# *Practical Manual on* GROUNDWATER QUALITY MONITORING

Peter Ravenscroft and Lucy Lytton

WORLD BANK GROUP

GWSP
GLOBAL WATER
SECURITY & SANITATION
PARTNERSHIP

## About the Water Global Practice

Launched in 2014, the World Bank Group's Water Global Practice brings together financing, knowledge, and implementation in one platform. By combining the Bank's global knowledge with country investments, this model generates more firepower for transformational solutions to help countries grow sustainably.

Please visit us at www.worldbank.org/water or follow us on Twitter: @WorldBankWater.

## About GWSP

This publication received the support of the Global Water Security & Sanitation Partnership (GWSP). GWSP is a multidonor trust fund administered by the World Bank's Water Global Practice and supported by Australia's Department of Foreign Affairs and Trade, Austria's Federal Ministry of Finance, the Bill & Melinda Gates Foundation, Denmark's Ministry of Foreign Affairs, the Netherlands' Ministry of Foreign Affairs, the Swedish International Development Cooperation Agency, Switzerland's State Secretariat for Economic Affairs, the Swiss Agency for Development and Cooperation, and the U.S. Agency for International Development.

Please visit us at www.worldbank.org/gwsp or follow us on Twitter: @TheGwsp.

# *Practical Manual on*
# GROUNDWATER QUALITY MONITORING

Peter Ravenscroft and Lucy Lytton

WORLD BANK GROUP

1818 H Street NW, Washington, DC 20433
Telephone: 202-473-1000; Internet: www.worldbank.org

**Rights and Permissions**

Please cite the work as follows: Ravenscroft, Peter, and Lucy Lytton. 2022. “Practical Manual on Groundwater Quality Monitoring.” World Bank, Washington, DC.

*Cover design:* Bill Pragluski, Critical Stages, LLC.

# Contents

**Boxes**

## Figures

## Maps

## Photos

## Tables

# Preface

This is a companion volume to "Seeing the Invisible: A Strategic Report on Groundwater Quality," which explains why groundwater quality is so important to managers of development programs in the World Bank and elsewhere. Its purpose is to provide managers and their teams with practical guidance on how to set up and manage a groundwater quality monitoring program. It provides a logical, step-by-step approach that can be tailored to, and grow with, the capacity to implement such a program. The guiding principle is that monitoring is the fundamental activity that shapes our identification of issues, the framing of problems, the design of solutions, and the measurement of the effectiveness of those solutions. Monitoring is often seen as simple and undervalued, but monitoring of groundwater quality, and its interpretation, is technically demanding. On the other hand, it is also extremely rewarding.

# Acknowledgments

This work was made possible thanks to financial support from the Global Water Security & Sanitation Partnership (GWSP).

The support of reviewers and advisors is gratefully acknowledged. Formal reviews were provided by peer reviewers: Dr. and Professor Yan Zheng, SUSTECH; Dr. Abedalrazq F. Khalil, World Bank Sector Leader Sustainable Development; Dr. Amal Talbi, World Bank Lead Water Resources Management Specialist MENA region. Professor John McArthur, UCL UK, provided invaluable advice and guidance during the drafting of this work. Additional comments and advice were received from World Bank colleagues Esha Zaveri, Aude-Sophie Rodella, Soma Ghosh, Nagaraja Rao Harshadeep, and Eileen Burke.

Delivery of this work would not have been possible without the unflagging support of the World Bank team, specifically Ayelen Nadia Becker, Erin Barrett, and colleagues from across the Water Global Practice and Communications Team.

# Abbreviations

| | |
|---|---|
| ABS | Acrylonitrile Butadiene Styrene |
| AD | alkali desorption |
| ADI | acceptable daily intake |
| AI | artificial intelligence |
| AMD | acid mine drainage |
| ANN | artificial neural techniques |
| BTEX | benzene, toluene, ethylbenzene, and xylene |
| CBE | charge balance error |
| CEC | chemical of emerging concern |
| CHM | conceptual hydrogeological model |
| DL | deep learning |
| DNAPL | dense nonaqueous phase liquid |
| DRASTIC | depth-recharge-aquifer-soil-topography-impact-conductivity |
| DT | differential temperature |
| EC | electrical conductivity (a proxy for salinity) |
| EIA | environmental impact assessment |
| EM | electromagnetic |
| EMP | environmental management plan |
| ESP | exchangeable sodium percentage |
| FAIR | findable-accessible-interoperable-reusable |
| FC | fecal coliforms |
| FIB | fecal indicator bacterium |
| FID | flame-ionization detector |
| FSP | field sampling plan |
| GC-MS | gas chromatography-mass spectrometry |
| GEMS | Global Environmental Monitoring System |
| GHS | Globally Harmonized System for Classification and Labeling of Chemicals |
| GIS | geographic information system |
| GPS | Global Positioning System |
| GRACE | Gravity Recovery and Climate Environment |
| GWB | groundwater body |
| GWMU | groundwater management unit |
| HDPE | high-density polyethylene |
| HSP | health and safety plan |
| HTPE | high-density polyethylene |
| ICP | inductively coupled plasma |
| InSAR | Interferometric Synthetic Aperture Radar |
| ISO | International Organization for Standardization |

| | |
|---|---|
| IT | information technology |
| LNAPL | light nonaqueous phase liquid |
| MCL | maximum concentration level, a legal definition used by the USEPA |
| MDI | maximum daily intake |
| ML | machine learning |
| MSP | multistakeholder platform |
| MTBE | methyl tertiary butyl ether |
| NAPL | nonaqueous phase liquid |
| PAH | polyaromatic hydrocarbon |
| PCE | per- or tetrachloroethene |
| PCP | personal care product |
| PFAS | per fluoroalkyl and polyfluoroalkyl substances |
| PFOA | perfluorooctanoate |
| PFOS | perfluoro-octane sulfonate |
| PID | photo-ionization detector |
| POP | persistent organic pollutant |
| PTFE | polytetrafluoroethylene |
| PVC | polyvinyl chloride |
| QA | quality assurance |
| QC | quality control |
| QHRA | quantitative health risk assessment |
| QRA | quantitative risk assessment |
| RBCA | risk-based corrective action |
| RD | reductive dissolution |
| RSC | residual sodium carbonate |
| SAR | sodium adsorption ratio |
| SDG | Sustainable Development Goal |
| SO | sulfide oxidation |
| SOP | standard operating procedure |
| SPR | source-pathway-receptor |
| TCE | trichloroethene |
| TDS | total dissolved solids |
| UNEP | United Nations Environment Programme |
| USEPA | United States Environmental Protection Agency |
| UST | underground storage tank |
| 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 strata of sufficient permeability to allow significant quantities of abstraction.

**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 for very saline waters, and the most commonly encountered units for the major ions encountered in groundwater. For example, calcium (Ca), magnesium (Mg), chloride (Cl) and sulfate ($SO_4$). |
| 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 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

The importance of natural groundwater quality and its contamination by human activities are constantly growing in importance. As the integrated water resources management paradigm emphasizes the importance of considering surface water and groundwater as a single resource, so also must the artificial disconnect between water quantity and water quality be bridged. Whether groundwater is depleted by pumping or rendered unusable by pollution, it is a lost resource and may lead to a failure to meet basic human needs.

## Background

In many countries, groundwater is the principal source of one or more of water requirements for drinking, irrigation, and industry; and notwithstanding the problems described later, it remains the inherently safest source of major water supplies. In low- and middle-income countries, direct extraction and use of untreated, and largely unmonitored, groundwater is the dominant source of drinking water for the rural and periurban poor; yet perhaps 30 to 50 percent or more of these supplies are contaminated by fecal bacteria by the time they reach a household. Furthermore, the water supplies of hundreds of millions of these people are contaminated by toxic levels of naturally occurring (geogenic) chemicals, such as arsenic, fluoride, and uranium. In addition, there is rapidly growing recognition of a wide range of anthropogenic pollutants entering, and accumulating in, the aquifers that feed the world's water wells and springs. These originate from the use of agrochemicals, such as nitrate and pesticides; municipal and industrial waste disposal; accidental losses of industrial chemicals, such as petroleum and solvents; a huge range of emerging environmental contaminants, such as pharmaceuticals, personal care products (PCPs), flame retardants, and chemical stabilizers; and many others.

The experience of high-income industrialized countries and global discoveries of the extent of natural contaminants, such as arsenic, provide salutary lessons that should shape all thinking about the conservation of natural groundwater quality and the prevention of groundwater pollution. The failure to proactively test for natural contamination has led to the accidental poisoning of many millions in the name of what was supposed to be a public good, with enormous health and economic consequences. When the failure to adequately control the hazardous substances that underpin the modern economy pollutes groundwater, its remediation (clean-up) is often extremely difficult, taking years or decades to achieve, and sometimes proving practically impossible. With the benefit of hindsight, it is self-evident that the costs of preventing, or at least greatly reducing, these occurrences would have been almost trivial compared with the costs of their mitigation or clean-up. This is not, however, a mere historical account; natural hazards continue to be discovered, and anthropogenic pollution remains commonplace. Limiting the damage from existing groundwater contamination and preventing further deterioration are core tasks of those who manage groundwater resources.

## Purpose and Readership

This report is the second of a complementary pair that describe the why and the how of managing groundwater quality problems. The readership is likely to be professionals and administrators in the water sector but not necessarily in the field of groundwater quality measurement, monitoring, and management.

This manual will support program managers and implementing teams in guiding the design of programs for the measurement, monitoring, and management of groundwater quality. It is not intended to replace detailed texts on the precise requirements of any one groundwater quality program but rather to support the user in taking the first steps for each component of such programs and provide guidance on where to find essential information and critically to ask the right questions of those responsible for the detailed implementation of each component.

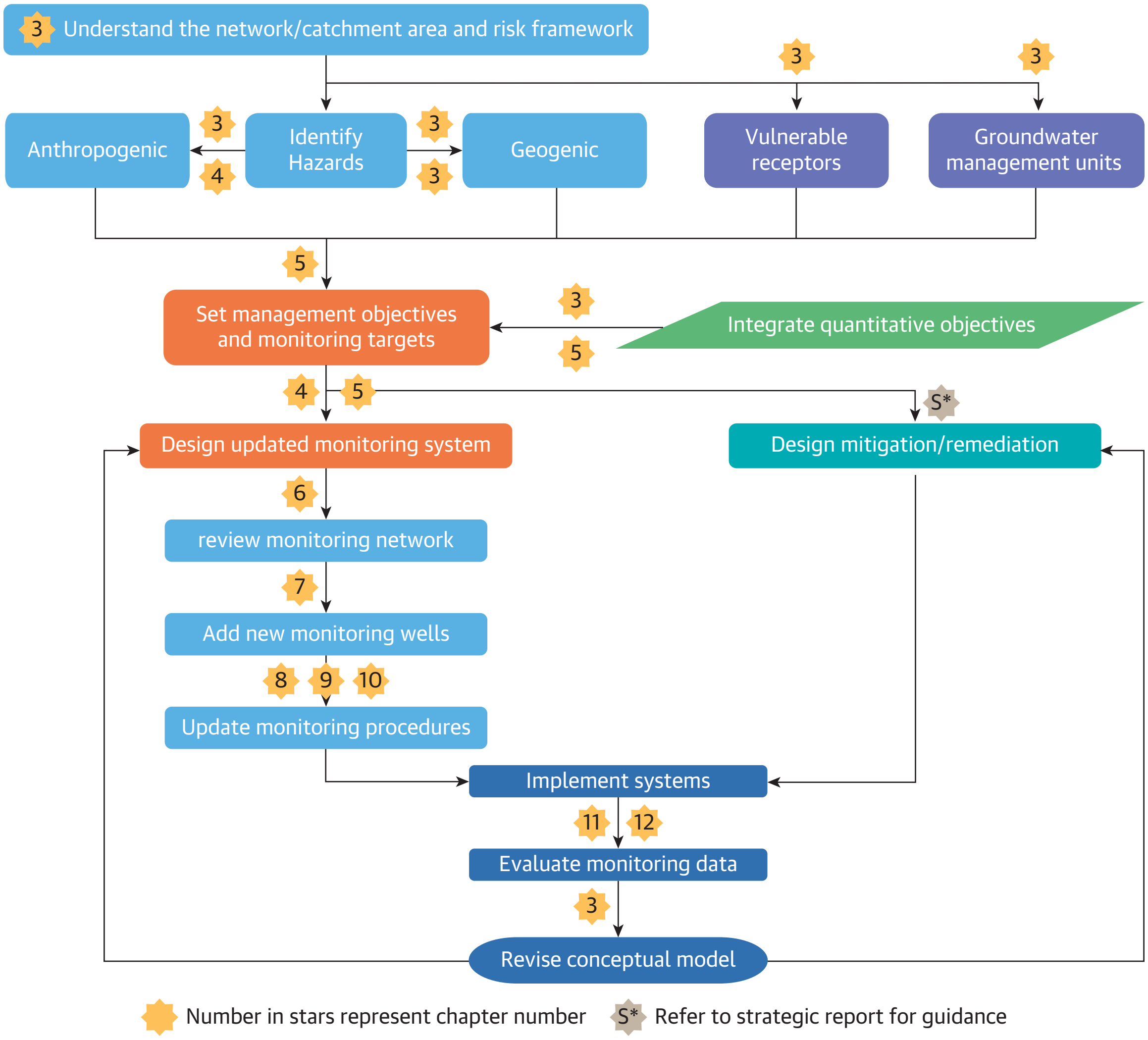
This manual goes beyond the scope of the strategic report, which emphasizes the understanding of why groundwater quality issues are so important, and will enable World Bank staff to put this understanding into practice. It describes how these topics can be incorporated into the practices of the operational departments of borrowing institutions, especially guiding World Bank staff and their counterpart agencies in understanding how groundwater quality monitoring supports sound investment decisions.

The manual is intended to serve as a guide to staff in water resources agencies looking to improve the capabilities in managing groundwater quality problems and to provide a practical step-by-step guide to establishing and running a groundwater quality monitoring program.

## Organization of the Manual

The management of groundwater quality issues is not entirely linear but does involve flows of activity with distinct feedback loops, as should be expected from monitoring as a process of collecting, analyzing, and learning from information. Figure 1.1 illustrates the generalized flow of activities and where in the report they are described (chapter 3 onwards). Chapter 2 presents a brief account of natural groundwater quality, including the criteria that determine its use and the chemical processes that control the behavior of contaminants in groundwater. Chapter 3 introduces the methodologies through which groundwater quality issues are assessed and is followed in chapter 4 by an account of the major natural and anthropogenic contaminants, with an emphasis on their monitoring aspects. Chapters 5 to 10 describe the practicalities of monitoring, starting with concepts and then proceeding through the review of networks and monitoring wells and on to sampling, field operations, and working laboratories. The final section of the manual discusses the interpretation of groundwater quality data and information systems (chapters 11 and 12) and closes with a brief account of mitigation and remediation as a bridge to working with those programs.

**FIGURE 1.1.** Groundwater Quality Monitoring and the Organization of the Manual



*Source:* Authors.

# Chapter 2

# Groundwater Chemistry and Use

This short chapter presents a brief account of the criteria that determine the suitability of groundwater for different uses, the chemistry of natural groundwater and how it may differ from well water, and the geochemical processes by which groundwater evolves as it flows through an aquifer and by which it modifies contaminants that have entered the aquifer. These subjects are described in detail in numerous books, such as Appelo and Postma (2005); Chapelle (2014); Hem (1985); and Langmuir (1997) and not repeated here.

## Groundwater Use Criteria

The primary concern over the chemistry of groundwater is its fitness for different purposes, such as drinking, irrigation, and various industrial purposes. This information is usually expressed in legally binding national standards and advisory guidelines produced by international organizations.

### Drinking Water

Most countries have published drinking water quality standards, many of which were based on the World Health Organization (WHO) guidelines at the time the standards were enacted. If legal standards do not exist, the WHO guidelines are generally adopted as a *de facto* standard. However, it should be noted that the WHO periodically updates its guidelines in light of new information concerning health effects, practical detection limits, and treatability, but national standards are not automatically brought into line.[1] In practice, in addition to regulating water supply, drinking water standards often become *de facto* standards for judging pollution of water bodies.

To comply with standards, in many countries it is customary to routinely test treated water as well as raw water before treatment. Such raw water testing is more frequent for surface water bodies as their quality can change more quickly, such that intakes may have to be closed at short notice to protect the public and/or the treatment works. Similarly, pollution events can pass quickly once the source of contamination is removed, so treatment works are rarely closed for extended periods. Groundwater presents a contrasting situation. Pollutant loads take a long time to accumulate but, once there, take much longer to remove.

It should be appreciated that drinking water standard guidelines are usually based on assumptions that may not be valid for individual countries and communities. Important assumptions include the volume of water consumed, average body weight, and intake from food. The guideline concentration is calculated from an acceptable daily intake (ADI), a lifetime average quantity expressed in terms of mass of chemical from all sources per kilogram of body weight. For example, the ADI for arsenic, considering a 60-kilogram adult, is 130 μg/day. Standard calculations make assumptions that may not apply everywhere such as that an adult drinks (about) 2 liters of water a day; thus, if the water contained 50 ppb (that is, 0.05 mg/L) of arsenic, consumption would be just below the ADI. However, if one considers a paddy farmer in an arsenic-affected area of South Asia who irrigates rice with groundwater and who may consume 400 g per day of rice, containing, say, 0.2 mg/kg of arsenic and, because of his lifestyle, perhaps 4 liters of tubewell water, his consumption will far exceed the ADI.

Groundwater managers should take care not to overlook the health risks of manganese (> 400 ppb) and molybdenum (> 70 ppb), which were withdrawn from the WHO's 2011 drinking water guidelines because they "occur … at concentrations well below those of health concern" and for aluminum, for which a guideline (900 ppb) "could be derived" but was not applied for similar reasons (Frisbie, Mitchell, and Sarkar 2015). The assumptions that these elements are not encountered in groundwater used for drinking are not sound, especially for manganese, so agencies should continue to apply these protective criteria and ensure that these elements have been tested for in baseline surveys (chapter 3).

### Agricultural Water

Standards and guidelines for irrigation water determine how groundwater might be used in agriculture (for example, Ayers and Westcott 1994). Globally and economically, the most important is salinity, which is important in itself and in combination with the amount of sodium, which affects the structure and drainage of soils. Guidelines vary according to type of crop, which are typically classified according to their salt tolerance as sensitive, semitolerant, or tolerant with thresholds of electrical conductivity (EC) of 1,500 to 3,000 µS/cm. Notwithstanding these guidelines, the impact of salinity on crop yields can be reduced if water is applied in excess and with good drainage. By contrast, if drainage is poor, the salt may be concentrated by evaporation and the impact exacerbated.

The effects of sodium on soil structure and drainage are commonly expressed in terms of various calculated parameters: residual sodium carbonate (RSC), exchangeable sodium percentage (ESP), and most commonly the sodium adsorption ratio (SAR), where:

$$\mathrm{SAR} = \mathrm{Na} / \sqrt{(\mathrm{Ca} + \mathrm{Mg})/2}$$

SAR values (measured in milliequivalents per liter, meq/L) of < 10 are considered excellent, 10 to 18 good, 18 to 26 medium, and > 26 bad.

Other elements that are particularly important for crops, though of minor impact on human health, include boron, to which many fruits are particularly sensitive. As with salinity, crops are classified according to their sensitivity to boron, which is also an essential element. The sensitivity is highly crop specific; a few crops begin to suffer at concentrations above 0.5 mg/L, and above 1.0 mg/L crop damage becomes increasingly common.

The chemicals described earlier affect the yield of crops (phytotoxicity), but some toxic contaminants accumulate in the edible parts of crops to enter the food chain; and some, such as arsenic, do both. Fluoride and heavy metals are notable examples of chemicals that can accumulate in this way. Arsenic in groundwater applied to paddy rice in the alluvial plains of many South and Southeast Asian river basins is particularly serious because arsenic co-occurs with iron and the bunded paddy fields retain water. As a result, arsenic concentrations in the soil build up year on year from the applied irrigation water and is retained by the precipitated iron flocs under dry conditions but remobilized when the paddy soil is flooded, each year transferring more arsenic to the grain until its phytotoxic effects prevent the rice grain from forming (Straighthead disease). Rice is affected more by arsenic than any other major crop, and because of the way arsenic accumulates it is not practical to define a water quality guideline because it is the soil-arsenic concentration that determines the hazard.

A benefit of using groundwater for irrigation or pisciculture is that content of pathogens will be low or absent, which is particularly important for fruit, vegetables, and shellfish.

### Industrial Water

Requirements of the production industry itself (bottled water, beer, pharmaceutical manufacture, and textile manufacture) are extremely diverse and may be more or less demanding than for drinking water.

### Environmental Protection

The criteria listed earlier apply to water at the point of extraction or use; however, one further aspect of standards is the regulation of industrial and other effluents that might enter groundwater. Although discharge standards are most commonly applied to surface water, they are equally relevant to effluents that could directly or indirectly enter groundwater. For example, a key element of the European Union's water protection strategy has been the specification of priority substances that must be prevented from entering groundwater. It is important to recognize that even if groundwater is of no interest as a resource, it can act as a conduit for contamination to surface water and wetlands.

## Natural Groundwater Quality

With the notable exception of shallow dug wells, most groundwater extracted by wells requires only precautionary disinfection because the soil and unsaturated zone are effective in filtering and degrading pathogens, many chemicals, and dissolved organic matter. Traditionally, the chemical quality of groundwater was often analyzed only at the time of commissioning for a short list of ions that constitute the majority of the dissolved load. These were typically

- Four metals: calcium, magnesium, sodium, and potassium, and possibly iron and manganese;
- Four nonmetals: bicarbonate, sulphate, chloride, and nitrate; and
- Indicator parameters, such as pH, EC, and temperature.

As described in standard textbooks, the chemical quality of groundwater is determined by a combination of the nature of the rock or sediment forming the aquifer and the climate and soil conditions under which it is recharged. The biggest influence of rock type is whether it contains calcium carbonate to neutralize slightly acidic rainwater. Under hot or humid conditions, organic matter in the soil soaks up atmospheric oxygen to create reducing conditions, dissolve iron and manganese, and remove nitrate. Under drier climates, dissolved oxygen survives longer, suppressing the release of iron and manganese and allowing nitrate to persist.

## How Contaminants Behave in Groundwater

Many factors slow down the movement, or reduce the concentrations, of contaminants in the subsurface. Before describing these, one critical distinction is drawn between dissolved contaminants, which constitute the great majority of contaminants, and immiscible or nonaqueous phase liquids (NAPLs), which are nearly all anthropogenic and behave differently.

Another important distinction is between, on the one hand, synthetic organic compounds that can be broken down into carbon dioxide, methane, and water and, on the other hand, toxic elements, such as arsenic or chromium, that cannot be destroyed but can be immobilized by being chemically bound to solids. In addition, the latter is potentially reversible, whereas the former is not. Textbooks describe these processes that control contaminants in depth (for example, Appelo and Postma 2005; Fetter, Boving, and Kreamer 2018; Langmuir 1997), and the following list gives a summary of the main ones:

- *Dissolution and weathering*. As water flows through the ground, it can dissolve or react with the minerals forming the aquifer to release ions into solution, while at the same time consuming dissolved oxygen and carbon dioxide.

- *Mineral precipitation*. As groundwater flows through the subsurface, its chemistry evolves and precipitates minerals such as calcium carbonate, iron oxides, and sulfides.

- *Adsorption and ion-exchange*. All minerals, but especially those like clays and iron and aluminum oxides, have charged surfaces that can bind (adsorb) ions like heavy metals and metalloids, such as arsenic, or perform a "water-softening" function by exchanging ions, such as calcium and sodium. Adsorption can be important for attenuating contaminants, but it should be appreciated that these processes are reversible. Although the mechanisms are different, comparable processes occur when synthetic organic contaminants are adsorbed to organic matter.

- *Oxidation and reduction (redox)*. Depending on the availability of oxygen, elements such as iron can be converted from a dissolved phase to a rust-like solid. Redox conditions also determine whether organic chemicals will be stable (box 2.1).

- *Biodegradation*. Most synthetic organic compounds will degrade in groundwater, but the rates at which this happens depend strongly on the type of compound, the redox conditions, and bacterial activity. For instance, benzene ($C_6H_6$) is easily degraded when there is a good supply of oxygen from the atmosphere or nitrate. On the other hand, in reducing groundwater, benzene is more persistent. The opposite occurs with a compound such as trichloroethene (TCE) ($C_2HCl_3$), which is degraded only under extreme reducing conditions.

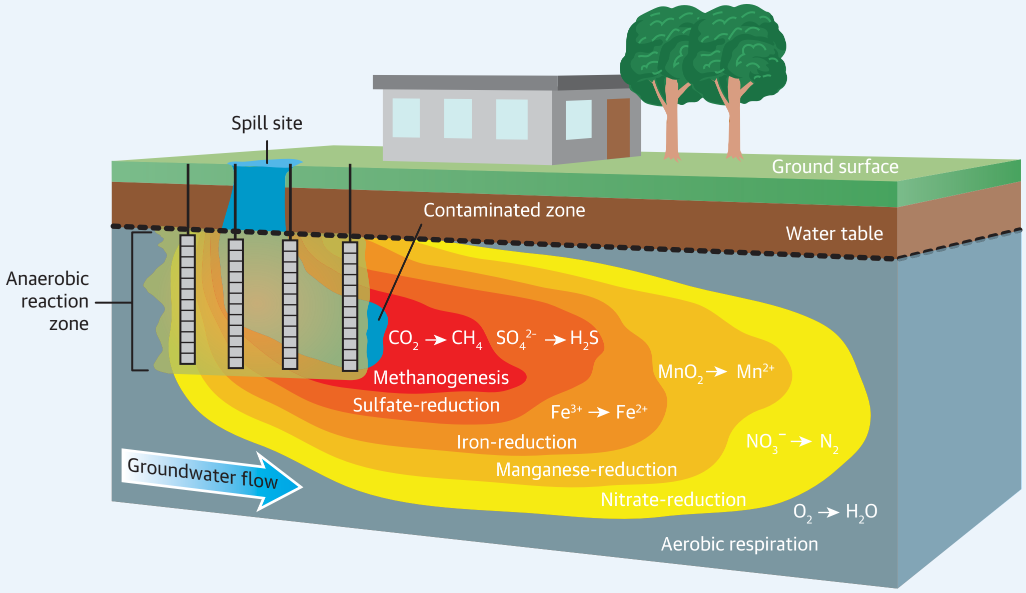
- *Volatilization*. Many industrial organic chemicals, such as solvents and components of petroleum, are more volatile than water and so may be lost by evaporation in the unsaturated zone, from the water table or floating light nonaqueous phase liquid (LNAPL), especially under hotter and drier climates.

## **BOX 2.1.** Oxidation and Reduction (Redox) Reactions

The occurrence of many substances depends on whether groundwater is oxidizing or reducing. Contaminants, such as iron and arsenic, are precipitated under oxidizing conditions and mobilized under reducing conditions, whereas others, such as uranium, follow the opposite trend.

A sequence of redox reactions typically occurs as water percolates into and through an aquifer (figure B2.1.1), mainly involving dissolved oxygen ($O_2$), nitrate ($NO_3$), manganese (Mn), iron (Fe), and sulfate ($SO_4$). The rate at which the reactions proceed depend greatly on the amount of organic matter present. If there is abundant organic matter, such as in a recent alluvium, $O_2$ from the atmosphere and $NO_3$ acquired in the soil zone are rapidly consumed. After these oxygen sources are consumed, oxides of first Mn and later Fe will be reduced and dissolve as $Mn^{2+}$ and $Fe^{2+}$, and finally $SO_4$ is reduced to form sulfides, such as the mineral pyrite. On the other hand, if there is little or no organic matter in the aquifer, oxygen sources persist far into the aquifer.

**FIGURE B2.1.1.** **Redox Zones at a Contaminated Site**



*Source:* Adapted from USEPA material.

- *Solubility and miscibility*. All contaminants have some limiting solubility in water and will vary with temperature, pH, or other factors. It matters greatly how the solubility relates to the toxicity. For instance, petroleum compounds, such as benzene, or solvents, such as TCE, have very low solubilities but are still high enough to pose significant cancer risks.

- *Dilution and dispersion*. As a plume migrates through an aquifer, the contaminants diffuse and disperse, expanding the plume but also diluting it.

- *Matrix diffusion*. Virtually all aquifers contain layers of high and low permeability, such as sand and silt in alluvium or fissures and blocks in hard rock aquifers. A pollution plume passes first through the high permeability zones; while doing so, it creates concentration gradients that cause pollutants to diffuse into the adjacent low-permeability zones. After the plume has passed, these gradients reverse and cause pollutants to diffuse back into the high-permeability zone, resulting in a plume with a very long tail.

## Note

1. Guideline values may be lowered or raised. For example, in 1993 the arsenic guideline was reduced from 50 to 10 ppb, whereas between 1998 and 2011 the boron guideline was progressively increased from 300 to 2400 ppb.

# Chapter 3
# Conceptual Models and Characterizing Risks

This chapter sets out generalized methodologies for understanding and assessing groundwater quality problems, whether natural or man-made.

## Introduction

Effective groundwater management, including its core tools of monitoring and risk assessment, can be built only on good understanding of how hydrogeological systems operate; how water enters and leaves the ground; how water moves through aquifers; how chemicals get added to or removed from groundwater; and so on. Later chapters will describe the different types of contaminants and the monitoring process.

