects as a natural groundwater contaminant, with about 200 million people at risk (EAWAG 2015). Like arsenic, fluoride is mobilized by multiple rock-weathering mechanisms. In South Asia, for example, fluoride and arsenic appear to be almost, but incompletely, mutually exclusive.

Fluoride contamination of groundwater is encountered widely on all continents but, unlike arsenic, is relatively rare in the great alluvial basins. Globally, high fluoride concentrations are more common in semiarid climates and in the vast weathered granitic basement terrains of Sub-Saharan Africa, India, and South America. High fluoride concentrations in groundwater are also associated with volcanic rocks, such as those that occur along the East African Rift Valley. The amount of fluoride that can be dissolved in groundwater is controlled by the solubility of the mineral fluorite such that in calcium-rich aquifers, such as limestone, less fluoride can be dissolved, but in calcium-poor aquifers, such as granite, higher fluoride concentrations are possible.

Commonly, basement aquifers are exploited by dug wells tapping the shallow weathered zone, from which much of the fluoride has been leached out. However, with increasing development, dug wells are replaced with drilled wells and encounter higher fluoride concentrations (for example, Madhnure et al. 2018). Such concentrations, possibly co-occuring with other toxic elements, are also encountered in areas of geothermal activity.

Mitigation of fluoride may be achieved through developing a new source; however, unlike with arsenic, drilling deeper is probably not a good solution, so treatment is the more likely option. The main treatment methods are adsorption (especially with activated alumina), coagulation methods, and membrane techniques, such as reverse osmosis (EAWAG 2015).

Iron

Iron is a common constituent in groundwater whenever reducing conditions apply. The presence of oxygen will precipitate iron as a rust-like oxide or hydroxide, so iron is almost always absent at the water table. Iron is not hazardous to health; and in some situations, health benefits have been reported for malnourished pregnant women (Merrill et al. 2010). However, at the milligram level, it is objectionable from the perspectives of taste, odor, staining of clothes and some cooked foods, and displeasure when washing bodies. For these reasons, drinking water guidelines and standards can be quite variable. A low concentration, commonly ≤ 0.3 mg/L, is normally required for piped water systems. However, because of the general health benefits of using well water compared with practical alternatives in rural settings, for hand tubewells concentrations of 1.0 mg/L are widely permitted and, in some cases, concentrations as high as 3 mg/L may be officially tolerated. Although iron removal by oxidation and filtration is scientifically simple, household and community treatment plants are difficult to maintain when water is manually pumped. In practice, many rural water authorities turn a blind eye to higher iron concentrations, which is regrettable because the bad taste often motivates people to switch to microbiologically unsafe sources. By contrast, in many areas iron avoidance has the desirable effect of also promoting arsenic avoidance, even though users may not be aware of this benefit.

Manganese

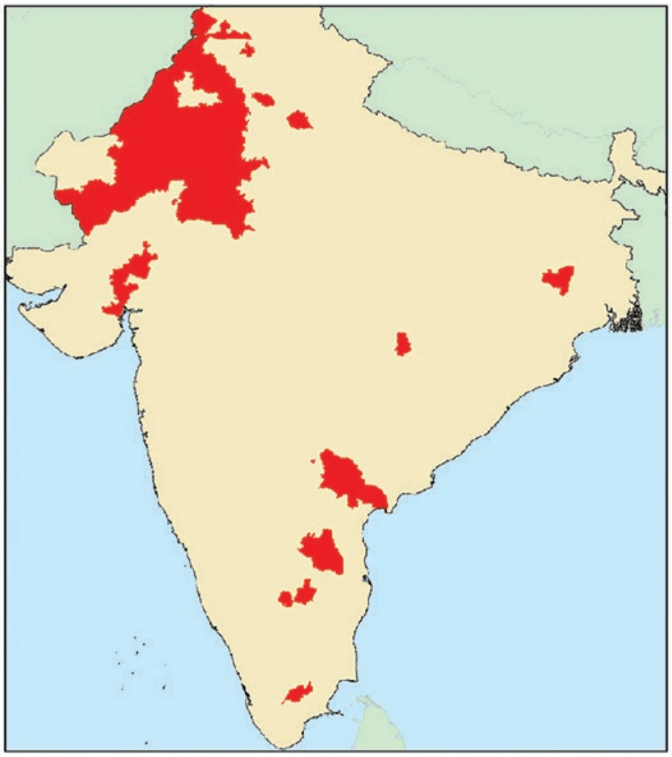
As a groundwater contaminant, manganese has similarities with iron, notably in terms of taste and odor, but with two important differences: First it adversely affects health of children (chapter 2) and second it has been widely neglected. Like iron, manganese has many mineral sources but is mobilized under less reducing conditions, so it appears first in groundwater as it flows through an aquifer and may disappear by the time iron appears. Thus, the sequence of manganese followed by iron indicates where the water is becoming more reducing as it evolves along a flow path.

High manganese concentrations (> 0.4 mg/L) are common and affect many millions of wells in the river basins draining the Himalayas from the Ganges to the Mekong in South and Southeast Asia and probably many other areas of the world. Many consumers may confuse manganese with iron, although the difference is easily recognized from the black (manganese) as opposed to red-brown (iron) staining on the concrete aprons and pipework.

Uranium and Other Radioactive Elements

Uranium, which is radiologically and chemically toxic, may be the most significant emerging natural contaminant. Over the past ten years there have been many "discoveries" of extensive uranium in aquifers where it had not been properly tested for previously, including in India (map 3.3) and China.[4] Natural uranium in groundwater results from simple weathering of uranium-rich rocks under oxidizing conditions and, so long as the water remains oxic, it continues to accumulate uranium (Riedel and Kubeck 2018).

MAP 3.3. **Uranium Contamination in India**



Source: Adapted from Coyte et al. 2018.

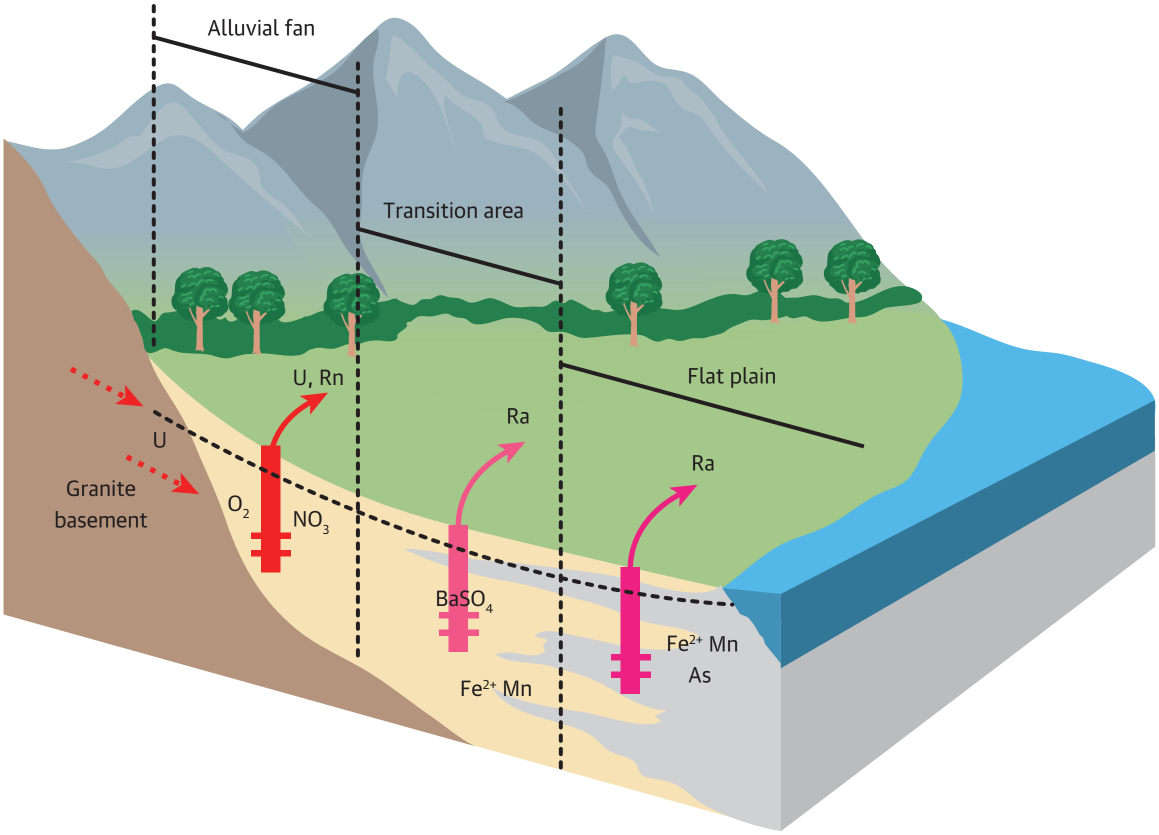
Therefore, any rocks, such as granite, and alluvium derived from them that are naturally enriched in uranium are potential sources of uranium contamination.

Other radioactive elements may be found in groundwater, notably radium and radon (decay products of uranium). As shown in the example of the Hetao Basin in northern China (figure 3.1), uranium, radon, and radium and other contaminants can co-occur at different positions in the same basin. As groundwater flows through the aquifer, it first mobilizes manganese, then iron, and eventually arsenic and radium.[5] In the recharge area, where groundwater is oxic, 80 percent and 97 percent of samples exceeded the USEPA guidelines for uranium and radon, respectively. Where surveys of uranium are planned, it would be prudent to test for other radioactive elements.

Anthropogenic Groundwater Contamination—The Unintended Consequences of Human Action

The list of potential anthropogenic contaminants of both surface water and groundwater is so enormous[6] that the threat could easily appear overwhelming. However, when placed in the context of systematic hazard mapping (chapter 4) the extent of the threats can quickly be rationalized to identify where to look for which contaminants. Accompanied by regulation of the sale and use of hazardous chemicals, systematic programs of survey and monitoring can rapidly assess the risks and reduce the monitoring

FIGURE 3.1. Occurrence of Uranium and Other Contaminants in the Hetao Basin, China



Source: Adapted from Guo et al. 2018.
Note: As = arsenic; $BaSO_4$ = barium sulfate; Fe^{2+} = iron; Mn = manganese; NO_3 = nitrate; O_2 = oxygen; Ra = radium; Rn = radon; U = uranium.

program to manageable proportions. The remainder of this chapter describes the major groups and sources of contaminants. Notwithstanding advances in assessment and remediation, the primary concern of every groundwater manager should be on preventing these chemicals entering the ground.

Agrochemicals: Fertilizers and Pesticides

In the twentieth century, global agricultural production expanded enormously through artificial nitrogen fertilizers, which produce dissolved nitrate in soil water for crops to take up. However, a proportion of this bypasses the root zone and either passes into surface drains or percolates to groundwater, where it poses risks to health (chapter 2). High nitrate concentrations can also originate from ploughing up of grassland, and human and animal wastes. Other fertilizers, such as phosphate, may also give rise for concern.

Leaching of nitrate fertilizer is both harmful to health and a huge economic waste. The persistence of nitrate in groundwater involves a delicate balance depending on the supply of oxygen. Nitrate itself is a source of oxygen to drive chemical reactions, so when there is organic matter present in the aquifer, such as in humid tropical river basins, nitrate disappears within a few meters of reaching the water table—the oxygen consumed by organic matter and the nitrogen gas releasing to the atmosphere. On the other hand, so long as there is a supply of oxygen, as in many semiarid climates, or aquifers containing little organic matter, such as the Chalk of Northwestern Europe, nitrate may persist for decades. Agricultural nitrate enters groundwater in such vast quantities and over such large areas that it can be managed only by reducing inputs, changing farming practices and land-use controls (catchment management), or by end-of-pipe solutions, such as blending and expensive treatment by anion exchange or reverse osmosis. In areas of groundwater irrigation, it may be possible to capture some of the escaping nitrate with shallow wells and return it to the fields as fertigation while concentrating potable abstraction in deeper parts of the aquifer.

Pesticide risks are associated with occupational exposure, wildlife, the food chain, and surface waters and give rise to widespread public concern. Pesticides are also common sources of diffuse groundwater pollution. Many pesticides are hazardous to health at the microgram or nanogram level, so a small amount of substance can contaminate a very large volume of groundwater. Pesticides vary greatly in both their toxicity and persistence, which is important in assessing the risk to groundwater. In the surface environment, adverse effects of pesticide may be acute and rapid (for example, fish kills) but also quickly flushed out of the system. By contrast, entry of pesticides into groundwater tends to be more diffuse and, if chemically persistent, more likely to lead to long-term low-level exposure. Over the past half century, the suite of pesticides in use has changed dramatically because of restrictions or bans on persistent, bioaccumulative, and toxic substances, such as DDT and many others since. In the United Kingdom, for example, the herbicides simazine and atrazine continue to be among the commonest groundwater contaminants, despite being withdrawn from use in 2003 (EA 2019a).

A detailed review of the pesticides currently in use is beyond the present scope; however, newer pesticides tend to be less persistent but not necessarily less toxic (for example, Hanson et al. 2015). Much of the applied pesticide that escapes its intended targets is trapped by a biologically active soil zone. Thus, aquifer contamination is likely to follow preferential pathways, such as runoff via drains, poorly sealed wells, or application to crops shortly before heavy rain. For groundwater managers, it is important to know which pesticides are, or recently have been, in use, for which purposes, and in which areas and then to ensure that a competent agency with appropriate laboratory and quality assurance procedures conducts targeted surveys and monitoring. Constantly emerging new substances that are hazardous to environmental and human health at very low concentrations create challenges for laboratories in terms of developing analytical techniques, purchasing equipment, and maintaining measurement accuracy.

Human and Animal Waste and Pathogens

Where populations rely on onsite sanitation and self-supply of drinking water, poor management of human and animal wastes can permit the entry of pathogenic bacteria, viruses, and protozoa, as well as nitrate, dissolved organic matter, pharmaceuticals, and personal care products into shallow aquifers[7] (box 3.3). Because identifying the many possible pathogens is difficult, drinking water surveillance relies on the fecal indicator bacterium (FIB) *E. coli* or variants, such as total and fecal coliforms, as a standard measure of microbial pollution. These are abundant and relatively easy to measure, and their presence establishes a chain of transmission from a fecal source to drinking water. However, disease is more likely

BOX 3.3. Latrines, Pathogens, Shallow Wells, and Drinking Water

A prevalent concern in the literature is that leaking latrines routinely pollute adjacent shallow wells, which may give rise to a disproportionate focus on well-spacing criteria. The reality is more complicated because of a confusion of cause and effect. It is correct that many surveys of village handpumps show a high frequency (about 40 percent of wells) of low-level fecal contamination at the point of collection and even higher frequencies (about 60 percent) and higher levels of contamination at the point of use in the household (for example, BBS/UNICEF 2019). These differences are well known and rightly give rise to the ubiquitous WASH initiatives to improve hygiene practice. What is less well known is the evidence that, in alluvial aquifers at least, groundwater between the wells and latrines is much less contaminated than the water collected at the pump and fecal bacteria are hard to detect in groundwater more than a few meters away from the latrine (for example, Caldwell and Parr 1937; Ravenscroft et al. 2017). The greater contamination at the pump is believed to be because of poor well and pump installation, inadequate sanitary protection, and inferior hygiene practices. When it comes to pathogens, well water and groundwater are not even approximately the same thing.

to be caused by other microbes, such as viruses, that are particularly significant because they are smaller, more mobile, and persistent. A global review of 649 groundwater outbreaks globally between 1948 and 2013 found that five pathogens (Norovirus, Campylobacter, Shigella, Hepatitis A, and Giardia) were responsible for most outbreaks. Complicating the utility of FIB in protecting health, an evaluation of twelve international studies of 718 drinking-water systems found that all microbial indicators have low sensitivity and predictive values for virus occurrence (Fout et al. 2017; Murphy et al. 2017).

Animal wastes pose similar risks to groundwater, but under intensive feedlots the microbial loading may be much higher and certain troublesome pathogens—such as the protozoan Cryptosporidium, which is resistant to disinfection—are particularly common. Some notable impacts have been associated with the disposal of animal carcasses, particularly following outbreaks of foot-and-mouth disease. In Taiwan, China, an outbreak of enteroviruses in 1998 led to more than 300,000 infections and the deaths of eighty-five children following the burial of five million infected pigs in coastal alluvium (Jean 1999).

The mobility and survival of pathogens in groundwater depends strongly on their size, which ranges over five orders of magnitude from protozoa, such as Cryptosporidium and Giardia, which may be mobile only in fissured rock and gravel, to viruses that may be able to move through the pores of most common aquifers. Bacteria are of intermediate size and mobility and may be able to survive for as long as one hundred days but probably much less if there is good supply of oxygen (for example, Lewis, Foster, and Drasar 1982), so most pathogens in most aquifers are unlikely to travel more than a few meters from their source. The notable exceptions are viruses and most pathogens in fissured rock aquifers.

Since the outbreak of the pandemic in 2020, surveys at Monterey in Mexico detected the ribonucleic acid (RNA) of the COVID-19 virus in 40 percent of well waters. Because this was correlated with the artificial sweetener sucralose, it was believed the viruses had infiltrated from sewers. Its high prevalence in well water serves as a powerful indicator of the penetration of wastewater, and potentially other viruses, into groundwater; however, the likelihood of the COVID-19 remaining infectious is judged to be extremely low to negligible (Jones et al. 2020; Mahlknecht et al. 2021).

Municipal, Industrial, and Mining Waste

Centralized disposal or treatment sites for municipal, industrial, and mining waste always present a threat to groundwater, although the risk varies with the type of waste and the type of aquifer. Increasingly such sites are subject to strict regulation with increasingly stringent assessment, enforcement, and monitoring. However, in many countries and in smaller settlements, solid waste is disposed of in unlined and unregulated dumps, posing an even greater risk to groundwater. With the introduction of sewerage and centralized sewage treatment, the juxtaposition of population and fecal waste loading is reduced, but new risks are created along the lines of sewers and drains, particularly where they carry chemical and industrial wastes.

Significant pollution risks, especially in aggregate, arise from the many small industrial operators, such as auto paint shops, dry cleaners, fuel stores, tanneries, mechanical workshops, and many other small industries to be found nestled among housing and general commercial activities in urban and periurban areas. Former coal gasworks can be serious sources of groundwater pollution. In addition, rural industries, such as agrochemical stores, sugar mills, and other agricultural processing activities, can pose significant risks.

A general concern regarding the risks to groundwater is whether and for how long a country or region has operated a comprehensive system of fecal and solid waste management. If the answer is yes and for a long time, then the risks should be well understood and controlled. However, most countries have experienced undocumented and irresponsible disposal of hazardous wastes, leaving a legacy of historical, ongoing, or potential groundwater pollution. A comprehensive regulatory regime is central to managing the risk to groundwater from these wastes. Engineered sanitary landfills include multiple barriers, the separation of hazardous waste, impermeable liners, drainage, and monitoring from the start of filling. However, if regulation is lacking, landfills may be little more than dumps for unsegregated waste with a high risk of pollution. Groundwater managers must engage with municipal authorities to implement policies and programs to ensure the spatial separation of waste facilities and sensitive groundwater bodies through the closure of polluting sites and the safe-siting and monitoring of new sites.