Groundwater quality management comprises three broad tasks:

- Respond to contamination already in the ground
- Identify hazards that might contaminate groundwater
- Develop protective actions

As a basis for assessment, each of these requires a conceptual hydrogeological model that guides the actions taken (particularly their location). When groundwater contamination is identified or suspected, evaluating the risks follows a sequence beginning with simple investigations that become progressively more detailed. Initially, detections should be double-checked for sampling or analytical error, followed by desk studies and inquiries with known or likely users of the relevant chemicals and sampling a few existing wells and any vulnerable surface water body. Subsequently this might expand into a program of drilling and subsurface testing, further sampling, and establishing a monitoring program. Once this information has been collected, the risks to water resources and users are evaluated using qualitative or quantitative risk assessment techniques, which may require numerical modeling. In practice, investigation and assessment are iterative and involve regular interaction with the regulator or relevant technical and local government agencies. Risk assessment is followed by risk management that involves various monitoring and/or remediation actions as described in later chapters.

If it is not known whether groundwater contamination is ongoing but risk is apparent, or if there is a perceived legacy of historical pollution, a different approach is needed and may lead to either or both protective and corrective action based on hazard mapping, qualitative risk assessment and ranking, and various risk management measures.

## The Conceptual Hydrogeological Model

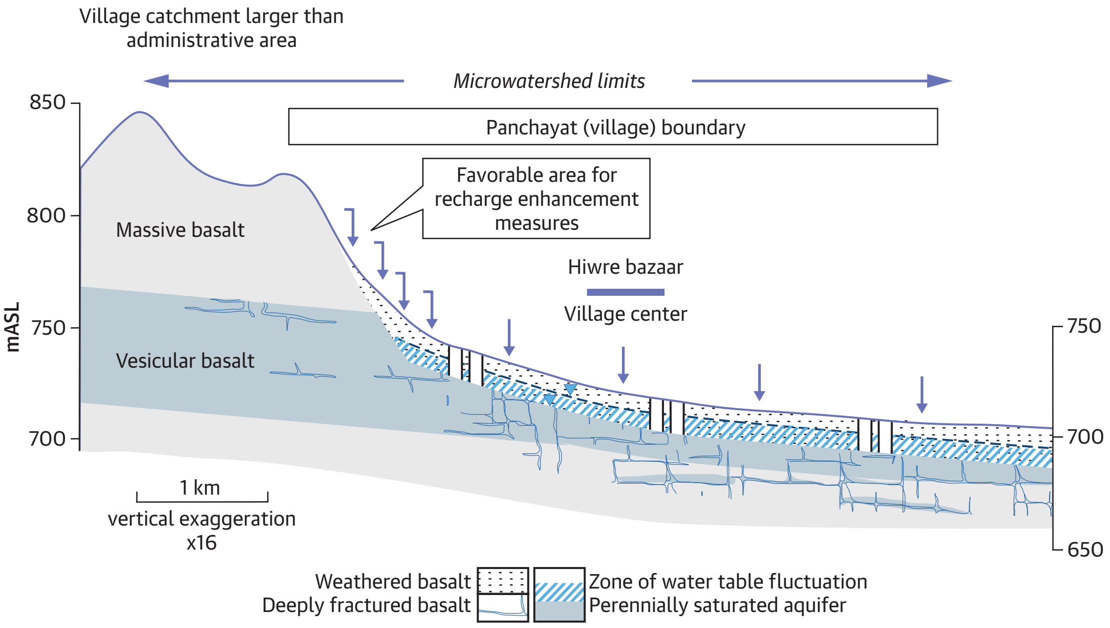
Conceptual hydrogeological models (CHM) provide a graphic and narrative description of aquifers, the mechanisms or recharge and flow, the distribution of water quality, natural and pumped discharges, and interactions with the surface environment. The CHM is now the standard framework for groundwater resources assessment (figure 3.1), essential for defining management objectives and actions and foundational for building numerical models and developing a monitoring network design and monitoring plan. A good CHM is the key to communication with specialists and nonspecialists alike and makes the design of risk assessments, monitoring, and mitigation relatively straightforward. Conceptual models do not have rigid specifications but general advice (for example, Brassington and Younger 2010; Enemark et al. 2019) indicates the core elements (box 3.1).

The conceptual model is first determined by the geology, topography, and climate, upon which is superimposed the influence of human activity through the use of groundwater and the use, transport, and disposal of hazardous substances.

The format and scale of conceptual models will vary greatly from models of shallow contamination associated with a single building to basin-wide models. A common element of all models is that the CHM is a live document that should begin with a simple preliminary CHM before the first hole is drilled and evolve continually as more information is collected. The subsurface is a complex place where uncertainty is the norm, so an evolving CHM is not a sign of error but of learning and a commitment to problem solving.

**FIGURE 3.1.** Examples of Graphical Representations of Conceptual Models

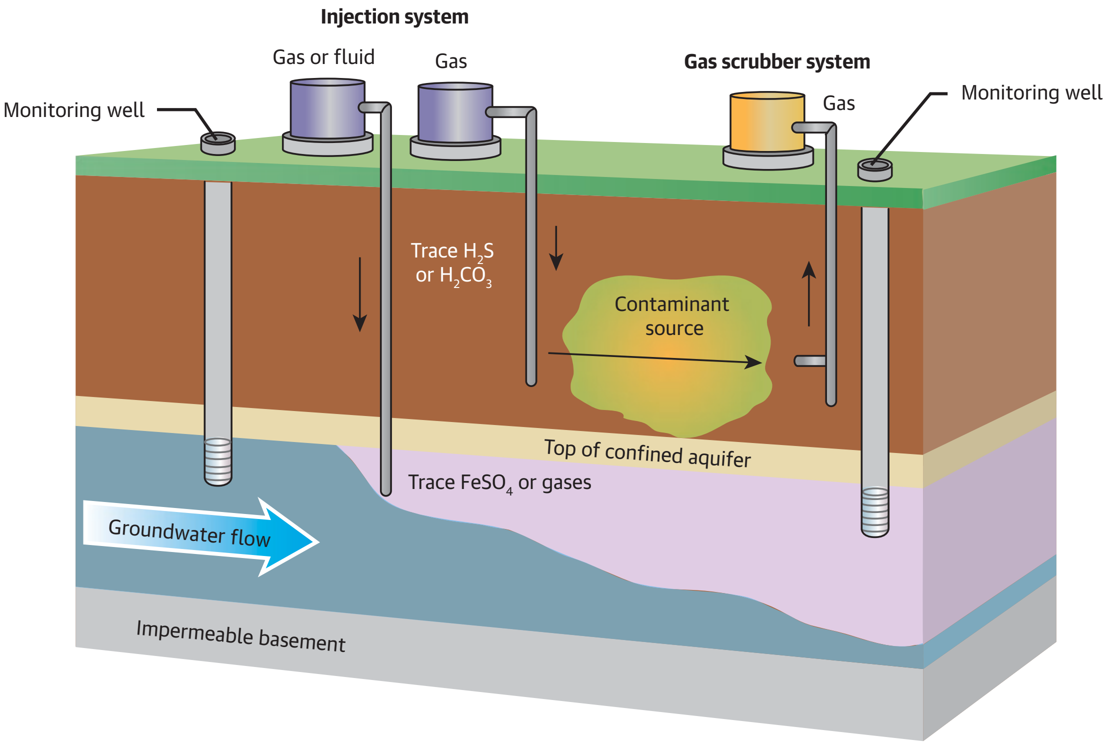
**a. Hydrogeological profile of Deccan Trap basalts around Hiwre Bazaar in Maharashtra, India**



*(continued)*

**FIGURE 3.1.** Continued

**b. Example of a generic in-situ treatment system at a contaminated industrial site**



*Sources:* (a) World Bank 2010; (b) adapted from Hashim et al. 2011.

The development of a CHM underpins almost everything in the following chapters. As far as possible, the core elements of the model should be stored and shared using a geographic information system (GIS).

## Establish a Baseline

The importance of establishing a baseline applies equally, whether you are managing an entire river basin or a single plot of land for commercial development and everything in between.

Consider these two end-member scenarios.

The first case (the basin) considers the water resource agency and public water utilities responsible for developing and authorizing groundwater for public or private supply. Although the risks from man-made chemicals should be evaluated on a site-specific basis, these agencies have a duty of care to know what naturally occurring hazards are present. Historically and globally, natural contaminants went undetected for many years because nobody thought to test for them. The extreme case is the unintended arsenic poisoning of more than 40 million Bangladeshis, which, in the space of five years, went from being unknown to the “largest mass poisoning of a population in history” (Smith et al. 2000).

### BOX 3.1. Elements of a Conceptual Hydrogeological Model

1. Background and purpose. Define objectives and confirm with resource agency/regulator.
2. Topography and surface water hydrology. Use maps and desk study.
3. Geology. Initially use maps, borelogs, and desk study; produce cross-sections.
4. Aquifer framework. Classify units and identify boundaries and expected properties.
5. Groundwater flow. Compile and map water levels; estimate flow directions and velocities.
6. Groundwater quality. Compile analyses and map lateral and vertical variations; identify processes.
7. Interaquifer and surface water-groundwater interactions. Use #2 to #6 to identify.
8. Water balance. Quantify flows, such as recharge, discharge, and abstraction.
9. Describe. In maps, diagrams, tables, and words.

Various attempts to apportion blame followed.[1] International donors had encouraged the Government of Bangladesh to exploit its abundant groundwater resources, but no one had tested the water properly. Everybody *assumed* the water quality was fine. The Bangladesh story is extreme but far from unique. Occurrences of arsenic, fluoride, uranium, selenium, and other elements continue to be discovered across the world where the groundwater has been *assumed* to be safe. The excuse that the science was not well understood is an evasion. A simple administrative solution to avoid repetition is for each basin authority to commission an expert agency to conduct stratified random sampling of each type of well in each aquifer. If concentrations exceed regulatory thresholds or even the local natural background, additional surveys can be initiated. This is the precautionary principle at work, and its cost—compared with not detecting a health issue—is small.

For the second scenario (a plot of land), there are several perspectives to consider. First, in some countries the law ensures there is a responsible person by attaching pollution to ownership of the land—when you buy the land, you buy the pollution. This does not prevent a private action against the original polluter, but it makes a powerful case for due diligence during purchase. Second, consider a company planning an industrial plant in a large port in a low-income country where enforcement of environmental standards is currently lax. In our example, there is a long and poorly documented history of commercial land use, and the new plant will have a working life of 30 years, after which it will be demolished and redeveloped for as yet unknown purposes. Thus, by the time of decommissioning, lax regulation will have become strong regulation, and the owner could face heavy costs for soil and groundwater contamination, not only for damage he has caused but also for claims from adjacent properties, former workers, the surrounding population and regulators, and reputational damage to the business. Companies that invest in baseline studies are also more likely to reduce future pollution risks.

## Water Bodies, Chemical Status, and Trends

As a generalization, groundwater contamination is managed at two scales: the individual pollution incident and at a subregional, or water body, level. The concept of a water body is simple but also relatively new in management practice. Water bodies may be defined for surface water, which is usually a subcatchment, or groundwater and often have the same surface representation. A groundwater body is simply a distinct volume of groundwater within an aquifer or aquifers. However, groundwater bodies may be subdivided to follow geological boundaries or groundwater flow divides, divided vertically into separate bodies because of layering, and sometimes enlarged where a dipping stratum is recharged in one catchment and discharges in another. In all cases, a key concept of a groundwater body is that it is practically homogenous in terms of its hydrogeology, its use, and the pressures[2] it faces. The water body concept is central to the European Union's WFD and also to Sustainable Development Goal (SDG) 6.3 for ambient water quality, establishing a trend that is likely to become universal in its application in the foreseeable future. The idea of good ambient water quality at the water body level is central to river basin planning and also necessitates the integrated assessment and management of surface water and groundwater. Unlike the response to pollution incidents, which is by definition reactive, the water body perspective leads to a proactive approach. SDG 6.3 involves "reducing pollution … and … minimizing release of hazardous chemicals" and increasing safe reuse of treated wastewater. Although intended for all waters, SDG 6.3 is formulated mainly with regard to anthropogenic pollution of surface water. For groundwater, two other factors must be integrated: (a) widespread geogenic contamination and (b) the lag time between stopping pollution and improving water quality.[3]

The definition of groundwater bodies fits naturally into the definition of CHM, wherein the groundwater body becomes the basic management unit for which a qualitative, or chemical, status is defined and the management objective is to prevent or reverse any deteriorating trend in key parameters specified in the conceptual model.

## Pollution Pathways

Although the predominant mode of groundwater pollution is by liquids infiltrating from the ground surface to an underlying aquifer, there are also man-made pathways by which pollutants can bypass the protective soil and pavements to enter an aquifer:

- *Abandoned wells*. Abandoned, and possibly forgotten, wells create perfect pathways for polluting groundwater. Whenever a well is decommissioned, it should be backfilled with cement grout or clay. This should be built into regulations.

- *Buried infrastructure*. Pipelines, latrines, sewers, and oil-filled electricity cables laid below the soil zone make infiltration easier and, unnoticed, will almost always leak to some degree, and utility trenches provide pathways that facilitate lateral contaminant movement. Maintenance and inspection are essential, and in sensitive areas, additional protection should be included according to industry best practice. Basements and tunnels pose similar risks according to how these spaces are used. All should be regulated.

- *Drilling and deep well activities*. To prevent leakage, boreholes drilled through aquifers should be sealed to the base of the aquifer before continuing drilling into a deeper aquifer. Deep wells normally encounter high pressures, and there are many cases of abandoned oil and gas exploration wells discharging high flows of water to the surface or into overlying aquifers for years or decades. Activities such as fracking and wastewater injection also pose significant risks of gases or liquids escaping to contaminate overlying aquifers.

In addition to these pathways *into* groundwater, there is one special pathway *from* groundwater to be aware of. This is vapor intrusion by volatile organics or escaping gases, such as methane or radioactive radon, which can rise from the surface of shallow groundwater to the surface or, worse, enter the basements of buildings.

## Pollution Hazard Mapping and Characterization

The first step in assessing anthropogenic pollution risk is hazard mapping, compiling information on present and historical land use into a GIS inventory of threats to soil and groundwater. It is also helpful to take a catchment scale view before zooming into the site. The principal sources of data for locating hazards will include

- Local government registers of businesses;
- Registered pollution events;
- Sequences of historical maps at different dates, which will identify sites where historical contamination might be present; and
- Google Earth, aerial photos, and high-resolution satellite images.

Compilation of these data leads to mapping the locations of hazards in GIS. The next step is to characterize the chemical as contaminants and estimate their magnitude by reference to standard guidelines on industrial activities (for example, UNIDO 2016; Weiss et al. 2016).

The chemicals of concern identified can be categorized and ranked according to standard data on toxicity and mobility in water, such as solubility in water, tendency to biodegrade, and tendency to be adsorbed onto aquifer solids (for example, Prager 1998). The quantities of chemicals used may sometimes be directly available, or estimates or weighting factors can be derived from proxies, such as the footprint, labor force, energy consumption, or tax records. The hazard mapping described earlier applies equally to risks to surface water.

## Chemical Registers and Toxicological Data

A central part of identifying pollution risks and reducing the likelihood of pollution occurring is knowledge of what chemicals are used and how, and where they are stored and transported. Although not every country has developed a national register of chemicals, there are various national and international registers of chemicals and their properties, which are accessible online and may be used to identify the properties of chemicals known to be in use in a country. Even countries that do not have a national register may have signed up to international agreements (such as the transport of chemicals), and there are initiatives by the United Nations Environment Programme (UNEP) to encourage establishment of national registers of chemicals permitted for use under the Stockholm Convention[4] to restrict the use of persistent organic pollutants (POPs). The WHO has produced guidance on approaches for setting up national chemicals registers (WHO 2018) and how they can be used to improve the management of hazardous chemicals. Some other sources of information and examples of national registers are listed in table 3.1.

Accessing consistent information is aided by the Globally Harmonized System for Classification and Labeling of Chemicals (GHS), which standardizes information on health and safety and chemical data sheets. A useful source of information on chemical hazard data is from the United States Environmental Protection Agency (USEPA) CompTox Chemicals Dashboard, which includes data on 883,000 chemicals.[5]

## Vulnerability Mapping

Given the difficulty of cleaning up polluted aquifers (see the strategic report), the maximum practical effort should be given to preventing it in the first place. Vulnerability focuses on the pathway component of the source-pathway-receptor (SPR) link (box 3.2). It is a land-use planning tool and adds to the value of hazard mapping when overlaid in GIS. The purpose of a vulnerability map is to give a qualitative indication of how easily a contaminant discharged on the land surface could enter the top aquifer. The contaminant is normally treated as an inert substance that moves at the same rate as water and, as such,

**TABLE 3.1.** **Examples of Sources of Information on Hazardous Chemicals and Their Control**

| Agency / Country | Link |
|---|---|
| United Nations Economic Commission for Europe (UNECE): | https://unece.org/about-ghs |
| United Nations Environment Programme (UNEP): | https://wedocs.unep.org/bitstream/handle/20.500.11822/28403/ChemContAut.pdf?-sequence=1&isAllowed=y |
| Australia: | https://www.industrialchemicals.gov.au/ |
| Canada: | https://www.ccohs.ca/oshanswers/chemicals/ghs.html |
| China: | https://msc.ul.com/en/resources/article/china-officially-launches-the-national-internet-platform-for-hazardous-chemicals/ |

**BOX 3.2. Hazard, Risk, and the SPR Link**

Risk can be thought of as simply the probability of a bad thing happening and described in pseudomathematical terms as

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

With regard to groundwater pollution, hazard is the existence of chemicals or pathogens that have the capacity to do harm, and vulnerability represents what might be affected by that hazard, which could be the aquifer, a well, or surface water.

For groundwater, the risk is often expressed in terms of a source-pathway-receptor (SPR) link. Here, source and receptor are equivalent to the hazard and vulnerability terms used earlier. The key difference is including the pathway term that focuses attention on how to cut the link between a pollution source and, for example, a well. For chemicals of concern, the SPR link should be illustrated in the CHM.

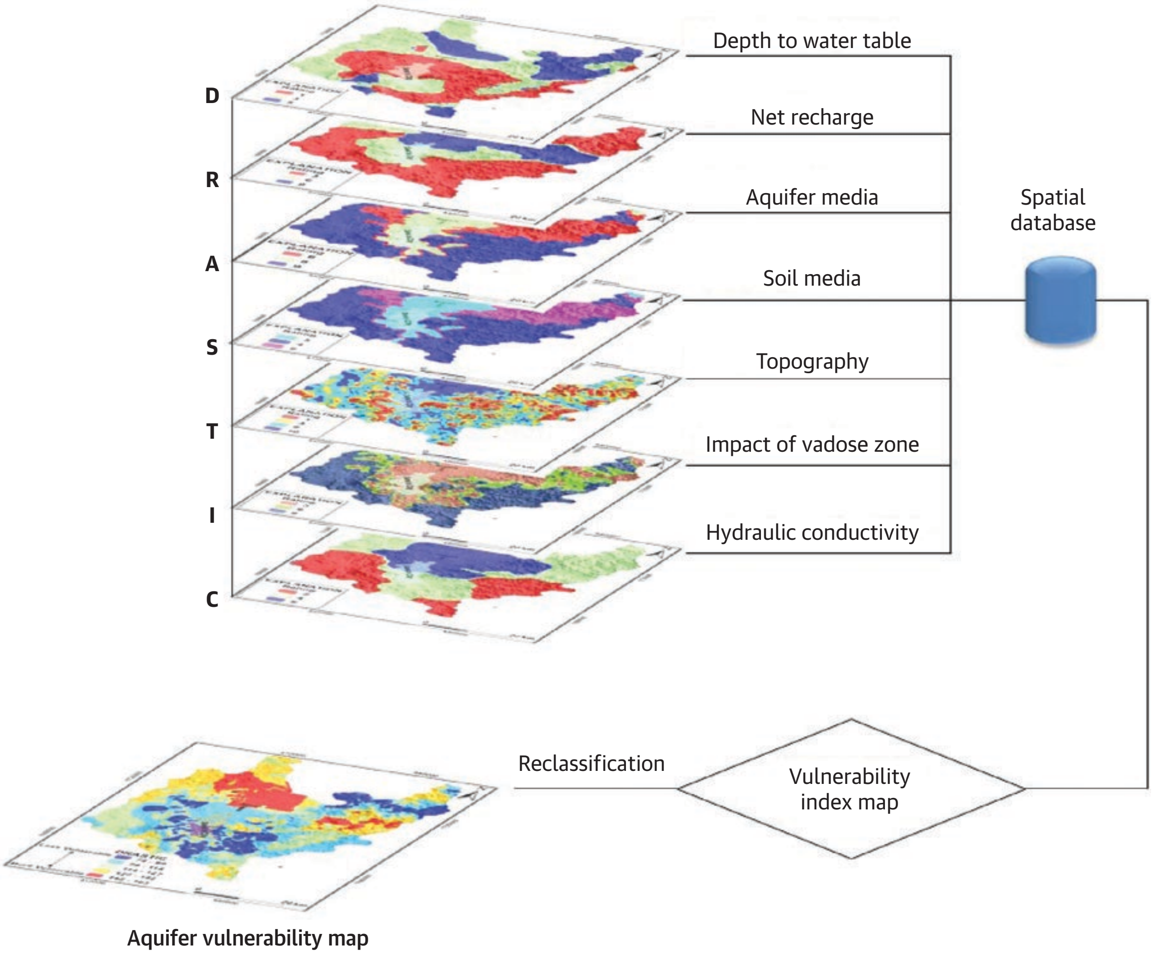
is closely related to recharge potential so that existing recharge studies will provide useful inputs to vulnerability mapping.

Vulnerability maps can have varying degrees of complexity, starting with the simple questions of where aquifers are located and for what purposes they are used. This information should be easily available from geological and, if available, hydrogeological maps. This will be added to information on the natural protective barriers formed by the soil characteristics, which can normally be obtained from the national soil survey, the thickness of the unsaturated zone between the soil and the aquifer, and overlying aquitards. These three elements (soil, aquitard, and aquifer) are the minimum requirements for a vulnerability map; however, there is much scope for adding additional information. The extent to which such maps are further refined will depend on the local circumstances and the local regulatory system. A common approach is known by the acronym DRASTIC: depth-recharge-aquifer-soil-topography-impact-conductivity. This methodology uses GIS to combine seven layers, as shown in figure 3.2. In all approaches, the map units are either assigned qualitatively into classes or each layer is assigned a set of scores and weights that are summed to give an overall numerical score. The original formulation and scoring of the DRASTIC model by the USEPA was based on readily available data sets; however, it can easily be modified to fit the data available in the country or region of interest, which should be available from national agencies in digital format. It is a simple and pragmatic approach to draw administrative attention to areas of higher or lower vulnerability.

## Risk Assessment

Risk assessment is an integral part of groundwater quality management and can be conducted at several stages. At the simplest level, superimposing hazard and vulnerability maps in a GIS provides a quick visual assessment of high-risk locations. This is easily extended by overlaying other GIS layers, such as

**FIGURE 3.2. The DRASTIC Methodology for Vulnerability Mapping**



*Source:* Alwathaf and Mansouri 2011.

abstraction wells and potential pollution sources. GIS can be used to determine the proximity between hazards and receptors and then used for risk ranking, which will help water utilities or public health agencies to identify water sources and communities most at risk and also for the owners of hazardous facilities to prioritize investments in risk reduction.

The next stage is quantitative risk assessment (QRA) employing models ranging from simple analytical models to sophisticated numerical models but all having the same basic objective of predicting the concentrations and time frame in which contaminants will reach a receptor. When there are multiple contaminants, the assessment may be reduced to evaluate only the most mobile and toxic ones.

A practical distinction is drawn between situations in which a contaminant *might* reach a point that results in actual exposure to humans or other organisms and situations in which the contaminant *has already* resulted in exposure. In the former case, the QRA[6] may be sufficient if it triggers corrective action.

In the latter, it is essential that health and environmental regulators be involved and the assessment extended to conduct a quantitative health risk assessment (QHRA), which combines predicted concentrations with exposure estimates and dose-response curves to predict the health impacts of nonintervention.

The details of risk assessment procedures are complicated and beyond the present scope; however, the overriding objective is not to conduct a work of definitive science but to initiate action to reduce risks to human health and the environment while avoiding unproductive expenditure that could be better spent elsewhere (box 3.3).

The main building blocks to understanding groundwater quality hazards were identified earlier. As indicated at the beginning of this chapter, the important role that conceptual models have in identifying the extent to which these hazards pose a threat cannot be overstated (box 3.4).

## Regulation and Its Consequences

Managing pollution requires an appreciation of the regulatory regime and, because groundwater pollution events take years to resolve, how it might evolve over that timescale. Although the European Union and North America have enacted fairly comprehensive legislation for groundwater during the past two decades, many countries have yet to develop a regulatory framework that meets the needs of protecting and restoring groundwater quality. Notwithstanding variably effective attempts to control groundwater abstraction, the prevention and remediation of groundwater pollution lag far behind.

The most basic regulatory measure is the drinking water standard, applied at the point of extraction or point of use, which controls what can be supplied to users without treatment. This standard is also used to quantify resources, but it can become complicated when water quality varies on a small

### BOX 3.3. Risk-Based Corrective Action (RBCA)

An understandable reaction to pollution is to demand clean-up to pristine conditions, demonstrating the polluter pays principle. For man-made chemicals that should not be present in groundwater, this is theoretically possible, but is it desirable? Or is it rather, as economists like to argue, that the optimum level of pollution is not zero because the costs of enforcement are so great (for example, Mishan 1974)? Early practice in the United States demanded clean-up to a pristine standard, but this was later revised because it was often practically unachievable and vast sums were being spent beyond the point of any practical benefit. Thus, the USEPA and many other countries have replaced this with the RBCA (pronounced "Rebecca") concept, which adopts the more realistic goal "to prevent adverse effects to human health and the environment." The devil in the detail here is to have (a) a competent regulator, (b) the necessary consultation to define "reasonable" targets, and (c) the definition of compliance points.

### BOX 3.4. Why We Need Conceptual Models

Groundwater can be difficult to conceptualize, even for water professionals. Apparently simple questions such as "What do we mean by 'the groundwater' or 'groundwater quality'?" defy simple answers. Knowing the average composition of all groundwater in a region is of no practical use; even the average for a single aquifer is of limited use. Groundwater, and its quality, varies from one place to another, laterally and vertically; it is divided between geological strata subject to an almost infinite variety of connectedness; its quality is not static but changes over time and space.

Thinking about groundwater requires a mental picture of where that water sits in some geological stratum, with other layers above and below, and how the well screen permits entry of water to the well. At the next level of conceptualization, one may ask: "Were and when did that water enter the ground?" "What path did it take to reach the well?" and "What happened to it along its journey?" This is where conceptual models help. Without such a model, it is easy to get confused. Consider two examples illustrating how this might play out:

1. A young engineer stands at a wellhead, close to where there has just been a fuel spill, with some sampling device and a standard operating procedure (SOP). He expects to find evidence of petrol but doesn't. Has he done something wrong? Perhaps the plume did not infiltrate here? Did it move in another direction? However, after asking about the well construction, he realizes the top of the screen is 10 meters below the water level in the well, the fuel could be present close to the water table, and he will need a shallower well to find out if it is there. The absence of hydrocarbons in the well does not prove an unpolluted aquifer.
2. A geochemist looks at a table of analytical results from a well in a particular aquifer. Her thermodynamic model tells her it is an unstable combination of parameters. Is there an analytical error? Or a software error? However, the borehole log shows the well is open over the full thickness of the aquifer. The sample is a mixture of waters from shallow and deep layers that doesn't represent anything that exists in the ground.

These simple examples illustrate how "picturing" the subsurface helps interpret results at a single well. Real conceptual models extend further in three or four dimensions, but the intellectual process is, in principle, the same and offers enormous benefits in understanding how aquifers work.

Another perspective, and warning, comes from numerical modeling of groundwater flow, which has a much longer record and is foundational to groundwater quality modeling. In the early decades of flow modeling, say up to the 1990s, it was common to pay lip service to conceptualization with the apocryphal saying, "Just collect the data and we'll sort it out in the model." This attitude was rejected to the extent that by the early 2000s, some agencies would not allow numerical modeling to proceed until the conceptual model was approved. The pioneering groundwater modeler Ken Rushton (2009), reflecting on his career, observed that every major modeling study he had worked on commenced with at least one major conceptual error. This is not an expression of poor work but a description of the nature of the challenge and the essential need for continuously evolving conceptualization. When groundwater flow and quality are involved, it is even more true.

scale or blending at the surface before delivery is an option. It is important to remember that some groundwater may be unfit for drinking (without treatment) yet suitable for agricultural or industrial purposes or as cost-effective raw water for desalination.

A more complicated issue is to define ambient standards or thresholds for groundwater. An example of this applies under the European Union's WFD in which a groundwater body containing elevated levels of nitrate, but not exceeding the drinking water standard, could cause eutrophication of a surface water body into which it discharges.

Controlling groundwater contamination is complicated by the varying nature of contaminants. Synthetic organic chemicals, such as PFAS, solvents, and pesticides, should never enter groundwater; hence, allowing entry of any measurable and attributable amount should be an offense. On the other hand, chemicals, such as chloride and nitrate or even arsenic and fluoride, occur naturally, so defining pollution must be based on a threshold or known background concentration.

With regard to where groundwater has already been contaminated by human activity, legal rules are required so that the polluter pays principle can be implemented through fines and/or requirement to remediate.