Mining is, or has been, an important source of pollution in most countries of the world, and one that often continues to pollute surface water and groundwater for decades after mining stops. Mining waste is usually deposited in spoil heaps, lagoons, or tailings ponds, where they may react with atmospheric oxygen to generate acid mine drainage containing high concentrations of sulphate and toxic metals, such as lead, zinc, copper, and arsenic, which may leak into groundwater and reemerge down-gradient as baseflow in rivers. All mining sites should be presumed to pose a high risk until determined otherwise. Many abandoned underground mines were not subject to such regulation and have no owner who can be held responsible, so water resource agencies will be obliged to take responsibility for the legacy pollution that results as groundwater floods old shafts and adits[8] and eventually rises to the surface.

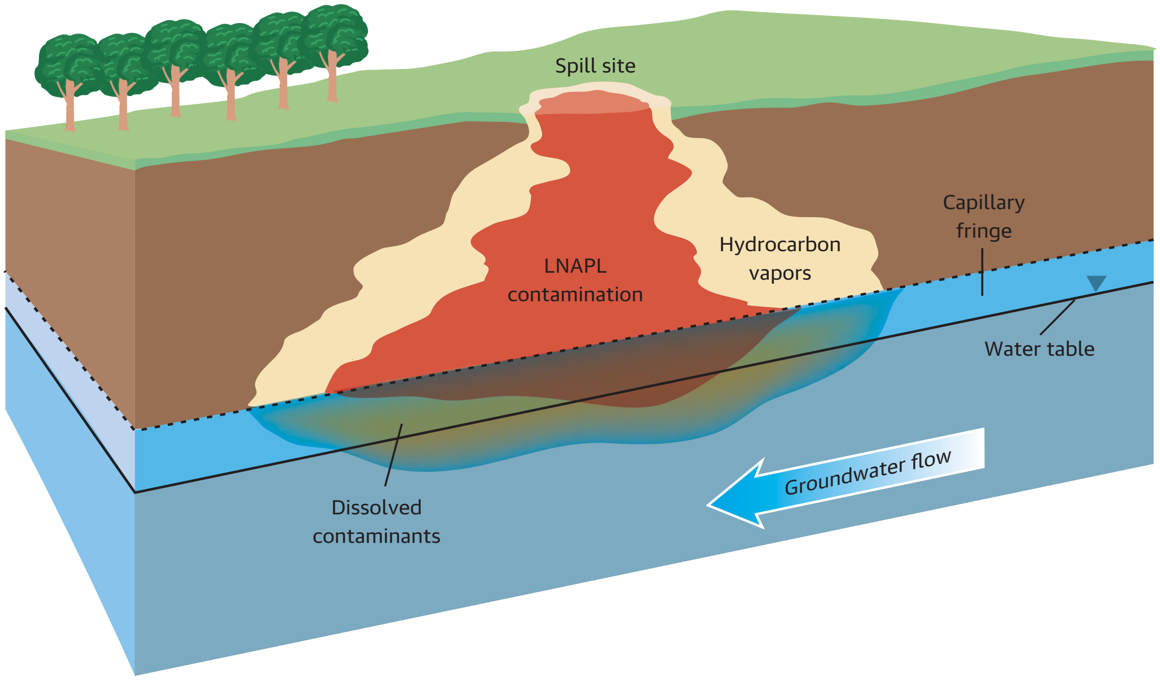
Petroleum and and Light Nonaqueous Phase Liquids (LNAPLs)

During the twentieth century, the use of petroleum products became so ubiquitous that shallow groundwater in every populated region of the Earth should be considered at risk of pollution. Oil refineries produce products ranging from light fuels to heavy furnace oils that contain a wide range of hydrocarbons, many of which are toxic and/or carcinogenic. Because of their ubiquity and mobility, fuels are the most common groundwater contaminants. Leaking underground tanks and fuel lines at petrol filling stations are the most common source, although leaking pipelines, spills from vehicles and aircraft, and runoff from trafficked areas are notable others.

Fuels such as petrol contain the well-known benzene, toluene, ethylbenzene, and xylene (BTEX) group of compounds, of which benzene is particularly significant because it is carcinogenic and has low maximum contaminant levels of just 5 and 1 μg/L in the United States and EU, respectively. Heavier fuels contain increasing quantities of polyaromatic hydrocarbons (PAHs) have maximum concentration levels (MCLs) defined at the nanogram level. Fuels also contain additives such as methyl tertiary butyl ether (MTBE), which is exceptionally mobile and causes taste and odor problems and can diffuse through plastic water pipes.

The essential characteristics of fuels as groundwater contaminants are that they have low solubility, they are lighter than water and volatile, and when they percolate through the unsaturated zone, they can form an LNAPL that floats on the water table (figure 3.2). At the same time, some of the volatile

FIGURE 3.2. Conceptual Model LNAPL Release and Migration



Source: Authors after Newell et al. 2003.
Note: LNAPL = light nonaqueous phase liquid.

compounds will evaporate, and another fraction of the petroleum will stick to the soil and aquifer. After the LNAPL has reached the groundwater, it slowly dissolves and migrates in the flowing groundwater. In addition, wherever oxygen sources are present, biodegradation reactions slowly decompose petroleum compounds.

Industrial (Chlorinated) Solvents and Dense Nonaqueous Phase Liquids (DNAPLs)

Chlorinated solvents are an important group of synthetic compounds that are used as degreasing agents and in dry cleaning. They are often known best by their acronyms and include trichloroethene (TCE), per- or tetrachloroethene (PCE), and 1,1,1-trichloroethane. As organic solvents, they are capable of dissolving organic compounds that are not soluble in water. Most are toxic and often carcinogenic and have distinctive properties:

- They are immiscible with, and denser than, water forming DNAPL, which can sink rapidly through the aquifer.
- They are only slightly soluble but at concentrations that are harmful to health.
- They are volatile, so they can evaporate in the unsaturated zone.
- Unlike petroleum compounds, they are resistant to aerobic biodegradation.

Pollution tends to originate as either accidental spills or slow leaks from storage tanks and then sink to uncertain depths, possibly to the base of the aquifer or become trapped on an interbedded low-permeability layer, where they can be difficult to locate and remediate (figure 3.3). As the DNAPL sinks or rests above a low-permeability surface, it slowly dissolves into the flowing groundwater.

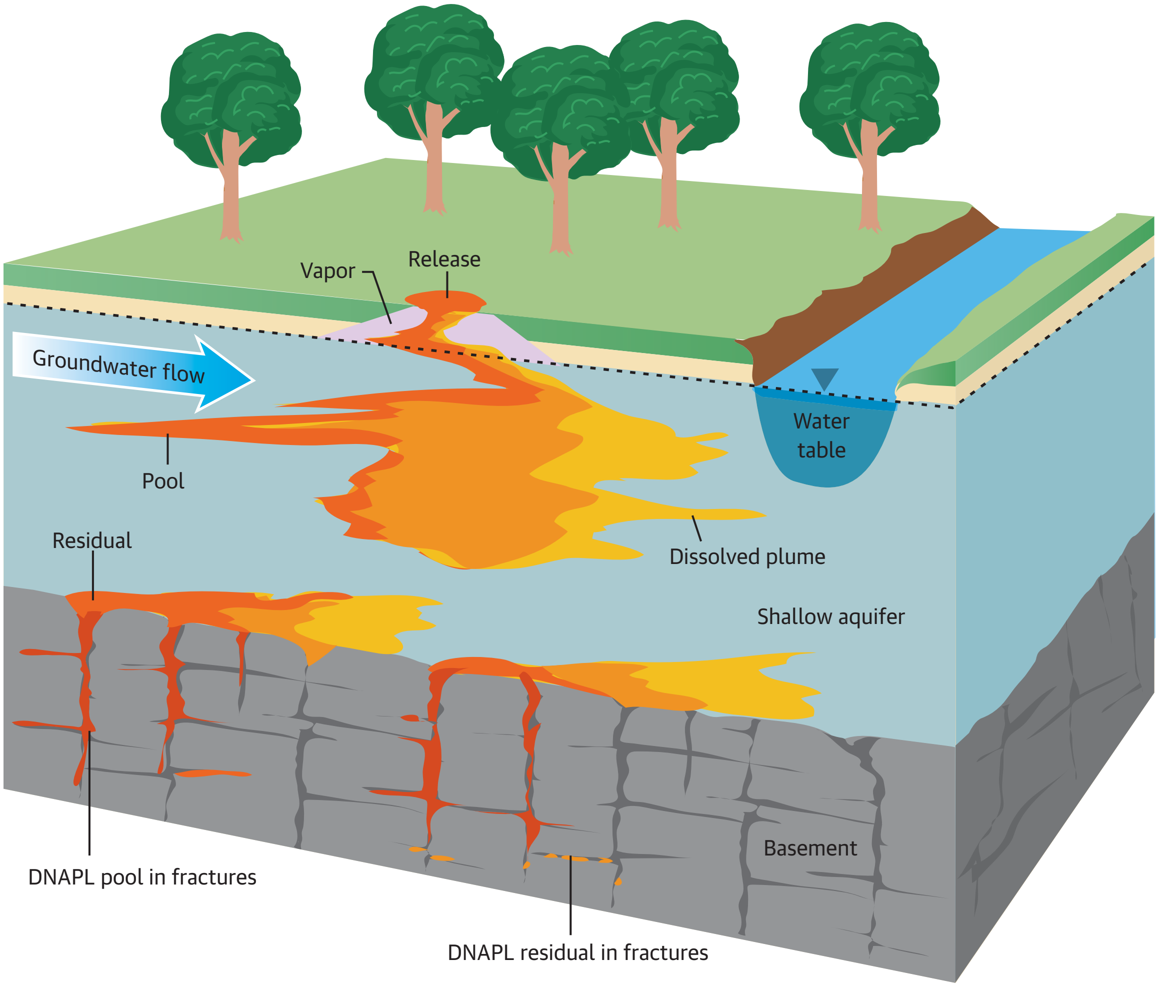
Chemicals of Emerging Concern

Contamination by solvents, petroleum, and pesticides has long been recognized, and its characteristics are reasonably well understood. However, over the past two decades, other synthetic organic compounds have come to the attention of regulators and the public. Some, such as PFAS (see the next section) and 1,4-Dioxane (chapter 2), have proved to be widespread and are particularly troublesome because of their high solubility, resistance to biodegradation, and adsorption. These chemicals of emerging concern (CEC) are increasingly entering groundwater through sewage, landfill, and other forms of deliberate or casual disposal (box 3.4 and table 3.1).[9] The health and environmental implications of many of these compounds are poorly understood;[10] however, at least some, such as PFAS, are significant. The precautionary principle demands that their presence be taken seriously and, as a minimum, measured. The variety between regions presumably both reflects their different economic histories and highlights the need for careful planning of surveys based on local knowledge of chemical use.

Per- and Poly-Fluoroalkyl Substances (PFAS)

Better known by the acronym PFAS, per- and poly-fluoroalkyl substances—notably PFOS and PFOA—are a group of 3,500 chemicals used as flame retardants, stain protectors, nonstick surfaces, and water repellents.[11] They are probably the most significant group of emerging groundwater pollutants.

FIGURE 3.3. Generalized Conceptual Model of DNAPL Occurrence



Source: DEET = N,N-diethyl-meta-toluamide; Adapted from EA 2003.
Note: DNAPL = dense nonaqueous phase liquid.
The darker orange color represents the locations of residual pockets or pools of nonaqueous phase liquid.

BOX 3.4. Chemicals of Emerging Concern (CECs)

A vast array of artificial organic substances (manufactured substances containing carbon atoms) is routinely entering the environment. They include fuels and lubricants; solvents and cleaning products; legal and illegal drugs; hormones; sweeteners; stimulants; food preservatives; corrosion inhibitors; fire retardants; plasticizers; surfactants; and personal care products (PCPs), such as soaps, skin care products, lotions, and fragrances; among many others (Damania et al 2019). An important subclass of these compounds are known by the self-explanatory name persistent organic pollutants (POPs).

TABLE 3.1. Selected Surveys of Emerging and Microorganic Contaminants, 2012–18

Country	Main emerging compounds	Main legacy compounds	References
China	Antibiotics (ofloxacin, lincomycin, norfloxacin, sulphapyridine)	VOCs: naphthalene, chloroform, 1,2-dichloroethane, 1,2-dichloropropane, 1,2,3-trichlorobenzene SVOCs: P,P′-DDT, 2,4-dinitrotoluene Phenol, Aldrin, heptachlor	Bi et al. 2012; Chen et al. 2014, 2018
England and Wales	Caffeine, DEET, bisphenol A, antimicrobial agents, and pharmaceuticals	Solvents (TCE, PCE), petroleum hydrocarbons (xylene, toluene), pesticides (atrazine, simazine), PAHs	Manasma et al. 2016; 2,650 sites
United States	N,N-diethyltoluamide, bisphenol A, tri(2-chloroethyl) phosphate, sulfamethoxazole, 4-octylphenol monoethoxylate	not reported	USGS[a]
Zambia	DEET, triclosan (bactericide), surfactants	Solvents (TCE, PCE), insecticides, herbicides	Sorensen et al. 2015

Note: DEET = N,N-diethyl-meta-toluamide; PAH = polyaromatic hydrocarbon; PCE = per- or tetrachloroethene; SVOC = semi volatile organic compound; TCE = trichloroethene; VOC = volatile organic compound.

a. For more information on the reconnaissance studies, visit the United States Geological Survey website at https://toxics.usgs.gov/highlights/gwsw_ec.html (accessed February 21, 2021).

These compounds are toxic, persistent, mobile, and bioaccumulating (chapter 2) and have been widely detected in municipal supplies across vast tracts of the United States, notably in Michigan, Minnesota, New Hampshire, and West Virginia. Elsewhere, widespread contamination of the Chalk Aquifer outside London followed a major fire in 2012 (Nicholas and Whitfield 2013). Although regulatory guidelines are not well established, the risk to health is clear. In 2016, the USEPA established a health advisory level of 70 parts per trillion (ppt), but in 2020 Michigan adopted a new groundwater standard of 8 ppt for PFOA and 16 ppt for PFOS (EGLE 2020). These thresholds are a thousand times smaller than better-known toxins such as arsenic, lead, benzene, or TCE. The usage of PFAS chemicals, and hence the likelihood of groundwater contamination, is becoming global, yet in many countries awareness of this risk is limited.

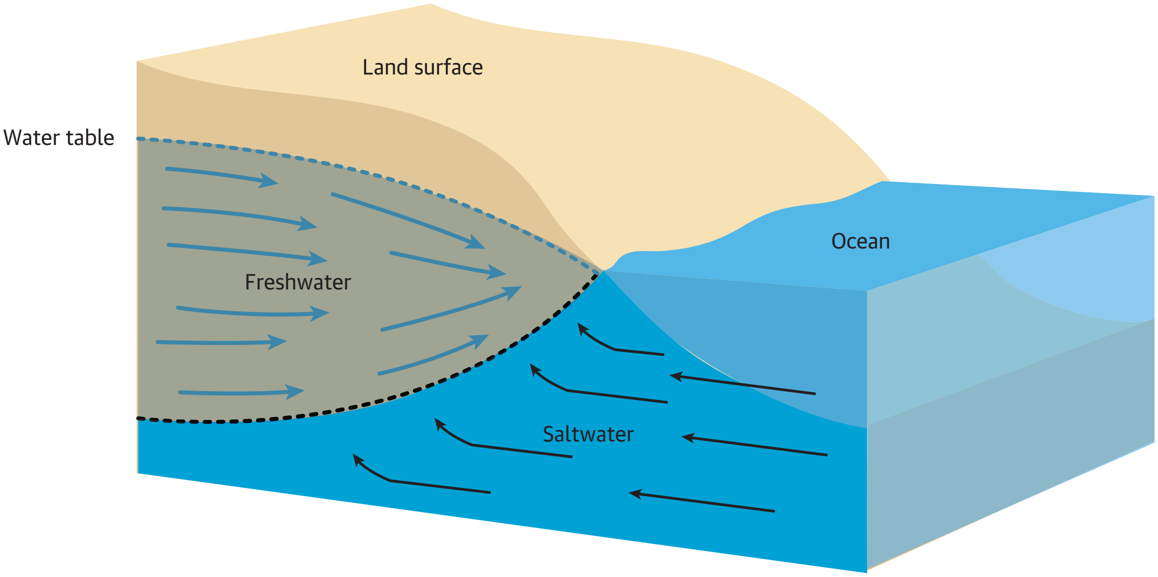
Salinity and Saline Intrusion

This important subject is described in many dedicated texts (for example, Jiao and Post 2019). Saline groundwaters are encountered in two main settings: near the coast and in low-lying arid plains where shallow groundwater is concentrated by evaporation. Saline groundwater can also result from dissolution of ancient evaporite rocks or simply rock weathering in exceptionally old groundwater, such as in the Great Artesian Basin of Australia. It should never be assumed that any detection of salinity means that seawater is flowing into the aquifer. There are several alternatives to the standard image of seawater intrusion (figure 3.4), and it is important to determine which of the following causes applies before defining a monitoring and management strategy:

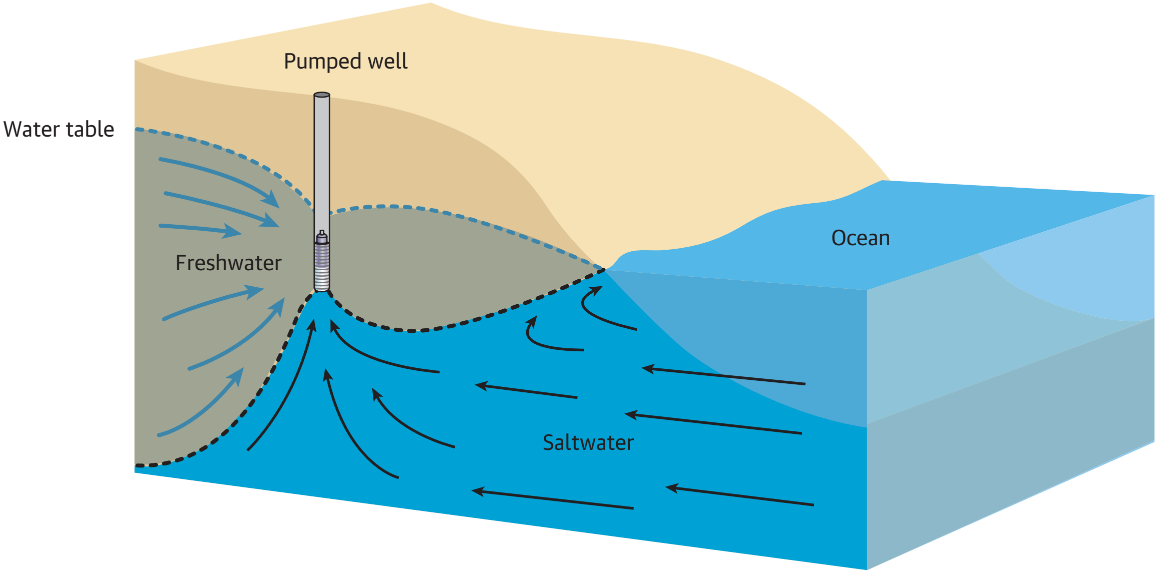
- *Conventional intrusion.* This occurs as horizontal movement of seawater beneath the land where there is a regional imbalance between recharge and abstraction.[12]

FIGURE 3.4. **The Standard Conceptual Model of Saline Intrusion and Upconing**

a. Natural conditions



b. Salt-water intrusion



- *Upconing*. Freshwater effectively “floats” on salty water, which can easily be pulled up immediately beneath a pumping well. This is a local, well-specific effect, not an aquifer-level imbalance, and it happens because the well is too deep or the drawdown is too big.

- *Ancient seawater*. It is usually assumed that freshwater is in direct contact with seawater. However, inland and coastal aquifers may contain trapped bodies of ancient saline water, relics of flow systems

> that have been inactive for hundreds or thousands of years. Many of these aquifers are layered and dip beneath the sea, where low-permeability layers separate them from the seabed. This is common in deltas, and it is usually good for sustaining water supplies, slowing down salinization, and allowing high pumping rates to be sustained for longer than expected by the standard model.

Salinity obviously makes water unacceptable or objectionable for drinking, albeit coastal populations tend to be more tolerant of mild salinity than most inland consumers. Salinity is also a major constraint on irrigated agriculture, especially under more arid climates where salt becomes concentrated in the soil zone. There is emerging evidence of significant of salinity-related health impacts on pregnant women and infants (World Bank 2019).

Some Special Issues

Here are some considerations that are becoming prominent for groundwater quality management.

Groundwater Quality and Surface Water

Streams that are hydraulically connected with aquifers are termed either gaining or losing streams according to whether groundwater seeps into or out of the stream, and many streams alternate between these conditions seasonally. The point here is that polluted surface waters can contaminate groundwater and vice versa; thus, the groundwater manager needs to know whether streams that flow across shallow aquifers are gaining, losing, or both. Although riverbed sediments may act as a sink for contaminants, special concern is given to situations in which fissured rock or gravelly sediment does not provide this protection and potentially allows pathogens, algae, and suspended solids to enter aquifers, then water wells or springs.

Groundwater Quality and Unconventional Uses of Aquifers

The techniques known as artificial recharge, aquifer storage and recovery (ASR), and managed aquifer recharge (MAR) are normally viewed as beneficial; however, the chemistry of the injected water and the aquifer must be matched to avoid any unwanted reaction—for example, when oxygenated water is injected, aquifers containing minerals such as pyrite can release sulphate, iron, and arsenic into the recovered water.

Fracking and coalbed methane production involve dramatically changing the hydraulic regime of groundwater systems and, in the former case, injecting chemical additives. Whenever interventions are considered, the groundwater manager should ensure that comprehensive groundwater quality monitoring is initiated with a well-defined baseline. The last point is important because fracking is often blamed for flaming methane discharges at taps, perhaps correctly, but this also happens in areas where such technologies do not operate (for example, Ahmed et al. 1998).

One approach to mitigating climate change is sequestration of carbon dioxide (CO_2) in exhausted gas fields or aquifers, raising concerns that CO_2 could escape from around wells or along geological pathways. The main concern is that escaping CO_2 will acidify groundwater, dissolve carbonate minerals, and create enhanced pathways for flow. As with energy production, a well-defined baseline and ongoing monitoring are vital.

Aquifers are used for heating and cooling buildings by circulating groundwater through a heat pump, which, depending on local circumstances, could change the thermal regime and, therefore, possibly the natural water chemistry. Although not always viewed as a water quality issue, heat is regarded as a contaminant under EU legislation, and this may apply elsewhere in the future. Small changes in temperature can have dramatic impacts for surface water bodies; their effect on groundwater is poorly understood.

Groundwater Contamination in Different Geographical Settings

To this point, this chapter has described contamination according to the different types of chemicals that may be encountered. To provide a balanced presentation, boxes 3.5, 3.6, and 3.7 describe the variety and extent of contaminants that occur in different geographical and hydrogeological settings: (a) a large unconfined alluvial aquifer in the Indian Punjab; (b) urban pollution in weathered basement aquifers in Sub-Saharan Africa; and (c) an extensive transboundary sandstone aquifer in South America.

BOX 3.5. Groundwater Contamination in the Indian Punjab

The Indian state of Punjab is underlain by thick alluvium laid down by tributaries of the Indus River, where groundwater is the principal source of drinking water and about 70 percent of irrigation water in India's "grain basket," which produces about 20 percent of the nation's wheat and 11 percent of its rice from just 1.5 percent of its land. Here, the interaction between surface water and groundwater is of profound importance, with 35 percent of the recharge to these wells estimated to originate as leakage from irrigation canals (World Bank 2010).

The Department of Drinking Water Supply and Sanitation (DWSS) tested more than 9,000 rural schemes, which were typically wells 100 to 150 meters deep with a submersible pump serving a few thousand consumers (one to three villages), with a minority having handpumps serving about twenty households. The groundwater, which was generally considered to be of good quality, was found to contain multiple chemicals in excess of drinking water standards. Three groups of contaminants—geogenic, anthropogenic, and microbiological—were recognized. The three principal geogenic contaminants—arsenic, fluoride, and uranium—are statewide issues (map B3.5.1), although arsenic is concentrated in different areas from the other two. Salinity (about 14% total dissolved solids (TDS) > 2,000 mg/L) was a major issue in the south and east of the state, as was iron (about 11% > 0.3 mg/L) in many areas. No data are available for manganese, but this is also likely to be a significant issue.

Identified anthropogenic contaminants included heavy metals, such as lead, chromium, mercury, nickel, and selenium, although the latter may be partly natural. These were tentatively attributed to industrial activity, but their distribution was not consistent in space and time, and it was suspected that the results are compromised by sampling protocols that acidified samples in the field before filtering in the laboratory. Nitrate (> 10 mg/L as NO_3^--N) was detected at 4.4 percent of sites. This was attributed to both fertilizer and fecal waste and considered to indicate significant downward flow, possibly following preferential pathways along the outside of

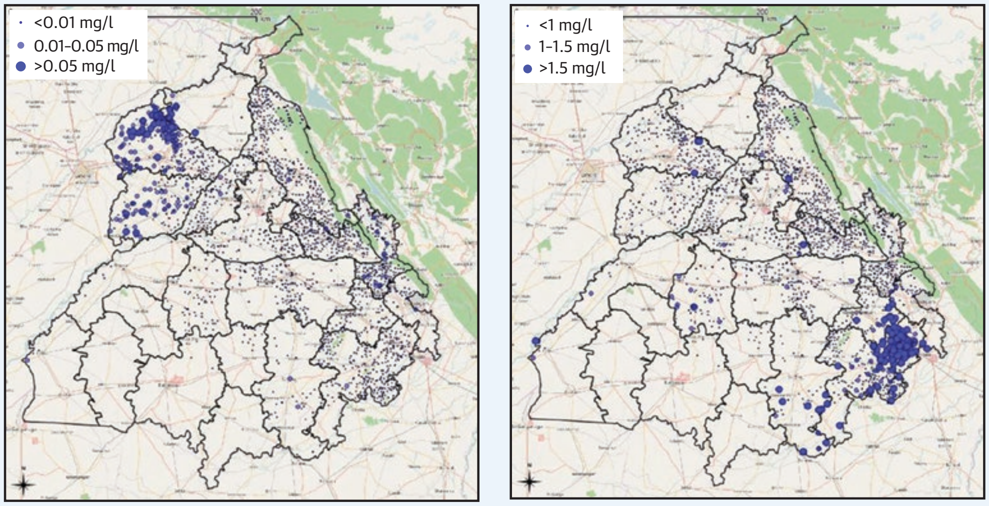
box continues next page

BOX 3.5. continued

wells, and therefore also to a significant risk of pesticide contamination (which was not tested). Pathogens were not tested; however, other investigations and the prevalence of diarrheal disease suggest their presence in groundwater is common.

The study proposed technical interventions, such as deepening wells and better sanitary sealing, and also emphasized the need for regular groundwater quality monitoring to improve understanding, development of a public communications strategy, and sensitization of the DWSS and related institutions to adopt a learning culture to actively manage water quality problems.

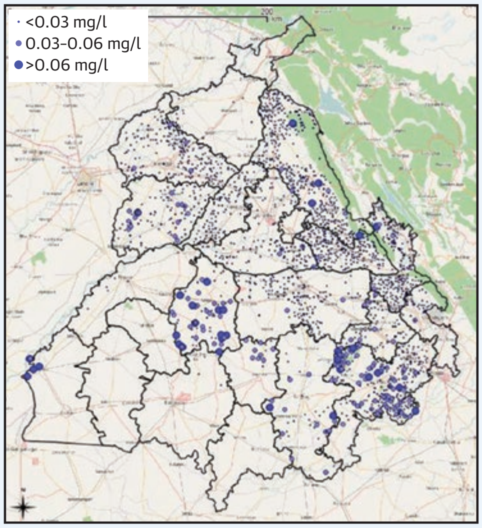
MAP B3.5.1. Concentrations of Geogenic Contaminants in Groundwater, Punjab, India



a. Arsenic

b. Fluoride

c. Uranium

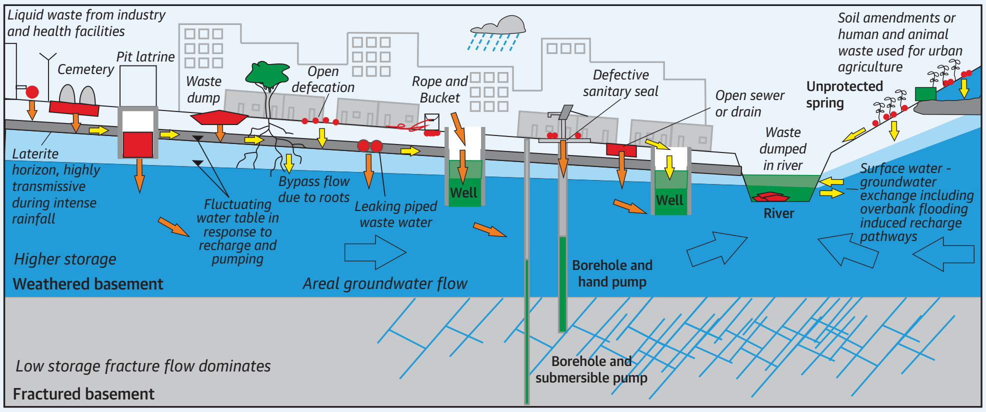


Source: World Bank 2020.

BOX 3.6. Anthropogenic Groundwater Contamination in Sub-Saharan Africa

There are many parts of the world where groundwater quality is not measured adequately. However, studies conducted in Sub-Saharan Africa since 2014 provide insight on how urban groundwater is being affected, as illustrated conceptually in figure B3.6.1. Reports of fecal contamination from eleven countries included ten with data on fecal coliforms and one on viruses, but none assessed protozoa or helminths; most also presented chemical indicators such as nitrate and chloride. Most studies found proximity to pit latrines to be a key determinant of fecal contamination and often nitrate. Rapid attenuation of bacteria was often observed over distances of 1 to 20 meters. Data on nonsanitary contamination were reported from three countries, including five landfill, two mining, and one industrial source. High concentrations of heavy metals, especially lead and zinc plus copper and cadmium, were recorded at several of these sites, as well as high concentrations of nitrate, ammonium, and phosphate at municipal sites. Information on emerging organic contaminants in groundwater are almost unknown outside South Africa, with

FIGURE B3.6.1. Key Potential Sources, Pathways, and Receptors of Fecal Contamination in Urban Settings in Sub-Saharan Africa



🟥

Sources of contamination providing an essentially diffuse input of hazards to the surface, for example open defecation by humans as well as animals, surface liquid discharge from household and municipal waste water, as well as sources that are buried in the subsurface, for example waste dumps, historical mining waste, pit latrines, septic tanks, and cemeteries.

🟩 🟦

Receptors of hazards including the groundwater resource as a whole as well as specific groundwater supplies including wells, boreholes, and springs. Surface water is also a receptor of hazards. Shallow wells and springs are at risk from septic tanks and shallow waste systems and in low-lying areas where shallow water tables persist and that are prone to flooding during high-intensity rainfall events.

⇨

Transient pathways for hazard to migrate to the subsurface linked to intense rainfall events. High risk from rapid lateral transport in/above laterite horizon when infiltration capacity of soil is exceeded. Limited vertical transfer beyond laterite horizon particularly during the early part of the rainy season when there are low moisture levels in the shallow subsurface below the laterite horizon and the water table is deeper.

☁

As the rainy season progresses, soil moisture and areal recharge increase and trigger pathways for surface-surbsurface migration of hazards. The intensity of the rainfall is an important factor and may lead to transient surface runoff, ponding, and lateral flow above and in the regolith and laterite horizon, (that is, pipe flow when vertical infiltration is exceeded). The first flush of contaminants during early rains can lead to a large pulse of contaminants from the surface to the subsurface due to focused urban recharge processes.

➡

Continuous pathway for hazard to migrate to depth within groundwater via (a) continuous source of recharge of liquid waste such as soak-aways, open sewers, or surface discharge providing continuous pathway to the water table or, (b) where there is direct bypass of the soil and unsaturated zone (that is, using a bucket and rope or cracks in well or borehole seal). This may be a particular issue at the end of the dry season/start of the wet season because of intense use of fewer nonseasonal sources.

⇨

Areal groundwater flow from piezometric high points toward natural discharge points, such as rivers.There may also be discharge from springs; flow from these sources will be linked to cumulative rainfall, rainfall intensity (especially in rapidly responding or transient springs), aquifer storage, and recharge processes.

Source: Lapworth et al. 2017.

box continues next page

BOX 3.6. continued

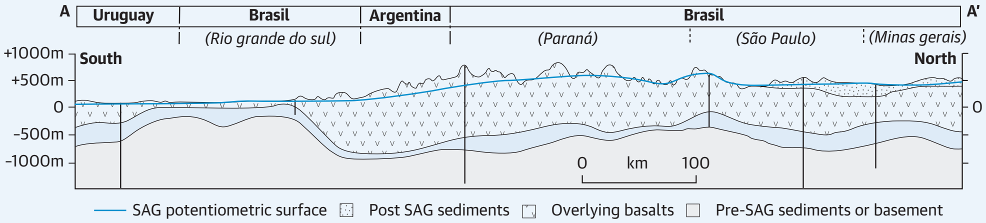
the notable exception of a survey testing for a range of over a thousand compounds from the city, and former mining center, of Kabwe in Zambia. Twenty-seven compounds were detected from twenty samples from wells in the underlying granitic basement. The insect repellent DEET was detected at every site. The bactericide triclosan, trihalomethanes, herbicides, and insecticides were detected only in residential areas. Chlorinated solvents were detected in industrial and low-cost housing areas. The concentrations measured were generally quite low but unambiguously establish the existence of pollution pathways to an aquifer that was previously thought to be well protected. Because they are isolated in time and space, these pioneering investigations cannot be considered representative, but they clearly indicate the reality of the anthropogenic pollution risk and the urgent need to instigate baseline surveys and targeted monitoring.

Sources: Lapworth et al. 2017; Sorensen et al. 2014; WWQA 2021.

BOX 3.7. Groundwater Quality in a Transboundary Aquifer—The Guarani Aquifer, South America

The Guarani Aquifer System (GAS) is South America's largest and most important aquifer, spanning Argentina, Brazil, Paraguay, and Uruguay, and the subject of the landmark Guarani Aquifer Agreement (GAA). The aquifer is formed of an average of 250 meters of weakly cemented sandstone of Triassic-Jurassic age that is extensively overlain by Cretaceous age basalts and contains such a vast store of freshwater that annual recharge is only a fraction of a percent of the stored water (figure B3.7.1). The GAS is a major source of public (80 percent) and industrial (15 percent) supply in four countries, as well as a geothermal resource. Notwithstanding an area of high salinity in the southwest, the natural groundwater quality is generally quite good, mostly with low mineralization, but changes as water flows from the outcrop area into the area where the aquifer is confined by the basalts—a zone that extends for more than a hundred kilometers. The pH increases from about 6.5 to as high as 9.5, and ion-exchange causes a decrease in calcium (from 30 to 2 mg/L) and a corresponding increase in sodium (from 1 to 90 mg/L), which accounts for high fluoride concentrations and occasionally elevated arsenic in the confined aquifer.

FIGURE B3.7.1. Guarani Aquifer Hydrogeological Cross-Section



Source: Foster et al. 2009.