The overriding objective of the regulator should be to protect the environment rather than maximize prosecutions, so it is prudent to provide for voluntary remediation with the expectation of avoiding prosecution or receiving a reduced sentence. There are several pragmatic reasons for such a dispensation. First, the number of polluters probably far exceeds the capacity to prosecute them. Second, many pollution events are accidental. The keys to limiting pollution damage are immediate reporting, emergency response, and early remediation. Laws and regulations that promote quick responses will protect the environment, reduce costs to the economy, and focus prosecution resources on the more recalcitrant members of society.

## Notes

1. Several court actions were attempted but none succeeded as international agencies asserted their right to legal immunity. It is questionable whether there would be recourse to such immunity in the future—certainly not in the court of public opinion.
2. Here the term *pressure* is used as in the European Union's WFD to refer to effects such as abstraction or pollution.
3. Of the five parameters required for Level 1 monitoring, only three (salinity as EC, nitrate, and pH) apply to groundwater and miss many important groundwater contaminants. However, Level 2 (optional) monitoring allows for including arsenic, fluoride, heavy metals, pesticides, and so on. Countries that wish to leverage the SDGs to improve groundwater quality must opt to include appropriate Level 2 monitoring parameters in their SDG reporting.
4. For more information on the Stockholm Convention, see its website at http://www.pops.int/
5. The USEPA CompTox Chemicals Dashboard is available at https://comptox.epa.gov/dashboard. For a discussion and tutorial, see Williams et al. (2021).
6. Such risk assessments are normally conducted by the site operator under the direction of the regulator.

# Chapter 4
# Groundwater Contaminants and Their Monitoring

This chapter describes the major natural and anthropogenic contaminants found in groundwater, including their occurrence and significance, but focuses on the practical considerations for monitoring and how to start addressing them. This is complemented in chapters 5 to 9 by general advice on network and well design, sampling procedures, and field operations.

## Natural Groundwater Contaminants

Although any constituent in excess can be harmful, there is a relatively short list of naturally occurring (geogenic) elements that cause widespread concern for public health or objections from water users (table 4.1). In terms of impact on global health, two contaminants—arsenic and fluoride—exceed all others in the capacity to cripple or even kill large numbers of people.

The two most common, however, that give rise to widespread nuisance are iron and manganese.[1] Every country or region should conduct high-quality baseline surveys of a representative sample of aquifers, including variations with depth, to know what's there. Only then can resources be properly targeted and adequate and efficient monitoring systems designed; yet many areas have not tested, and occurrences of arsenic or other toxic elements may be awaiting discovery.

### Arsenic

Arsenic is the world's most important natural groundwater contaminant and, since the 1980's has been recognized to have poisoned more than 150 million people in more than seventy countries (map 4.1), with a huge toll of mortality and morbidity, and effects ranging from debilitating skin conditions to fatal heart and lung disease and cancers (see the strategy report for details). The occurrence of arsenic is global, but particularly common along river valleys draining young mountain belts. This hazard becomes a grave risk when it coincides with poor rural populations who rely on self-supply from shallow wells. Because arsenic can be mobilized into groundwater by four different mechanisms,[2] predicting where arsenic pollution will occur is complicated (figure 4.1), but identifying which mechanism is most likely to apply will guide sampling. This is important because there are still significant areas that have not been tested.

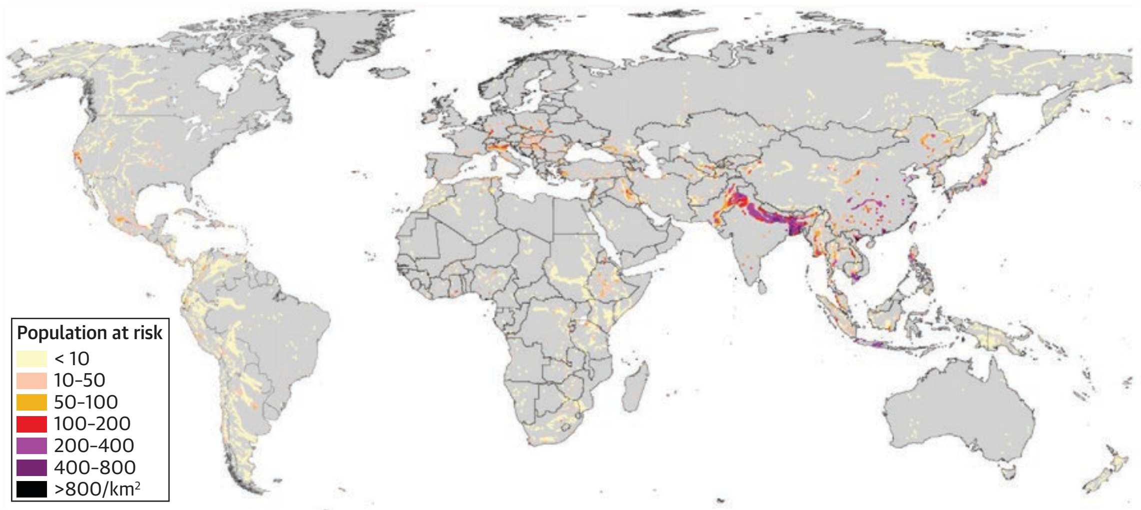
Arsenic in groundwater is also a major problem for irrigated crops, especially rice, which accumulates arsenic far more than any other major crop. When irrigated with iron- and arsenic-rich tubewell water, arsenic accumulates in the soil year on year, transferring progressively more and more arsenic to the rice plant, which enters the food chain and is phytotoxic. Therefore, monitoring must include testing of both drinking and irrigation sources and, if the latter is significant, should also include periodic sampling of agricultural topsoil. The associations between exposure from drinking, cooking, and irrigation water highlight the necessity for water resource agencies to liaise with both public health and agriculture agencies.

**TABLE 4.1. Important Natural Groundwater Contaminants**

| Substance | GV/MCL | Occurrence/environment | Effects/significance | Examples/extent |
|---|---|---|---|---|
| Arsenic (As) | 10 ppb | In alluvium around young mountain belts; also in crystalline rocks with sulfide mineralization, some sandstones, and geothermal areas;<br>accumulates in irrigated crops. | Skin lesions, liver and kidney disease, heart and lung disease, multiple cancers | Global, especially South and Southeast Asia;<br>about 150 million exposed since about 1980. |
| Barium (Ba) | 70 ppb | Sedimentary rocks containing the mineral barite (barium sulphate) | Nephropathy | United States, localized |
| Boron (B) | 2.4 ppm | Sodium-rich alluvial groundwater; geothermal areas | Nephropathy, hypertension | Bangladesh, United States |
| Cadmium (Cd) | 3 ppb | Associated with sulfide-rich sediments; also anthropogenic; accumulates in irrigated rice | Chronic kidney disease, possibly carcinogenic | Germany, Pakistan, Sri Lanka |
| Chloride (Cl) | 250–600 ppm | Ubiquitous, especially in coastal areas | Taste, suspected adverse pregnancy outcomes | Global |
| Chromium (Cr) | 50 ppb | Occurs in two states: highly toxic Cr (VI) and low toxicity Cr (III) | Carcinogenic | California |
| Fluoride (F) | 1.5 ppm | Global | Dental and skeletal fluorosis | Global; 200 million at risk |
| Iron (Fe) | 0.3–1.0 pm | Ubiquitous | Taste, odor, staining | Global |
| Lead (Pb) | 10 ppb | Groundwater with low pH and alkalinity; also anthropogenic, including leaching of lead pipes | Impaired neurodevelopment in children, cardiovascular diseases, kidney malfunction, hypertension, adverse impaired fertility and pregnancy outcomes | Punjab (India); generally rare |
| Manganese (Mn) | 0.1–0.4 ppm | Ubiquitous | Impaired mental development in children | Global |
| Molybdenum (Mo) | 70 ppb | Volcaniclastic alluvium; granitic basement | Uncertain | Argentina, Burkina Faso, Ethiopia, United States |
| Selenium (Se) | 40 ppb | Alluvium with marine shale source rocks | Keshan disease, Kashin-Beck disease, gastrointestinal disturbance, tooth decay, hair and nail loss | China, India, Japan, Jordan, United States |
| Uranium (U) | 30 ppb | Mostly in crystalline, especially granitic, rocks and alluvium derived therefrom | Kidney disease | China, India |

*Sources:* Bailey 2017; Coyte et al. 2019; EAWAG 2015; Kubier et al. 2019; Moore et al. 1984; Oze et al. 2007; Ravenscroft, Brammer, and Richards 2009; Ravenscroft and Mcarthur 2004; Riedel and Kübeck 2018; Smedley and Kinniburgh 2017; World Bank 2020.
*Note:* GV/MCL = WHO guideline value (GV) for drinking water or USEPA maximum concentration level (MCL) if GV is not available.

**MAP. 4.1.** **Areas and Populations at Risk of Arsenic Pollution of Groundwater**

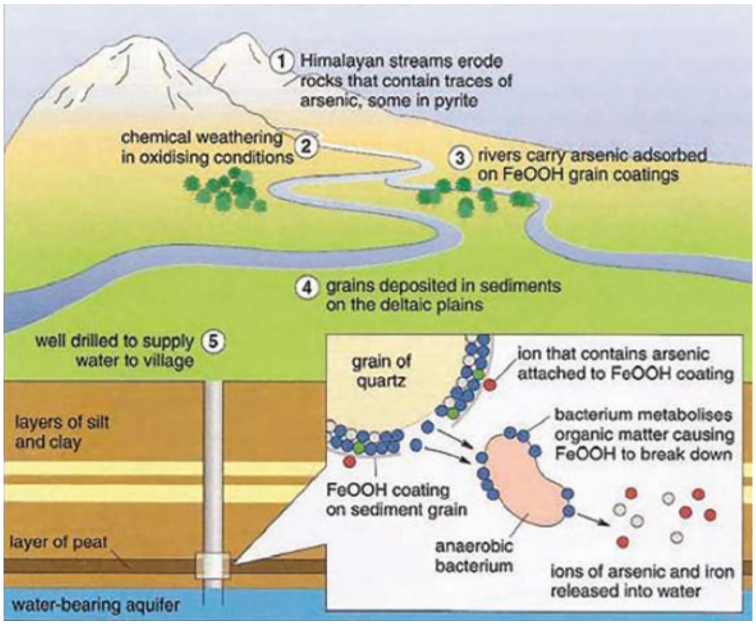


*Source:* UNICEF and WHO 2018.

### Monitoring Advice for Arsenic

The distribution of arsenic contamination varies particularly strongly with depth and also with subtle differences in the age[3] of sediment, and provides a strong indicator of arsenic risk. The design of monitoring and surveys must take explicit account of differences in well depth and surficial geology. Failure to do this in the past has led to severe pollution being overlooked, even while it was poisoning people. Because of depth variations, maps of arsenic can be misleading, with areas that appear to be thoroughly contaminated having safe water available at specific depths and vice versa (see chapter 11).

**FIGURE 4.1.** **Arsenic Mobilization by Reductive Dissolution**



*Source:* The Open University ©.

Arsenic concentrations vary over time, increasing and decreasing depending on local circumstances. Seasonal changes are most likely in the zone of water table fluctuation. At greater depth, concentrations can increase steadily over periods of months to a few years from below detection limits to more than 100 ppb under the influence of pumping (for example, McArthur et al. 2010). The implication of temporal trends is that one-off surveys are not sufficient, and wells must be monitored regularly at intervals reflecting the time required for adverse health effects to develop (≤ two years).

Because of its highly toxic nature, it is to be hoped that contaminated drinking water wells will not provide long-term time-series monitoring data unless the well is equipped with an arsenic removal plant and the raw water monitored, in which case it will offer a good practical alternative to dedicated monitoring wells. This synergy can also save costs for water resource agencies.

The procedures for monitoring arsenic will depend on the socioeconomic setting and the severity of the problem. In cases of recently discovered mass poisoning, there is likely to be heavy reliance on the use of field test kits for arsenic testing as single-parameter monitoring. It is important that (a) random samples are sent for laboratory checking and (b) procedures are developed for results that are borderline for safety (for example, As = 10 ppb or As = 50 ppb). In the latter case, either borderline samples can be sent for laboratory analysis or, applying the precautionary principle, borderline analyses can be treated as "unacceptable" exposure. When an arsenic problem is of smaller scale or more under control from the public health perspective, laboratory analysis at annual or shorter intervals will become the norm and should include at least measurement of iron, manganese, pH, sulfate, and bicarbonate.

When collecting water samples for laboratory analysis of arsenic, the samples should be immediately filtered with minimum contact with air to remove any suspended particles and then acidified to prevent oxidation and precipitation of iron and arsenic. If there is doubt, it may be useful to analyze both filtered and unfiltered samples. If arsenic speciation analysis is required, further field preservation is needed; for this, as with all aspects of sample collection and preservation, procedures should be agreed with the laboratory before ordering sample bottles (for example, McCleskey, Nordstrom, and Maest 2004).

Currently, most arsenic field tests are based on the Gutzeit method.[4] Used appropriately, these are adequate for public health surveillance but not sufficiently accurate for water resource trend monitoring. However, some new generation arsenic test kits are under development that should provide quicker and more accurate analyses.

As of late 2021, there are areas of the world where groundwater had not been tested for arsenic, including some where arsenic contamination is suspected (UNICEF and WHO 2018). All agencies should ensure they have confident knowledge of the presence or absence of arsenic in the groundwater sources.

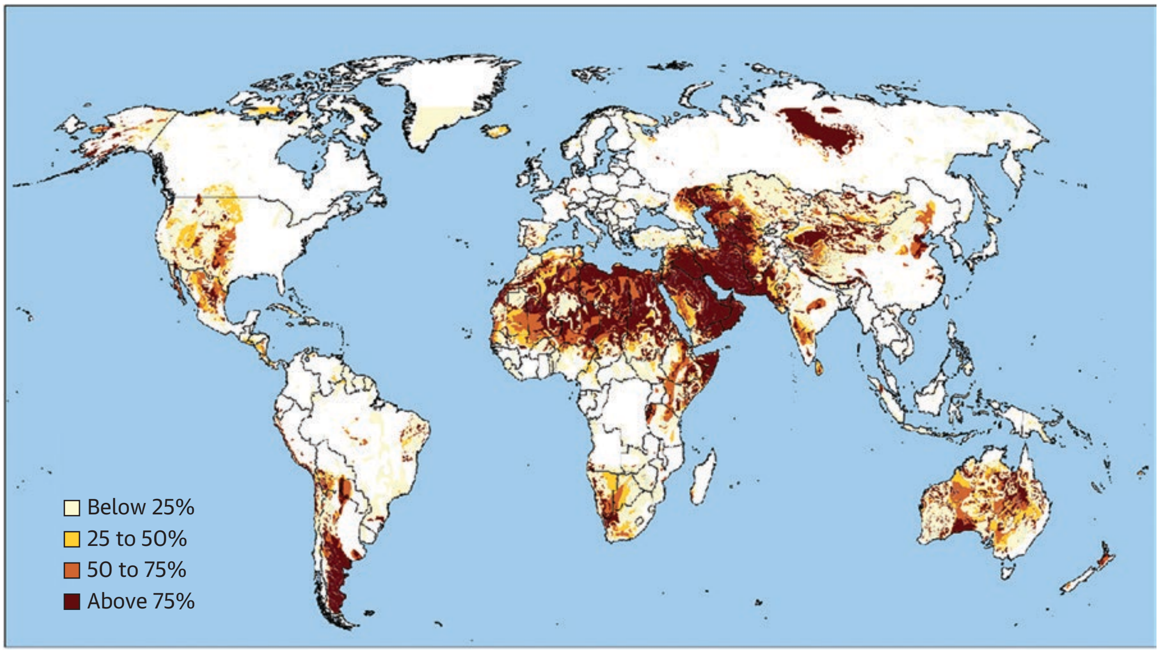
Geostatistical methods[5] are useful to display and summarize risk from large data sets and methods, such as artificial intelligence (AI), and might offer new insights; but, like all models, they should be used with care and based on sound conceptualization. Caution should be applied if such methods, which require arsenic concentrations as inputs, are used in predictive mode. The quality of prediction is inversely proportional to the density of arsenic data and hence least useful when no data exist. In the latter case, predictive models will use readily available proxy data, such as iron or pH, or environmental variables to determine where testing is required.

### Fluoride

Fluoride is the only natural groundwater contaminant that compares with arsenic in its global extent and impact on health and is estimated to place about 200 million people at risk of developing fluorosis (EAWAG 2015). Fluoride is also mobilized by multiple geochemical mechanisms, complicating prediction, and in some situations fluoride and arsenic co-occur. The maximum acceptable concentration for fluoride in most countries is 1.5 mg/L. There is also emerging 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).

Fluoride contamination of groundwater is encountered on all continents (map 4.2). Unlike arsenic, it is relatively rare in the great alluvial basins, but it is commonly associated with hard rock aquifers in semi-arid climates. The main sources of fluoride are weathering of silicate minerals such as mica, apatite, and amphibole, which are common in granitic rocks and some volcanic rocks. The amount of fluoride in groundwater is controlled by the solubility[6] of the mineral fluorite ($CaF_2$), such that high concentrations of calcium, as found in limestone aquifers, depress the maximum fluoride concentration (figure 4.2). Conversely, in aquifers with little calcium, like granites, high fluoride concentrations are possible. Given that geological maps and calcium measurements are widely available, this relationship

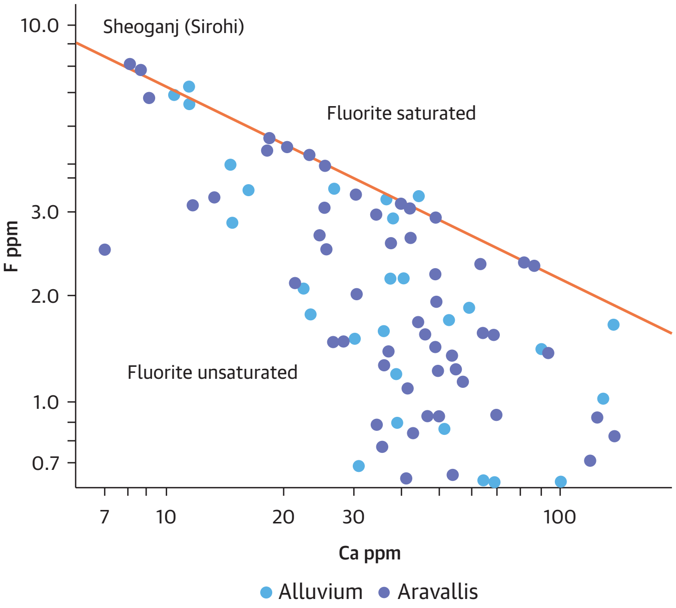
**MAP 4.2. Predicted Probability of Fluoride Concentrations in Groundwater Exceeding 1.5 mg/L**



*Source:* Adapted from EAWAG 2015.

can be used to guide sampling for fluoride. Such conditions are common and important in the weathered basement terrains of Sub-Saharan Africa, India, and South America. Commonly, these basement aquifers are exploited by dug wells tapping the shallowest, most weathered part of the profile, from which much of the fluoride had been leached out. However, with increasing development, dug wells dry up and are replaced with drilled wells that encounter higher fluoride concentrations (for example, Madhnure et al. 2018). High fluoride concentrations are also encountered in areas of geothermal activity.

**FIGURE 4.2. Inverse Correlation Fluoride and Calcium Concentrations in Northwest India**



*Source:* Adapted from Handa 1975.
*Note:* In northwest India, high fluoride concentrations are inversely correlated with calcium. The Aravallis are a hill range formed of metamorphosed Precambrian sedimentary and volcanic rocks.

Baseline measurements of fluoride should be conducted for all aquifers. An important aspect of monitoring for fluoride is to consider variation with depth of well to ensure likely vertical variations are accounted for in the network design. Figure 4.3 shows examples from Ghana and India of how fluoride concentrations vary spatially and with depth and hence how this would influence the design of monitoring networks.

### Monitoring Advice for Fluoride

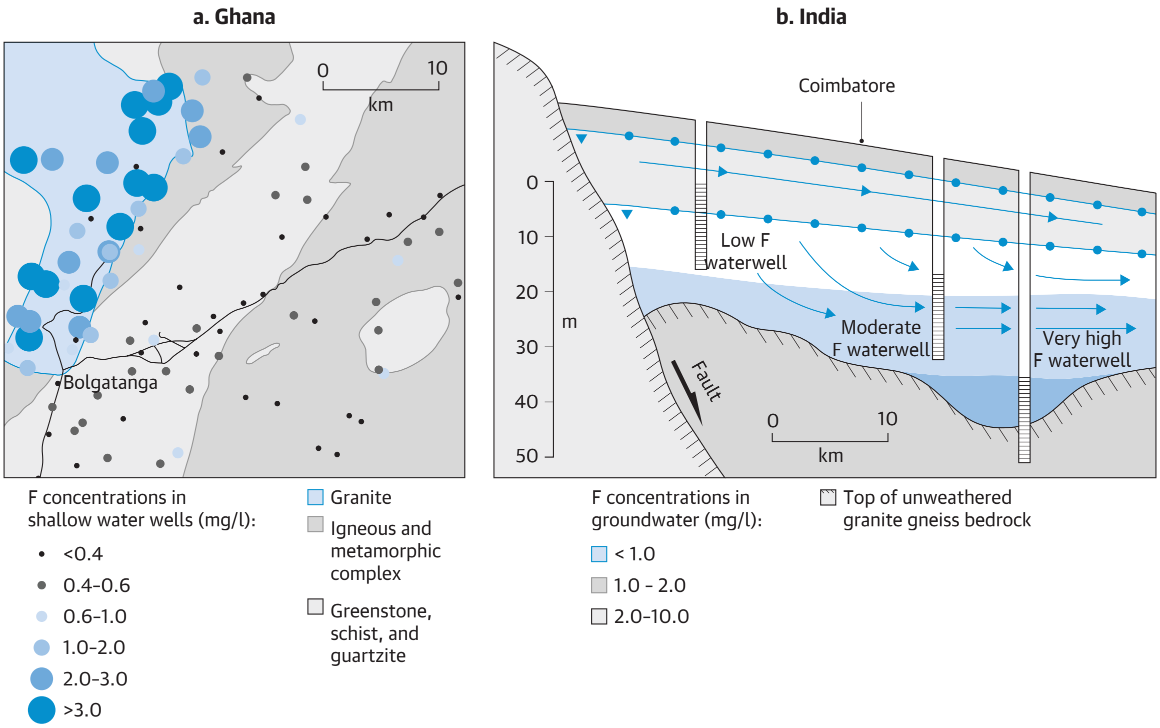
Although long-term temporal trends of fluoride in groundwater are not well-constrained, it is clear that weathered basement aquifers are sensitive to the impact of falling water levels and deepening of wells, leading to increased exposure to fluoride. Therefore, monitoring networks must be designed to sample different depths to track the related changes in water level and quality. In addition, seasonal fluctuations are likely in shallow wells and, therefore, should be monitored at least twice a year.

In areas where fluoride has been recently discovered, or wherever the number of affected or vulnerable wells is large, agenices should seek to take advantages of emerging technologies for field testing of fluoride. Because of its possible phytoxic and food-chain effects, monitoring should include irrigation wells and liaison with agricultural departments.

## Iron

Iron is common in reducing groundwater, which commonly displays concentrations of the order of 1 to 10 mg/L. Iron is not hazardous to health but is highly objectionable from the perspectives of taste, odor, washing bodies and clothes, and cooking. Hence guidelines and standards are quite variable,

**FIGURE 4.3. Spatial and Vertical Variations of Fluoride (F) in Ghana and India**



*Source:* GW-MATE 2006b.

commonly requiring ≤ 0.3 mg/L for piped water systems but permitting higher concentrations (≥ 1.0 mg/L) in rural settings where treatment systems are difficult to maintain. The presence of dissolved iron is one of the most reliable indicators of strongly reducing conditions and should not normally coexist with chemical species, such as dissolved oxygen or nitrate. If this happens, it suggests mixing of different waters inside the well. Iron is usually absent close to the water table and in aquifers that contain little or no organic matter.

### Monitoring Advice for Iron

When groundwater containing dissolved iron comes into contact with the atmosphere, it is liable to precipitate flocs of iron oxyhydroxides (that is, rust) at a rate that can vary from seconds to hours. These newly formed flocs contain iron that is naturally dissolved in groundwater and should be part of the analysis, unlike genuine suspended solids that are mobilized during sampling. Therefore, the water should be filtered and acidified as quickly as possible. In some situations, it may be useful to analyze both filtered and unfiltered samples.

Because iron concentrations are strongly depth dependent, the monitoring design should include wells of different depths or at least explicitly recognize that either high- or low-concentrations may have been overlooked.

Also, because the presence of elevated iron is usually self-evident to users by taste and by sight (photo 4.1), user feedback using smartphones is possible. Although this introduces the possibility of lobbying, agencies failing to appreciate people's dissatisfaction risks people switching to unsafe sources.

## Manganese

Manganese not only gives rise to taste and odor problems but also adversely affects health[7] and has been widely neglected. Manganese is mobilized under mildly reducing conditions, so it appears early along the flow path through an aquifer and may disappear by the time iron is mobilized.

Although not included in the 2011 WHO drinking water guidelines, it has a health-related guideline of 0.4 mg/L and an even lower aesthetic guideline (0.1 mg/L). The latter drives water utilities to act, whereas the health effects of manganese in private supplies are often overlooked because of a lack of awareness, which explains why some countries still do not routinely test for it.

### Monitoring Advice for Manganese

Agencies should ensure their routine monitoring schedules include manganese. When concentrations approach or exceed 0.4 mg/L, the matter should be discussed with relevant public health and education authorities.

It is also likely that many users confuse manganese with iron, although the difference is easily recognized by looking at the black (manganese) and red-brown (iron) staining on the concrete aprons at handpumps (photo 4.1).

**PHOTO 4.1.** **Examples of Iron and Manganese Staining at Handpumps**

**a. Red-brown iron staining**

**b. Black manganese staining**

*Source:* Authors.

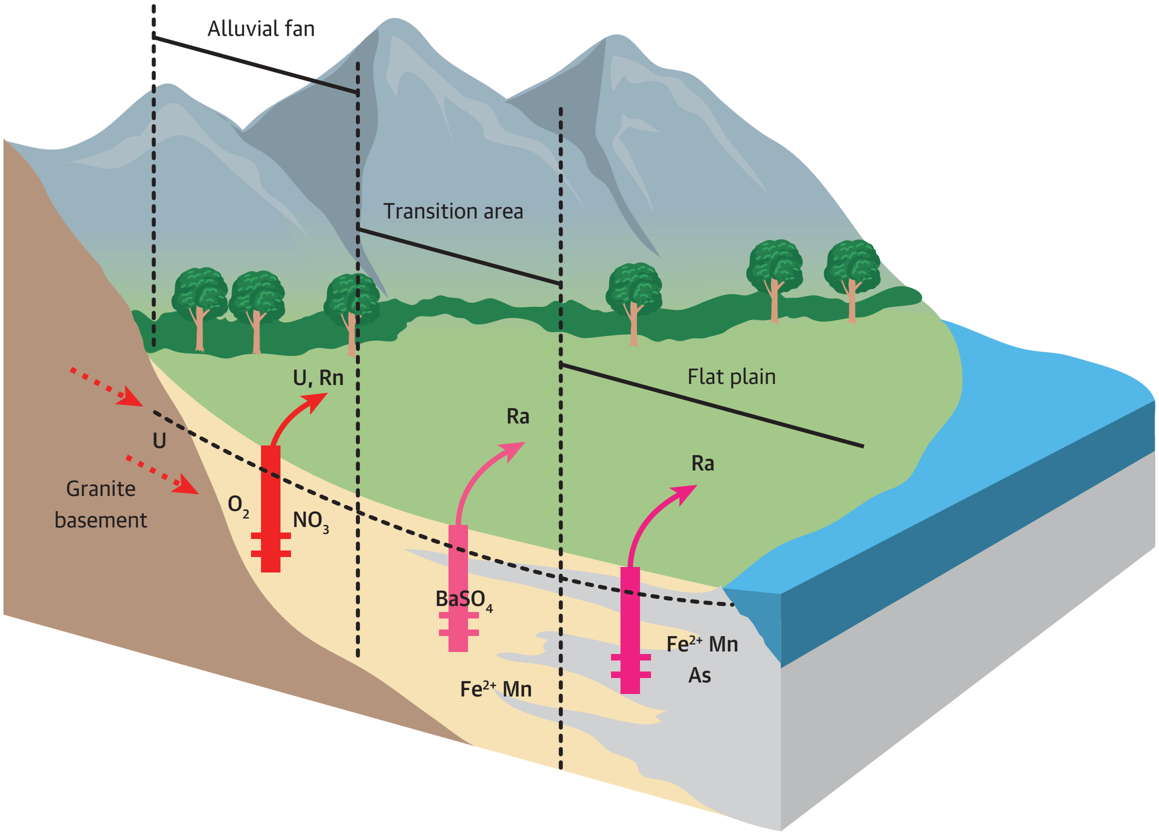
As with iron, the occurrence of manganese is strongly depth dependent, and this should be reflected in the selection of wells of different depths; to avoid oxidation and precipitation, water samples should be immediately filtered and acidified after reaching the surface.

### Uranium and Radioactive Elements

Uranium, which is radiologically and chemically toxic with a WHO guideline of 30 ppb, is an emerging natural contaminant,[8] though it is also associated with industrial and mining operations. 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 significant occurrences in India and China (CGWB 2020; Guo et al. 2018). Most occurrences of uranium in groundwater result from simple weathering of uranium-rich minerals under oxic conditions, especially when combined with high bicarbonate concentrations (Riedel and Kubeck 2018).