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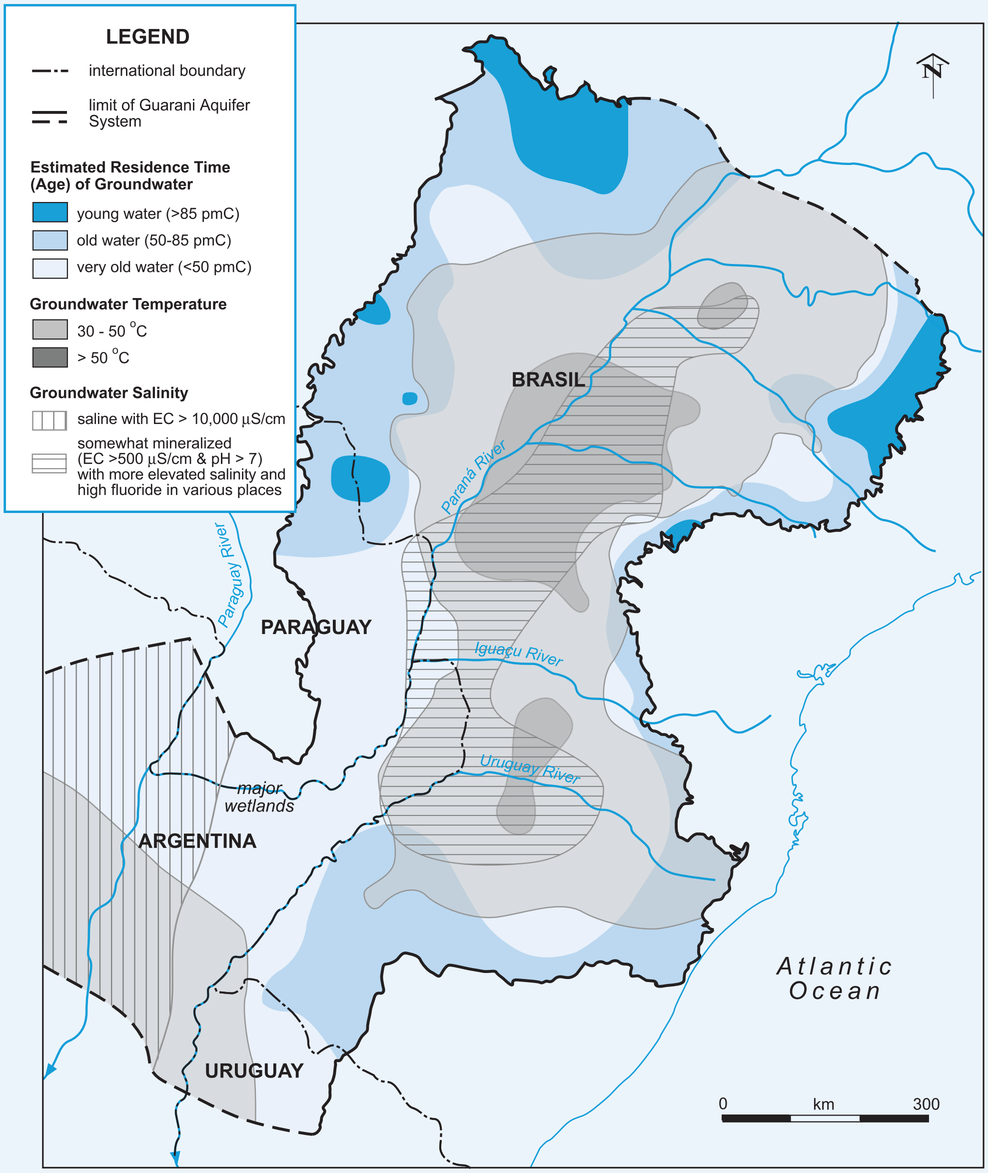
BOX 3.7. continued

There are also reasons to suspect that deep confined groundwater might contain significant levels of uranium, radium, and radon. Studies to support the GAA, such as joint monitoring exercises and isotopic studies, have led to advances in understanding and enabled the definition of five "resource management zones" (map B3.7.1). In the unconfined zone and beneath "windows" in

MAP B3.7.1. Guarani Aquifer System

a. Groundwater "ages" based on δ14C analysis of percent modern Carbon (pmC) and its regional temperature and salinity variation



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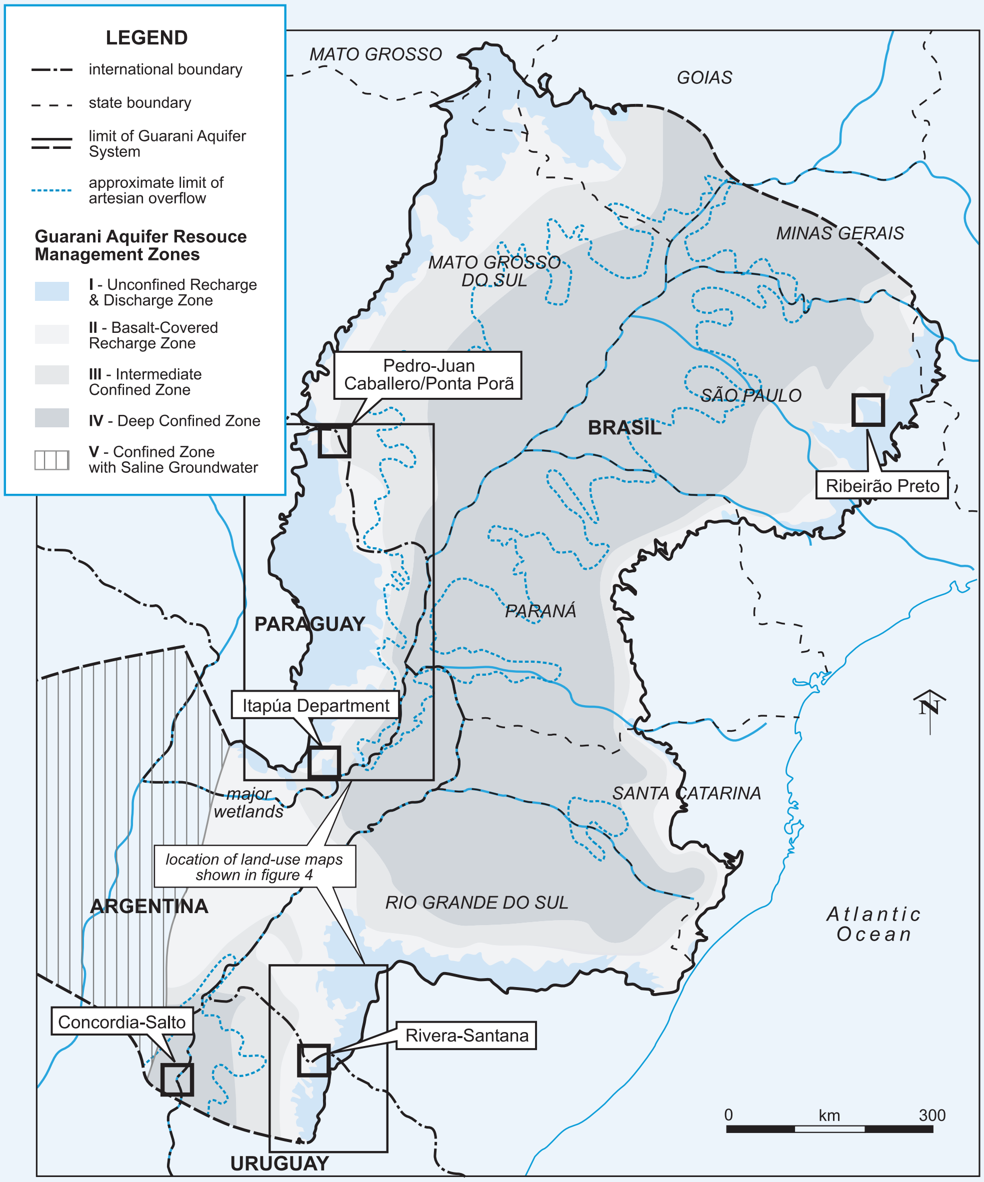
BOX 3.7. continued

MAP B3.7.1. Guarani Aquifer System (continued)

b. General delineation of resource management zones



Source: Foster et al. 2009.

the basalt cover, groundwater is "modern" (that is, recharged in the past fifty years or so) and is significantly vulnerable to pollution from the land surface by urban wastewater, storage of hazardous chemicals, disposal of liquid effluents, and agricultural intensification. Also, where the

box continues next page

BOX 3.7. continued

water table has been drawn down, there may be induced leakage of contaminated surface water. To date, nitrate has not exceeded 10 mg/L (as NO_3^--N), and herbicides and chlorinated solvents known to be in use have not yet been detected in groundwater. In the confined zones, groundwater is as old as 700,000 years and considered to be completely protected from anthropogenic pollution. The political process involved in drawing up and ratifying the GAA, which includes separate articles (#3 and #4) on legally backed monitoring and institutional structures, has had a major impact on developing public understanding and dispelling myths about groundwater and in raising finance for its management.

Sources: Foster et al. 2009; Hirata and Foster 2020; Sindico, Hirata, and Manganelli 2018.

Notes

1. The unsaturated zone is that between the soil and the water table.
2. Typically four metals (calcium, magnesium, sodium, and potassium) and three nonmetals (bicarbonate, sulphate, and chloride), plus pH and possibly iron and manganese.
3. Mining and industrial sources can cause significant confusion in areas where geogenic arsenic is present, as occurred in West Bengal and Bangladesh (Ravenscroft, Brammer, and Richards 2009). On the one hand, extensive pollution was wrongly attributed to arsenical wood preservatives in electricity pylons, but on the other hand, in Kolkata arsenic pollution from a factory producing the pesticide Paris Green was superimposed on natural contamination.
4. Plus countries as diverse as Finland, Kosovo, South Korea, Switzerland, and the United States (Sahoo et al. 2021).
5. It may be noted that, in this semiarid area, as the water moves through the basin, it also becomes increasingly saline.
6. There are thought to be about 150,000 chemical substances in commercial use.
7. Schmoll et al. (2006) provide a detailed and wide-ranging discussion of these issues.
8. A subhorizontal tunnel in a mine.
9. The United Kingdom study in table 3.1 revealed the important, if not surprising, finding that differences in microorganic contaminants' occurrence are closely related to land use. This should be a lesson for surveys that have not yet been conducted.
10. Some, such as bisphenols, phthalates, and estrogens, are suspected endocrine-disrupting chemicals.
11. PFAS may also be found in tannery wastes.
12. In some thick beach sand deposits and massive limestones, such as the Floridan Aquifer, the Chalk of Northwestern Europe, and the Umm Er Radhuma in the Arabian Peninsula, this is a reasonable approximation of what happens.

Chapter 4
Characterizing the Risks of Groundwater Contamination

Key Points

- Conceptual models are the foundation of characterization.
- The source-pathway-receptor (SPR) concept provides a framework for understanding risks.
- Modest, low-cost actions can provide a solid basis for assessing risks.
- Baseline water quality is an essential management tool.

Three broad tasks face the groundwater quality manager: (a) respond to known contamination, (b) identify hazards that might contaminate groundwater, and (c) develop protective actions to prevent contamination. The prerequisite for assessing these issues is a sound conceptual hydrogeological model. Then the characterization of risks from suspected or identified contamination follows a sequence of steps, beginning with simple investigations that become progressively more detailed. An assessment of the risk is made by understanding the physical and chemical nature of the contaminant and the pathways by which it enters the groundwater.

A convenient way to think about risk is as the probability of a bad thing happening, in which

risk (R) = hazard (H) * vulnerability (V)

where, for groundwater pollution, the hazard is the chemical or pathogen that could do harm and vulnerability is what might be affected, which could be the aquifer, a well, or surface water. Another useful way to think about groundwater risk is the source-pathway-receptor (SPR) linkage, where source and receptor are equivalent to the hazard and vulnerability terms used earlier but the pathway term focuses attention on how to cut the link between the source and the receptor.

The Conceptual Hydrogeological Model

A conceptual hydrogeological model (CHM) is a graphic and textual description of the nature of the aquifer's, groundwater flow and quality, its uses, and its interaction with the surface environment (photo 4.1). This is the essential framework for defining objectives and designing a monitoring program. The CHM also aids communication between specialists and nonspecialists. Its core elements are geology, topography, climate, and human activities, such as groundwater abstraction and the handling of hazardous substances (Brassington and Younger 2010; Enemark et al. 2019). An example of a generic

PHOTO 4.1. **What a Real Aquifer Looks Like**

a. Cliff near Rousdon, Devon, United Kingdom

b. Cliff at Hive Beach, Dorset, United Kingdom

Source: Author's photos.

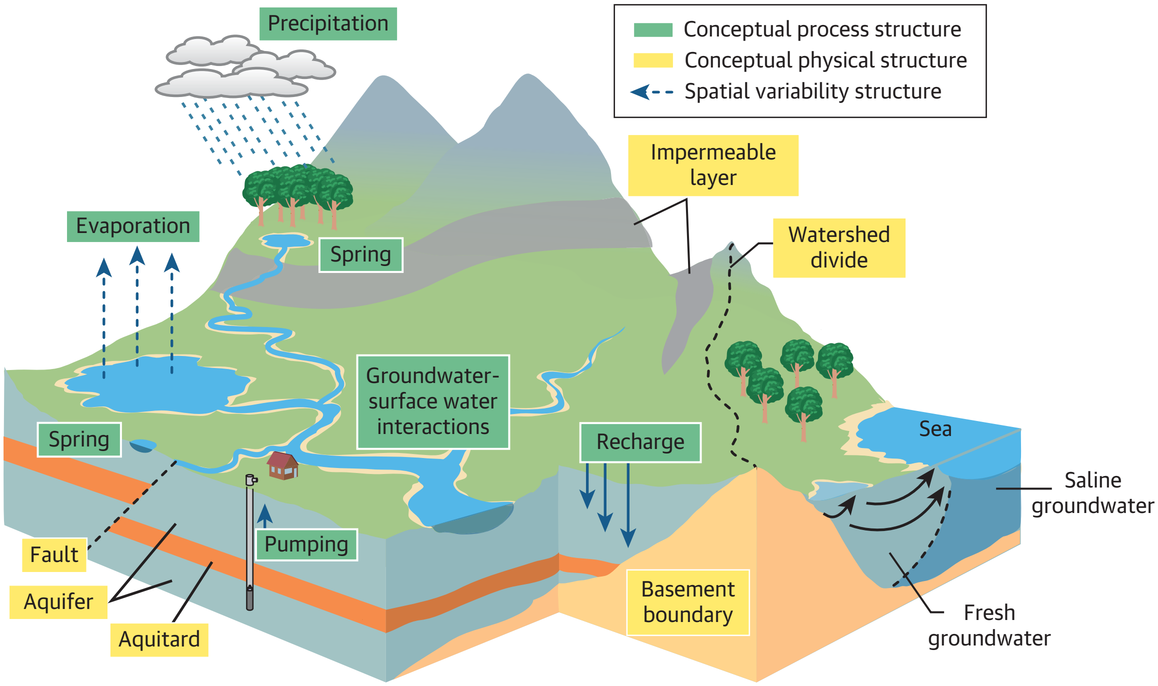
conceptual model is shown in figure 4.1. The conceptual model is a live document that should be updated regularly as more information is collected.

Establish a Baseline

Commonly, serious monitoring begins only after problems are discovered, which leads to unresolvable arguments about the initial state of the aquifer and therefore the foreseeability of, and liability for, the problems (box 4.1). The importance of establishing a baseline applies equally to managing an entire river basin or a single plot of land for commercial development and everything in between.

There are multiple reasons why a comprehensive baseline is important. The first and most obvious is to detect the presence of any natural hazards, such as fluoride or arsenic, before harm results.[1] A good hydrochemical baseline makes it possible to design a monitoring system that is prioritized on the parameters of most relevance. The detection of synthetic compounds, such as pesticides, solvents, or PFAS, will be unambiguously attributed to human activity. Other contaminants, such as nitrate or phosphate from fertilizer, sewage, or saline intrusion, result in higher concentrations of naturally occurring chemicals. In the latter cases, it may be difficult to differentiate the cause of higher-than-expected concentrations and to initiate—and justify—appropriate action. Similarly, a robust baseline is needed to know the natural state of groundwater against which the impact of physical stresses, such as changes in land use or modification of river regimes, may be evaluated.

FIGURE 4.1. **Generic Example of a Conceptual Hydrogeological Model**



Source: Adapted from Enemark et al. 2019.

Managers Message

Concentrating on developing and updating a good conceptual hydrogeological model (CHM) is likely to be much easier and more useful than trying to apply "fancy mathematics" that is conducted by a small group of experts (who may lack practical experience of monitoring) and is not communicable to many stakeholders, and still may not capture the proper determinants of good monitoring. By contrast, a visual presentation of geology and water flows, abstractions, and pollution sources will allow healthy discussion by all and produce a robust solution that is communicable to budget holders.

Preferential Pollution Pathways

Although most groundwater pollution results from liquids infiltrating from the ground surface, there are important man-made pathways by which pollutants can bypass the normal protection provided by soil and pavements. The most important of these are (a) abandoned wells; (b) buried infrastructure, such as pipelines, latrines, sewers, oil-filled electricity cables, basements, and tunnels; and (c) drilling and deep well activities, such as fracking and wastewater injection. In addition to pathways *into* groundwater, vapors from shallow groundwater can enter the basements of buildings.

BOX 4.1. Absence of Evidence Is Not Evidence of Absence: What Haven't You Tested For?

In the 1980s and 1990s, long-industrialized countries witnessed an explosion of discoveries of industrial chemicals and pesticides in groundwater supplies. This was not a real increase in pollution, simply better testing equipment and more monitoring.

A naïve reading of the literature might suggest that this type of pollution is a problem only of old industrialized countries. There are relatively few reports from low- and middle-income countries, yet towns and cities across the world that draw groundwater from beneath their feet have used the same chemicals for decades. It is likely that such pollution has already occurred and has entered water supplies unrecognized.

Monitoring for industrial chemicals requires sophisticated equipment and skills that may not be easily accessible. Utilities often declare their water has been tested safe when relevant chemicals have not been tested for. Many water managers don't know what they don't know. There is an urgent need to compare what water providers test for with the hazardous chemicals that are in use. If the lists don't match, a research organization should be commissioned to conduct a rapid baseline survey.

Pollution Hazard Mapping and Characterization

A priority action in assessing anthropogenic pollution risk is hazard mapping, which can be done by compiling information on present and historical land use in geographical information systems (GIS) based on the following data sources:

- Local government and trade association registers
- Registered pollution events
- Historical maps that identify previous potentially contaminating land uses
- Google Earth, aerial photos, and high-resolution satellite images
- NGOs and citizen reporting

The next step is to characterize the toxicity and mobility of potential contaminants that could be associated with these activities and, if possible, estimate the magnitude of chemicals used in terms of volumes and persistence.

Vulnerability Mapping

Groundwater vulnerability is a measure of how easily a contaminant discharged on the land surface could reach the water table. It focuses on the pathway component of the SPR link, and its presentation

BOX 4.2. Ambient Groundwater Quality and SDG Indicator 6.3.2

SDG 6.3 aims to improve water quality by "reducing pollution, eliminating dumping and minimizing release of hazardous chemicals, halving the proportion of untreated wastewater and increasing safe reuse," with indicator 6.3.2 defined as "the proportion of water bodies with good ambient water quality." Although intended for all waters, it is formulated mainly with regard to surface water where anthropogenic pollution is the overwhelming cause of poor water quality. For groundwater, this introduces two complications: widespread geogenic contamination and the lag time between stopping a polluting activity and improving water quality. The so-called Level 1 monitoring parameters are good for surface water quality but not sufficient (only EC, nitrate, and pH) for groundwater. Countries that wish to leverage the SDGs to improve groundwater quality must include "optional" Level 2 parameters in their SDG reporting.

as a vulnerability map serves as a powerful land-use planning tool, especially when combined with hazard mapping in GIS. These maps vary in complexity and start with the locations of aquifers, to which can be added information on soil characteristics, the unsaturated zone, and the nature of the aquifer, as in the well-known depth-recharge-aquifer-soil-topography-impact-conductivity (DRASTIC)[2] methodology (figure 4.2). Each layer is assigned a set of scores and weights that are summed to generate an overall numerical score for vulnerability.

Groundwater Quality Investigations

Most significant pollution events will require field investigations, and their scope should be worked out by an interdisciplinary team. A typical sequence of investigations would be composed of the following four steps:

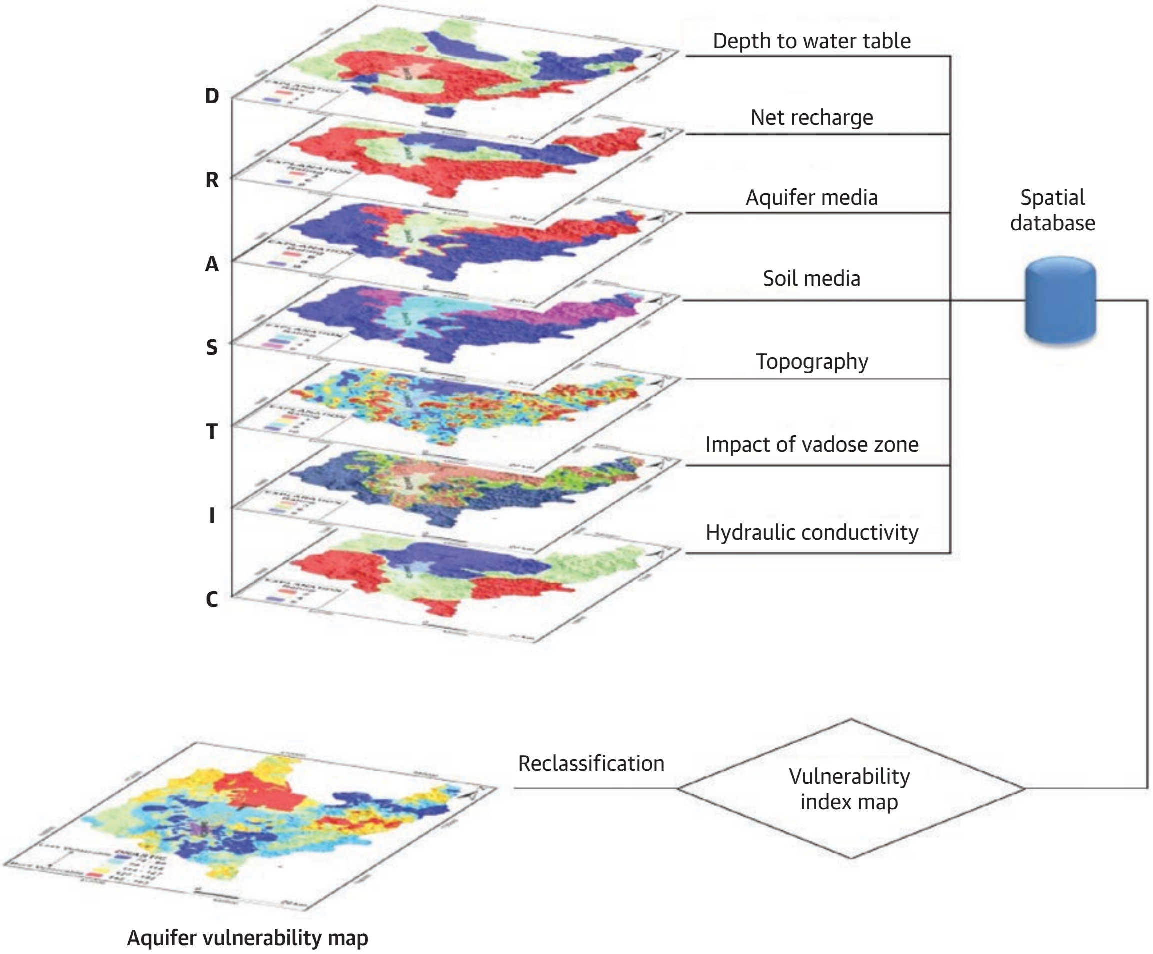
(a) Reconnaissance surveys of existing wells, boreholes, and springs.

(b) Sampling surveys. In the case of natural contamination, this would be blanket surveys of all wells in the area—if possible, using field test kits to provide immediate feedback to water users. In the case of anthropogenic contamination, this would involve targeted surveys in the vicinity of the pollution event to identify any impacted wells and establish a baseline against which any further impact can be measured.

(c) Site investigations or research studies in pollution hot spots or source areas. For natural contamination, this will concentrate on understanding the geochemical processes that release contaminants into groundwater. For anthropogenic contamination, the focus will be quantifying the concentrations of pollutants and their distribution in the source area and delineating any plume that has migrated away.

(d) Regular monitoring, starting as soon as possible, based on the findings of these steps.

FIGURE 4.2. The DRASTIC Methodology for Vulnerability Mapping



Source: Alwathaf and Mansouri 2011.

Risk Assessment

Risk assessment, which may be qualitative or quantitative, should guide the conduct of groundwater quality management and follow the philosophical approach of risk-based corrective action (RBCA) developed in the United States. Risk assessment is most commonly applied to anthropogenic events, but it is equally applicable to natural contamination. The simplest application is to overlay hazard and vulnerability maps and abstraction wells in GIS. This will help water utilities or public health agencies identify water sources and communities most at risk and for the owners of hazardous facilities to prioritize investments in risk reduction. As a pollution incident is recognized to be potentially significant, it will be appropriate to carry out a quantitative risk assessment (QRA) employing models to predict when and at what concentrations contaminants might reach a receptor. An important distinction can be drawn between when a contaminant *might* reach a receptor and results in actual exposure and situations when the contaminant has *already* resulted in exposure.

In the latter case, health and environmental regulators must be involved and a quantitative health risk assessment (QHRA) may be required.

The details of risk assessment can become quite complicated; however, the manager's duty is to ensure that the risk assessment is conducted by competent professionals so that the results are defensible, in court if necessary, and that the results are used to initiate action to reduce risks to human health and the environment while avoiding unproductive expenditure that could be better spent elsewhere.

Regulation and Its Consequences

Managing pollution requires understanding the regulatory regime and how it might change in the foreseeable future. The EU and North America have enacted fairly comprehensive legislation for groundwater since the 1980s to address gaps in water quality protection. Outside these areas, the adequacy of the existing regulations to protect and restore groundwater, including implementing the polluter pays principle through fines and/or the requirement to remediate, probably requires review.

The basic regulatory measure is usually the drinking water standard, applied at the point of extraction or point of use, and is used to classify resources, but remember that water may be unfit for drinking (without treatment) yet suitable for agricultural or industrial purposes. Changes to drinking water standards that occur in response to improved scientific understanding will affect the classification of water (box 4.3).

Assigning responsibility for groundwater pollution can be complicated. Synthetic chemicals, such as PFAS, solvents, and pesticides, should never enter groundwater and originate only from human action. Others, such as chloride, nitrate, arsenic, and fluoride, occur both naturally and through human action,

BOX 4.3. Changes in Drinking Water Standards and Guidelines

The scale of a water quality problem can be transformed by administrative decisions. Despite strong evidence that synthetic organic compounds (SOCs), such as PFAS and 1,4-Dioxane, are harmful, defining scientifically justifiable thresholds is difficult, and opposition to low standards comes from the high cost of delivering uncertain benefits, especially in more litigious societies. In the United States, in the absence of clear federal guidance, states specify vastly different thresholds. Even when the evidence is clear, there may be political opposition. In 1991, the WHO reduced its guideline value for arsenic from 50 to 10 ppb. This value was adopted by the EU and the USEPA; however, many of the most affected countries retain a 50 ppb standard, apparently because a lower standard for arsenic would approximately double the officially exposed population. In the United States, in 2001 the outgoing Clinton administration instituted a lower (10 ppb) arsenic rule, which was almost immediately revoked by the incoming Bush administration under pressure from Southwestern states about the financial costs of compliance. However, following a review by the National Research Council (NRC), the 10 ppb arsenic rule was quickly reinstated because the scientific evidence review suggested an even lower limit was appropriate.

so pollution is defined on a threshold or known background concentration. Assigning responsibility may be debatable and illustrates the importance of carefully drafted regulations.

The overriding objective of the regulator should be to protect the environment, not maximize prosecutions. This can be advanced by promoting voluntary remediation with the expectation of either avoiding prosecution or receiving a reduced sentence. There are several pragmatic reasons for such dispensation. First, the number of polluters often far exceeds the capacity to prosecute them. Second, most pollution events are accidental, and because the key to limiting damage is immediate reporting and early remediation, the most effective emergency response will be when the user of hazardous chemicals deploys real-time monitoring and a contingency plan. Prosecution resources should be concentrated either where pollution is particularly severe or where gross negligence or malice require a point of principle to be established.

Notes

1. Such as occurred with the unintended poisoning of more than forty million Bangladeshis by arsenic, which in the space of five years went from being unknown to being the “largest mass poisoning of a population in history” (Smith et al. 2000).
2. DRASTIC is an acronym for the DRASTIC methodology seven layers: depth (to water), recharge, aquifer, soil, topography, (vadose zone) impact, and (hydraulic) conductivity (Aller et al. 1987).

Chapter 5
Groundwater Quality Monitoring

Key Points

- Know why and what you are monitoring.
- Understand the limitations of monitoring infrastructure.
- Be ready to challenge monitoring results—there usually are alternative explanations.
- Ensure monitoring protocols, infrastructure, and network design are aligned with the monitoring purpose.
- Ensure staffing and logistics are consistent with the scope of monitoring required.
- Integrate monitoring into designing responses (for example, alternative source, remediation, and treatment) that match the capacity to implement it.

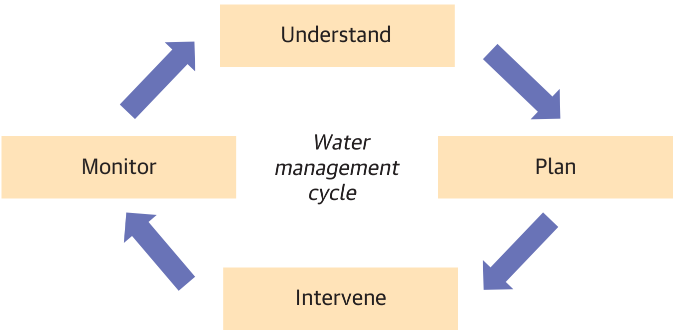
This chapter takes a high-level view of monitoring, emphasizing the principles and applications, some systemic reasons for how it can go wrong, and how they can be avoided.

The Purposes of Monitoring

Monitoring involves making regular measurements over time. It reveals how hydrological systems work and support the development and implementation of plans and programs (figure 5.1). Without monitoring, these plans may be no more than wishful thinking. To realize their potential, monitoring data must be verified and then displayed imaginatively using graphs, maps, geological sections, and statistical analysis. In addition, groundwater professionals must take time to explain the benefits of groundwater quality monitoring, which include

(a) Resource accounting—that is, quantifying the volumes of different water qualities;

FIGURE 5.1. The Monitoring and Management Cycle



(b) Identifying trends in the water quality status of groundwater bodies;

(c) Tracking pollution plumes and supporting management decisions; and

(d) Identifying the fingerprints of climate change and other human activities.

A monitoring system comprises a network of monitoring stations and practices and clear objectives. In practice, monitoring of groundwater quality and quantity will be integrated. Individual agency monitoring networks may have a variety of purposes as listed here:

- *Water resource surveillance*: to know the status and trends of groundwater quality in aquifers or water bodies. The planning horizon is typically years to decades.

- *Operational monitoring*: for agencies to demonstrate they are satisfying their mandates to deliver a particular quantity and quality of water to consumers. They may include sentinel monitoring in which one or more monitoring wells are positioned between contaminated groundwater and abstraction wells to provide advance warning of encroaching pollution. The planning horizon is days to a few years.

- *Water supply surveillance*: similar to operational monitoring but is consumer-focused, irregular, and randomized. Groundwater is monitored incidentally.

- *Site surveillance:* precautionary monitoring for known risks associated with activities such as landfills, industrial estate, or mining but where pollution is not known to have occurred.

- *Monitoring pollutant plumes*: similar to earlier but concerned with managing positioned pollution events.

Multiple agencies conduct monitoring for different purposes, but their outputs should be combined into what can be called the *total monitoring network*, created as an online cooperative venture.

Two complementary tiers of objectives are required: first for individual monitoring points and second for the groundwater body in terms of overall status, the latter being essential to deciding the appropriate number and type of wells, the parameters to analyze, and the frequency of measurements. Objectives should be confirmed with regulators, water utilities, private abstractors, surface water monitoring agencies, local authorities, and other groups affected by, or dependent on, groundwater, ideally through a multistakeholder partnership (MSP).

Monitoring is also required to comply with international commitments, such as tracking the SDGs and the United Nations Environment Programme's Global Environmental Monitoring System (GEMS).

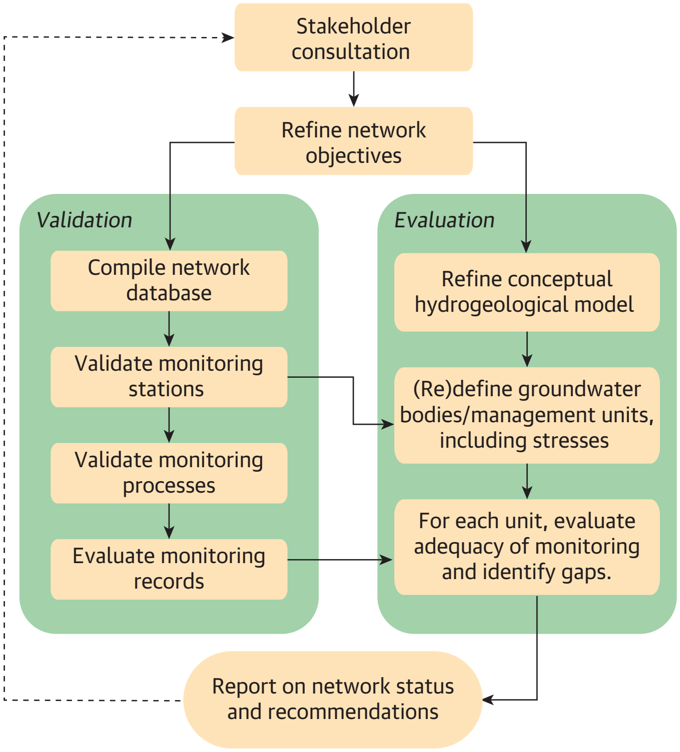
Reviewing Groundwater Monitoring Networks

Networks are rarely, if ever, designed from scratch. They begin by adopting existing wells and springs and progressively adding purpose-built monitoring wells. The purpose of review is to rationalize the network, which is done through an iterative process (figure 5.2), which proceeds by way of (a) stakeholder consultation, (b) defining groundwater bodies[1] and a conceptual model, and (c) fixing objectives at the station and network levels. Stakeholder consultation is important to build a consensus around the objectives, sharing data, local knowledge, and concerns.

In parallel with refining the conceptual model of the groundwater management units (GWMUs), the review should systematically validate the monitoring stations and check the sampling and testing procedures before evaluating the actual monitoring records.

In the final stage, the review will examine the validated stations and monitoring records as a group to decide whether they provide the necessary and sufficient information to determine the status and trends of groundwater quality in that water body. The completed review is shared with stakeholders to (a) explain the status and trends of groundwater quality, (b) explain any gaps in knowledge, and (c) agree on a plan of action.

FIGURE 5.2. Network Review Process



Design of Monitoring Wells

A monitoring well is “a window into the aquifer” (Weight 2008), and like any window, how it is positioned determines what is seen. The perception that any well in an area is “monitoring the groundwater” is a fallacy. Wells must be designed to suit the local geological environment and the type of

Managers Message

There are many details of monitoring well design that the manager does not need to know, but what she or he needs to understand is that there are many ways in which inappropriate or faulty designs can yield false results. The manager must exhibit “interested scepticism” and feel confident to ask, “How do you know?” when unexpected results are presented, even more so in the face of unexpected “nothingness.” The absence of a response in monitoring data may mean that a well is not doing its intended job.

contaminant to be monitored. Aquifers are three-dimensional, and water quality is almost always layered (box 5.1). Taking groundwater samples from different layers is like collecting river water from different streams. If the construction of a well is not known, then neither is the source of the water pumped from it (box 5.2).

The difference between monitoring and abstraction well designs is illustrated in figure 5.3. For monitoring dissolved contaminants (that is, no NAPL), the design is quite straightforward. The exact screen length and position will be decided during drilling, but the approximate position should be known from the conceptual model. Screen lengths and diameters should ideally not exceed about 3 meters[2] and 50 millimeters. The pipe materials should not corrode or react with the water and are usually thermoplastic or high-grade stainless steel; however, Teflon may be used in special cases. The annular space above and below the screen must be carefully sealed to prevent cross-contamination of aquifers.

Well screen length and hydraulic sealing are generally the most important aspects of monitoring well design because wells with long (≥ 6 meters) screens or poorly sealed pipes are likely to mix waters from different layers. The simple maxim of "one aquifer, one piezometer" will go a long way to (a) obtain representative water samples and (b) not give the false impression that uncontaminated aquifers are contaminated or vice versa (box 5.3).

BOX 5.1. Monitoring Wells and Piezometers

The terms *monitoring well* and *observation well* simply describe how a well is used. The term *piezometer* has specific meaning: a well designed and constructed to measure water level and/or water quality at a point in the subsurface. Practically, this means a short well screen of minimum diameter.

BOX 5.2. Design Versus Construction

Always be aware that not all wells are constructed as per their design, and neither do they remain so ever after. For example, wells may not be drilled to their reported depth, and this explains many anomalous cases of pollution. Also, wells can become clogged or corroded over time. Whenever unexpected results are obtained, always check for construction defects.

Monitoring Nonaqueous Phase Liquids

Petroleum hydrocarbon pollution floating on the water table as a LNAPL poses special problems. Normal piezometers are not suitable for measuring LNAPL thickness. This requires wells screened across the full thickness of the LNAPL and extending only a small distance into the underlying groundwater. By contrast, if chlorinated solvents form a DNAPL, wells must be screened at the bottom of the aquifer or on the top of interbedded aquitards, and because these surfaces are often not of predictable shape, it is difficult to locate pools of pure solvent.

Monitoring Saline Interfaces

The density difference between freshwater and saline water poses similar problems to NAPLs, and because flow in coastal aquifers is usually complicated by tidal effects that can cause rapid vertical flows of water inside a well or borehole, the saline interface cannot be directly measured in a conventional well. Instead, its position has to be either inferred from a vertical "nest" of closely spaced, short-screened piezometers or deduced using geophysical logging tools that can "see" through the well pipe.