Other radioactive elements, notably radium and radon, are derived from uranium. Radon is released as gas, whereas radium remains in solution under reducing conditions. Thus, where suitable source rocks exist, uranium, radon, and radium might all occur at different positions in a basin as observed in the Hetao Basin in northern China (figure 4.4).

**FIGURE 4.4. 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.

### Monitoring Advice for Radioactive Elements

It is likely that more occurrences will be reported in coming years. Water resource agencies should examine their monitoring schedules and historical surveys for evidence of testing of radioactive elements. If the evidence is lacking or incomplete, it is recommended to commission a national research institution to first conduct a rapid desk study and second, provisionally, to conduct a targeted baseline survey. Any aquifers that are naturally enriched in uranium, such as granites and alluvium derived therefrom, are potential sources of uranium contamination if the groundwater is oxic. Agencies should discuss this issue with the national geological surveys. As indicated in figure 4.4, redox-sensitive parameters that are usually already available, such as iron, manganese, and nitrate, may help in the design of sampling programs.

## Other Heavy Metals and Metalloids

Although not as extensive as those elements reviewed earlier, other elements listed in table 4.1 can be locally significant natural contaminants. Chromium and selenium deserve special mention (see later in this section) and natural contamination by nickel, cadmium, and mercury have been documented.[9] Many heavy metals also occur as anthropogenic contaminants; however, in most cases the context should make the origin obvious, and cases involving anthropogenic pollution often record the highest concentrations of heavy metals. In some cases, multiple elevated heavy metal concentrations coincide with one another and high concentrations of arsenic or fluoride. When considering the likelihood of natural pollution by these elements, the regional geology may provide warnings: For example, reports of rocks containing the mineral barite[10] should lead to testing for barium. More generally, two conditions—geothermal activity and sulfide mineralization—should be taken as default warnings to screen for heavy metals and metalloids. However, when apparently natural contaminants are unexpectedly detected, it would be prudent to consider whether the concerned metals (particularly lead and zinc) could be derived from pipework or pump fittings.

**Chromium** in its hexavalent form is highly toxic and occurs in shallow oxic groundwater associated with ultrabasic (ophiolite) rocks, which commonly contain accumulations of the mineral chromite and sediments derived therefrom. Elevated levels of chromium (VI) associated with ultrabasic igneous rocks are known to be widespread in northern California and in parts of Italy and Mexico (Oze, Bird, and Fendorf 2007) and have also been reported from deep alluvial basins in northern China. The extent of natural chromium in groundwater is probably underrecognized.

**Selenium** is an essential element, but significant disease can result from either excess or deficiency. Guidelines, which range from 10 to 50 ppb, are exceeded in various parts of the world, including China, Finland, India, Japan, Jordan, and the United States (Bailey 2017). Natural concentrations in groundwater can exceed 2,000 ppb and have been positively correlated with soil concentrations such that both soil and groundwater contribute to exposure through drinking and the food chain. The geological associations of high selenium vary, but an association with alluvium derived from oxidized marine shale source rocks seems to be important (Bailey 2017).

#### Monitoring Advice for Heavy Metals and Metalloids

The occurrence of heavy metals should be determined through discussion with national geological surveys followed by baseline studies (chapter 3) before deciding what level of routine monitoring is required. The surveys should be designed and conducted by a suitable research organization, taking account of any previous surveys and experience of similar regions, especially if there are transboundary aquifers. Because many of these elements are liable to be adsorbed onto freshly precipitated iron oxyhydroxides, samples should be filtered and acidified in the field before sending to a well-equipped laboratory with a track record in high-resolution trace element analysis.

## Anthropogenic Contaminants

The list of potential anthropogenic contaminants of both surface water and groundwater is so enormous[11] that the threat could easily appear overwhelming. However, when placed in the context of systematic hazard mapping, the extent of the threats can quickly be rationalized by identifying where to look for which contaminants. Accompanied by pragmatic regulation on the sale and use of hazardous chemicals, systematic programs of survey and monitoring can rapidly assess the risks and reduce the monitoring program to manageable proportions.

### Agrochemicals

In terms of groundwater quality, two groups of agrochemicals are important: fertilizers and pesticides. The former is dominated by nitrogen fertilizers, which come in various forms but end up as nitrate in groundwater. The latter are extremely diverse and can be discussed only generally here.

#### Nitrate

Nitrate in drinking water has long been associated with blue baby syndrome (methemoglobinemia) and, particularly since the turn of the millennium, with increased risks of colorectal cancer, thyroid disease, and childhood stunting (Ward et al. 2018; Damania et al. 2019). In the twentieth century, global agricultural production expanded enormously with artificial nitrogenous fertilizers, such as ammonium or nitrate compounds, which produce dissolved nitrate in soil water for crops to take up. A proportion of this nitrate bypasses the root zone and either passes into surface drains or percolates to groundwater. The fate of nitrate in groundwater depends heavily on redox conditions. Only mildly reducing conditions are required to convert nitrate to nitrogen gas. Where there is abundant organic matter, such as in many humid tropical river basins, nitrate virtually disappears within a few meters of reaching the water table. However, in many semiarid climates or in rock aquifers containing little organic matter such as the Chalk of Northwestern Europe, nitrate can be highly persistent. To prevent misunderstandings it is important to take note of how nitrate is measured and reported (box 4.1).

### **BOX 4.1.** Reporting Nitrate Concentrations

Care is needed because nitrate and related parameters are commonly reported in different ways. Confusion sometimes arises because nitrate is sometimes expressed as the nitrate ion ($NO_3^-$) and sometimes as an equivalent weight of nitrogen ($NO_3$-N). Most countries follow nitrate guidelines of 45 to 50 mg/L when measured as $NO_3^-$ or 10 to 11.3 mg/L when measured as $NO_3$-N. Most laboratories and regulatory schemes include nitrite ($NO_2^-$) in their schemes and may report the sum of oxidized nitrogen species (that is, $NO_2^- + NO_3^-$). However, nitrite rarely exceeds 1 to 2 mg/L (as $NO_2$-N) and is almost always a small proportion of the total.

Measurement as $NO_3$-N is useful for comparing with the equivalent amounts of ammonium and nitrite, expressed as $NH_4$-N and $NO_2$-N. For example, if 1 gram of ammonium, reported as $NH_4$-N, is oxidized to nitrate, depending on the reporting format used, it will produce either 1 gram of $NO_3$-N or 4.4 grams of $NO_3$. Hence, there is a need for care reading reports and the essential need for clarification if only “nitrate” is written.

#### Pesticides

Pesticides are also a common source of diffuse groundwater pollution and can be hazardous to health at the microgram or nanogram level. Pesticides vary greatly in their toxicity and persistence, and new pesticides are regularly being introduced and older ones withdrawn. Nevertheless, because of their persistence, some pesticides that are no longer in use remain important groundwater contaminants. In the United Kingdom, for example, the herbicides simazine and atrazine continue to be among the most common groundwater contaminants, despite being withdrawn from use in 2003 (EA 2019).

Much of the applied pesticide that escapes its intended targets will be prevented from entering groundwater by the presence of a biologically active soil zone. Aquifer contamination often follows preferential pathways, such as runoff via drains, poorly sealed wells, or application to crops shortly before heavy rain. Groundwater managers should be aware which pesticides are, or recently have been, in use, for which purposes, and in which areas and then ensure that periodic surveys and/or monitoring are conducted by a competent agency with appropriate laboratory and quality assurance procedures.

#### Monitoring Advice for Agrochemicals

While sampling, preservation and analysis for nitrate is quite straightforward but requires prompt analysis. For pesticides, it is likely to be more demanding, and it is essential to (a) conduct a detailed desk study of current and historical pesticide use in the area and (b) liaise closely with the intended laboratory on all aspects of the sample collection, analysis methods and detection limits, and QA procedures.

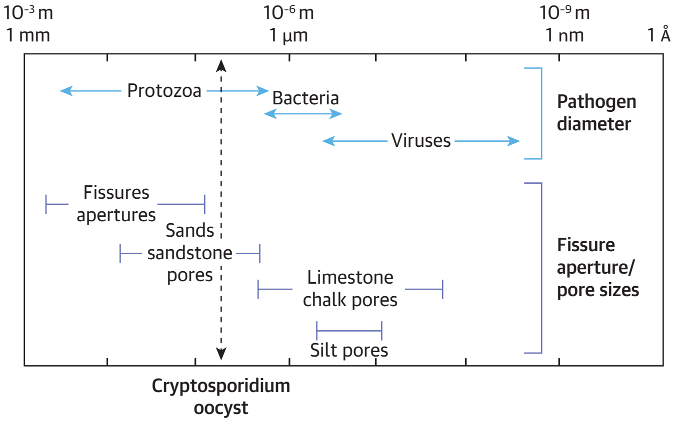
### Pathogens

The entry of pathogenic bacteria, viruses, protozoa, and other microbes into shallow aquifers is a major concern for drinking water, especially where populations rely on onsite sanitation and self-supply of drinking water. Detection of the many possible pathogens is difficult, so for surveillance the fecal indicator bacterium (FIB) *E. coli* or variants, such as total and fecal coliforms (FC) or thermotolerant coliforms, is the standard measure of microbial pollution. FIB are abundant and easily measured and, if present, establish a chain of transmission from a fecal source to drinking water. FIB are the working tool of water surveillance but generally are not what causes disease. Viruses are more likely to cause illness and are smaller, more mobile, and persistent.

Animal wastes pose similar risks to groundwater but with some specific differences. First, where animals are kept in large groups, the microbial loading can be much higher. Second, pathogens, such as the protozoan Cryptosporidium, are particularly abundant in the feces of young cattle and troublesome because they are quite resistant to disinfection.

As shown in figure 4.5, pathogen sizes vary over five orders of magnitude. Protozoa are effectively filtered by most aquifers except karst limestone, some other fissured rocks, and gravel. The mobility of bacteria in groundwater is debatable but should be assumed to be somewhat mobile unless there is evidence to the contrary. Viruses may be able to move through the pores of most aquifers. Transport of microbes is also limited by biodegradation and adsorption so that their attenuation will be more effective than implied by pore size measurements alone. Fecal bacteria that live naturally in the gut of mammals tend to die off in the aquatic environment.

**FIGURE 4.5.** **Pathogens and Aquifer Pore Sizes**



*Source:* Adapted from ARGOSS 2001.

Field information for FIB suggests they can survive for up to a hundred days under anaerobic conditions but much less under aerobic conditions. By contrast, there is strong evidence that fecal bacteria can survive and regenerate when living attached to porous elastomeric materials inside handpumps. Also, groundwater located in between latrines and shallow handpumped wells may be less contaminated than water collected at the handpump and illustrates how, particularly with regard to microbes, there can be profound differences between groundwater and well water (Caldwell and Parr 1937; Ferguson et al. 2011; Lewis, Foster, and Drasar 1982; Ravenscroft et al. 2017).

### Monitoring Advice for Microbes and Pathogens

Monitoring of microbes by water resources agencies overlaps with, and tends to be overshadowed by, the surveillance work of water utilities and water supply, sanitation, and hygiene (WASH) professionals. Although this monitoring should be complementary, it is critical to understand that they have different objectives. The evidence that fecal bacteria leaking from latrines are responsible for only a small proportion of the pathogen risk associated with water drawn from adjacent shallow hand tubewells is important but does not mean that latrines do not contaminate groundwater. The designers of monitoring and surveys must be clear about what they seek to measure: Are they measuring groundwater quality or human exposure? In other words—and this is even more critical for pathogens than chemical contaminants (see chapter 5)—do they wish to measure the quality of a water supply or the quality of a water resource? Chemicals and pathogens, such as viruses, may survive longer and still reach nearby wells. Elevated concentrations of nitrate or chloride may be better indicators of the extent of leachate migration. This may be supplemented by measurement of both chloride (Cl) and bromide (Br) because Cl:Br ratios, along with artificial tracers, such as sucralose, are good indicators of a human waste origin.

It is highly recommended that a microbiologist be involved in the design and conduct of such monitoring (and not only its analysis), paying close attention to field hygiene and sample transport and storage. The microbiologist should also advise on what role, if any, field testing should play and how this is done.

If the objective is to understand the microbial quality of groundwater, sampling should be done using dedicated monitoring wells and sampling equipment that can be cleaned and demonstrably disinfected between sampling events.

### Municipal, Industrial, and Mining Waste

Treatment and disposal sites for municipal, industrial, and mining waste, and the sewers and drains that carry such wastes, always present a threat to groundwater. Increasingly, countries are adopting dedicated regulation[12] with stringent assessment, enforcement, and monitoring. Notwithstanding the current system, most countries also have a historical legacy of undocumented and irresponsible disposal of hazardous wastes as part of a general category of contaminated land, leaving ongoing or potential groundwater pollution that requires investigation.

Modern regulatory regimes should greatly reduce the risk of groundwater pollution from active wastes. For example, modern sanitary landfills are likely to include multiple barriers, the separation of hazardous waste, drainage, and monitoring from the start of filling. However, where unregulated, landfills may be little more than dumps for unsegregated waste with a high risk of pollution. In this situation, groundwater managers must undertake a range of actions. Obviously, they should ensure regular monitoring of surrounding groundwater resources and 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. However, the practical difficulty is to know where the high-risk locations are, so they must commission inventories of current, historical, official, and unofficial waste disposal sites and other polluting activities following the approaches described in chapter 3.

Although there is extensive literature on monitoring groundwater at landfills (for example, EA 2003), many groundwater managers must contend with situations in which regulation and awareness are lacking. In this situation, second-best approaches must be adopted until regulation is forthcoming.

Examination, or development of, a conceptual model will identify the groundwater flow direction and where water users are most at risk. Although toxic substances are the primary concern, mapping of simple parameters, such as EC, pH, and possibly dissolved oxygen, which can be measured quickly and cheaply in the field at public and private operating wells, will delineate areas of concern for targeted sampling for laboratory analysis. These field measurements can also be part of long-term monitoring. Interviews with local well owners and residents, especially regarding any historical changes at their wells, should also be helpful in designing long-term monitoring plans.

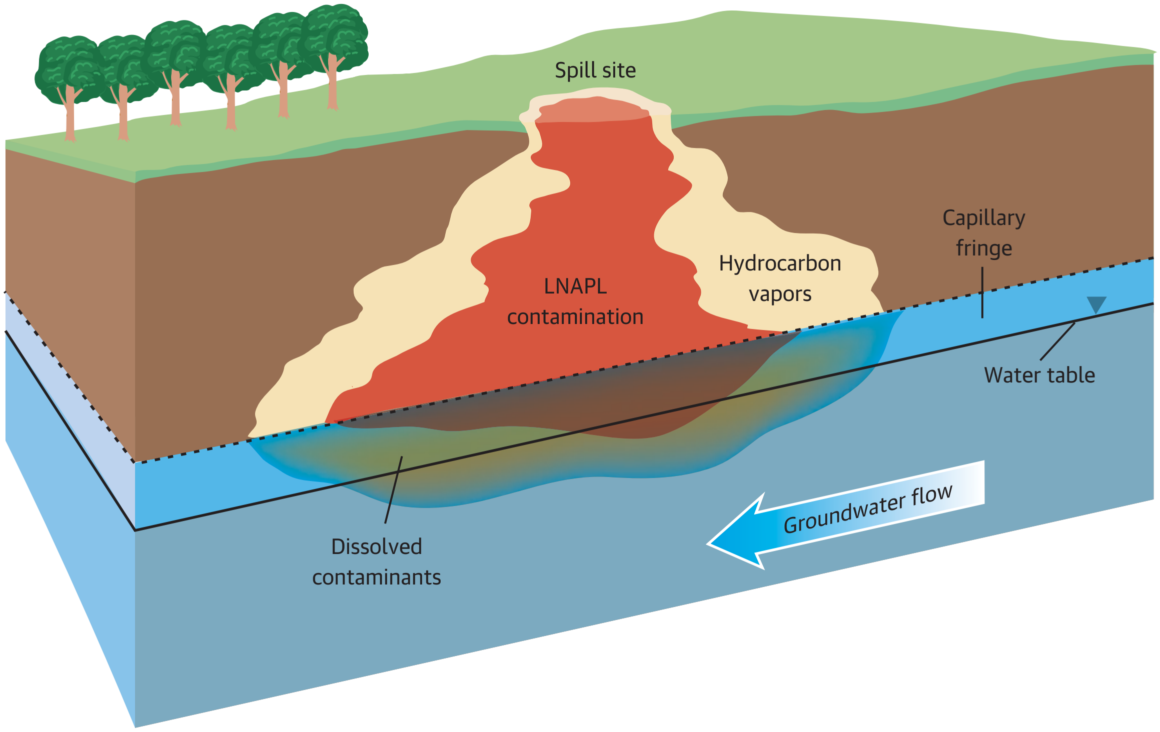
Mining waste is typically deposited in spoil heaps, lagoons, or tailings ponds and may generate acid mine drainage (AMD) containing high concentrations of sulphate and toxic metals, such as lead, copper, and zinc. AMD may leak into groundwater and also reemerge down-gradient as baseflow. All mining sites should be regarded as high risk unless determined otherwise. Although current mining operations will probably have been subject to an environmental impact assessment (EIA) and an environmental management plan (EMP), including regular monitoring, the groundwater manager should check these records and confirm with random spot checks. In addition, many abandoned underground mines were not subject to such regulation and give rise to surface water and groundwater pollution for many decades after mining has stopped, not only from spoil heaps but also from rising groundwater that floods old shafts and adits, leaching oxidized ore minerals, and eventually rising to the surface. Lastly, unmined parts of mining areas contain subeconomic amounts of the same minerals and can give rise to naturally contaminated groundwater; a common example of this arsenic contamination of dug wells is in gold mining areas. As earlier, in the absence of bespoke regulation and limited budget, valuable insights can be gained from field testing (EC and pH) and collecting anecdotal information through interviews to justify further investigation.

### Petroleum and LNAPLs

The use and storage of petroleum products is always a risk to shallow groundwater, ranging from light fuels to heavy furnace oils. They contain a range of groundwater contaminants that vary widely in their toxicity, mobility, and degradability. Fuels are the most common source of contamination, with leaking underground storage tanks (USTs) at petrol filling stations being number one, though leaking pipelines, spills from vehicles and aircraft, and runoff from trafficked areas are notable others. Fuels are characterized by short chain alkanes and the benzene, toluene, ethylbenzene, and xylene (BTEX) compounds, which are relatively mobile and have low maximum contaminant level (MCLs) but are relatively degradable. The heavier fractions contain longer chain alkanes and, among others, polyaromatic hydrocarbons (PAHs), which have MCLs defined at the nanogram level. Risk assessment should be built on a profile of the hydrocarbons present, including additives, such as methyl tertiary butyl ether (MTBE), which is exceptionally mobile and causes offensive taste and odor and can diffuse through plastic water pipes. The key characteristics of fuels that determine their migration, monitoring, and mitigation are that they are

- Immiscible in water and form LNAPL, which are volatile and also tend to float on the water table (figure 4.6);

**FIGURE 4.6.** **Schematic of LNAPL Occurrence**



*Note:* LNAPL = light nonaqueous phase liquid.

- Only slightly soluble but at concentrations above drinking water standards;
- Contain toxic and carcinogenic compounds; and
- Biodegradable in oxic groundwater but relatively stable under reducing conditions.

Monitoring hydrocarbons in groundwater is complex and poses special problems when an LNAPL is present, which requires wells screened across the water table, as described in chapter 7, and the use of special probes that respond to both the air-petroleum and the petroleum-water interfaces.

It may also be appropriate to construct special wells in the unsaturated zone to monitor vapors rising from the plume and possibly screen underground utility spaces with a flame-ionization detector (FID) or photo-ionization detector (PID) device (see chapter 9).

Analysis of hydrocarbons requires different tools than are traditionally used in groundwater studies, so before sampling it is essential to consult with laboratories regarding sampling protocols and detection limits and, where applicable, also with risk assessors regarding which compounds will determine the protection of health and clean-up standards.

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

An important group of chlorinated organic solvents are widely used as degreasing agents in engineering works and in dry cleaning, including TCE, per- or tetrachloroethene (PCE), and 1, 1, 1-trichloroethane. As solvents, they have the potential to carry other organic compounds not soluble in water and create practical difficulties for monitoring agencies because of their distinctive properties:

- Immiscible and denser than water, so tend to sink as a DNAPL
- Slightly soluble but at concentrations above drinking water standards
- Highly toxic and/or carcinogenic
- Volatile, so tend to evaporate
- Chemically stable in oxic groundwater but degradable under strongly reducing conditions

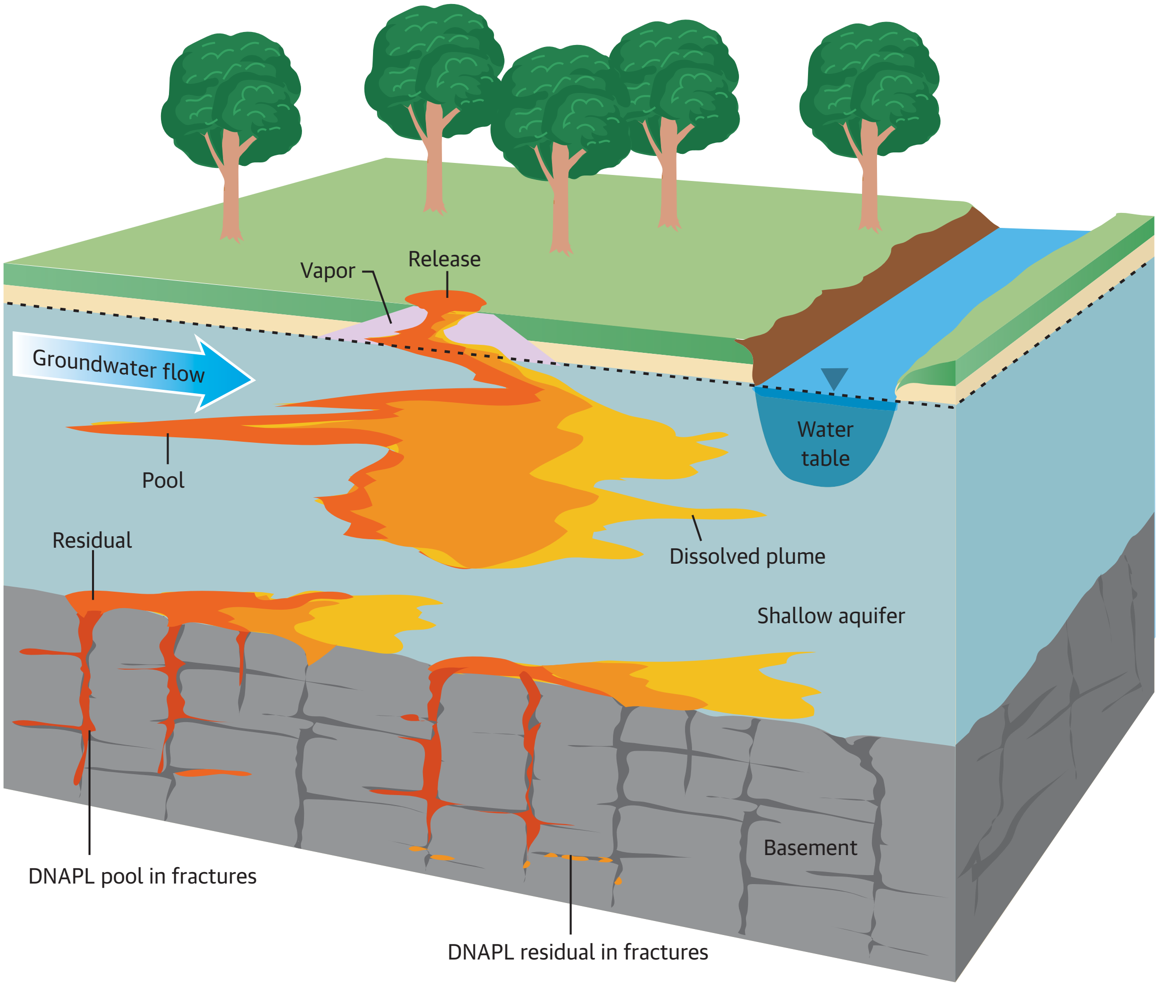
Pollution originates as either accidental spills or slow leaks from storage tanks. DNAPLs sink and accumulate on low-permeability surfaces while slowly dissolving into flowing groundwater (figure 4.7). Because DNAPLs sink to uncertain depths, they are hard to locate or even to prove whether a DNAPL still exists. Monitoring wells and sampling devices must not be formed of plastic pipes that can be leached by these solvents; they typically require the use of Teflon or stainless steel (see chapter 7).

Compounds, such as PCE ($C_2Cl_4$) and TCE ($C_2HCl_3$), are biodegraded under strongly reducing conditions by progressive dechlorination whereby, for example, PCE is transformed to TCE, then dichloroethene ($C_2H_2Cl_2$), vinyl chloride ($C_2H_3Cl$), and finally ethene gas ($C_2H_4$). Some of the degradation products may be more toxic than the original contaminant, so the sampling and analytical procedures should consider the degradation products; however, measuring these products has the additional advantage of providing proof that degradation, not just dilution and dispersion, are occurring.

### Pharmaceuticals, Personal Care Products, and Other Microorganics

In the past two decades, many new synthetic organic compounds, the so-called chemicals of emerging concern (CEC), have been detected in groundwater, entering through sewage, landfill, and other forms of deliberate or casual disposal. These include legal and illegal drugs; hormones; sweeteners; stimulants; food preservatives; corrosion inhibitors; fire retardants; plasticizers; surfactants; and PCPs, such as soaps, skin care products, lotions, and fragrances. Two of the most important of these PFAS and 1,4-Dioxane) are considered separately later. The health and environmental implications of many of these compounds are poorly understood; however, their use should be documented, mapped, and monitored. The diversity of these compounds requires regular attention to national chemical registers and international literature to identify emerging threats.

**FIGURE 4.7. Generalized Conceptual Model of DNAPL Occurrence**



*Source:* 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.

## PFAS

Per- and poly-fluoroalkyl substances, notably perfluoro-octane sulfonate (PFOS) and perfluorooctanoate (PFOA), are part of a group of 3,500 chemicals used as flame retardants, stain protectors, water repellents for nonstick surfaces like Teflon, and in tannery wastes. They are toxic, persistent, mobile, and bioaccumulating. The scientific basis for regulatory guidelines is still evolving, but the basic risk to health—and need for action—is clear and the values of these guidelines are so low[13] that they pose challenges for laboratories[14] and monitoring practices, being about a thousand times smaller than better-known toxins (for example, arsenic, lead, benzene, or TCE). Water managers should compile information on PFAS usage and instigate monitoring in close consultation with laboratories and raise awareness of the risks with municipal authorities.

### 1,4-Dioxane

The volatile compound 1,4-Dioxane has diverse industrial uses as a chemical stabilizer for solvents and in PCPs, detergents, electronics, fibers, and pharmaceuticals. It is a likely human carcinogen and causes liver and kidney damage. In countries where it has been monitored, such as the United States, 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. 1,4-Dioxane is a troublesome groundwater contaminant with high solubility, low degradability, and little tendency to be adsorbed, and it may even migrate ahead of other contaminants.

### Monitoring Advice for Chemicals of Emerging Concern

Monitoring agencies should consult national chemical registers to define areas of high risk for regular monitoring and conduct extensive baseline surveys of urbanized areas. If this is a new activity, it may be prudent to take guidance from international organizations that have relevant experience, which could include a review of the analytical capabilities and needs.

## Salinity and Saline Intrusion

Salinity makes water unacceptable or objectionable for drinking and is a major constraint on irrigated agriculture, especially where salt becomes concentrated in the soil zone. Saline groundwater is mainly encountered near the coast and in low-lying arid plains, where shallow groundwater is concentrated by evaporation. It also occurs where ancient evaporite rocks are dissolved or simply where groundwater is exceptionally old. To monitor and manage salinity, it is important to understand its origin and avoid jumping to the conclusion that the detection of salinity means that seawater is flowing directly into an aquifer because there are several variants, each requiring a different monitoring and management strategy:

- *Intrusion or upconing*. In the standard model (figure 4.8), intrusion occurs as horizontal movement of saltwater from the sea beneath the land because of a regional imbalance between recharge and abstraction. However, where freshwater effectively "floats," salty water can easily be pulled up immediately beneath a pumping well (upconing). This is a local, well-specific effect and happens where the well is too deep or the drawdown is too big.