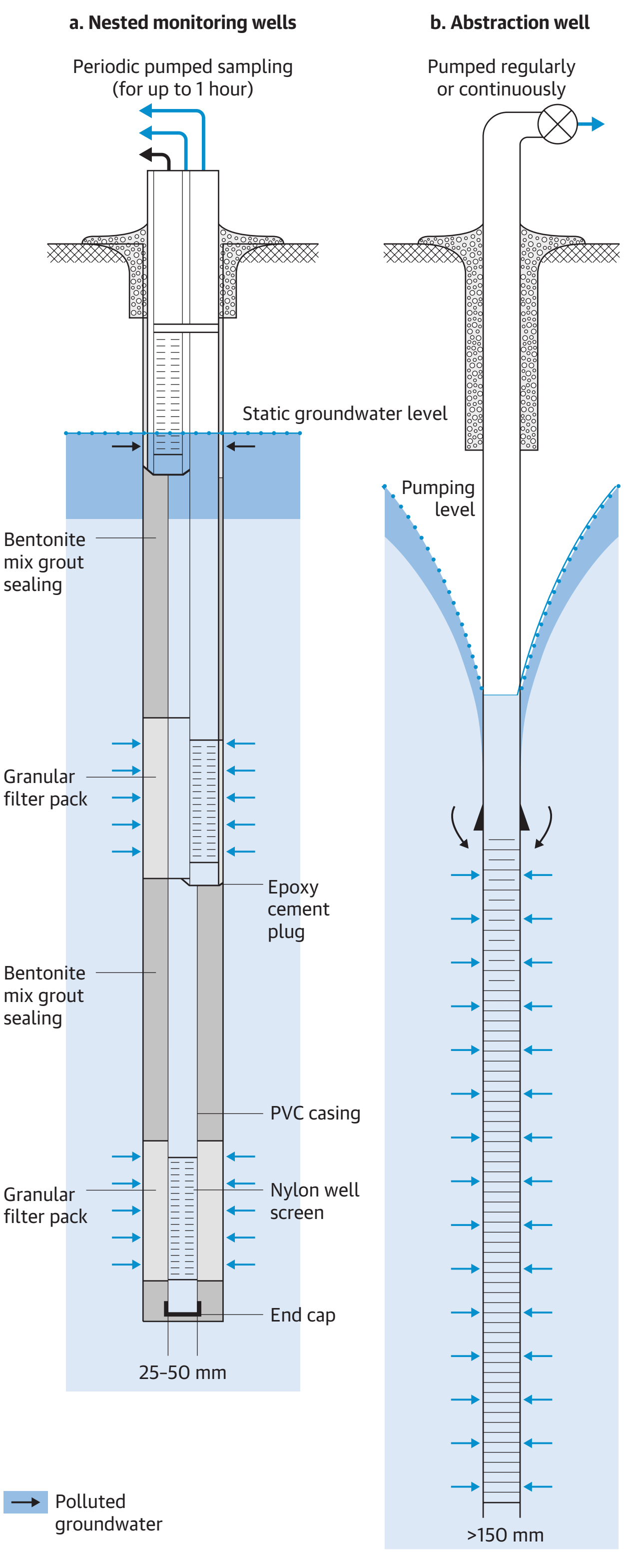
Including Abstraction Wells in Monitoring Networks

Notwithstanding the importance of dedicated monitoring wells, operational abstraction wells should be included within the total monitoring network. Abstraction wells provide different and complementary information, and if already done by a water utility, it saves cost. The advantages of abstraction wells are that they sample large volumes of aquifer and do not require purging. Their disadvantage is that they also tend to mix water from different layers.[3] Combined monitoring also facilitates dialogue between utilities and monitoring agencies.

Groundwater Sampling

Properly constructed wells will produce only a *representative* water sample (boxes 5.4 and 5.5) if appropriate sampling procedures are followed. The conventional thumb-rule approach, known as purging, is to pump out three to five well volumes before collecting a sample. This is usually effective, but for deep or large diameter wells, this can easily require

FIGURE 5.3. Comparison of Typical Well Designs



Source: GW-MATE 2006.

BOX 5.3. Systemic Misrepresentation of Water Quality in Monitoring Networks

Systemic error can easily arise if the depth distribution of monitoring wells is not representative of water quality variations in the aquifer. This is particularly common when the monitoring network has a high proportion of shallow wells. An example of this is found along the Ganges and Brahmaputra plains, where monitoring networks often comprise about 90 percent of dug wells, in which water is exposed to the atmosphere, giving the impression that groundwater is only slightly impacted by arsenic and iron. If monitoring were conducted in hand tubewells and/or motorized production wells, the picture of pollution would be completely different. Thus, an unrepresentative depth distribution of wells misrepresents the state of water quality, and where depth differences exist, which is often, reporting must reflect this.

pumping for hours, and if the purge water is contaminated, it will have to be safely disposed of, adding further time and cost.

Given these constraints, much attention has been given to reducing the amount of purging required based on the concept of a flow-through well that causes minimal disturbance to flow in the aquifer and using low-flow pumps or no-purge sampling devices.[4] In all cases, the use of special purpose sampling pumps made from inert materials is preferred.

Once groundwater has been brought to the surface, it may need to be filtered and then stored in precleaned bottles, with barcoded labels. It should also contain the appropriate preservatives,

BOX 5.4. The Representative Water Sample

A representative groundwater sample has

(a) No mixing of water from different horizons;

(b) Minimum disturbance of temperature and pressure; and

(c) No reaction with any part of the well.

BOX 5.5. The Sad State of Groundwater Quality Sampling

Worldwide the conduct of groundwater quality monitoring has lagged behind other areas of groundwater science. Nielsen and Nielsen's 2007 *Handbook of Groundwater Sampling* describes the prevailing attitudes in the United States at the turn of the millennium, noting that professionals remain entrenched in practices that have consistently been proven to be unreliable for providing representative samples (the primary objective of virtually every groundwater sampling program). The authors further note that these practices continue to dominate, despite research that demonstrates convincingly that they provide neither accuracy nor precision.

Managers Message

Proper sampling poses serious logistical challenges, starting from the selection and design of monitoring wells and continuing through field procedures to delivering the sample to the laboratory and following appropriate analytical procedures. These determine both the validity of the sample and the time and cost. It also explains why many agencies give so much emphasis to minimizing purging by using small-diameter wells and avoiding heavy pumps where possible. To conduct monitoring efficiently, teams need to be equipped with dedicated vehicles to carry a variety of pumps, winches, generators, field testing equipment, and storage facilities for water samples. Failure to provide this support results in false economies, a disillusioned workforce, poor quality work, insufficient monitoring conducted, and poor management decisions.

supplied by the laboratory, which should maintain a chain of custody record and quality assurance (QA) program.

Field Testing of Groundwater Quality

Field testing is conducted for two purposes: (a) to measure unstable parameters (for example, temperature, dissolved oxygen, pH, and bicarbonate) that are likely to change before reaching the laboratory and (b) for public health surveillance where low cost, speed, and immediate follow-up are prioritized. A classic example of the latter is the blanket testing of arsenic in millions of domestic wells in South and Southeast Asia since the year 2000. The arsenic test kits require some skill and training but do not require a professional chemist[5] and can be completed in 20 minutes at a cost of about US$1 a test. They produce semiquantitative results that can reliably classify the risk to health (photo 5.1) but are not accurate enough for resource monitoring.

In-Situ Monitoring of Groundwater Quality

Certain parameters (for example, EC, temperature, and pH) are suitable for continuous monitoring by suspending a probe, connected to a data logger and telemetry system, inside the well screen. Other probes are normally used only in research studies. The popularity of EC is that it is an excellent proxy for salinity, the measurement is reliable, and it is sensitive to other changes that might indicate the approach of a pollution plume. This type of monitoring should be seen as an addition, not an alternative, to conventional monitoring to track trends and fluctuations and to trigger field investigations. It is particularly useful for determining the timescale of water quality changes. Another approach to in-situ monitoring of salinity is to lower an electromagnetic (EM) logging tool into a piezometer constructed with PVC pipe. The EM tool can “see through” the solid PVC pipe to estimate the continuous profile of groundwater salinity outside and is not affected by intraborehole flow and density effects described earlier.

PHOTO 5.1. **Training and Use of Arsenic Field Kits in Bangladesh**

a. Colour chart for reading concentration

b. Female mechanic conducting test in field

c. Adding reagents to water sample

d. Training course for hygiene promoters

Source: Photos taken by the authors.

Monitoring Frequency

Optimal monitoring frequency is a compromise between science and logistics. The initial decision is usually administrative, following a thumb-rule approach (for example, pre- and postmonsoon), and should not go unchallenged. Seasonal monitoring has obvious relevance for water level monitoring but less so for groundwater quality.

Irrespective of scientific reasoning, monitoring wells should be sampled at least once a year, preferably twice, and many guidance documents advocate quarterly sampling for resource status monitoring of unconfined aquifers. Beyond this, deciding an appropriate frequency must follow from the purpose of the well. Elsewhere, in cases in which a particular risk is being guarded against, the regulator will specify the monitoring interval. If not, it is helpful to ask questions such as "How quickly could something go wrong?" "What is the longest period you are willing to accept not knowing what is happening?" and "Will you have enough measurements to establish a credible trend for the status of the resource?"

At the start of monitoring, it is impossible to know whether long-term or progressive trends can be separated from shorter-term fluctuations with a particular monitoring frequency. The answer will become clear only as more time-series data are collected, so the frequency of monitoring must be periodically reviewed in the light of results. This can be aided by temporarily increasing the frequency or, even better, installing a continuously recording water quality probe. In special cases, it may be useful to conduct numerical modeling of pollutant travel times or to examine epidemiological data to understand the consequences of sudden and unexpected pollutant breakthrough at a supply well.

Laboratories and Analytical Services

Traditionally, most agencies relied on internal laboratories for testing groundwater for low-toxicity major ions. Growing recognition of toxic geogenic and anthropogenic contaminants means this is no longer adequate and places new responsibilities on agencies to protect public health. Agencies should resist the temptation to buy complex and expensive equipment without considering the institutional, logistical, financial, and liability aspects. This not only is expensive but also requires highly skilled staff, rigorous quality control, and possibly laboratory accreditation.[6] Failure to meet these standards might even result in legal action. To be cost-effective, there must be sufficient workload and budget to keep the equipment in regular operation. For these reasons, agencies are increasingly outsourcing water quality testing to commercial laboratories operating on a near 24/7 basis with the best available technologies, staffing, and QA procedures, resulting in more cost-effective, reliable, and quicker analytical results. On the other hand, agencies should probably resist complete outsourcing and maintain an in-house testing capacity based on a guaranteed workload to (a) act as a check on external services, (b) provide specialist support to the agency, and (c) retain a core of professional competence as part of the transition from being a testing service to managing water quality.

Reporting of Monitoring Results

Although reporting obviously begins with the results at individual monitoring stations, to make strategic assessments, there is a need to aggregate results to represent the status of groundwater bodies (chapter 4) and hence determine the scale of management actions. For example, the water body is the basic reporting and assessment unit of the EU Water Framework Directive, which also allows for grouping of water bodies into so-called river basin districts for high-level reporting.

Costs of Groundwater Quality Monitoring

The costs of groundwater quality monitoring are rarely reported, usually only from Europe and North America, and even where available are difficult to transfer between regions. However, a reference case is ambient (surveillance) monitoring in the United States. A 1996 USEPA report estimated the cost of annual sampling of a network of 100 monitoring wells (excluding installation) for 185 parameters US$267,000 a year (or US$451,000 at current prices[7]) plus a one-off cost of US$200,000 (or US$338,000 at current prices). The bulk of costs comprise analytical costs; however, when resources are limited and the regulatory regime permits, costs could be dramatically reduced by a risk-based focus on chemicals of particular concern, which might well be measured more frequently to provide better guidance. Such decisions must be based entirely on the local context.

Agency costs can be further reduced by using field test kits and measuring proxies at alternate sampling events. Depending on the regulatory context, a carefully selected schedule of thirty to forty parameters might satisfy needs in many settings. For recurrent budgets that are most limited, measuring only a handful of locally critical parameters, such as arsenic or fluoride, could meet most needs.

Notes

1. Also referred to as groundwater management unit (GWMUs).
2. This length is common for water resources monitoring but is usually shorter at anthropogenically contaminated sites.
3. In other words, it proves that a contaminant is present but not where and not at what concentration.
4. These are described in the accompanying manual.
5. Although they should be backed up by a laboratory-based quality assurance program and should include laboratory checks on borderline results.
6. Public health concerns increasingly require compliance with international standards such as ISO-15000.
7. For more information, see the CPI Inflation Calculator at https://www.in2013dollars.com/us/inflation/1997 (accessed August 3, 2021).

Chapter 6

Mitigation and Remediation

Key Points

- The expected response to anthropogenic contamination is remediation, but natural contamination is met with a mitigation approach.
- Notable exceptions are agricultural pollution and sanitation-related pathogens, which are also met with a mitigation approach.
- Remediation of anthropogenic contamination should be based on "smart characterization," risk assessment, targeted monitoring, and close collaboration with the regulator.
- Diverse and bespoke remediation methods may be applied differently and/or sequentially to source zones and dispersed contaminant plumes.
- Natural contamination is managed with conventional water supply technologies.
- Carefully designed monitoring and periodic evaluations are vital to both mitigation and remediation.

The key differences between natural and anthropogenic contaminants are that (a) anthropogenic contamination tends to be intense but localized, whereas natural contamination tends to be less intense but more widespread, and (b) for natural contamination, there is nobody to hold accountable and responsible for clean-up.

The following sections provide a generalized overview of the management approaches, activities, and technologies used in addressing groundwater contamination problems.

Groundwater Remediation and Mitigation Strategies

Strategies for remediation and mitigation are largely guided by the contaminant origin.

For anthropogenic contamination, agencies will seek remediation to either pristine conditions or an acceptable level of risk. For natural contamination, it is highly unlikely that removal of the contamination will be attempted, so the adopted approach will be mitigation by managing risks through a combination of education, monitoring, and water supply interventions to ensure safe water at the lowest practical cost. Both approaches require sound understanding and good monitoring to guide action.

Two notable exceptions to a mitigation approach being taken to anthropogenic pollution are (a) agricultural pollution, which is liable to be extensive and involve too many stakeholders, and (b) pathogens from onsite sanitation, which require mitigation through better WASH practices.

Anthropogenic Contamination

In discussions of anthropogenic contamination, the term *source* is used in two ways: first the original pollutant source, such as a leaking storage tank or spill, and second as a concentration of nearly pure pollutant held in the subsurface that feeds a spreading plume of contaminants. The latter is particularly important in the case of NAPL phases in which a tiny amount of free-phase product can contaminate large volumes of groundwater. Broadly, remediation of anthropogenic contamination comprises the steps described in box 6.1, wherein the first priorities are to stop ongoing pollution and then to delineate the pollution below ground before moving to the detailed assessment and design of a remediation program.

Natural Contamination

The approach for natural contamination differs because the source is simply where the contaminated groundwater is located. To understand how the source will evolve during the mitigation program, it is

BOX 6.1. Stages in Responding to an Anthropogenic Pollution Event

1. Find and close the pollution source above ground so that no further pollution enters the ground.
2. Delineate the pollution plume in soil and groundwater, including the distribution of contamination between high- and low-permeability layers.
3. Rationalize the site monitoring network to protect sensitive receptors and track the progress of remediation.
4. Conduct a risk assessment and a remedial options study.
5. Agree on the end game with the regulator: (a) whether groundwater will be restored to a pristine condition or to an acceptable level of risk and (b) compliance point(s) and standard, together with a time scale for action.
6. Aggressively remediate (for example, in-situ treatment or pump and treat) the below-ground "source" until diminishing returns are observed and then explore with the regulator options to switch to a less aggressive and expensive method. To justify switching, demonstrate that the plume is stable or shrinking.
7. After depleting the source zone, contain or treat and monitor the dispersed plume to prevent it reaching sensitive receptors using methods such as monitored natural attenuation or permeable reactive barriers.
8. Continue to monitor and critically review results until regulatory sign-off.

important to understand the mobilization mechanism of the contaminants. For instance, is there just a finite amount of contaminant dissolved in groundwater that, once removed, ends the problem? Or will it, as with arsenic and fluoride, continue to release contaminants from the aquifer solids as water is removed? And if so, will this be at a constant or a declining rate? In addition, it is necessary to know how it will move under the influence of natural or pumping-induced groundwater flow. The generalized sequence of actions to mitigate a natural contamination or agricultural pollution scenario is described in box 6.2. This focuses on the default case in which drinking water sources are at risk but could be easily adapted if an environmental receptor is at risk.

Investigation of Contaminated Sites

Natural contamination is generally investigated at the regional or subregional scale using conventional water resources and public health surveillance methods. Research organizations may be involved to undertake detailed investigations for finite periods and have considerable freedom in choosing their methods. By contrast, the investigation of industrially contaminated sites is generally more complicated, working in a small geographical area, requiring different equipment and skill sets, and conducted by specialist companies operating under a prescriptive regulatory regime. Investigations of industrially contaminated sites differ fundamentally in scale with interest in the properties of individual layers

BOX 6.2. Stages in Mitigating a Geogenic Contamination Problem

1. Reconnaissance surveys to determine the extent of contamination.
2. Blanket testing with concurrent awareness raising and health education to identify and inform the affected water users.
3. Source switching as an emergency response to immediately stop unacceptable exposure from drinking water, such as sharing safe sources with neighbors, water trucking, or bottled water.
4. Groundwater monitoring to track changes in the extent and concentrations of contamination.
5. Quantitative risk assessment to identify the scope and timing of required action.
6. Options assessment and economic analysis to identify practical alternatives, their technical and economic efficiency, and social acceptability.
7. Develop a mitigation strategy to bring together the best options for specific institutions and water users.
8. Formulate water supply projects or programs to implement the strategy.
9. Operational and impact monitoring to ensure that interventions work as planned and reach the intended beneficiaries.
10. Conduct ongoing evaluation to determine whether the desired outcomes are being achieved and, if not, reshape the strategy.

rather than whole aquifers. They use small, maneuverable drilling rigs capable of precision sampling and centimeter scale profiling of water quality. This so-called smart characterization (Suthersan, Potter et al. 2016), combined with "decades of failed attempts to clean-up Superfund sites" (NAP 2013), has transformed the practice of remediation, shifting the focus from the high-permeability zones to the adjacent low-permeability ("low-K") zones that act as stores for their long-term release of contaminants.

Remediation Methods for Point Source Anthropogenic Pollution

A variety of remedial techniques have been developed to cope with the diverse combinations of contaminants, receptors, and hydrogeological conditions that can arise. Not only is there no single best method, but often the optimum solution involves a combination of two or more methods. The optimum choice will also depend on the client's attitude to time and cost. For instance, a landowner who wants to sell or redevelop the property may choose an aggressive and capital-intensive approach to deliver the quickest result, whereas a factory owner who intends to continue operation will choose a solution that defers costs into the future. The main tools in the remediation toolkit are summarized here.

- **Containment**. Here the objective is to physically stop contaminants migrating toward a sensitive receptor by one of two methods: The first is a physical barrier, such as a sheet-pile or slurry-trench wall. The second is hydraulic containment by pumping, or possibly injecting, water to modify the flow direction. The pumped water may have to be treated and possibly reinjected to enhance the hydraulic barrier. Containment is often used in combination with other methods.

- **Pump and treat (P&T)**. Earlier this was the dominant approach and remains important but has been increasingly displaced by other methods because of the high cost of long-term operation. Early popularity stemmed from using long-established industrial treatment technologies and appealed to regulators and the public because of the (apparent) visible proof of method. The pumping also has a containment effect. The effectiveness of P&T, measured as cost per unit mass of contaminant treated, declines over time. It is now appreciated the continued slow release of contaminants happens because of back-diffusion from low-K layers. P&T quickly removes contamination from high-K zones, but sustained pumping simply draws in increasing volumes of uncontaminated water from distance and is inefficient at drawing water out of adjoining low-K layers (figure 6.1).

- **Dual-extraction systems**. A special form of pumping system is deployed when a substantial thickness of LNAPL is present. It is popular for large fuels spills in which the petroleum can be potentially recovered for reuse. The system requires installation of a well screened across the full thickness of the NAPL and with a diameter large enough to accommodate two pumps. One pump is placed in the NAPL and the other in the water, and they are operated simultaneously. As far as practical, the relative pumping rates are adjusted so that the two liquids are separated. Of course, the two phases cannot be perfectly separated, and some treatment will be required.

- **Air injection and vapor extraction**. These methods are used to remove light and volatile compounds in the unsaturated zone or shallow groundwater, most commonly fuel spills. They involve installing wells to either apply suction to permeable soils or to actively inject air into shallow groundwater to "strip" volatile compounds. Both techniques work best in sandy or gravelly sediments. Vapor extraction is favored when the natural water content in the unsaturated zone is low and the ambient air temperature is high. The introduction of oxygen also promotes biodegradation of hydrocarbons, such as BTEX compounds.