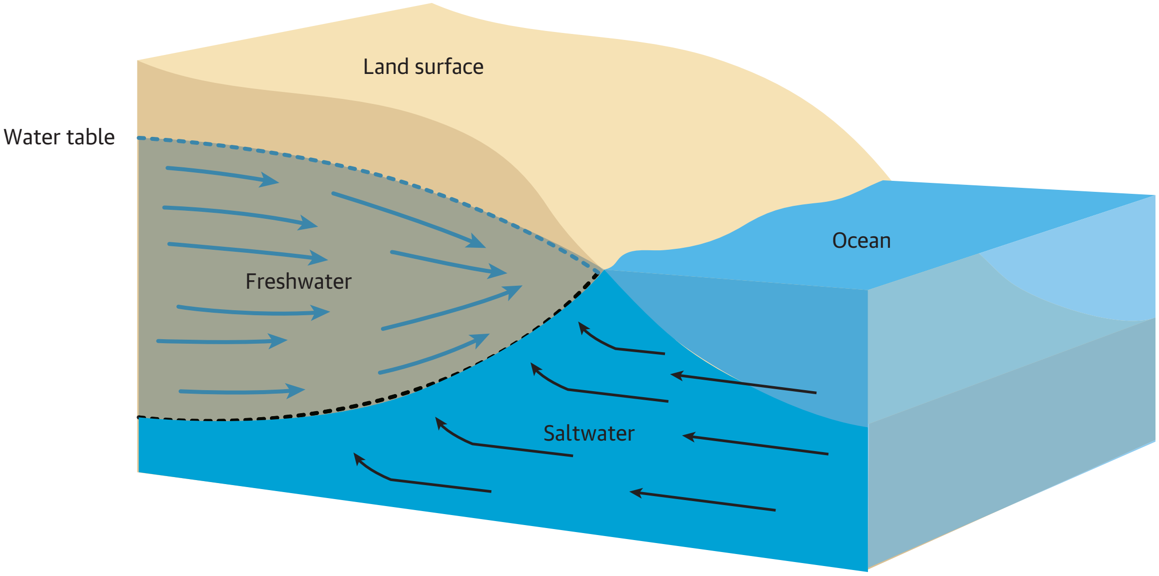
- *Ancient seawater and/or an aquifer not connected to the sea*. Coastal aquifers, especially in deltas, often contain trapped bodies of ancient saline water, relics of flow systems that have been inactive for tens of thousands of years. Many aquifer systems are layered, with interbedded high- and low-permeability layers dipping beneath the sea where the overlying strata protects the aquifer from intrusion and the saltwater is much less easily drawn inland. These situations are exemplified in the densely populated Asian mega-deltas where deeper layers may sustain high rates of pumping.

### Monitoring Advice for Saline Groundwater

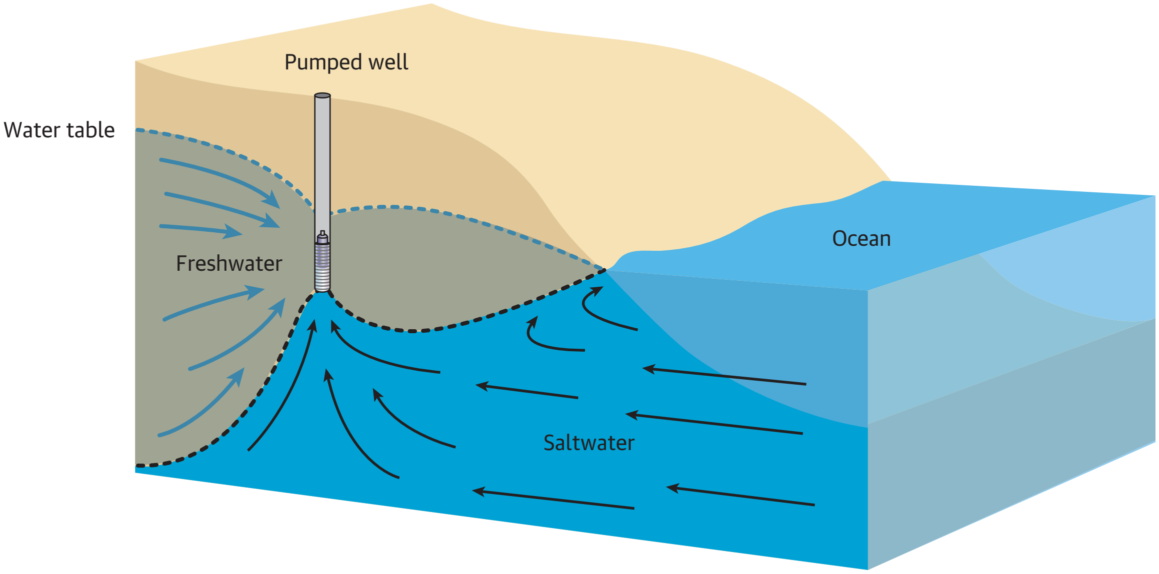
The actual measurement of salinity as EC, as a proxy for total dissolved solids, is easy, but monitoring saline groundwater is difficult. At the outset, there should be a validated conceptual hydrogeological

**FIGURE 4.8. Coastal Saline Intrusion**

**a. Natural conditions**



**b. Saltwater intrusion**



model that explains which salinity scenario applies. The holy grail of salinity monitoring is locating the saltwater interface, although it is usually not "sharp" but a transition zone, typically meters thick, in which freshwater and saltwater actively mix. Unfortunately, the use of water quality profiling inside long-screened (> 3-meter) monitoring wells or boreholes is unacceptable.[15] The practical alternatives are either to install piezometer nests or use an indirect method, such as electromagnetic logging (see chapter 7).

Whenever salinity is monitored using probes inside piezometers, measurements must be made in the screened section, and whenever a change of water quality is indicated, the cased section of the well must be completely flushed out so that there is a uniform water column and the correct water level can be measured.

These forms of dedicated monitoring will be demanding on resources and therefore expensive. When logistics are lacking, a second-best approach may have to be employed; and when accurate delineation of the saltwater interface may be impossible, the collection of the data required for numerical modeling will be very difficult. Thus, when an extended dedicated monitoring network is not possible, agencies should concentrate on a combination of (a) as many pairs of shallow and deep piezometers as possible, plus (b) extensive surveys of EC in operating wells of all types. The latter may not provide the best quality information for assessment, but it will ensure the agency's work remains relevant and well informed in conversations with stakeholders.

## Notes

1. Manganese is also a health issue.
2. Most importantly by reductive dissolution (RD) of iron oxide particles deposited in organic-rich sediments, such as applies in South and Southeast Asia and the Po and Danube rivers of Europe. Mobilisation of arsenic is normally minimal at the water table but increases rapidly with depth before slowly declining. Alkali desorption (AD) occurs under highly alkaline ($pH \geq 8.5$) conditions without dissolving the iron and does not have a simple relationship with depth. Sulfide oxidation (SO) is caused by the breakdown of minerals, such as pyrite, under oxidizing conditions; arsenic concentrations are highest close to the water table but decline rapidly with increasing depth. Geothermal waters produce the most extreme arsenic pollution, and all geothermal areas should be considered suspect until tested. For more information, see Ravenscroft, Brammer, and Richards (2009) and WHO/UNICEF (2018).
3. For example, Holocene versus Pleistocene, and this is often reflected in a difference in sediment color between gray (potentially unsafe) and brown (probably safe) sand.
4. This involves adding acid and trapping highly toxic arsine in a mercuric bromide and a reaction time of ten to twenty minutes.
5. See chapter 11 for further discussion.
6. Strictly speaking, its solubility product, a constant that reflects multiplying the concentrations of calcium and fluorides.
7. For instance, manganese is now known to significantly impair the intellectual development of children (Wasserman et al. 2006 and others since).
8. As opposed to fluoride and arsenic, which are now widely recognized.
9. Kubier, Wilkin, and Pichler (2019) report Cd up to 10 ppb in Pakistan and 20 ppb in northern Germany; Barringer, Sazbo, and Reilly (2013) report Hg at a few locations in the United States.
10. Moore and Staubitz (1984) report concentrations of up to 23 ppm in a basement in New York, United States.
11. There are thought to be about 150,000 chemical substances in commercial use.
12. If not, they probably will be in the foreseeable future.
13. In 2016, the USEPA established a health advisory level of 70 parts per trillion (ppt). In 2020, Michigan adopted standards of 8 ppt for PFOA and 16 ppt for PFOS (EGLE 2020).
14. USEPA methods 533 and 537.1, which use solid phase extraction and liquid chromatography/tandem mass spectrometry, allow laboratories to effectively measure 29 PFAS in drinking water.
15. One alternative is to conduct EC logging while pumping, first with the pump intake placed above the well screen and second with the pump intake placed below the well screen. By controlling the direction of flow, the exact positions of changes in incoming water quality can be located. This method is better suited for investigation than monitoring.

# Chapter 5
# Groundwater Quality Monitoring Basics

Monitoring is the tool and measure of management. The foundations for monitoring design are the conceptual hydrogeological model and the objectives of the monitoring agency and other stakeholders. To realize the potential of these data, they must be verified and then displayed imaginatively on maps and geological sections, supported by graphs and the judicious use of the GIS, modeling, and statistical software. The topics introduced here are expanded in chapters 6 to 10.

## Purposes

The benefits of groundwater quality monitoring include

(a) Resource accounting—that is, knowing the volumes of bodies of different water quality, their status and trends, and how they may be used and conserved;

(b) Tracking pollution plumes to assess threats and provide early warning of encroaching pollution at potable water sources; and

(c) Being an archive of climate change and human activities at the local scale, such as the long-term effects of canal leakage, the impact of agriculture on recharge, and the fate of agrochemicals.

A good groundwater quality monitoring system comprises a network of monitoring stations, practices, and skilled personnel and must be integrated with monitoring of groundwater levels, abstraction, and discharges. Monitoring is conducted by different agencies for different purposes, but the objective should be to produce a total monitoring network—an amalgam of all agency networks. The objectives of individual networks include the following:

- *Water resource surveillance*: to know the quantitative and qualitative status and trends of groundwater quality in aquifers, with a planning horizon of years to decades.

- *Operational management*: to demonstrate an agency is satisfying obligations with regard to delivering a particular quantity and quality of water to consumers and may include sentinel monitoring. The planning horizon is days to a few years.

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

A complementary approach to network design (table 5.1) considers primary to tertiary perspectives with a hierarchy that descends from characterizing regional water quality to specific cases of controlling individual pollution events.

**TABLE 5.1.** **Classification of Groundwater Monitoring Systems by Function**

| System | Function | Well locations |
|---|---|---|
| Primary (reference monitoring) | Evaluate general groundwater status, trends from climate and land-use change, diffuse pollution, and recharge | In areas of "uniform" hydrogeology |
| Secondary (protection monitoring) | Protect strategic resources like wellfields and springsheds, infrastructure, and sensitive ecosystems | Around areas or facilities requiring protection |
| Tertiary (pollution containment) | Provide early warning from known pollution risks from industry, waste facilities, mines, agriculture, and so on | Immediately up- and downgradient of hazard |

*Source:* After GW-MATE 2006a.

National monitoring should also be able to satisfy commitments to monitoring the SDG and the UNEP Global Environmental Monitoring System (GEMS).

## Design of Monitoring Systems

The design of groundwater quality monitoring systems comprises the following elements:

- Network- and site-specific objectives
- Unifying agency networks into a virtual Total Network
- Verifying that the network area has been divided into groundwater bodies (or management units) consistent with the conceptual model
- A network of existing wells, dedicated monitoring wells, and natural discharge points, such as springs
- A suite of sampling methods and protocols to collect representative groundwater samples
- In-situ monitoring methods, such as downhole probes or logging tools
- A suite of parameters to be measured onsite or in laboratories comprising standard constituents and targeted analyses based on the known risks in the catchment
- Sampling and measurement frequencies
- The logistical resources of staffing and budget

## Setting Objectives

Without clear objectives, it is impossible to know the appropriate number and type of wells, the selection of parameters, or their frequency of measurement. These objectives should be consistent with the conceptual model and what is practical given the specific institutional and budgetary constraints.[1]

This requires consultation with regulators, water utilities, private abstractors, surface water monitoring agencies, local authorities, and other groups affected by, or dependent on, groundwater convened through a multistakeholder platform (MSP). However, before forming an MSP, the monitoring agency must define the spatial boundaries of monitoring and divide aquifers or basins into groundwater bodies.

For each groundwater body, the monitoring agency should agree on objectives in three stages: (a) the concerns and objectives of each stakeholder group; (b) consensus objectives for the water body; and (c) a set of verifiable measurements comprising location, depth or geological target, parameters and threshold concentrations, and frequency of measurement. This list triggers the iterative review of the monitoring network described later and creates a framework for reporting.

## Groundwater and Well Water

The perception that the quality of water drawn from wells represents the quality of groundwater in the aquifer is not necessarily true. This difference has two aspects, which may be called the modification problem and the sampling problem.

*The modification problem*. Water passing through a well and pump is affected by changes in temperature or pressure, leading to degassing and possibly precipitation of minerals. If the intake zone is long, different water qualities mix inside the well and react with one another or the well materials. Rusted steel pipes may adsorb trace metals, and the inside of pipes and pumps can act as reservoirs for the growth of bacteria (Ferguson et al. 2011). It is also important to avoid mobilizing particulates and grain coatings (artifactual colloidal material) by extracting water too quickly (for example, Nielsen and Nielsen 2006). If these particles are acidified without filtration, they can dissolve, adding chemicals that are not part of the groundwater.

*The sampling problem*. This is more profound (see also chapter 11). Because groundwater quality is normally layered, wells usually sample only a small proportion of the aquifer profile, and long-screened wells mix waters of different quality from different levels. Such mixed samples are problematic because they may indicate the presence of a contaminant somewhere in the aquifer but not where or at what concentration. Therefore, long-screened wells are generally unsuitable for water quality monitoring. In most cases, the number of wells required to comprehensively define this three-dimensional distribution of the composition of groundwater exceeds what most agencies are willing to spend. Thus, in all except very thin aquifers, the network manager must decide which parts of the aquifer will be monitored using short-screened wells. Recognizing this uncertainty is central to understanding aquifer systems and appreciating how misinterpretations about water quality arise.

## Well Types and Their Influence on Groundwater Quality

The design and operation of different well types influence the quality of water extracted and therefore our understanding of the characteristics of groundwater quality (box 5.1).

### **BOX 5.1.** Systemic Error in Monitoring Wells

Systemic error from an unrepresentative depth distribution of monitoring points is surprisingly common. Examples are found in monitoring of arsenic along the Ganges and Brahmaputra alluvial plains, where official monitoring is conducted dominantly in very shallow dug wells whereas abstraction is dominantly drawn from slightly deeper hand tubewells and even deeper motorized production wells. Dug wells are, in fact, well known as a means of arsenic avoidance, so the official monitoring significantly underestimates the prevalence of arsenic that is found in drinking water wells. This example illustrates the importance of updating conceptual models to reflect changes in water use.

**Dug wells** often yield different water quality from drilled wells. Dug wells are shallower and allow atmospheric oxygen to mix with the groundwater. Furthermore, dug wells in hard rock and alluvium differ from one another. In hard rock, dug wells tap the weathered zone, which is the most porous and permeable part of the aquifer, whereas alluvial dug wells are completed in fine-grained sediment just above the main aquifer. Both tend to encounter a perched water table. Because dug wells are pumped intermittently to empty the well storage and then allowed to recover, this raises awkward questions: (a) What is a representative sample of a dug well? and (b) what do dug well samples represent? The first question cannot have a single answer and must be addressed by defining a protocol, say collecting the sample approximately halfway through a pumping cycle. The second question requires defining the purpose of monitoring. If it is to assess its acceptability for use, then it is acceptable. However, if the purpose is to monitor the aquifer water quality, then it is not acceptable and should be replaced with one or more piezometers.

Whatever strategy is adopted, dug-well water is more prone to fecal contamination by pathogens, ammonium or nitrate, and chloride. Because of its reaction with air, the water will tend to be low in iron, arsenic, and manganese, even when these parameters are highly enriched a few meters below.

**Borewells** are boreholes in fractured rock unsupported by casing, except for a surface casing, and raise complications for use as monitoring wells. If the locations of productive fractures are proved during drilling or test pumping, and the borehole is completed with solid casing cemented at the top of an open section that is no more than 3 to 6 meters long, then it should be acceptable. Unfortunately, in practice many borewells adopted into existing networks have surface casings that do not reach the static water level or have open sections that extend to depths of tens or even hundreds of meters. This can lead to situations in which either (a) percolating recharge cascades into the borehole; and/or (b) the saturated section becomes a conduit for intraborehole flow, cross-contaminating aquifers and producing unrepresentative water samples. When this happens, the borewell should be converted into a piezometer by installing a small-diameter casing attached to a short length of screen placed against the fracture horizon of interest and careful sealing of the annulus.[2]

**Tubewells and piezometers** are both completed with casing and screen and hydraulic sealing of the annulus. A good piezometer with a short length (preferably ≤3 meters) of small diameter (≤ 50 millimeters) well screen should yield representative samples when properly sampled. Tubewells with longer screens may be compromised by internal vertical flows. Those with large diameters may provide valid samples but will require purging of larger volumes before collecting samples.

**Springs** are a greatly underappreciated component of monitoring networks, especially in hilly and mountainous regions. Because they are the end point of a flow system, springs have the great advantage in monitoring the status of a large volume of aquifer. Any change in recharge will result in a change in flow, and any water quality impact will be transmitted to the spring. Springs have the advantage that they require no purging and no sampling equipment. Unlike with production wells, this mixed sample is a true aquifer process, so the sample is representative and a good target for monitoring. Nevertheless, a spring sample may disguise the presence of multiple water qualities within the springshed (that is, the catchment area of the spring).

## The Representative Groundwater Sample

One of the principal objectives of monitoring is to collect a representative groundwater sample, a working definition of which is a water sample that accurately represents the quality of groundwater at a specified point or level in an aquifer. This is easy to specify but not so easy to collect. The nonintuitive distinction between groundwater quality and well water quality was described earlier. Collecting a representative groundwater sample involves the following:

- Identify the target horizon in the aquifer.
- Have a well that isolates the target horizon and does not react with the water.
- Remove (purge) any stagnant water between the collection point and the target aquifer. Collect water with the minimum physicochemical disturbance or mobilizing fine particles.
- Discharge the extracted water into suitable sample bottles without exposure to air, with filtration, and adding preservatives as required.
- Label bottles and place in cool boxes for early dispatch to the laboratory.

A fully representative water sample cannot be delivered to the laboratory, so to represent groundwater quality, unstable parameters must be measured either in situ or in the field (chapter 9).

## How Groundwater Quality Monitoring Can Go Wrong and How to Avoid It

Groundwater quality monitoring can go wrong for all the reasons that any form of monitoring can go wrong—human error, machine error, inappropriate detection limits, transcription errors, and so on—but groundwater monitoring has special attributes that can lead to misinterpretation and slight or serious misunderstanding. If these risks (box 5.2) are understood, there is a good prospect they can be avoided.

### BOX 5.2. How Groundwater Quality Monitoring Can Go Wrong in Practice

**1. Not knowing what the target is**

This is the Alice in Wonderland question of groundwater monitoring and perhaps the principal underlying cause of monitoring failures: If you don't know what you're monitoring, then any well will do. Without a sound conceptual model, there may be a failure to precisely specify which aquifer or horizon is being characterized and what the chemicals of concern are. Only when this is defined can the adequacy of the well design and sampling procedure be judged. Such imprecision may result in errors, such as misidentifying the aquifer, inappropriately targeting remediation, failing to identify trends or to protect sensitive receptors, and wasting time and money.

**2. Inappropriate well design**

Groundwater quality is usually layered. Many so-called monitoring wells were installed for other purposes, with long well screens or open boreholes, and later adopted for monitoring without converting them to target specific horizons—resulting in waters mixing from different layers. The resultant monitoring information has some value, but it is difficult to interpret what changes are happening in what places.

**3. Vertical flows through well or annulus**

Groundwater head (pressure) almost always varies with depth, so there are always vertical flows of groundwater. In a natural state, these flows are very slow because of the presence of low permeability layers. However, constructing a well can connect the two sides of these layers and allow water to flow almost instantaneously from one part of an aquifer to another. This can also happen if the annular space between the pipes and the borehole wall were not properly sealed. This type of cross-contamination of aquifers is serious and can completely invalidate the monitoring function. This problem cannot be solved by additional purging.

**4. Inappropriate well and pump materials**

Depending on what chemicals are present, groundwater can react with well pipes or pumps. For major ions the effect is usually small, but for trace metals and synthetic organic compounds it can be significant. Steel pipes with rusty coatings adsorb heavy metals and arsenic between sampling events. Plastic pipes have little effect on inorganic chemicals, but they can affect organic compounds, which can be either added to or removed from the groundwater, particularly if the contaminants include organic solvents.

**5. Incomplete or inadequate purging**

Poor sampling technique results in unrepresentative water samples and incorrect measurements. For instance, if the stagnant water sitting above the screened section or response zone of a well is not purged, the water sampled will not represent the target aquifer. Conventional purging needs to remove the water from around the well screen and gravel pack. It is also important that the pumping rate not cause excessive drawdown, which could disturb both the water and the local flow regime.

(*continued*)

**BOX 5.2. Continued**

**6. Wrong selection of analytes**

In network operations developed without a sound and updated conceptual model, the important parameters may not be tested for. This is particularly likely in urban-industrial areas, but there are other examples where arsenic and manganese are not tested for in known affected areas, giving the false impression that they are not issues.

**7. Density and miscibility effects**

If a monitoring well screen crosses a zone of variable density (for example, salinity) or a light or dense nonaqueous phase liquid, measurements in the well are likely to completely mispresent the condition in the aquifer.

Table 5.2 provides a summary of the particular ways monitoring for specific contaminants, or groups of contaminants, can lead to error and a guide to what actions should be prioritized to prevent this from happening. The details are described in the following chapters.

Beyond these technical concerns, the overriding cause of many, if not most, problems is the failure to employ, supervise, and support properly trained field staff.

## Budget and Logistics—Cutting Your Coat According to Your Cloth

Although cheap compared with the costs of contamination, the costs of groundwater quality monitoring may appear expensive to budget holders, especially when starting from a low baseline or without a strong regulatory driver. If this happens, the smart groundwater quality manager will have to find ways to manage with limited resources by applying a risk-based approach.

The first step is to conduct a qualitative risk assessment of the entire aquifer or groundwater body; focus attention on the most at-risk receptors and the associated SPR links; and at the same time engage with the owners or users of those water sources and, if anthropogenic, the owners of the known or potential pollution sources.

The second step is to concentrate the number of stations monitored, the frequency of measurements, and the selection of analytes on those links. The cost of analysis can be reduced by alternating the measurement of indicator parameters and “full” analyses and substituting some laboratory analyses with field testing.

Third, agencies might look to outsource some of the work to local, perhaps voluntary, organizations and citizen monitoring. In both cases, the monitors can be supplied with field testing equipment or requested to collect samples. Verification of these processes can be greatly increased by using the Global Positioning System (GPS) and video functions of smartphones.

**TABLE 5.2.** Common Problems in Monitoring Specific Groundwater Contaminants and Indicators

| | **Inorganic** | | | | | | | | | | | **Organic** | | | | **Pathogens** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sampling problems/issues** | **Arsenic** | **Bicarbonate/carbonate** | **Dissolved oxygen** | **Fluoride** | **Heavy metals** | **Iron** | **Manganese** | **Nitrate** | **pH** | **Salinity** | **Sulphate** | **Chlorinated solvents** | **Petroleum hydrocarbons** | **Pesticides** | **Emerging contaminants** | **Bacteria** | **Viruses** | **Parasites** |
| *Well design* | | | | | | | | | | | | | | | | | | |
| High sensitivity to well depth/screen length[a] | ☑ | ✓ | ✓ | ☑ | ✓ | ☑ | ☑ | ☑ | ✓ | ☑ | ✓ | ☑ | ☑ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Incorrect screen position disguises density/NAPL effects | | | | | | | | | | ☑ | | ☑ | ☑ | | | | | |
| Reactions because of in-well mixing | ✓ | ✓ | ✓ | | ✓ | ☑ | ☑ | ☑ | ✓ | | | | | | | | | |
| Release from or binding to well/pump materials | ✓ | | ✓ | | ✓ | ☑ | | | | | | ☑ | | ✓ | ✓ | ☑ | | |
| Well/pump materials | | | | | ✓ | | | | | | | | | | | ☑ | | |
| *Field protocol* | | | | | | | | | | | | | | | | | | |
| Excessive pumping rate | ✓ | ✓ | ☑ | | ✓ | | | | ✓ | | | | ✓ | | ✓ | ✓ | | |
| Failure to measure parameter in field | | ✓ | ✓ | | | | | | ☑ | | | | | | | | | |
| Failure to filter samples in field | ☑ | | | | ☑ | ☑ | ☑ | | | | | | | | | | | |
| Inappropriate bottles or bottle materials | | | ☑ | | | | | | | | | ✓ | ✓ | ✓ | ✓ | ☑ | ☑ | ☑ |
| *Transport and storage* | | | | | | | | | | | | | | | | | | |
| Losses because of volatilization | | ☑ | ☑ | | | | | | ☑ | | | ☑ | ☑ | | ✓ | | | |
| Losses in storage because of inadequate preservation | ✓ | ✓ | ☑ | | ☑ | ☑ | ☑ | ☑ | ☑ | | ☑ | ✓ | ✓ | ✓ | ✓ | ☑ | ☑ | ☑ |
| Additions because of acid-dissolution of suspended sediment | ☑ | | | | ☑ | ☑ | ☑ | | | | | | | | | | | |
| Laboratory issues | | | | | | | | | | | | | | | | | | |
| Detection limits in laboratory | ✓ | | | | ✓ | | | | | | | ☑ | ☑ | ☑ | ☑ | | | |
| Excessive temperature/slow delivery to laboratory | ✓ | | | | | | | ✓ | ☑ | | ✓ | | | | | ☑ | ☑ | ☑ |
| Lack of refrigeration/excessive storage time in laboratory | | ☑ | | | | | | ☑ | ☑ | | ☑ | | | | | ☑ | ☑ | ☑ |

*Note:* NAPL = nonaqueous phase liquid.

a. Well screen and length are important for all parameters, especially close to the water table, but some are more critical than others.

**Legend**

☑ Major ✓ Significant Minor/not important/not applicable

Finally, when a problem is faced and internal resources unavailable, engaging with academic resources may bring about a temporary solution.

## Notes

1. If there is a gap between what ought to be done and what can be done, these limitations should be made explicit in the introduction of reports. Failure to do this has occasionally caused serious problems in the past.
2. During the investigation phase, inflatable packers may be used to isolate specific sections of a borehole for sampling and permeability testing; however, this is generally not practical for long-term monitoring.

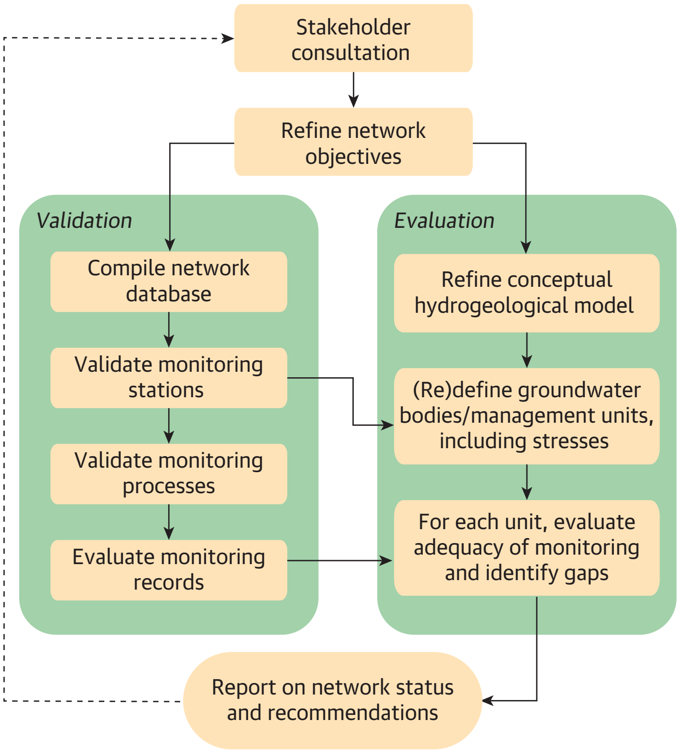
# Chapter 6
# Establishing and Reviewing Groundwater Quality Monitoring Networks

Networks are usually initiated by adopting existing wells and then progressively augmenting these with purpose-built monitoring wells and dropping wells that prove unreliable. The literature notion of network optimization is probably an illusory goal that can never be reached because it is constantly moving.

## Network Review

In practice, the purpose of a review is to modify, rationalize, and/or expand the network. Network review is iterative and multifaceted (figure 6.1). The starting points for effective review are (a) stakeholder consultation, (b) a sound conceptual model, and (c) clear objectives at the station and network levels. Stakeholders help define objectives and share data, knowledge, and concerns. The basin or aquifer is divided into groundwater bodies (GWB) or groundwater management units (GWMU) that are practically homogenous in terms of groundwater flow, quality, and stresses. These water bodies should be recognizable to stakeholders as areas for joint management and are normally consistent with surface

**FIGURE 6.1. Network Review**



water bodies. When there are multiple aquifers, each will potentially be defined as a separate unit with its own bespoke monitoring and management objectives.[1]

In parallel with refining the CHM and GWMUs, the review should systematically validate the monitoring stations. The first step is to compile the network databases of each agency, verify the coordinates, and check the well construction is appropriate for the stated purpose of each well (chapter 7). Next the sampling and testing procedures are validated to ensure that they are capable of providing representative water samples and measurements. The third part of station validation is to examine the actual monitoring records for completeness and credibility.

The final stage of the review examines the set of validated station and monitoring records in each GWMU to decide whether they are sufficient to determine the status and trends of groundwater quality with particular regard for the concerns of stakeholders.

When the review is complete, the findings and recommendations must be effectively communicated to network managers, institutional stakeholders, and relevant members of civil society to explain (a) the status and trends of groundwater quality, (b) what is not known and its consequences, and (c) what needs to be done to fill these gaps in knowledge.

## Including Abstraction Wells in Monitoring Networks

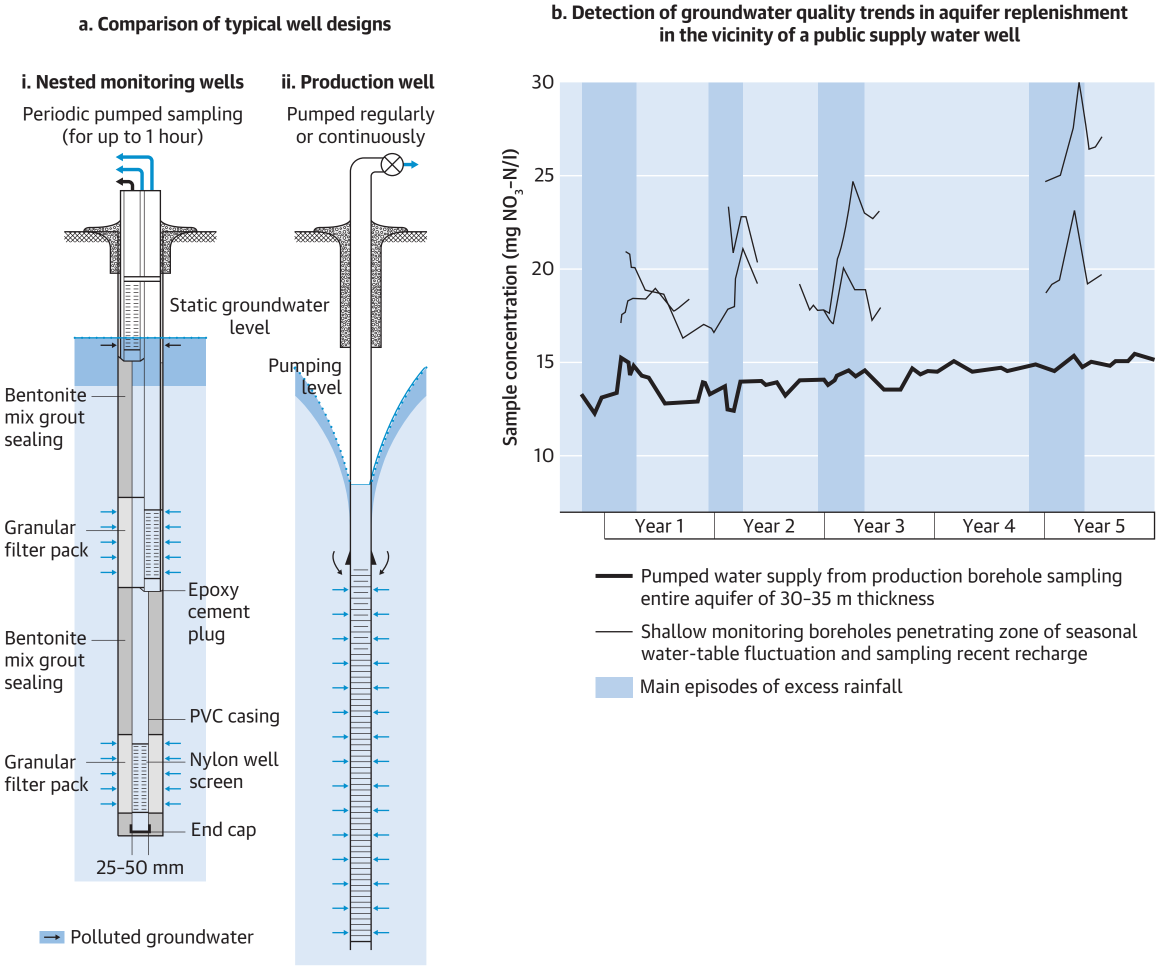
Both dedicated monitoring wells and public water supply wells should be included in the Total Network. However, it should be understood that they represent different things. The information is complementary, and combined monitoring allows for sharing of costs and facilitates dialogue among the utility, water resources agency, and regulator. Abstraction wells are important in their own right—they have the advantage of sampling a large volume of aquifer but the disadvantage of mixing water from different layers. For example, detection of traces of an industrial contaminant at a large municipal well might easily be missed in conventional monitoring wells and should quickly trigger a detailed investigation to locate and close the source. The opposite scenario may also be of benefit, as shown in figure 6.2, where shallow monitoring wells provide advance warning of dangerously rising nitrate concentrations.

## Spacing of Monitoring Wells

When considering well spacings, one should draw distinctions between (a) the design of a custom local network for tracking an anthropogenic pollution incident and the design of a routine resource monitoring network and (b) between the vertical spacing of well screens and the horizontal spacing of wells.

The latter is the main concern here and requires considerable judgment. Theoretically, this lateral spacing could be calculated for uniform and extensive aquifers using parameters such as hydraulic diffusivity or contaminant travel times and can be useful thumb-rule guides, but generally other factors will dominate. The most important is the distribution of existing monitoring wells, the geology, and the location of potable abstractions and other sensitive receptors. Additional factors may include proximity to features, such as surface water monitoring stations, and logistical considerations. All these factors will be refined through the lens of risk and the conceptual hydrogeological model.

**FIGURE 6.2.** **Comparison of Monitoring Production Wells and Piezometers**



*Source:* GW-MATE 2006a.

Although direct calculation of monitoring well spacing is rarely practical, it may be prudent to specify a maximum spacing or minimum spatial density for all groundwater management units based on local knowledge and practice. The spacing requirements of resource monitoring of water quality is different from that for water-level monitoring. The latter responds to pressure signals that travel much faster than the flow of water. Although it might be possible to install a level network that reflects events over a whole water body, this is very unlikely to be possible for groundwater quality. Instead, it will be necessary to ensure that monitoring wells are located at *representative locations,* which requires expert judgment and preferably stakeholder consultation. It is desirable to locate monitoring stations where groundwater flow is concentrated, such as along the center line of a buried channel or where it converges, such as a spring, and therefore carries a chemical signal that is derived from a large area of aquifer. In general, using the SPR framework will guide the cost-effective and risk-based location of monitoring points.

Geology and hydrogeology are always critical to determining the spacing of monitoring wells. For instance, wells in large alluvial or sandstone aquifers with high transmissivity may represent larger volumes of aquifer than in other aquifer types. Karstic limestones are particularly complicated because of the extreme concentration of flow along a dominant fissure system, and expert advice must be sought. Aquifers in weathered crystalline basement, and massive basalts like the Deccan Traps of India, pose practical problems because they have limited lateral continuity and are controlled by the geomorphological history of each subcatchment. Regional maps are easily misinterpreted to suggest an extensive aquifer, whereas, in reality, it comprises many small aquifers with little interaction. If funds allow, each microaquifer requires separate monitoring wells; otherwise, monitoring of operational wells or springs may be an appropriate compromise. Finally, the presence of faults, which may act as either barriers or conduits for flow, should always be considered when judging whether the spatial coverage is adequate.

## Unconventional Components of Monitoring Networks

The conventional view of a groundwater network is a collection of wells and springs at which water levels, discharges, and quality are measured or sampled. However, there is a growing tendency for technological innovations to extend the scope of monitoring to include the following:

- Soil gas sampling, measuring volatile or flammable gases rising from the water table.
- Geophysical techniques, such as surface electrical resistivity surveys, and especially downhole methods, such as electromagnetic logging, which are useful for monitoring salinity. The latter is able to measure through the walls of polyvinyl chloride (PVC) piezometer pipes. Airborne electromagnetic surveys can potentially be used for salinity mapping.
- Remote sensing from satellites, which is finding favor for monitoring quantitative aspects of groundwater resources—for example, the Gravity Recovery and Climate Environment (GRACE) satellite for measuring regional changes in abstraction or the Interferometric Synthetic Aperture Radar (InSAR) for measuring land subsidence. However, currently there are no direct satellite methods for measuring groundwater quality.

## Note

1. This commonly happens in areas of dipping sedimentary strata, where the recharge area of an aquifer lies on one surface water catchment and dips beneath the divide to discharge as springs or baseflow in another catchment.

# Chapter 7
# Understanding Monitoring Wells

Dedicated monitoring wells are an essential part of any monitoring system, and this chapter summarizes some of the essential issues and principles involved in their design and construction (box 7.1).

## Principles

The previous chapter highlighted where and when existing wells should and should not be adopted into a groundwater monitoring network. Using existing wells will always be cheaper in the short run, but if the information is not reliable, it is a false economy (box 7.2). As Weight (2008) puts it, the monitoring well is "a window into the aquifer," and how that window is positioned determines what is seen. Overlooking the fact that groundwater quality is three-dimensional will lead to error and misinterpretation. The well designer and network operator should be explicit in defining what the target of monitoring is.

For dissolved contaminants, the design of monitoring wells is quite straightforward. The target aquifer is defined from the conceptual model and determines the position and length of the well screen, which should be as short as possible, and the pipe diameter should be the minimum for sampling and logging. Further, the annular space above and below the screen should be carefully sealed. Other aspects of well design (for example, pipe strength, slot size, gravel pack, and development) are basically the same as for

### BOX 7.1. Observation Wells, Monitoring Wells, and Piezometers

Unlike monitoring wells and observation wells that have no particular design, a piezometer is designed and constructed to measure hydraulic head and/or water quality at a specific point in the subsurface. True point measurements are not possible, but practically a piezometer will have a short length of well screen, typically 0.2 to 3 meters. The screen should be inert, of minimum diameter, and hydraulically sealed above and below.

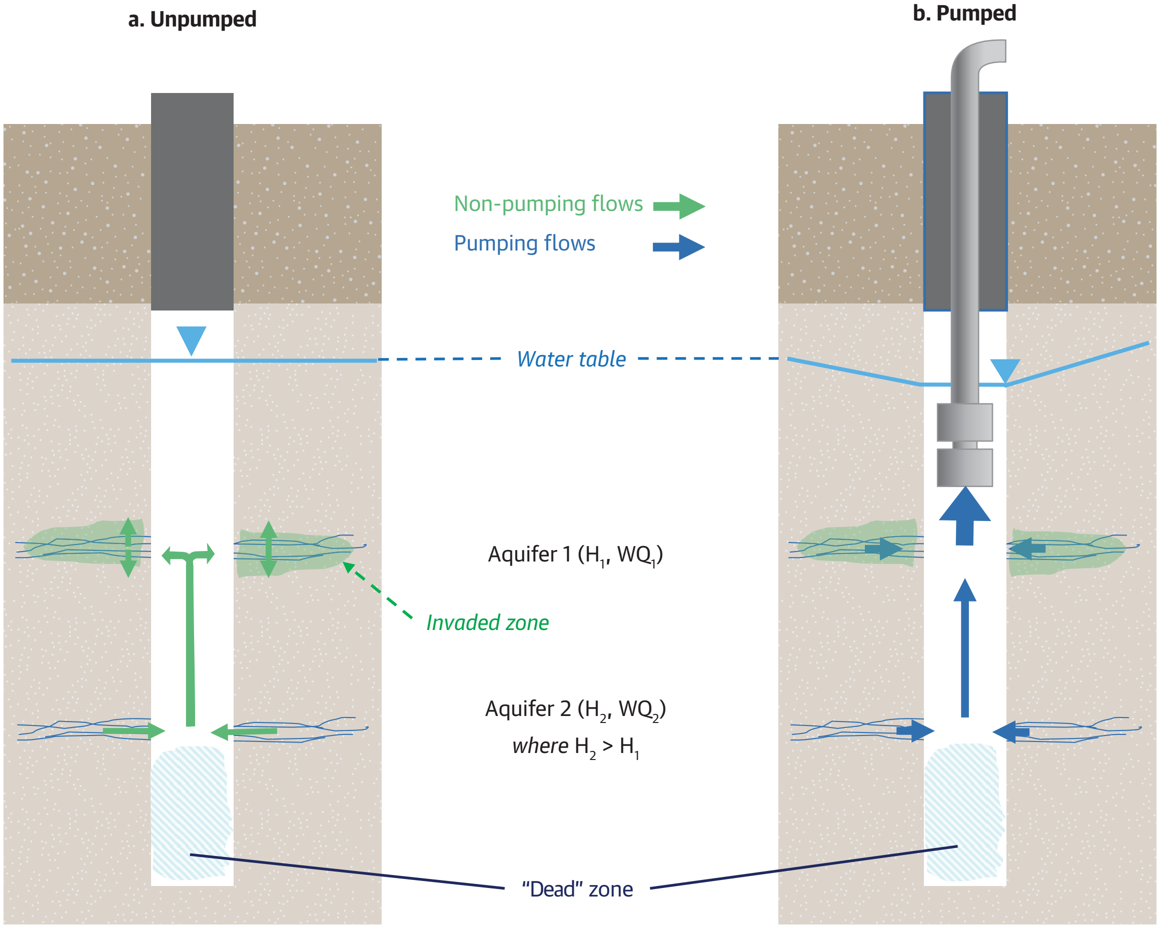
### BOX 7.2. Design Versus Construction

The main text assumes wells are constructed exactly as per their design and remain so ever after. This is not a safe assumption. Unfortunately, wells are not always drilled to their reported depth, and this explains many anomalous cases of pollution and poisoning (for example, Choudhury et al. 2016). Also, wells can fail in service because of incrustation, sedimentation and corrosion, or mechanical failure of pipes. Thus, whenever unexpected results are obtained, construction defects should always be considered and the depths of monitoring wells verified.

other types of wells. However, drilling methods should be chosen to avoid using chemicals that could interfere with monitoring.

Screen length and hydraulic sealing are emphasized strongly because many wells used for monitoring were installed for other, yield-maximizing, purposes and have long open sections (≥ 6 meters) that create pathways to short-circuit flow through the aquifer, allowing water to move from the horizon with higher pressure into those with lower pressure (figure 7.1). Such mixing can be prevented by following

**FIGURE 7.1. Effect of Intraborehole Flow on Water Sampling**



*Note:* The diagram shows a borehole in an idealized aquifer with two inflow zones under (a) static (unpumping) and (b) pumping scenarios. The well connects two aquifer horizons that have different water qualities ($WQ_1$ and $WQ_2$), with the head (pressure) in the lower aquifer higher than the upper aquifer. In the nonpumping condition, water flows upward from Aquifer 2 via the borehole into Aquifer 1. This water occupies an "invaded zone," the size of which is practically unknowable.

When the well is pumped, water enters the borehole and moves upward to the pump. The quality of this water changes over time. Initially it is a mixture of water from Aquifer 2 and the invaded zone of Aquifer 1. Eventually, it becomes a simple mixture of water from the two aquifers, but it is never representative of any actual aquifer. The proportion of water qualities in the pumped sample depends on the relative pressures and permeabilities of the aquifers.

At all times, the water in the borehole between the two aquifers represents only Aquifer 2. In the "dead" zone below Aquifer 2, the water is completely stagnant, of unknown quality, and has no relevance for monitoring.

the simple rule of never installing monitoring wells that connect two sides of a low permeability layer. Ideally there will be at least one piezometer in each aquifer. In thick aquifers piezometers should be installed near the base and, if the aquifer is unconfined, close to the water table. Similar problems arise  if the annular space between the well pipes and the borehole wall is not properly sealed, creating even longer pathways from layers far above the screened section. Thus, a shallow plume of pollution can seep down the outside of the pipe, creating the false impression that the deeper aquifer is contaminated, whereas in truth the only deep pollution is that introduced by the monitoring well. This type of cross-contamination is most likely where the deeper layer experiences greater drawdowns.

## Well Screen and Casing

This section outlines important aspects monitoring well design—the diameter and the screen length.

### Casing Diameter

For water-level monitoring, an internal diameter of 50 millimeters is sufficient to accommodate a water level dipper or pressure transducer. For water quality sampling, it is also desirable to minimize the diameter to reduce purging requirements (chapter 8); however, the internal diameter will be determined by the external diameter of the planned sampling device, so the sampling method should be decided before designing the well.

### Screen Length and Position

The most important design decision is the screened interval, which, if only one well is being installed, will normally be positioned in the center or toward the base of the main producing zone. It should contain no vertical flows or variations in water quality and should be as short as possible. In complex shallow aquifers, this could be as little as 0.3 meters, but more typically 3 meters and no longer than 6 meters. Historically, some wells were completed with longer response zones because of uncertainty in accurately locating aquifers, but with improved methods of aquifer characterization, such practices are no longer justifiable.

In alluvium, lithological boundaries and brackish water horizons can be precisely delineated using geophysical (electrical resistivity and natural gamma) logs. In hard rock, the necessary information for well design can be obtained by combining multiple lines of evidence, including

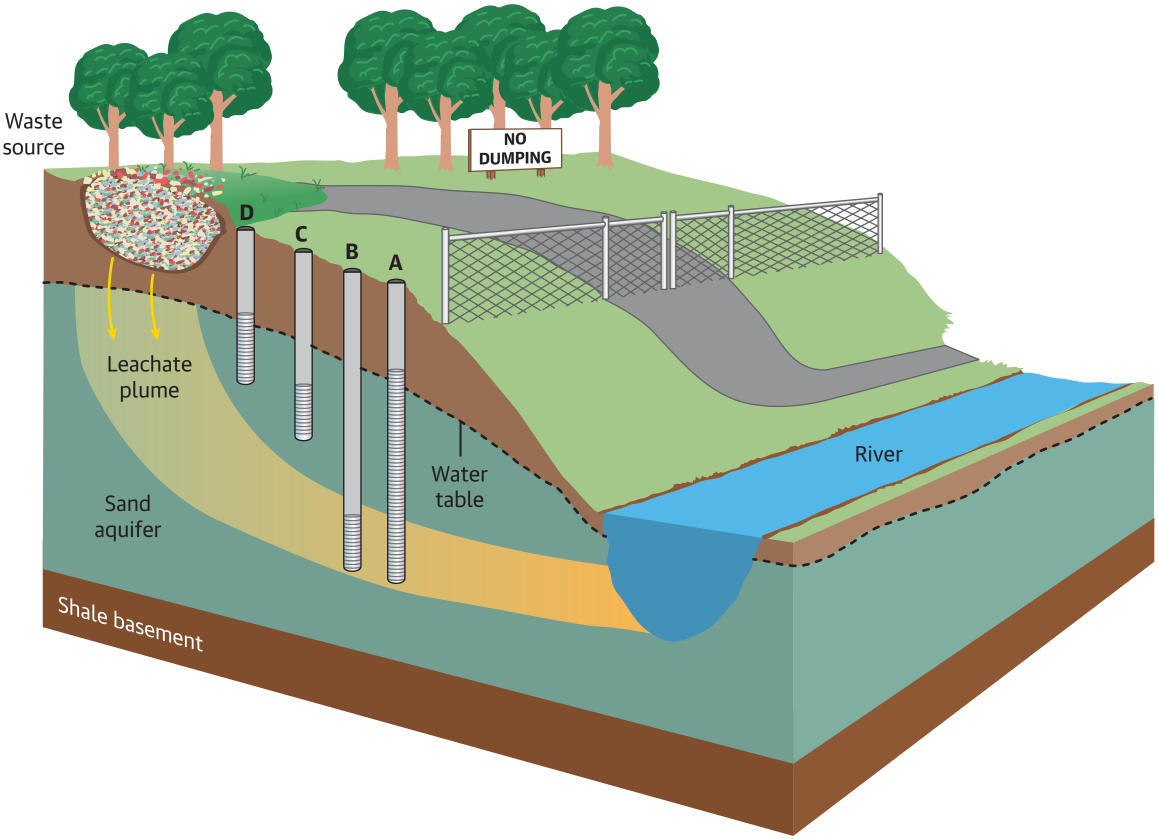
- Drill time and lithological logs;
- Monitoring of return flows during drilling;
- Additional geophysical logs (including sonic, gamma-gamma, neutron) to identify fracture zones;
- Packer testing and pumping tests; and
- Geophysical fluid logs (Temperature [T], differential temperature [DT],[1] electrical conductivity [EC], and flow) under static and/or pumping conditions.

Figure 7.2 uses the example of a contaminant plume to show how different well designs would determine the characterization of groundwater quality. In this case, at least two, and preferably three, monitoring wells would be needed to provide the information needed for management.

### Casing and Screen Materials

Pipes for monitoring wells must be robust and inert. Except for surface casing to prevent collapse during drilling, metals other than stainless steel are best avoided. Unlike mild steel and some grades of stainless steel, which can corrode, releasing iron (Fe), manganese (Mn), copper (Cu), lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), and molybdenum (Mo) into water (Nielsen and Nielsen 2006), thermoplastic pipe does not release metals into water and is unlikely to adsorb trace metals and metalloids. Thermoplastic well casing (for example, PVC, acrylonitrile butadiene styrene [ABS], high-density polyethylene [HDPE], and polytetrafluoroethylene [PTFE]) is strong enough for most conditions to depths of 300 meters, resistant to corrosion, easier to work with, and cheaper. However, the use of solvent cement should be avoided. Well screen should normally be factory-made, machine-cut or molded pipe. Except in very shallow wells, centralizers should be used to allow proper placing of gravel pack and hydraulic sealing.

**FIGURE 7.2.** **Influence of Screen Length and Position on Quality Monitoring**



*Source:* Adapted from Fetter 1993.

*Note:* Well A intersects the plume, but the concentration is diluted and may mix water between layers. Well B correctly measures the plume concentrations. Wells C and D confirm unpolluted groundwater above the plume, and well D alone monitors the water table.

**TABLE 7.1.** Comparison of Monitoring Well Waterials

| Pipe material | Advantage | Disadvantage | Relative cost |
|---|---|---|---|
| PVC | Lightweight; resistant to acids, alkalis, alcohols, and oils | Can adsorb VOCs or react with ketones or esters | 1.0 |
| Teflon | Lightweight; resistant to most chemicals | Lower wear resistance and tensile strength | 20.7 |
| Polypropylene | Lightweight; resistant to acids, alkalis, alcohols, and oils | Weak, flexible, and difficult to make slots | 2.1 |
| Stainless steel types 304 and 316 | High strength and least reactive with organic chemicals | Heavy; may corrode in AMD-type waters | 6.0, 11.2 |
| Mild steel | Low-cost; strong | Heavy; not as chemically resistant as stainless steel | 1.1 |

*Source:* After Weight 2008.
*Note:* AMD = acid mine drainage; PVC = polyvinyl chloride; VOC = volatile organic compound.

The advantages and disadvantages of different pipe materials are summarized in table 7.1. There is no single best material. PVC will serve well for most routine applications, but particular geological conditions and chemicals of concern require other choices. If wells are to be used for sampling for volatile or semivolatile organics, pesticides, pharmaceuticals, or similar, the material selection needs to be checked carefully because some common organic contaminants are solvents that can leach chemicals from plastics. Moreover, PVC and PTFE can sorb some chlorinated solvents (Fetter 1993; Weight 2008).

## Special Issues in Monitoring Well Design

Some important considerations that affect monitoring well design are outlined here.

### Multilayered Aquifers

The general rule is that multiple aquifers require multiple monitoring wells. Many thick sequences, assigned to a generalized geological type (for example, alluvium, granite, or sandstone) are described as "single aquifers" but actually have distinct vertical differences in piezometric level and water quality. A practical compromise will be to install one piezometer close to the water table and another in a high-yielding zone near the base of the aquifer (Rushton 2003). When installing multilevel piezometers, there are three basic options:

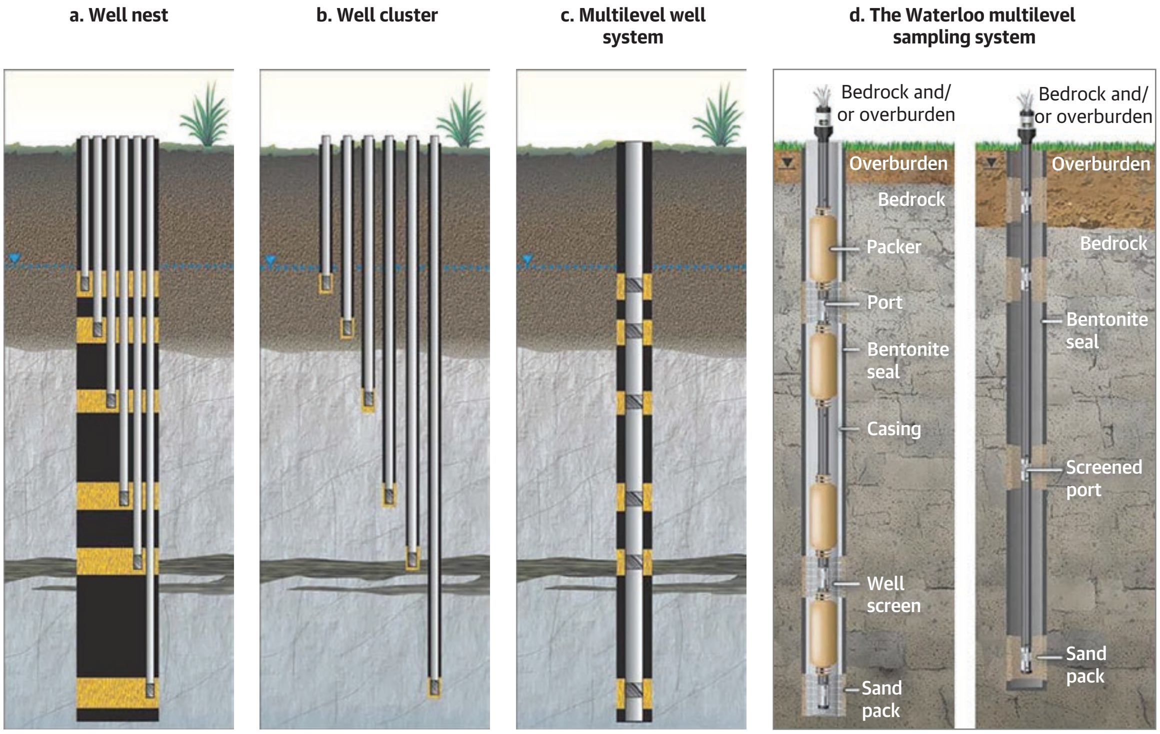
(a) Multiple pipes inside a single borehole (well nest; figure 7.3 panel a)

(b) Separate pipes in separate boreholes (well cluster; figure 7.3 panel b)

(c) Proprietary multilevel monitoring systems (figure 7.3 panels c–d)

The first two do not require special technology or skills, but option b is more secure in terms of avoiding leakage between layers. The choice is also influenced by cost; option b is preferred in shallow aquifers and requires only small borehole diameters. With increasing depth, there is an increasing cost incentive

**FIGURE 7.3.** General Approaches to Obtain Vertical Water Quality Profiles



*Sources:* (a), (b), and (c) Cherry et al. 2015; (d) courtesy of Solinst Canada Ltd.
*Note:* Well nest is shown with multiple casings with short screens installed in a single hole with sand packs surrounding the screens and bentonite seals between the sandpacks. Well cluster is shown with short-screened wells at different depths in individual holes.

to install multiple pipes in a single borehole (option a). This requires more skill and careful supervision, and overambitious designs should be avoided. As a rule of thumb, a borehole diameter of 200 to 250 millimeters is recommended to install two piezometer pipes.

An alternative approach is the use of proprietary multilevel sampling devices, such as the Waterloo® system, in which between two and twenty-four discrete sampling ports can be installed in a single borehole (figure 7.3). Such systems can produce high-definition monitoring of profiles of groundwater quality and hydraulic head; however, they are expensive and require accurate definition of the strata and skilled installation, operation, and maintenance. They are best suited to shallow pollution plumes.

## Nonaqueous Phase Liquids

When a LNAPL, such as petroleum hydrocarbon, is present or suspected, normal piezometers are not suitable. Measuring the LNAPL thickness with an interface probe[2] in a piezometer or former production well can give a false impression of the presence, absence, or thickness of an LNAPL in the aquifer. To measure the LNAPL correctly requires a monitoring well that is screened across the full thickness of the LNAPL but extends only a small distance into the underlying groundwater.

By contrast, if chlorinated solvents are suspected to form a DNAPL, which is one of the most difficult monitoring situations, wells must be screened at the bottom of the aquifer or on the top of interbedded aquitards. Furthermore, if these surfaces are not flat or at least of predictable shape, it will be difficult to locate pools of pure solvent. As noted, because they are organic solvents, plastic pipes and sampling devices must be carefully selected to avoid leaching.

### Saline Interfaces and Saline Intrusion

Because of density differences and intraborehole flow, a saline interface cannot be directly measured in a conventional well. Its position must be inferred either from a vertical "nest" of closely spaced, short-screened piezometers or using geophysical logging tools that can "see" through the well pipe. The density difference between freshwater and saltwater, combined with the effects of tides and pumping, create special problems for monitoring well design. Attempts to directly measure the profile of salinity inside a borehole or well screen do not work and generate data that mispresent and confuse. The valid techniques for monitoring saline interfaces include the following:

- Piezometer nests (with screens about 1 meter long) installed at as many levels as practical or affordable, but at minimum at least one short-screened piezometer in the freshwater and one in the fully saline zone and preferably in the transition zone. Measured water levels must be converted to equivalent freshwater head (Post et al. 2007), and this requires that the water column have a constant density. Therefore, piezometers must be thoroughly flushed (purged; figure 7.4) after installation and whenever there is a change in the salinity of water measured *inside* the well screen. Such piezometers are ideal for installing automatic water quality probes *inside* the screened section.