- **In-situ treatment**. This involves injecting chemical treatment directly into the contaminant source zone so it does not continue to feed a diffuse plume (figure 6.1). Its popularity has increased with the recognition of low-K layers as stores of pollution, and its design requires "smart characterization." The chemicals injected depend on the type of contaminant. For instance, highly reduced chemicals, such as BTEX, will be treated with strong oxidizing solutions, such as permanganate or hydrogen peroxide. On the other hand, oxidized compounds, such as chlorinated solvents, will be treated with a reducing agent, which overlaps with a variant known as in-situ bioremediation, in which conditions are modified to promote microbial degradation. An example is adding molasses or vegetable oil to degrade PCE and TCE. In-situ treatment is also conducted using heat or steam injection.

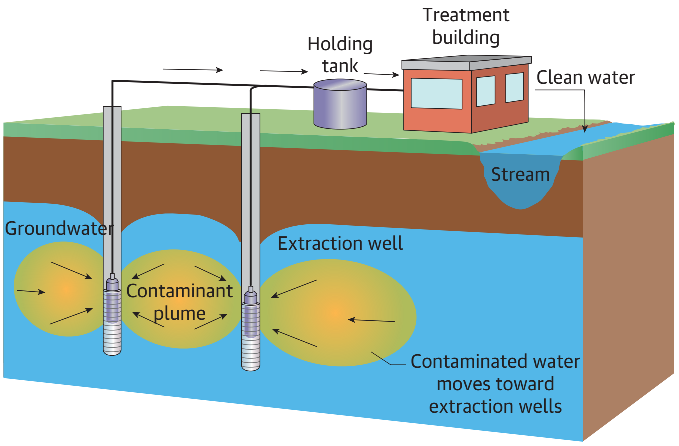
- **Permeable reactive barriers (PRB)**. This approach involves creating an underground reactor vessel and diverting groundwater flow toward it (figure 6.1) and may be combined with impermeable barriers to funnel contaminated water to the reactor. The applicability of reactive barriers depends strongly on the site hydrogeology, and because it requires excavation, it is limited to shallow depths where a suitable low-cost reactant, such as zero-valent iron or organic matter, can be placed. Once constructed, PRBs have relatively low maintenance requirements and costs.

- **Monitored natural attenuation (MNA)**. Experience over decades has conclusively demonstrated the ability of nature to degrade a wide range of contaminants under a range of conditions, including many chemicals previously considered to be highly persistent. It must be emphasized that not all contaminants are attenuated under all conditions, but if the chemicals and the site conditions are properly understood, MNA can be cost-effective for dissolved phase contamination at relatively low-risk sites and when time is not of the essence. MNA is suited for use in combination with other methods. However, there is also a danger that MNA can be advocated as an excuse to avoid active remediation when it will not be effective. It therefore requires a well-informed regulator to ensure the proponent conducts detailed site investigations, hydrochemical testing, and analysis of monitoring data to prove that contaminants are actually being degraded and that the plume dimensions are declining. The regulator must be authorized and willing to order a reversion to active remediation if these conditions are not being met.

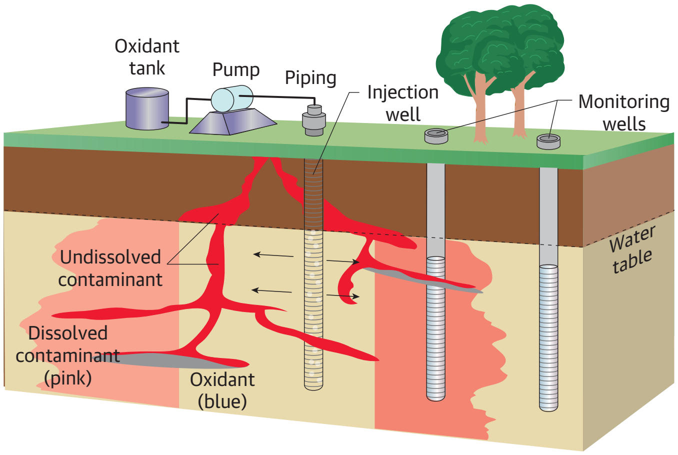
Groundwater remediation has ballooned into a huge subject, for which the reader is referred to the books by Payne et al. (2008); Suthersan, Horst et al. (2016); and Fetter, Boving, and Kreamer (2018), among others, but good starting points for these topics are found in the USEPA's "Citizen's Guides" at https://clu-in.org/cguides/.

FIGURE 6.1. **Schematics Showing Some Groundwater Remediation Methods**

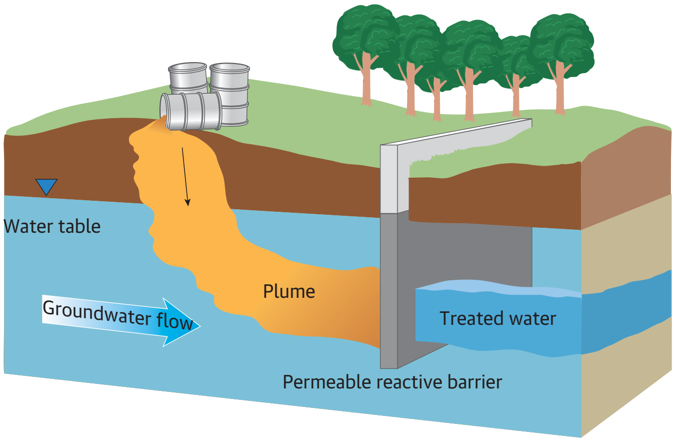
a. Pump and treat



b. In-situ treatment



c. Permeable reactive barrier



Source: Adapted from USEPA 2012.

Ex-Situ Groundwater Treatment and Water Supply Mitigation

Although it is always preferable to restore contaminated groundwater to its natural state, this is not always achievable, and there are situations in which contamination had already affected water supplies before the hazard was recognized. Whatever the cause, safe water supplies must be restored as soon as possible and, in the case of anthropogenic contamination, supplemented by clean-up of the aquifer if possible. There are two basic strategies: either treat the contaminated groundwater or develop an alternative water source. Whichever path is chosen, it should be accompanied by awareness raising and public health education.

Treatment of groundwater at the surface for direct supply is the subject of standard water treatment texts, but a few comments may be made regarding the interrelated issues of technology, scale, and cost. When a large public supply well is affected, all technologies and economies of scale are available. However, when household or small-community systems are affected, the options are more limited, especially in low- and middle-income countries, because of the availability of skilled staff, support services, and operation and maintenance (O&M) requirements (photo 6.1). For municipal systems, skills, finance, and management are readily available, so a treatment system may be selected based on conventional financial analysis. Although there are exceptions (for example, German et al. 2019), small rural treatment systems tend to have poor performance records and locating an alternative safe-groundwater source will almost always be preferred. If no good alternative is available, maximum effort should be given to establishing an O&M system that involves the community in operation and financing but also has external support for maintenance, monitoring, and awareness raising. The most common ex-situ groundwater treatment methods include:

- **Reverse osmosis (RO)**. This is a standard technique for desalination, in which cost is proportional to salinity but can also be used for removing nitrate and other contaminants and for treating wastewater for reuse.

- **Granulated activated carbon (GAC)**. For groundwater, the main application of GAC is in removing low concentrations (microgram level) of toxic microorganics, such as pesticides.

- **Air stripping**. Blowing air through groundwater falling through a specially packed column of water is an effective method of removing volatile compounds, such as BTEX and chlorinated solvents (photo 6.2). If the removal efficiency is not high enough, the water may be polished using GAC.

- **Anion exchange**. Although there are others, the principal application of this technology for groundwater is removing high concentrations (tens to hundreds of milligrams) of nitrate.

- **Adsorption**. Adsorbents, such as activated alumina and synthetic granulated iron oxyhydroxides (granular ferric hydroxide (GFH) for example, shown in panel c of photo 6.1), can be highly efficient at removing negatively charged contaminants, such as fluoride and arsenic, when adjusted to optimum pH. The cost of the adsorbent is an important part of the total cost, so it is best suited to low-level pollution.

PHOTO 6.1. Household, Community, and Municipal Arsenic Removal

a. Sono filter, Bangladesh

b. Amul filter, West Bengal, India

c. Granular ferric hydroxide adsorption plant, Severn-Trent Water, United Kingdom

Sources: (a) and (b) authors; (c) Severn-Trent Water.

PHOTO 6.2. **Example of an Air Stripping Column for VOC Removal**

Source: © Delta Cooling Towers, Inc. Used with permission.
Note: VOC = volatile organic compound.

- **Oxidation-coagulation-coprecipitation-filtration**. Oxidation by aeration is the simplest method of removing iron and manganese from groundwater. Freshly precipitated iron will also coprecipitate toxic trace elements, such as arsenic, but may not reliably achieve drinking water standards, so a coagulant, such as ferric sulphate or chloride, is added. The water then requires settling or more commonly passing through a sand filter. In a well-managed utility, this can be a cost-effective method of treatment, especially when contaminant concentrations are high.

  In small arsenic-removal systems (for example, panels a and b of photo 6.1), if 24/7 electricity is lacking, coagulation may be omitted but oxidation of naturally high iron concentrations is exploited to remove much of the arsenic before polishing with an activated alumina or GFH adsorbent.

The topic of locating alternative water sources, from another aquifer or surface water, is too diverse and dependent on local conditions to discuss in detail, but a few general points deserve mention. First, contaminants should not be drawn from one aquifer into another because of shifting the balance of abstraction; second, one risk should not be substituted for another of equal or greater magnitude. For instance, chronic and possibly irreversible poisoning from fluoride or arsenic should be weighed against acute poisoning from pathogens, using metrics such as disability adjusted life years.

Finally, diffuse agricultural contaminants, such as nitrate, require an approach that combines catchment management, adaptive management of abstractions by utilities, and economic incentives, such as increasing taxation on fertilizer. In most countries, widespread cessation of fertilization is not realistic, but local changes in farming practices, backed by financial incentives, can be achieved. A prerequisite for nitrate reduction is to understand the contributing areas to borehole catchments and targeting restrictions and incentives (for example, for switching crop types) in areas where the impact is large and rapid. In addition to cropping changes, other measures would include awareness raising and education campaigns to make farmers aware of the financial waste of leached fertilizer and also requiring or promoting the relocation, or lining, of features like slurry pits.

Remediation and Risk Assessment

As noted earlier (chapter 4), groundwater risk assessments are conducted mainly to predict the likelihood and magnitude of harm that might result from a pollution source. Risk assessment models can also be used in remedial design, essentially running the models backward to determine how much remediation needs to be done to the source to reduce risks (at the receptor) to an acceptable level. Remediation is conducted in discussion with the regulator to agree on compliance criteria (or remedial targets), which are critical determinants of remedial cost. To provide a factor of safety, the compliance point may be a monitoring well positioned upgradient of the vulnerable receptor. The compliance standard might be related to drinking water, but other standards might be applied at environmental receptors. The objective of the assessment is to ensure that the concentration of the contaminant never exceeds this level at the receptor or compliance point.

Chapter 7
Governance and Institutional Support

Key Points

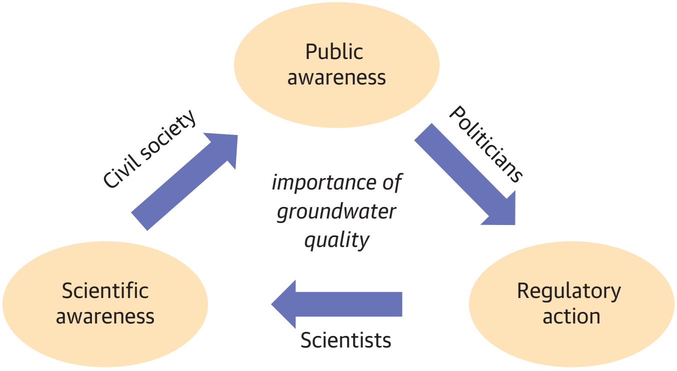
- A problem ignored can have enormous economic cost and even turn into a national disaster.
- Groundwater quality management has been almost universally neglected until the human and economic costs become too obvious to ignore; only senior managers and budget holders can correct this.
- Institutional strengthening is essential for better groundwater quality management and is driven by a proper legislative framework.
- Institutional strengthening is implemented by providing adequate budget, proper recruitment, and training matched to the needs of management objectives. Its success will be seen in a change in culture and public awareness.
- Poor regulation and compliance transfer costs from the polluter to the government both directly in treatment and remediation costs and indirectly in impaired health and life expectancy.
- A checklist of questions for senior managers will identify where and how institutional performance needs to be improved.

The problems of groundwater contamination and protection described in this report will not be resolved unless the responsible institutions are properly aligned and adequately resourced and motivated. This chapter explores the scope of institution support and regulatory drivers required.

Drivers for Action

The development of effective groundwater quality monitoring and management systems is likely to be driven by the continual interaction of scientific and public awareness and legislative action (figure 7.1). Initially, awareness among the public and the legislature is low. At some stage, measurements from a scientific organization become the concern of public health officials, journalists, and NGOs, possibly following a scandal or accident. This then becomes the concern of the general public and drives politicians to enact legislation. New legislation both obliges resource managers to conduct more rigorous monitoring and, critically, to access money for better equipment and more personnel. With these resources, the quality and quantity of investigations, monitoring, and knowledge increase, and so the cycle continues.

FIGURE 7.1. **Drivers for Action on Groundwater Quality**



Experience suggests that legal drivers are critical not only to improving groundwater quality monitoring but also to sustaining action beyond the first "crisis." Breaking out of the initial low-awareness condition can be difficult. When scientists in water agencies feel trapped in their bubbles, talking only to their own communities, there are several things they can do to raise awareness at little cost. They should look at ongoing human activities and ask what unrecognized risks these pose, what the consequences of these activities are, whether anybody has tested for these chemicals, and why these problems are not happening here—or are they? They can look at surrounding or similar countries to see what problems they experience. For instance, although the boundary between West Bengal in India and Bangladesh runs straight down the middle of a delta, it took more than ten years for knowledge of arsenic on the Indian side of the border to cross into Bangladesh, even though some international agencies operated on both sides of the border. It would be prudent to review the local legislation to check, for example, whether it is a criminal offense to *cause* or *allow* pollution of groundwater or, notwithstanding a polluter pays statement in an environmental policy, there is an enforceable obligation to remediate polluted groundwater.

Groundwater Quality Governance

The governance of groundwater quality, a subject that has received much less attention than overabstraction, has four dimensions, as discussed in the following sections. These are

- Law and regulation;
- Institutional strengthening;
- Policies and practices; and
- Information and education.

Law and Regulation

Although legislation is usually driven by policy (see later in the section), it is evident from the experiences of Europe and North America that many countries will require new primary legislation to ensure the integrated management of surface water and groundwater—and water quality and quantity—and to provide a legal basis for protecting and restoring groundwater.

Precise requirements will depend on the national context and will require a formal regulatory review, but the following list presents some core elements of an effective system:

- The pollution of groundwater per se, and not just a well or spring, should be a criminal offense and carry with it the legal duty to remediate the resource to an acceptable level (that is, ensuring the polluter pays).
- Environmental impact assessments should be required to consider the impacts of, and on, groundwater quality.
- The conduct of risk assessments should be built into the regulatory process together with a risk-based (that is, proportionate) assessment of reasonable response.
- Groundwater source and resource protection measures should be established as part of legally binding planning and land-use controls.

Institutional Strengthening

Most countries developed their water resource institutions to deal with quantitative issues and, if not already done, will require reform and restructuring with an expanded mandate. Job descriptions, promotion prospects, and incentives for professional development must reflect this.

Management Needs

Water resources agencies should expand their departmental mandate, structure, facilities, and job descriptions to better accommodate groundwater and water quality. Further, they should incentivize professional development paths to reward diversity of knowledge and experience in advancing careers in management. Other measures that could support institutions in giving appropriate importance to groundwater quality issues include

- Specific budgetary allocations for groundwater quality monitoring;
- Creating an independent auditor to examine networks and records;
- Mandatory public reporting; and
- Facilitating citizen science.

Capacity development should not be conducted as an abstract training exercise. Training and recruitment should be oriented to fill gaps in knowledge or practice where the verifiable indicators of progress are measured in terms of implementing policies and regulations.

Education and Institutional Culture

Although regulation is the primary driver of change, this has to be implemented through changes in institutional culture and practice. In many countries, reform is constrained by outdated professional culture and gaps in education, both in terms of the academic curricula of universities and in-service training. To become an expert in groundwater quality requires knowledge of aspects of geology, chemistry, hydrology, hydraulics, and well drilling. Professionals who manage groundwater come from different backgrounds. Only those with postgraduate qualifications in hydrogeology are likely to have received dedicated training in groundwater chemistry. Those from an engineering background bring strong skills in hydraulics but may be weak in chemistry and sometimes geology. Conversely, water quality practitioners (especially in laboratories) coming from a chemistry background may lack appreciation of geology and hydraulics. These skill sets should be complementary but only as specializations that span a common knowledge base. The needed changes include the following:

- Updating university curricula so that all courses in hydrology and water resources include components on groundwater that include groundwater quality and contamination.
- Water resources agencies and utilities should provide or procure in-service training, including
  - Introduction to groundwater quality for engineers and ecologists;
  - Basic groundwater hydrology for chemists, environmental engineers, and ecologists; and
  - Groundwater contamination and protection for all relevant professionals.

This type of training can be incentivized by building it into professional development programs that are preconditions for promotion.

- Water resources agencies and utilities should encourage staff to commission or participate in applied research on groundwater quality issues of concern.
- The organograms of water resource agencies should be aligned with the importance of water quality (and ecological) issues to the economy and society.

Specialist Support

Given the complexity and diversity of groundwater quality issues, agencies should retain a list or register of experts to advise on and periodically review subjects that go beyond the organization's core skills, including

- Analytical chemistry;
- Emerging pollution threats from novel chemical usage;
- Water treatment and groundwater remediation technologies;

- Hydroecology;
- Epidemiology; and
- Information technology and information dissemination.

Policies and Practices

The intended impacts of new regulations and the targeted strengthening of institutions are realized through tangible actions.

- Improved monitoring is a precondition for all other actions and should not, and need not, wait for anything.
- The resource assessment framework should include defining the chemical status and trends of water bodies integrated with their quantitative status.
- Surface water and groundwater should be managed as an integrated resource, and groundwater quality should be incorporated into river basin planning.
- Stakeholder participation and formal public reporting are essential components of water resources management.
- Good information management, which includes an open-data policy, is vital to communicating messages to policy makers and the public and to ensuring good governance.