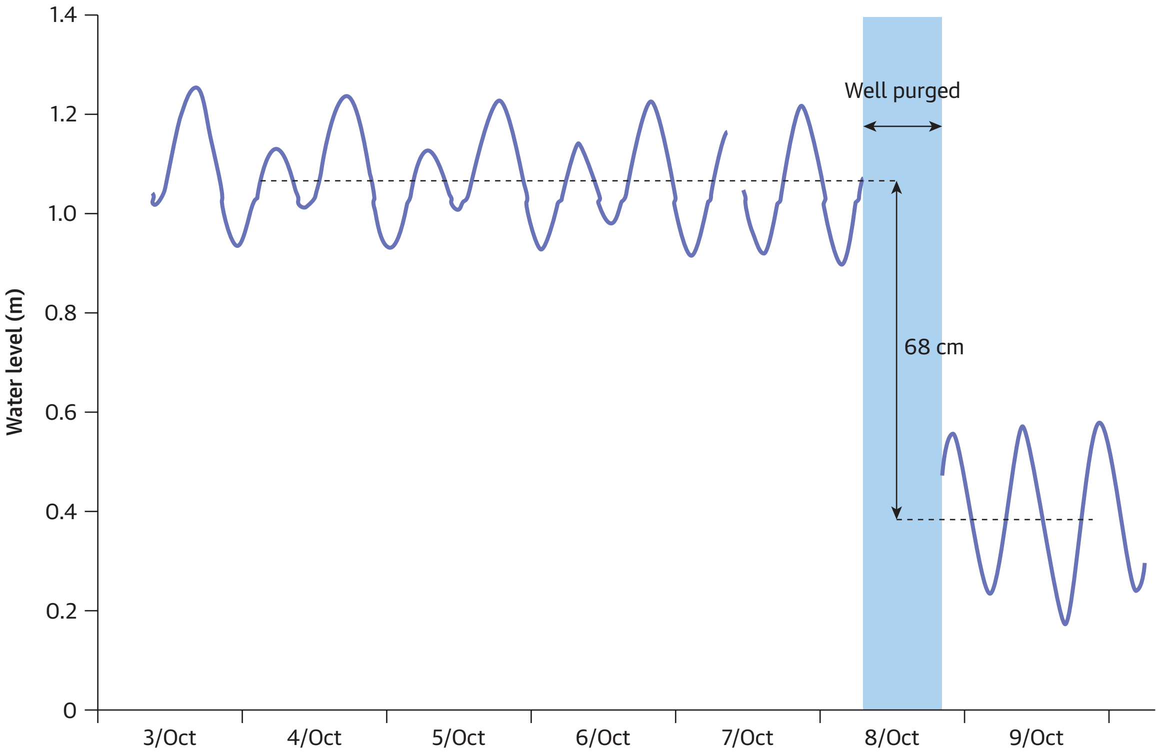
- An alternative concept involves burying an array of resistivity electrodes in a borehole backfilled with alternating layers of sand and bentonite (Sherrod et al. 2012). This can provide cost-effective, high-precision salinity profiles but is limited for long-term monitoring because, once installed, measurements cannot be checked or the electrodes replaced.

- Another alternative is to use electromagnetic induction logging inside PVC casing (for example, Stumm and Como 2017). This technique responds to the conductivity of water outside the solid PVC pipe, so the water quality is inferred rather than measured. In addition, the well serves as a conventional piezometer for the deepest part of the aquifer.

## Piezometer Inspection and Maintenance

Network management also requires monitoring the monitoring wells to ensure they are performing their intended functions and carrying out maintenance as necessary. Common problems include clogging of screens by sediment, biofouling or chemical incrustation, corrosion, and physical damage or obstruction. Wells also become dysfunctional because of falling water levels. The simplest means of identifying problems is a visual inspection during monitoring. Field staff should also systematically report problems with installing or operating equipment. Inspections can be conducted by lowering a plumb line to full depth, running a temperature-conductivity log, or a closed-circuit television (CCTV) camera. Screen clogging can be identified by comparing simple hydraulic tests, such as a slug test

**FIGURE 7.4.** **The Importance of Purging Saline Monitoring Wells**



*Source:* Adapted from Jiao and Post 2019.

*Note*: The figure shows groundwater level over time for a coastal observation well. The fall in measured head of 68cm is caused by purging the stagnant water from the well which had a lower average density prior to pumping than after. This density difference was caused by a salinity stratification that existed before the well was purged. After pumping, all the water in the well became saline (reflecting the conditions of the aquifer).

(using a solid slug) with the original testing records or by recording discharge and drawdowns during purging. If rehabilitation is done before specific capacity is halved, the original yield can be restored. However, notwithstanding this, it is prudent to conduct periodic preventive maintenance.

## Sources of Further Information

Fetter, C. W., T. Boving and D. Kreamer. 2018. *Contaminant Hydrogeology*, 3rd ed. Long Grove, Illinois: Waveland Press Inc.

ISO (International Organization for Standardization). “ISO 5667-22:2010: Water Quality – Sampling – Part 22: Guidance on the Design and Installation of Groundwater Monitoring Points.” Geneva, ISO.

Weight, W. D. 2008. *Hydrogeology Field Manual*, 2nd ed. New York: McGraw-Hill.

## Notes

1. DT for measuring small, sudden changes, such as where water enters or leaves the well.
2. That responds to both the air-petroleum and the petroleum-water interfaces.

# Chapter 8
# Groundwater Sampling

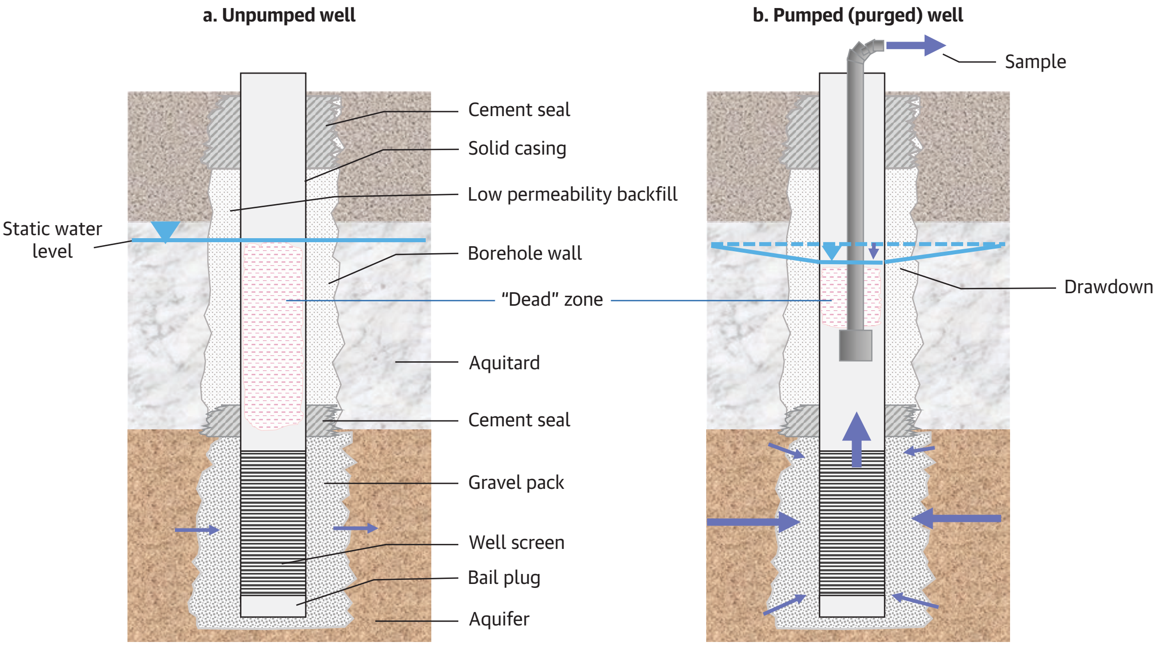
Even with a properly constructed well, a representative water sample will be obtained only if appropriate sampling procedures are followed. In describing the approaches to sampling, two key themes emerge: the validity of the sample and the practicality of the process.

## Conventional Sampling Techniques

The conventional precondition to sample collection, known as purging, is to pump out the stagnant water from inside the well and its immediate surroundings. The amount of water purged can be calculated, but most agencies follow a thumb-rule approach of purging three to five well volumes before collecting a sample. If the well is deep or has a large diameter, this can require pumping for several hours, making the monitoring process quite slow. Furthermore, if the purge water is contaminated, it should be disposed of at a treatment plant or other approved location, adding much time and cost to the operation. Other important considerations in purging (figure 8.1) are

- The pump materials should be inert;
- The pump position and flow rate should not disturb either the aquifer solids or water because of turbulence or degassing;

**FIGURE 8.1.** Terminology Relating to Purging



- If water is contaminated, the equipment needs cleaning and/or disinfecting between wells; and
- Special purpose sampling pumps may be required.

During purging, a pump is operated in the stagnant ("dead") zone[1] above the screen until all water discharged at the surface comes directly from the aquifer. When the pump is started, water is drawn first from above the pump until the drawdown stabilizes and then successively from the dead zone below the pump, inside the screen, the gravel pack, and finally the aquifer. Placing conventional pumps inside the screen is normally avoided because it can induce sand pumping or uneven flow. The pump should be lowered gently and pumped at a rate low enough (say ≤ 1 L/s) to minimize vertical flow and not mobilize any solids from the aquifer.

### Reduced Purging Considering Hydraulics

A pragmatic approach to reducing purging volumes and time required by thumb-rule approaches, especially for deep wells, is to calculate the minimum volume required considering the well hydraulics and pump position by adding the following volumes:

- The volume of (stabilized) drawdown inside the well
- The internal volume of the casing from 3 meters above the pump intake to the bottom of the well
- The volume influenced by the well using the screen length plus 2 meters, a porosity of 0.2, and a diameter of two or three times the drilling diameter
- Multiply the sum of these volumes by a safety factor of two or three

This approach can be recommended only when the agency is confident of, and preferably has independently verified, the depths of the casing and screen.

### Purging Based on Physicochemical Stabilization

A popular approach is based on the proposition that, with a pump placed above the screen, stagnant and near-well effects are eliminated when sensitive chemical parameters, such as pH, temperature, EC, dissolved oxygen, and redox potential (Eh), become uniform, and then a representative sample can be collected. Pumped water is passed through a cell at the surface until the parameters stabilize. This approach has merit but should be accompanied by a minimum purge volume requirement. A limitation is that flow-through cells are designed for low flow rates and can take a long time for deep or large-diameter wells to stabilize.

### Handpumped Wells

Providing the depth is reliably known, there can be advantages in sampling operational handpumped tubewells in alluvial aquifers. Because they have short, typically 3- to 6-meter, screens and low pumping rates, they approximate point measurements. Such wells are most conveniently sampled after the well has been in operation for an hour or so, avoiding both the need for purging and the effects of leaking casing joints.[2] A limitation is that it is not possible to measure the water level without removing the pump, which is time-consuming and unpopular and introduces liabilities in the event of damage. Although appropriate for chemical parameters, domestic handpumps are unsuitable for measuring the microbiological quality of *groundwater* as opposed to *well water* because fecal bacteria can survive and grow inside pumps even when largely absent in flowing groundwater.

When sampling a handpumped well that has not been in continuous use before sampling, a convenient rule of thumb for evacuating the stagnant water in the casing is one stroke of the handle for each foot (three per meter) of depth of the well. Generally, it is recommended to avoid monitoring inactive hand tubewells.

## Low-Flow Sampling Techniques

Given the constraints associated with conventional purging, much attention is given to low-flow sampling (or micropurging) based on the concept of a *flow-through well*, which causes minimal disturbance to flow in the aquifer and is combined with stabilization of physicochemical parameters (for example, pH, EC, temperature, and Eh). This technique is most suitable for piezometers. Provided the flow-through assumption is valid (figure 8.2), the pump intake is lowered gently inside the screen and pumped very slowly (typically less than 1 L/min), until the drawdown is small (preferably < 0.1 meter) and stable so that groundwater flow is almost perfectly horizontal and only the internal volume of the well screen and gravel pack require purging.

Low-flow sampling is widely regarded as best practice for sample collection (figure 8.3). In this way, water is extracted from an accurately known location without mobilizing particles and minimizes turbulence and degassing. The sample should better represent the natural groundwater and reduces the purge water volume by as much as 95 percent, as well as sampling time (Nielsen and Nielsen 2006).

**FIGURE 8.2.** The Flow-Through Well Concept

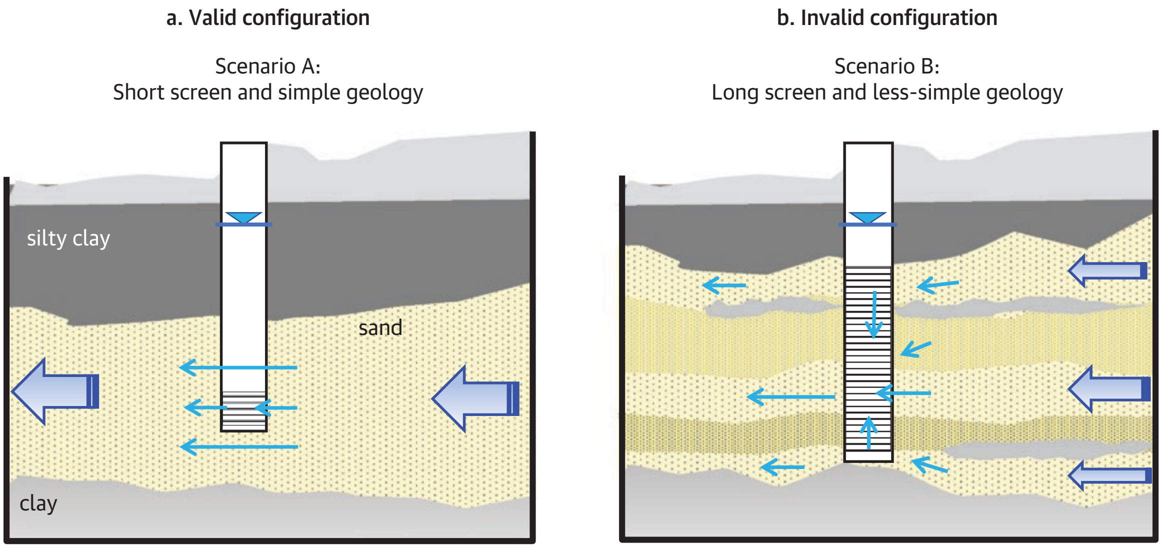
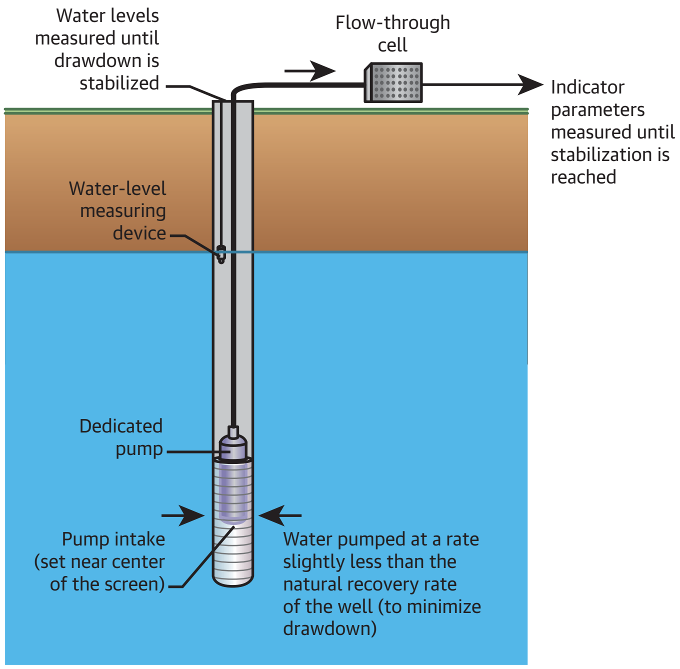


**FIGURE 8.3.** Components of Low-Flow Purging and Sampling



## Sampling Pumps and Bailers

The most important types of pump for purging and sampling are the following:

- *Surface-mounted centrifugal and jet pumps* are sometimes used for sampling wells when water levels are within suction limits; however, this is to be discouraged because they encourage degassing and are not suited for constant and low discharge, and the materials used may not be inert.

- *Peristaltic pumps* only work when the pumping level is within suction limits (about 8 m) and operate by squeezing water through silicon tubing using a surface mounted electric motor. Peristaltic pumps provide high quality samples at low cost, and although they operate only at low discharge, are suitable for low-flow sampling at shallow depth.

- *Submersible centrifugal pumps* are positive displacement pumps and can operate with higher flow rates than bladder or peristatic pumps. They tend to be the default choice for conventional purging and sampling. Most major pump manufacturers produce separate ranges of sampling pumps incorporating inert materials and with low and variable discharge.

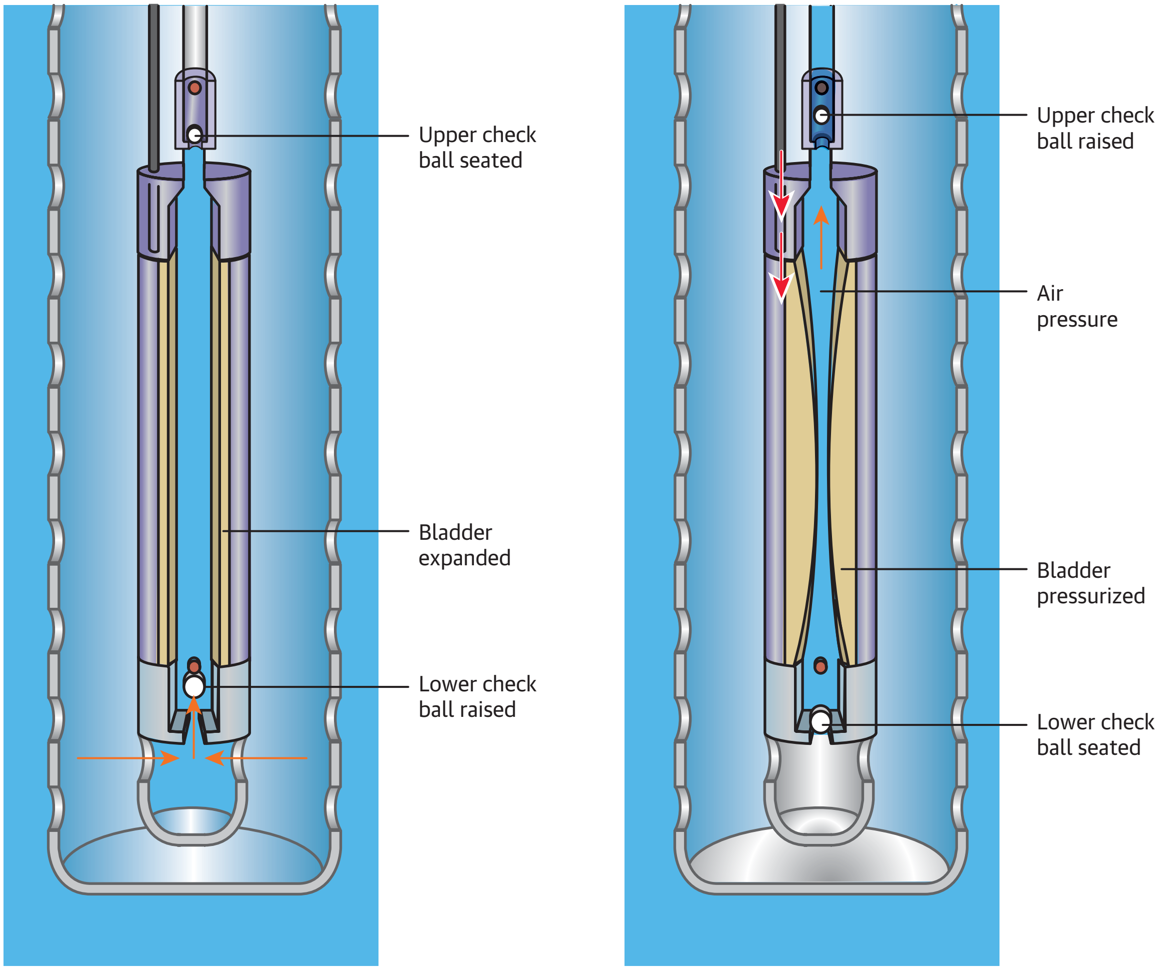
- *Manually operated inertial pumps* are a simple, reliable and inexpensive type of positive displacement pump, comprising a continuous length of HDPE or PTFE tubing with foot valve, which is raised and lowered manually to push water to the surface. Their low cost makes them popular for dedicated installation, avoiding the need for setup and decontamination between sampling events.

However, they cannot provide the quality of sampling obtained with low-flow methods and are unsuitable for large-diameter wells.

- *Bladder pumps* are used almost exclusively for low-flow sampling (figure 8.4). They work by successively expanding and contracting a bladder below the water level, powered by a gas tank at the surface. The method avoids contact with metallic components and does not subject the water to high velocities and is well suited to sampling organic chemicals.

Bailers are sometimes used as a substitute for pumps for either purging and/or sample collection. They are cheap, easy to use, unaffected by suction limits, and they require no power supply. If used for purging, they should be used carefully so as not to disturb particles around the well screen. At contaminated sites, disposable PTFE bailers may be used to eliminate the risk of cross-contamination. One advantage in purging is that they can ensure that stagnant water at the top of the water column is removed before collecting samples, which helps ensure the integrity of the sample.

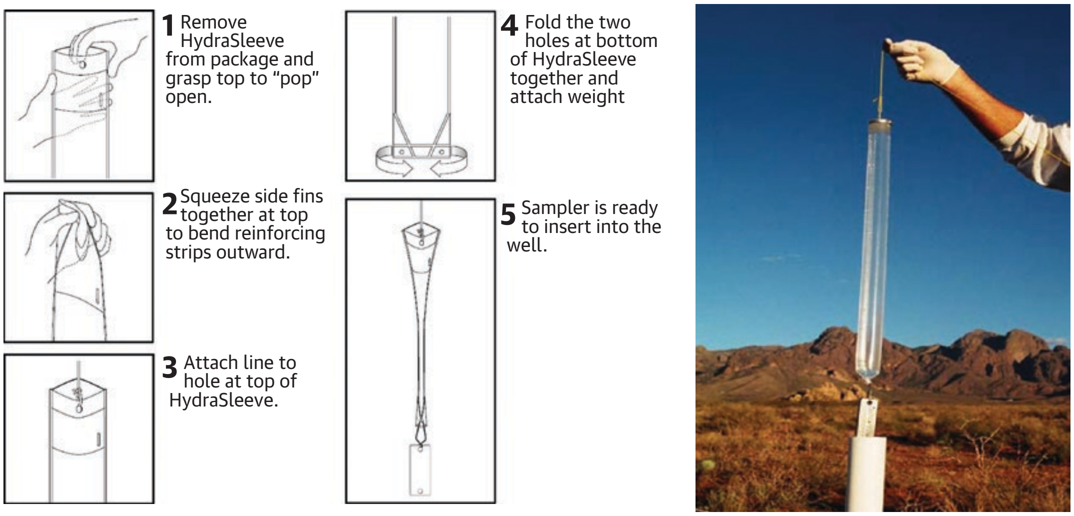
**FIGURE 8.4. Bladder Pump Operation**



## No-Purge Sampling Techniques

The no-purge concept requires a flow-through well as described earlier, whereby it is believed that water collected inside the well screen without significantly disturbing the water column will provide a representative groundwater sample. Several commercial technologies offer no-purge solutions based on *coring* the water column and passive diffusion bags (figure 8.5). Regulatory guidance (ITRC 2007;

**FIGURE 8.5.** **No-Purge Sampling Devices**

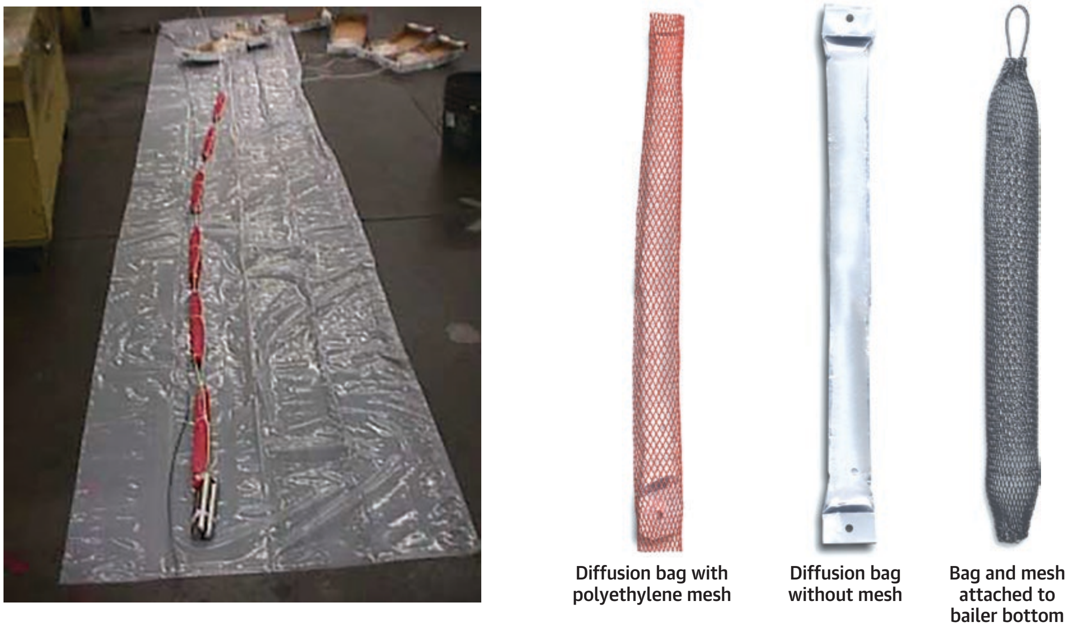


a. HydraSleeve assembly (1,2,3,4,5)

b. Full HydraSleeve retrieved from a well

c. Example of multiple passive diffusion bag samplers prepared for deployment

d. Typical water-filled passive diffusion bag samplers used in wells



*Source:* (a) and (b) ITRC 2007; (c) and (d) Vroblesky 2001.

Parker and Clark 2002) from the United States validates the ability of these devices to produce valid samples. However, sample integrity is contingent on the well being properly constructed and maintained. Also, passive techniques will be more vulnerable to well construction defects than purging techniques.

An example of a water coring device is the HydraSleeve® (panels a and b of figure 8.5), in which a flattened and weighted plastic bag is gently lowered into the well until a triggering mechanism opens the bag and captures the water at that depth. With the passive diffusion bag (panel b of figure 8.5; Vroblesky 2001), a special slightly permeable cylinder, or string thereof, is lowered into the well screen and left there for a period of weeks or months to equilibrate with the ambient water. The procedure averages the concentrations over a period rather than being a snapshot as with all other techniques; this may be useful for monitoring highly transient concentrations of pollutants, such as chlorinated solvents and pesticides.

## Monitoring Frequency

Optimal monitoring frequency is a compromise between science and logistics. The initial decision on frequency is usually administrative and should not go unchallenged forever. Compared to groundwater levels, groundwater chemistry changes slowly and thumb-rule approaches are widely followed. Some jurisdictions conduct seasonal monitoring (for example, pre- and postmonsoon), which is relevant to water levels but less so for groundwater quality monitoring unless the well samples are very close to the zone of water level fluctuation.

A distinction should be drawn between routine (resource status) monitoring, in which no particular risk is being guarded against, and purposive (or sentinel) monitoring, which typically responds to regulatory requirements following anthropogenic pollution or a specific natural risk to abstraction wells to provide an early warning of danger. When the regulator does not specify the monitoring interval, this can be approached by asking the following questions:

- How quickly could something go wrong (in terms of contaminants reaching a receptor)—that is, what should be the maximum interval between measurements? This judgment can be guided by experience of the contaminants in similar settings.
- What is the longest period for which it is acceptable to not know what is happening? For instance, are there enough measurements to establish credible trends of resource status?

As more time-series data are collected, it is possible to refine these decisions using observed variations. It is also possible to estimate intervals by modeling pollutant travel times and, therefore, how quickly a well might be polluted. If human health is at risk, it is also prudent to consider the consequences of a contaminant reaching a safe water supply. For instance, chronic exposure to arsenic is understood to take two years or more to produce clinical symptoms; so monitoring vulnerable wells at intervals of no more than six to twelve months should be protective of health, though shorter intervals are desirable if logistics permit.

When continuous in-situ monitoring with water quality probes is employed, recording once a day should be sufficient except (a) when tidal fluctuations are of interest or (b) in karstic systems in which rapid pulses of pollution are suspected. A good strategy for optimizing monitoring frequencies is to install in-situ monitoring devices with continuous recording of indicator parameters at a few wells on a rotational basis to determine what short- and medium-term fluctuations occur.

## Logistics and Management

For managers, sampling poses logistical challenges that start with the selection or design of monitoring wells, which, without thorough planning, will result in either poor and insufficient monitoring or excessive time and cost. This is why agencies give so much emphasis to minimizing the amount of purging by using small-diameter wells and avoiding the need for heavy pumps. To conduct this work, monitoring teams should 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 work, and insufficient monitoring conducted.

Managers must ensure a quality assurance program is in place with standard operating procedures, equipment checks, training and supervision, interlaboratory comparisons and certification, and so on.

## Costs of Groundwater Quality Monitoring

Estimating a universal set of groundwater monitoring costs is difficult, if not impossible, because of aquifer variations, local logistical factors, changes in analytical costs, and most importantly the number and type of parameters to be tested for. Although data are generally lacking, 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 (or US$451,000 at current prices[3]) a year 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 significantly reduced by a risk-based focus on chemicals of particular concern, and that might be measured more frequently to provide better guidance.