Building a Consensus for Action

Until a strong regulatory regime is in place, there is likely to be resistance, or inertia, to protecting, monitoring, or remediating groundwater quality. Advocates of reform should garner support from potential allies who may not naturally see a common cause. For example:

- Water utilities who fear for the sustainability of their high-quality, low-cost water sources.
- Public health agencies, which can easily be persuaded to lobby in favor of safe water.
- Industries, especially those involved in food and drink, should be acutely aware of the financial and reputational costs of polluted water wells, even simply near their premises. Other than the progressive attitudes of many industrialists, multinational or export-oriented companies will recognize the benefit of complying with standards that apply in other markets they trade in. Furthermore, some multinational companies require common standards in these countries and, in demanding a level playing field, can lobby effectively for compliance from less-progressive companies in their sectors.
- Civil society organizations with interests in ecology, human rights, or simply clean water can be expected to provide strong advocacy.

BOX 7.1. Multistakeholder Partnerships and Textile Industries in Bangladesh

Since 2016, the 2030 Water Resources Group (2030 WRG), an international alliance of public and private sector and civil society groups, has supported the Bangladesh Water Multi-Stakeholder Partnership in improving efficient and sustainable water resources management through establishing multistakeholder partnerships (MSP) for different sectors and regions. A particular interest has been the garments industry, which is vital to the economy but has a legacy of polluting rivers and groundwater and is overwhelmingly dependent for its water supply on privately owned wells in an aquifer that is being seriously depleted. Recognizing the unsustainability of such practices, and the commercial risk of negative publicity in export markets, there is strong support within the sector for change. Through the MSP process, 2030 WRG has been able to build a coalition of government and industry interests and facilitate funding for a package of measures including: a Public-Private Partnership (PPP) for centralized wastewater treatment; volumetric water allocation for efficiency and life-cycle monitoring; advanced water quality monitoring; support for managed aquifer recharge and reuse of treated wastewater; and strengthening water resources management institutions. (See https://www.2030wrg.org/bangladesh/.)

It can be particularly powerful if these groups are given voice through MSPs of public, private, and civil society groups of the kind promoted by the 2030 WRG (box 7.1). In such forums, it is possible to mobilize these diverse groups into a coalition for action and to argue the economic case of groundwater protection in a way that can reach even the Ministry of Finance.

A Checklist of Questions for Senior Managers

To assist in identifying where and how institutional performance may be improved for groundwater quality monitoring, a checklist of questions is presented in table 7.1.

TABLE 7.1. Ten Questions for Senior Managers

The following questions are to help senior managers assess whether agencies are adequately managing groundwater quality issues and, if not, what they can do about it.

Nr	Question	Explanation/elaboration	Scope for action
1	What proportions of (a) drinking, (b) irrigation, and (c) industrial water are obtained from groundwater in your jurisdiction?	To appreciate the value of groundwater as a resource.	If not easily known, quantitative monitoring or information systems need upgrading.
Legal			
2	Is the legislative and regulatory regime adequate to manage groundwater quality?	• Do drinking water or environmental quality standards apply to groundwater? • How are the storage and use of hazardous substances controlled? • Is pollution of groundwater per se an offense, and is remediation required? • Do regulations require risk assessment and impose risk-based clean-up targets?	Commission a regulatory review.
3	Are water bodies and status and trend indicators defined?	• Dividing basins into water bodies with hydrological (not administrative) boundaries for assessment of quality and quantity and defining status and trends are norms of international practice. • Defining water bodies is a prerequisite for SDG 6.3 monitoring (UN-Water. 2017).	Water policy may need updating. Instruct resource agencies to define water bodies (rivers, lakes, and groundwater).
4	Are measures in place to prevent or reduce the likelihood of pollution?	• Have legally supported (water) source protection zones been defined? • Is the storage and use of hazardous chemicals controlled? • Has groundwater vulnerability been mapped?	Commission (a) feasibility study of protection methods, followed by (b) project(s) to define protection zones. Establish dialogue with municipalities, industry ministry, and industry associations regarding hazardous substance regulation.
Knowledge and management			
5	Are all water bodies, and the appropriate parameters, being monitored?	• Are all groundwater bodies being monitored? • Are the hazardous chemicals identified being monitored in the relevant groundwater bodies?	Require review by agency? Evaluate constraints on noncompliance.
6	Is there a GIS-based inventory of pollution hazards?	• The locations of waste sites, mines, pipelines, factories, and other industries and hazardous chemicals associated with each.	Municipalities and environmental/pollution control departments to prepare inventory.

table continues next page

TABLE 7.1. continued

Nr	Question	Explanation/elaboration	Scope for action
7	Is it known whether there are serious geogenic or anthropogenic groundwater quality problems within your jurisdiction?	• How many people are exposed to arsenic, fluoride, or manganese in their drinking water? • How many incidents of groundwater pollution by petroleum, pesticides, and pharmaceuticals? • Do fertilizers pollute groundwater? • Do you have estimates of the human and economic costs of groundwater pollution?	If not known, there is a knowledge/reporting gap that requires more and better monitoring and/or information systems.
Institutional			
8	Are responsible agencies appropriately staffed to manage groundwater quality?	• Are the numbers of staff assigned to considering (a) surface water and groundwater and (b) quality and quantity proportionate to their importance. • What percentage of staff have responsibilities for groundwater quality? • Do surface water, groundwater, and water quality professionals have equal opportunities to becomes heads of department? Has this ever happened?	Commission review of organogram.
9	Are proportionate budgeting and human resource allocated to groundwater quality?	Adequacy to be judged by considering: • Surface water versus groundwater • Quality versus quantity in terms of (a) importance to economy and (b) status and trends in water bodies	Commission joint review by monitoring agency and independent experts.
10	Does professional staff education include the study of groundwater quality?	• Is groundwater quality included in university syllabi? • Do agencies conduct/contract in-service professional training? • Is groundwater quality recognized as a core skill for career development?	Create funding for training courses. Partner with academic institutions?

Source: Authors.
Note: GIS = geographic information system; SDG = Sustainable Development Goal.

Chapter 8

Groundwater Quality Protection

Key Points

- Cost-effective groundwater protection measures can be taken in almost every scenario.
- Source protection zones (SPZs) can be simple or complex. Simple ones can be set up quickly and cheaply and refined later.
- SPZs should be integrated into land-use planning and the regulation of hazardous chemicals.
- Saving just one major abstraction from serious pollution could pay for an entire protection program.

By far the most cost-effective means to ensure safe and low-cost groundwater supplies is to invest in protection measures.[1] Protecting groundwater from pollution normally involves a combination of

(a) Controls on hazardous chemical storage and use;

(b) Land-use controls;

(c) Definition of groundwater source protection zones;

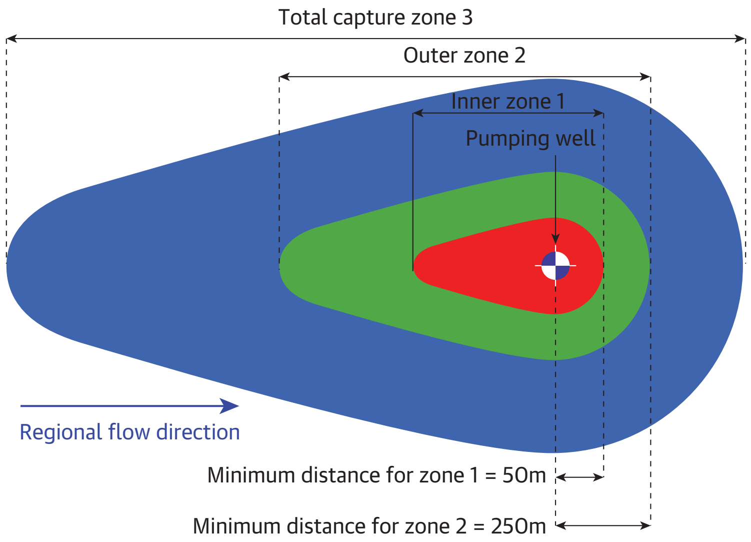
(d) Sanitary protection of wells; and

(e) Monitoring of drinking water wells.

The first will be part of a broader chemical regulation but should include a list of priority groundwater pollutants based on national and international experience. For water agencies, a unifying concept is the groundwater SPZ—the area from which recharge at the ground surface leads to a particular well or spring and within which area land use and the use of specified chemicals can be controlled to reduce risk (figure 8.1). This requires cooperation between water agencies and local planning departments.

SPZs can be simple or complex and so, to some extent, can be implemented everywhere. At the simplest level, they can involve just drawing a circle, or "teardrop," of specified radius on a map. This approach may be satisfactory for very small sources or wells in a confined aquifer with a well-defined protective clay layer above the aquifer. At the first level of refinement, these zones can be drawn using professional

FIGURE 8.1. Schematic Representation of Source Protection Zones

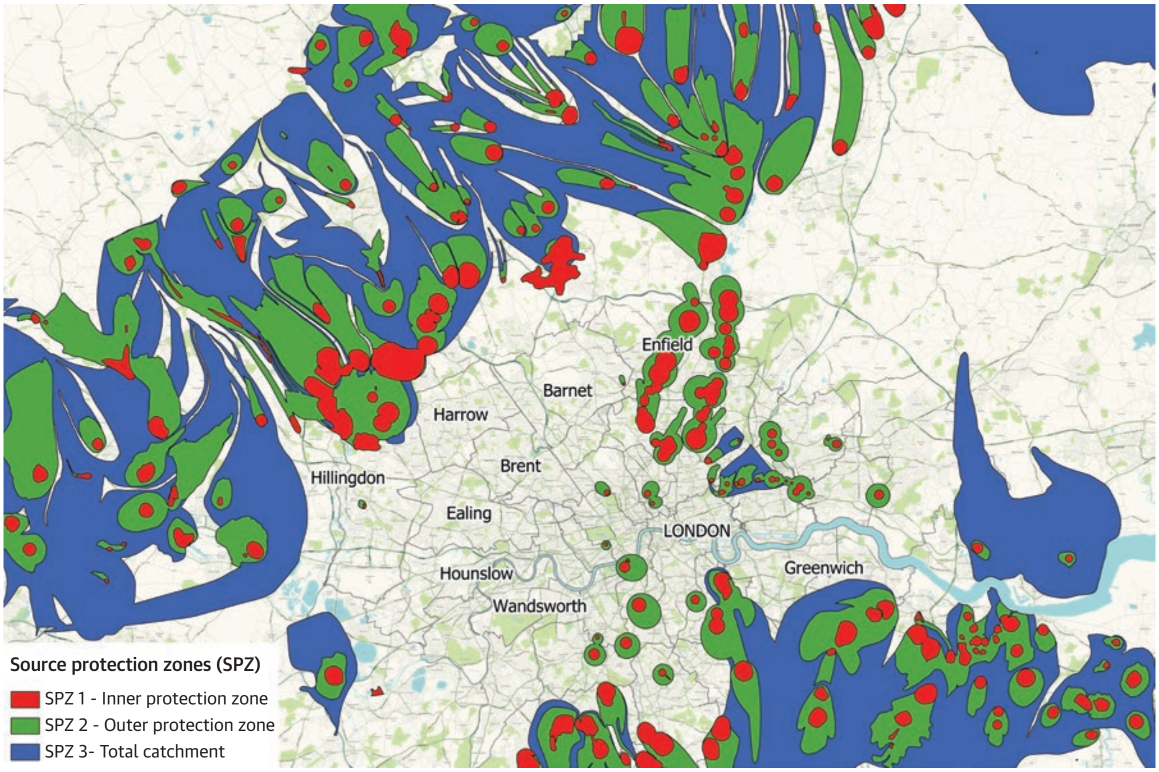


judgment and/or manual calculations. For larger sources and areas where there are multiple sources, SPZs are drawn by considering the time of travel for infiltrating water reaching the water table to flow to the well. The time of travel is mapped out using often bespoke mathematical models, and the results classified into zones of the type shown in figure 8.1. In simple aquifers, the zones are tear-shaped and elongate in the upgradient direction of flow. The exact travel times for defining zones varies between countries and may be supplemented by some minimum geometrical dimensions but are broadly the same. In the United Kingdom example shown in map 8.1, the inner zone (SPZ1) is based on a fifty-day travel time and must extend for at least 50 meters in all directions.[2] The fifty-day criterion is based on the likely survival of pathogens. Within this zone, there are strict controls on land use, affecting such activities as pipelines, cemeteries, effluent discharges, underground storage of pollutants, livestock housing and transport, underground construction, and so on. The outer zone (SPZ2) is based on a 400-day travel time and must extend for at least 250 meters. This criterion is based on moderating the risks of chemical pollution and is subject to less stringent restrictions than in SPZ1. Finally, the total catchment zone (SPZ3) is the total capture zone of the well has fewer restrictions.

The final element in protecting groundwater takes place at the water source itself, which is referred to as wellhead protection, and includes sanitary sealing of the well, drainage around the wellhead, and tight restrictions on what can be done inside the facility. When a water safety framework is in place, water utilities and critical private abstractors, such as food and beverage manufacturers, will have conducted their own risk assessment and ideally prepared contingency plans and initiated proactive measures regarding the sources of highest risk.

Many national water resources agencies have developed guides or manuals to suit their particular hydrogeological conditions; a general and practical guide is given by Foster et al. (2002).

MAP 8.1. **Example of Source Protection Zones in the United Kingdom**



Note: Red represents inner zone (SPZ1), green the outer zone (SPZ2), and blue the total catchment (SPZ3).
Source: Own elaboration based on DEFRA Data Services Platform (DEFRA 2016), accessed on November 22, 2021.

Notes

1. These measures overlap with the scope of water safety plans (WHO 2005), which aim at a catchment-to-consumer approach to drinking water quality protection.
2. Procedures for delineating SPZs are given by the United Kingdom Environment Agency (EA 2019b).

Chapter 9
Concluding Remarks

This chapter summarizes the key drivers and recommendations for monitoring groundwater quality outlined in this report.

Why Groundwater Quality Matters

Groundwater is critical to the health and survival of populations, economies, and the environment around the world. Although its importance is principally noted for its contributions to drinking water, food production, and industry, it is increasingly regarded as an essential component of adaptation to climate change. Neither present nor future uses of groundwater can be guaranteed without protecting its quality.

The Changing Quality of Groundwater

Groundwater naturally takes its quality from the infiltrating recharge water and the aquifer through which it passes. Although most groundwater is naturally of good quality, some aquifers naturally contain hazardous contaminants—arsenic, fluoride, and salinity being the most well-known. Furthermore, the quality of recharge water is affected by human activities, either through warmer or increasingly acidic rainfall that affects how the water reacts with the aquifer or from the cocktail of chemicals and effluents discharged to land and water. These changes to recharge water are inexorably changing the quality of the groundwater that is pumped from wells and boreholes, and consequently affecting its usability.

The scale and severity of the effects of natural contaminants has been widely underestimated. They touch hundreds of millions of people who are affected by crippling and potentially fatal illnesses and, in some countries, make a significant contribution to total morbidity. Some contaminants, such as arsenic, threaten the sustainability of irrigated agriculture, a cornerstone of the Green Revolution. The lack of awareness of the scale of these issues is because many cases were discovered only in the past two to three decades in regions that previously had not been tested, and it is almost certain that more occurrences are yet to be identified.

Analytical techniques have become more sophisticated and, combined with improved monitoring, have led to an ever-increasing recognition of anthropogenic groundwater contamination on a global scale. It is inevitable that the more groundwater quality is measured, the more pollution will be found. Furthermore, today's limits are tomorrow's toxic concentrations, so water classed as safe today may not be in the future, even if its measured quality remains unchanged.

Recommendations for Managing Groundwater Quality

Managing groundwater quality can seem complicated, but many common pitfalls are easily avoided with just a little insight. Furthermore, given the technical complexity and the huge time and cost required to clean up polluted groundwater, prevention is unquestionably easier to achieve, and better than having to cure, from the perspective of economic, environmental, and population health.

Monitoring and Assessing Risks to Groundwater Quality

To manage groundwater quality, it must first be measured, then the risks characterized, and then mitigation measures developed to limit exposure to them. Many groundwater monitoring networks have been developed piecemeal without systematic planning or construction of dedicated monitoring wells and may misrepresent the status and trends of groundwater quality in an aquifer.

Modest, low-cost actions can provide a solid basis for assessing risks, starting with a conceptual model of the groundwater system being measured and an evaluation of the pollution risks. These will help design a monitoring strategy with well-positioned wells and piezometers, appropriate sampling procedures, and adequate laboratory facilities. This approach allows the determination of a groundwater quality baseline and creates a monitoring system that will continually illustrate the status and trends of groundwater quality and enable managers to act, prevent, or reduce unacceptable outcomes and then plan treatment and mitigation action.

Mitigation and Remediation

Responses to pollution incidents and adverse trends in groundwater quality are guided by the nature and extent of contamination. Natural contaminants cannot practically be removed and require treatment or the development of alternative sources. Large-scale anthropogenic contamination (such as nitrate and pesticides from agriculture and pathogens from inadequate sanitation) requires both government support and a community-scale response to change practices and gradually reduce contaminant inputs. Localized pollution, such as from industrial sites and urban landfills, can be prevented by breaking the link between these activities and the groundwater through improved operations and other preventive measures. If it cannot be prevented, the impact can be greatly reduced by fast response, innovative remedial measures, and a regulatory regime that encourages voluntary remediation. This requires effective site characterization, risk assessment, targeted monitoring, and collaboration between the site owner and the regulator. Placing these actions in a risk-based approach will prioritize action when it is most effective in reducing harm and also avoid the unnecessary expenses associated with blanket responses.

Governance and Institutional Support

An ignored problem of groundwater quality can have an enormous and long-term economic cost and even turn into a national disaster. Poor regulation and compliance have the effect of transferring costs from the polluter to the government and society, both directly in treatment and remediation costs and indirectly in impaired health and life expectancy.

Groundwater quality management is almost universally neglected until the human and economic costs become too obvious to ignore. Because of the predictability of the impact, this reflects unfavorably on any government that does not already pursue a proactive groundwater quality protection program.

Institutional strengthening is essential for better groundwater quality management and is driven by a well-founded legislative framework, an adequate budget, proper recruitment, and training matched to the needs of management objectives.

Protecting Groundwater Quality—Taking the First Step

As with all other aspects of groundwater management, the protection or restoration of groundwater quality is based on a conceptual model that is progressively refined, in a continuous feedback loop, through the evaluation of monitoring data that, when supported by the right regulatory framework, leads to a reduction in vulnerability to increasing water scarcity while optimizing investment in infrastructure and systems.

Groundwater protection is the first and most cost-effective step in managing groundwater quality, and cost-effective measures can be taken in every scenario. Simply designed SPZs can be used to support land-use planning and the regulation of hazardous chemicals. Groundwater protection is implemented not only through water sector projects but also administrative procedures to ensure that nonwater projects and activities improve their handling of hazardous substances though physical protection, monitoring, and avoiding high-risk locations.

The Economic Imperative for Groundwater Quality Protection

The challenge and cost of cleaning up polluted groundwater, or treating it in perpetuity, is far greater than protecting it in the first place, and the intergenerational human and economic costs of these avoidable phenomena are measured in hundreds of millions of people and hundreds of billions of dollars. Compared to these, the financial costs of groundwater quality monitoring and protection are negligible. Saving just one major abstraction from serious pollution could pay for an entire protection program. Not adopting these measures is to neglect a moral duty and represents a massive and long-term waste of financial resources that could be used much better elsewhere.

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