Such decisions must be based entirely on the local context; however, the scope for costing and cost savings can be seen by examining the build-up of the 1996 USEPA costs for a single well in a one hundred-well network sampled once a year. These costs (table 8.1) are presented as a preliminary planning guide and are expected to vary significantly with changes in technology and local availability of services. The reader should concentrate on the relative costs of items because analytical costs may not correlate well with the overall inflation rate.

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

**TABLE 8.1.** Unit Costs of Ambient Groundwater Quality Monitoring in the United States

| Item/subitem | Cost (US$) |
|---|---|
| Labor and travel cost for sampling | 375 |
| Monitoring equipment | 20 |
| *Analytical costs* | |
| Metals | 261 |
| Nonmetals | 85 |
| General water quality | 43 |
| Nutrients | 76 |
| Radionuclides | 107 |
| Acid/base/neutral hydrocarbons | 313 |
| Herbicides | 357 |
| Pesticides | 381 |
| Volatile organic compounds | 380 |
| *Subtotal for analysis* | **2,003** |
| Data management | 56 |
| Data interpretation | 461 |
| Reporting and communication | 83 |
| **Total unit cost** | **2,998** |

*Source:* USEPA 1996.
*Note:* Costs are in 1993 US$ averaged across 100 wells sampled once in a year.

might satisfy needs in many settings. When recurrent budgets are most limited, measuring only a handful of locally critical parameters, such as arsenic or fluoride, could meet most needs. Note the cost of installing the network will vary enormously depending on the local hydrogeology, but this may also be reduced by judicious inclusion of existing wells.

## Sources of Further Information

### Books and Reports

Brassington. R. 2007. *Field Hydrogeology*, 3rd ed. Chichester: Wiley.

CL:AIRE (Contaminated Land: Applications in Real Environments). 2008. “Principles and Practice for the Collection of Representative Groundwater Samples.” Technical Bulletin 3, CL:AIRE. Haddenham, Buckinghamshire, United Kingdom. https://www.claire.co.uk.

ISO (International Organization of Standardization). “ISO 5667-11-2009. Water Quality – Sampling – Part 11: Guidance on Sampling of Groundwaters.” ISO, Geneva

Nielsen, D. M., and G. L. Nielsen. 2006. *The Essential Handbook of Ground-water Sampling*. Boca Raton, United States: CRC Press.

Sundaram, B., A. Feitz, P. de Caritat, A. Plazinska, R. Brodie, J. Coram, and T. Ransley. 2009. *Groundwater Sampling and Analysis - A Field Guide*. Geoscience Australia. Canberra.

### Websites

Environment Agency (United Kingdom): https://www.gov.uk/government/publications/guidance-on-the-design-and-installation-of-groundwater-quality-monitoring-points

USEPA: https://www.epa.gov/quality/compendium-ert-groundwater-sampling-procedures

United States Geological Survey: https://water.usgs.gov/owq/Fieldprocedures.html

Waterloo Multilevel Systems, Solinst Canada Ltd.: https://www.solinst.com/products/multilevel-systems-and-remediation/401-waterloo-multilevel-system/

## Notes

1. Wells may contain up to two "dead" zones where water is stagnant: one above the well screen, as shown in figure 8.1, and another below the well screen and extending to the bottom of the well.
2. This is recognized in some coastal areas as the "salt in the morning well" phenomenon.
3. For more information, see the CPI Inflation Calculator at https://www.in2013dollars.com/us/inflation/1997 (accessed August 3, 2021).

# Chapter 9
# Field Operations

The proper conduct of monitoring in the field is often poorly understood and therefore overlooked by managers, leading to frustration and poor-quality work. This chapter seeks to make managers aware of how they can support field staff in doing their work well and cost-effectively.

## Planning Monitoring Trips

The planning of a monitoring trip should be documented in a field sampling plan (FSP), which should be an essential part of the agency's quality assurance program and must consider many factors, including

- Personnel and transportation logistics;
- Health and safety;
- Standard operating procedures
- Sampling, purging, and field-testing equipment; and
- Chain of custody.

Each trip should have a designated trip leader, who is responsible for the field team, and a trip manager, who is not present in the field yet responsible to approve and track the trip. Field staff should be prepared and equipped for the many eventualities that arise in the course of fieldwork (box 9.1). Training in

### BOX 9.1. The Hydrogeologist's Toolkit

Field staff conducting monitoring should routinely carry the following:

- Water level dipper
- EC and pH meters and field test kits
- Mobile phone and camera
- Compass, GPS, and maps
- Measuring tapes and gauges
- Spanners, wrenches, and so on
- SOPs and data tables
- Sample bags, bottles, and filters
- Personal protective equipment
- First aid kit

groundwater quality monitoring should be mandatory. The trip manager must ensure that trip members are suitably trained or supervised.

### Health and Safety

Trip managers may delegate tasks but not responsibility for the quality and safe conduct of work. Detailed specification of health and safety is beyond the present scope; however, every agency should have a health and safety policy and a designated health and safety manager. The trip leader and trip manager have a duty of care to themselves, staff sent to the field, contractors, and site visitors. Critical aspects of trip planning include the following:

- Safe vehicles and driving practices
- Notification of trip itinerary and return
- Communications
- Working alone
- Location of emergency health facilities
- Public order/personal safety issues
- Carriage and use of personal protective equipment
- Handling of toxic or corrosive chemicals
- Isolation of public from hazards through signs and fencing
- Recognition of onsite hazards
- Working at height or below ground level
- Proper use of appropriate tools

Approval of a health and safety plan (HSP) should be a mandatory duty of the trip manager. All trip leaders must receive health and safety training. For most trips, the necessary information can be included in a generic HSP supplemented by a short form highlighting special features of the trip.

### Standard Operating Procedures

To ensure high-quality and reproducible results, each agency should adopt SOPs for each task or group of related tasks. These might include activities such as purging and sampling or field water quality tests. The trip leader must carry copies of all relevant SOPs.

### Equipment Checks

Before travel, the trip leader should ensure that all equipment has been checked by the team or by the stores or laboratory issuing it. Batteries must be fully charged, spare batteries carried, and fuel and lubricants available as appropriate.

### Conducting the Site Visit

Notwithstanding what is described in the FSP, HSP, and SOPs, the site visit is never only about making a particular set of measurements. No site can be fully appreciated from remote data, and conditions change over time. Observation of the site environment and activities and conversations with local people and water users are vital to updating the conceptual model. Each professional should look for the unusual and unexpected and record and report these observations, which will include but not be limited to the following:

- On arrival, recording the weather conditions and examining the surroundings before focusing on the condition and security of the well.

- Validating the visit by transmitting a photograph and GPS position by smartphone.
- Verifying the identity of the well(s) or spring and cross-checking with the information on the paperwork so that is not wrongly assigned later. Two common problems are
    - Identifying wells of different depth at piezometer nests; and
    - For private, or nonagency, wells, establishing whether any changes have occurred since the most recent visit.[1]
- On opening the well, examining the headspace for odors, blowing or sucking motions, and sounds, such as bubbling gases or dripping water. If hydrocarbons, solvents, or flammable gases are suspected, the headspace should be tested with a photo-ionization detector (PID) or flame-ionization detector (FID), see box 9.2.

## Sample Collection, Preservation, and Storage

Once at the surface, samples must be carefully preserved, transported, and stored. Because of the various types of analysis that may be scheduled, a variety of bottles and preservatives will be required. Bottles should be supplied by the laboratory, and the trip leader must liaise with the laboratory to ensure the correct combination. The laboratory should supply the prepared bottles together with barcoded labels and cover sheets in prechilled boxes. This forms part of a chain of custody record within an overall QA program and allows for easy “assembly” of results from the field and each sample. To prevent the possibility of particulates being later dissolved, some samples require filtering through a 0.45-µm (micrometer) cartridge, often using a simple syringe, but must be sealed against air exposure for redox-sensitive elements, such as arsenic, iron, manganese, and heavy metals. The bottles are then placed in cool boxes and transferred to the laboratory as quickly as possible. Table 9.1 provides a summary of the recommended field procedures.

### BOX 9.2. Checking for Volatiles and Flammable Gases: Headspace Screening

The *headspace* (that is, atmosphere inside a well that has been closed with a cap) is an indicator of what is happening in the aquifer and also a warning of danger. If volatile hydrocarbons or flammable gases are suspected, the headspace should be tested with a PID or FID. The PID and FID perform broadly similar functions. Both are effective in detecting and measuring aromatic compounds and many aliphatic compounds. PIDs are usually lighter, smaller, and less complex and measure volatiles in the range from parts per billion to thousands of parts per million, including chlorinated aliphatics and ethane but not methane. FIDs will measure hydrocarbon gas concentration, including methane. These devices can also be used in urban settings for checking under utility covers.

**TABLE 9.1. Sampling Procedures for Specific Compounds**

| Determinand group | Sampling procedure | Preferred materials | Storage time/ temperature | Operational difficulty/cost |
|---|---|---|---|---|
| **Major Ions**<br>Cl, SO$_4$, F, Na, K | • 0.45-µm filter only<br>• no acidification | any | 7 days/4 °C | minimal |
| **Trace metals**<br>Fe, Mn, As, Cu, Zn, Pb, Cr, Cd, and so on | • sealed 0.45 µm filter<br>• acidify (pH <2)<br>• avoid aeration through splashing/head space | plastic | 150 days | moderate |
| **N species**<br>NO$_3$,NH, NO$_2$ | • sealed 0.45 µm filter | any | 1 day/4 °C | moderate/low |
| **Microbiological**<br>TC, FC, FS | • sterile conditions<br>• unfiltered sample<br>• onsite analysis preferred | dark glass | 6 hours/4 °C | moderate/low |
| **Carbonate equilibria**<br>pH, HCO$_3$, Ca, Mg | • unfiltered well-sealed sample<br>• on-site analysis (pH, HCO$_3$) (Ca/Mg at base laboratory on acidified sample) | any | 1 hour<br>(150 days) | moderate |
| **Oxygen status**<br>pE(Eh), DO, T | • on site in measuring cell<br>• avoid aeration<br>• unfiltered | any | 0.1 hour | high/moderate |
| **Organics**<br>TOC, VOC, HC, ClHC, and so on | • unfiltered sample<br>• avoid volatilization<br>• direct absorption in cartridges preferred | dark glass or Teflon | 1–7 days<br>(indefinite for cartridges) | high |

*Source:* GW-MATE 2006a.

*Note:* As=arsenic; Ca = calcium; Cd = cadmium; Cl= chloride; ClHC = chlorinated hydrocarbons; Cr = chromium; Cu = copper; DO = dissolved oxygen; Eh = redox potential; F = fluoride; FC = fecal coliforms; Fe = iron; FS = fecal streptococci; HC = hydrocarbon; HCO$_3$ = bicarbonate; K= potassium; Mg = magnesium; Mn = manganese; N = nitrogen; NH$_4$ = ammonia; NO$_3$ = nitrate; NO$_2$ = nitrogen dioxide; Pb = lead; pE = redox potential; T = temperature; TC = total coliforms; VOC = volatile organic compounds; Zn = zinc.

## Field Testing of Groundwater

Field testing is conducted for two distinct purposes. First, even when samples are being sent to the laboratory, some parameters are measured in the field because they are unstable and likely to change during transport and storage. All of these measurements should be made as quickly as possible after groundwater reaches the surface and in a way that minimizes contact between the water and the atmosphere. The most common and important field measurements are the following:

- *Multiprobe* measurements measured in a flow-through cell, continuously or regularly recording EC, temperature, pH, dissolved oxygen, and Eh. As described earlier, this is also done as part of the sampling protocol to demonstrate that the chemistry of the pumped water has stabilized. It should be appreciated that the Eh parameter may not stabilize and is best regarded as a semiquantitative indication of the redox state (Appelo and Postma 2005).

- *pH*. If a very accurate measurement is required, such as when equilibrium calculations will be performed to stability or mobility of contaminants, a dedicated pH meter should be used and calibrated onsite against multiple buffer solutions before each measurement.

- *Alkalinity*. Accurate measurement of alkalinity and its components (bicarbonate and carbonate) should be conducted by field titration (photo 9.1) using either a conventional burette and a pH meter to identify the inflection points or more easily using a digital titrator with methyl orange indicator.

The second major reason for field testing is public health surveillance. Here, high precision is not required, and the focus is on just one or two parameters plus a desire for low cost and speed to allow immediate follow-up action. A classic example is the blanket testing of arsenic in millions of domestic wells in South and Southeast Asia (photo 9.2) since the year 2000. The test kits require some skill and training and should be backed up by a quality assurance program but do not require a chemist to operate. Tests can be completed within fifteen to twenty-five minutes, cost about US$1 a test, and produce a semiquantitative result that can reliably classify the risk to health, albeit that samples

**PHOTO 9.1. Digital Titrator for Alkalinity Measurement**

*Source:* © Hach Company (www.hach.com). Used with permission.

**PHOTO 9.2.** **Using Arsenic Field Kits in Bangladesh**

a. Color chart for reading concentration

b. Mechanic conducting test in field

c. Adding reagents to water sample

d. Training course for hygiene promoters

*Source:* Photos taken by the authors.

should be sent to a laboratory in borderline cases. The great advantage of this type of testing is that the results can be communicated immediately to well users together with appropriate health and mitigation advice. However, these kits 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 in flow-through wells by suspending a probe, connected a data logger and telemetry system, inside the well screen. Other probes are available but normally used only in research studies. The most commonly used probes measure EC, which is an excellent proxy for salinity and also sensitive to other changes that might indicate the approach of a pollution plume. It is the most reliable measurement when left unattended for long periods. This type of monitoring should be seen as an addition, not alternative, to conventional monitoring to track trends and fluctuations and to trigger field investigations.

An alternative in-situ approach for monitoring salinity is to install a conventional PVC piezometer with a short screen at the maximum depth of interest but can also be used for periodic lowering of an electromagnetic (EM) logging tool, which can "see through" the solid PVC pipe to estimate the continuous profile of groundwater salinity outside. This method avoids the problems of intraborehole flow and density effects described earlier.

## Quality Assurance: Blanks, Standards, and Duplicates

Although they rarely get the attention they deserve, quality assurance (QA) and quality control (QC) are vital to reliably interpreting, and acting decisively with confidence on, water quality data. Key elements of the QA/QC process include the following:

- *Blanks* are usually bottles filled with deionized water but processed identically to real samples to identify false positive detections (that is, substances not actually in the groundwater). Blanks can be divided into trip blanks, field blanks, and lab blanks to identify where errors arise (box 9.3).

- *Accuracy and precision* are related but different concepts. Accuracy is a measure of how close the result is to the "true" value. Precision is a measure of the reproducibility of results. Good analyses are both accurate and precise.

- *Standards* are samples of known concentration, usually obtained from reference laboratories, that are used to check accuracy. However, because standards are normally pure solutions, they do not guarantee accuracy in real groundwater where other parameters may interfere. Accuracy is mainly the business of laboratories, but one useful procedure to check recovery is to make a standard addition to real groundwater samples.[2]

- *Duplicate and triplicate samples* are used to check precision and are very much the business of water quality professionals; but as a guide, the difference between duplicates sets a benchmark for what a significant difference between two real samples is.

## **BOX 9.3.** The Utility of Trip Blanks

A large airfield, underlain by an alluvial aquifer, abandoned its wellfield because of contamination by jet fuel and chlorinated solvents. Following investigations, the location for a new wellfield was identified on the opposite side of the airfield. However, when the new production wells were tested, the samples collected were found to contain chloroform ($CHCl_3$). This caused great consternation, but fortunately the sampling program had included trip blanks—bottles filled with deionized water before going to the field and then submitted to the lab together with the field samples. It was found that the trip blanks contained the same concentration of $CHCl_3$ as detected in the groundwater samples. This was a relief to all concerned—except the laboratory—because this was the only place where all the samples could have been contaminated; therefore, groundwater contamination could confidently be ruled out. Indeed, no further cases of $CHCl_3$ contamination were reported, but without the trip blanks, the possibility of pockets of groundwater contamination could never have been eliminated.

- *Interlaboratory comparisons*—given a spirit of cooperation, sending identical samples to different laboratories is an excellent way to quickly check both precision and accuracy. This can be done either ad hoc as part of a normal survey or as a formal process involving many laboratories. Because of bureaucratic sensitivities, the latter can be done with varying degrees of anonymity.
- *Accreditation and certification* are important but are mainly the concern of laboratory managers rather than practicing water quality professionals.

Although accreditation is generally viewed as a gold standard for laboratories, it can be slow and expensive to implement and something of a blunt instrument if there is a particular parameter of concern, so preference may be given to interlaboratory comparisons. This occurred in the early days of arsenic investigations in South Asia when many laboratories were not accustomed to analyzing any groundwater parameters to the level of parts per billion. A good QA/QC program (box 9.4) is non-negotiable.

## **BOX 9.4.** Five Tips for Good QA/QC programmes

1. All laboratories should follow well documented procedures with a public commitment to auditable QA and QC processes.
2. Ensure SOP's exist and are always in the hands of field staff.
3. Ensure bottles and caps are gas- and water-tight, and that acidified and unacidified bottles are kept separate.
4. Field instruments should be calibrated before leaving the laboratory.
5. Collect, analyze, and report the appropriate blanks and duplicates, and cooperate with other labs to check reproducibility of results.

## Sources of Further Information

Barcelona, M. J., J. P. Gibb, J. A. Helfrich, and E. E. Garske. 1985. "Practical Guide for Groundwater Sampling." State Water Survey Publication 274 (EPA 600/S2-85-104), USEPA, Cincinnati, Ohio.

Brassington. R. 2007. *Field Hydrogeology*, 3rd ed. Chichester: Wiley.

CL:AIRE (Contaminated Land: Applications in Real Environments). 2008. "Principles and Practice for the Collection of Representative Groundwater Samples." Technical Bulletin 3, CL:AIRE. Haddenham, Buckinghamshire, United Kingdom. https://www.claire.co.uk.

ISO (International Organization for Standardization). "ISO 5667-14-1998. Water Quality — Sampling — Part 14: Guidance on Quality Assurance of Environmental Water Sampling and Handling." ISO. Geneva.

Nielsen, D. M., and G. L. Nielsen. 2006. *The Essential Handbook of Ground-water Sampling*. Boca Raton, United States: CRC Press.

Sundaram, B., A. Feitz, P. d Caritat, A. Plazinska, R. Brodie, J. Coram, and T. Ransley. 2009. *Groundwater Sampling and Analysis - A Field Guide*. Geoscience Australia. Canberra.

## Notes

1. For instance, in long-term monitoring in West Bengal (India), McArthur et al. (2010) found many hand tubewells had been redrilled at exactly the same location in order to avoid arsenic or iron, and with the original pump fitted to the new well.
2. For example, duplicate samples with and without addition of a known quantity of a chemical.

# Chapter 10
# Working with Laboratories and Laboratory Data

The interface between field monitoring and laboratories is usually also an interface between disciplines and cultures and accompanied by a lack of mutual understanding. This is regrettable, and in the long run efforts should be made to break down this barrier by deploying field staff with better understanding of water chemistry and hydrology. In the meantime, water managers are advised to hire a competent individual to advise them on analytical matters.

## Preliminary Data Assessment and Validation

Before interpreting water quality results, their credibility must be checked. The first subjective check is whether the results feel credible with the hydrogeology and consistent and previous results: If not, talk to the laboratory. If this test is passed, proceed to standard procedures to identify analytical and reporting errors, including the following:

- Compare the measured total dissolved solids (TDS) with the calculated sums of anions and cations to identify possible errors or missing items. If the error is large (> 5 percent) or zero,[1] check with the laboratory.
- Calculate the charge balance error (CBE) by summing the anions and cations (after converting to milliequivalents). The CBE should be as small as possible, but ± 5 percent is generally considered acceptable (Weight 2008).
- Compare parameters measured in the field with the corresponding laboratory measurements. Parameters such as EC should be similar, but differences in, say, pH or alkalinity could indicate degassing or precipitation.
- Conduct logical checks, such as for redox-sensitive parameters, where oxygenated species, such as dissolved oxygen and nitrate, should not normally coexist with reduced species, such as iron or sulfide.
- Check for outliers on cross-plots of EC versus major ions for waters from the same aquifer.

## Detailed Assessment of Laboratory Data

When examining suspect data, an open mind is essential. Apparent analytical errors may originate outside the laboratory. The entire monitoring and analysis chain, from the design of wells through sampling and storage to the supply of reagents and equipment, as well as information technology (IT) errors in data compilation and reporting, should be kept in mind. The assessment should be conducted by a minimum of two people—one who understands field operations and the significance of the data and the other an expert in analytical chemistry who could come from the laboratory or be independent. If, after the routine checks described earlier have been conducted, doubts about the accuracy or veracity of analytical results persist, further investigations may include but not be limited to the following:

- A detailed examination of blanks, duplicates, and interlaboratory comparisons.
- Examination of parameters values and combinations by a chemist familiar with the particular type of equipment used.
- Checks of current and historical records by a competent statistician to search for patterns suggesting fabrication of data by repetition of either old results or water sources.
- Examination of statistical ranges of parameter results that suggest truncation of results, such as at regulatory limits or the effective range of a machine or method.
- Commission an audit, which may be divided into two parts: one for the internal operations of the laboratory and data processing, the other for the entire chain of events from planning the visit to delivery of samples to the laboratory. This will involve continually asking the Deming question (Hunter 2011)—How do we know what we know?—with regard to every step, such as: Did the visit happen at the appropriate time? Was the well sampled correctly? Does the water represent the aquifer? How and when was the sample delivered? and so on. These questions should guide our reading of a groundwater quality report (box 10.1).

## The Nondetect Problem

Chemical and microbiological concentrations are never zero, only "not detected." Nondetects create several problems in data processing given the understandable desire to convert them to numeric values.

### BOX 10.1. How to Read a Groundwater Quality Report

It is easy to be handed a report on groundwater quality and, because you are not a chemist or a monitoring specialist, accept its validity at face value, whereas it is quite easy to determine whether it passes a basic test of acceptability. This is important because many reports are accepted and acted on without passing the most elementary of checks.

As a general rule, the more information that is provided about what was done and how, the more likely it is that the results meet a basic level of acceptability. The reader should expect to see the following described:

- Dates, times, and methods for sample collection
- Sample filtration, preservation, and bottle types
- What tests were done in the field and, if none were, parameters such as pH and alkalinity should be considered as approximate and possibly systematically biased
- Evidence of following QA/QC program, including a chain-of-custody record

The first problem arises when databases store results as text, which is ideal for recording detection limits but a problem when processed in spreadsheets for statistical summaries or graphing. Substituting a blank record confuses nondetect with no data. Substituting zero is common and may be tolerable for some applications but will cause large errors in others. A common rule of thumb is to substitute half the detection limit. This is easy to apply and better than using zero; it recognizes that some amount of the substance may be present and avoids division-by-zero errors, allowing geostatistical calculations to be performed. This is probably "adequate" for many practical purposes, but it has no scientific basis. One solution to test the significance of this substitution is to do calculations twice, once substituting zero and then substituting the detection limit, thus giving a confident range of answers. Alternatives, such as the maximum likelihood estimate (Gardner 2012), exist but take more effort to apply.

## In-House Laboratories and Analytical Services

Faced with the growing demand for accurate testing of toxic geogenic and anthropogenic contaminants at low concentrations, water utilities and water resource agencies may find it impractical for internal laboratories to support elaborate and increasingly expensive monitoring programs. It is not sufficient to buy complex and expensive equipment, such as inductively coupled plasma (ICP) and gas chromatography-mass spectrometry (GC-MS) and their numerous variants, without considering the institutional, logistical, and financial aspects. This equipment is not only expensive but also difficult to operate reliably, requiring highly skilled staff and demanding quality control. To be cost-effective, there needs to be sufficient workload and budget to keep the equipment in regular and routine operation. Also, public health concerns increasingly require compliance with international standards, such as ISO-15000 and laboratory accreditation. 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/QC procedures, resulting in more cost-effective, reliable, and quicker analytical results.

This, however, is not an argument for complete outsourcing of testing. Agencies should retain an in-house testing capacity based on a guaranteed workload, which will act as a check on the quality and cost of external services, perform the intelligent customer function, provide specialist support to the agency, retain a core of professional competence as part of a cultural change from being a testing service, and be a manager of water quality.

## Improving Analytical Techniques and Instrumentation

Senior managers and donors are often faced with requests to procure new equipment or to generally upgrade laboratories. There is no doubt that laboratories do require regular expenditure to maintain performance, and there are also regular developments in analytical equipment, plus ever-evolving demands for analyzing more parameters and with greater accuracy. For the manager who lacks detailed knowledge of these matters and is only partially aware of outsourcing options, it is difficult to evaluate the best course of action. This problem becomes acute when a budget is in hand and there is pressure to spend it. When funding for laboratory refurbishment comes from external sources, there is often a sad cyclical history of reequip, neglect, and decline. In such situations, there is a desperate need to change the culture from one of equipment procurement to a perspective of running an analytical services business. So long as the focus is on buying the best equipment, there is unlikely to be an overall improvement. What is required is an evaluation of medium- to long-term performance measured in terms of the unit costs of delivering analytical results that satisfy quality and time standards. When this becomes the new management paradigm, the best allocation of funds between equipment, personnel, and service procurement will take care of itself. Achieving this is likely to require (a) independent advice from an individual experienced in running commercialized laboratory and (b) a resource agency and/or donor who understands the importance of sufficient reliable water analyses and pays attention to the quality of service it obtains.

## Note

1. This could occur if a parameter has been calculated by difference.

# Chapter 11
# Interpreting Groundwater Quality Data

Groundwater quality investigations generate large data sets that may require varied and complex processing. This chapter presents a structure for information processing and evaluation and describes a few of the pitfalls that may emerge along the way.

## Methodologies

Once a validated set of groundwater quality data has been obtained, it should be processed to extract scientific and practical meaning. This should be done in three phases: standard reporting, exploratory data analysis, and hypothesis testing.

*Standard reporting* describes the basic presentation of results for others to understand what has been done and opens the door for interpretation. The main presentation is tabular, supported by descriptive graphics, such as box-and-whisker plots, emphasizing range and exceedances of standards or guidelines, and supplemented by simple temporal trends of single parameters at a point and summary statistics, such as mean and median and so on. Tables and text should be clear about units and accuracy. If duplicates were analyzed, it may be worth noting what constitutes potentially significant differences. An essential component of reporting is to state the purpose of the survey and the exclusions that followed from it. No survey can be truly comprehensive, and it would be mindboggling and disingenuous to list every chemical or group not tested for. A survey can, however, be judged fit for purpose or not, and this is where a thoughtful statement of limitations is both protective to the author and helpful to the reader.[1]

*Exploratory data analysis* is a vital and much underestimated or misunderstood part of data analysis. When examining large groundwater quality data sets, it is easy to jump to premature conclusions and miss important associations. This stage can be thought of as hypothesis identification, conducted with an open mind and guided by the adage that "correlation is not causation." Data exploration is done most efficiently by visual techniques, typically beginning with preparing two-parameter cross-plots and parameter-versus-depth plots, as well as in parallel mapping parameters in GIS. Qualitative interpretation of these graphical displays is greatly enhanced if the points are classified by geological unit, land-use differences, and the age and ownership of wells. In searching for patterns, it is also useful to display data on trilinear plots, such as the Piper or Durov diagrams.

*Hypothesis testing* is the natural successor to data exploration and can involve many different techniques, such as statistical analysis, drilling investigations, tracer or isotopic studies, geochemical modeling, or even epidemiological studies. Statistical testing is a core part of hypothesis testing, but the hypothesis must precede the test. Random trawling of large data sets with statistical tools is best avoided or at least treated with skepticism. As the Nobel Prize-winning economist Ronald Coase put it, "If you torture the data long enough, it will confess to anything." Because unguided data trawling is as likely to confuse as to throw up new insights, a recommended precaution is preregistration of the statistical protocols (for example, Spiegelhalter 2018).

## Working with GIS and Geostatistics

Although GIS and geostatistical analysis is not a separate phase, they are so widely used and so important in evaluating water quality data that they deserve special mention. Despite their different origins, geostatistics (for example, kriging and its variants) is treated as an extension of GIS because it is widely embedded in standard GIS software and has huge potential for understanding, analyzing, and communicating groundwater quality information. However, like all statistical methods, it can be misused, and a few cautionary notes are offered to help its best use. Particular concerns that arise in interpolating and extrapolating point data include the following:

- Unlike the water table, many groundwater quality parameters do not form a continuous field that exists in an aquifer. Parameters such as pH, TDS, or bicarbonate have a value everywhere and can be safely interpolated; however, most contaminants are not present everywhere, so the range of interpolation and extrapolation must be specified with care.

- Probabilistic solutions, such as the most probable concentration, risk hiding small-scale variation, such as where there are some (critical) safe wells in a heavily polluted aquifer or vice versa.

- Similarly, because most spatial analyses are two-dimensional, they risk hiding vertical variation, such as when there are particular layers of good- or bad-quality water.

- Interpolations from point data should respect geological boundaries or hydrological features, such as major rivers. Analyses should consider truncating interpolated surfaces at such boundaries or features. In general, analyses should be conducted only within single aquifers.

- Special care is needed in comparing time series of interpolated surfaces because of what has been termed *numerical migration,*[2] because measured change at a point propagates change at all distances toward points when no change has been recorded. However, this is not what happens in reality. Rather there is movement of a sharp chemical front away from the high concentration point but beyond which there is no change.

- Before interpolating concentrations, the data set should be tested to see if it approximates a normal distribution, and if not, various transformations[3] may be explored.

## Groundwater Quality Maps and Sections

Maps and their rotated equivalent, the cross-section, and three-dimensional images are powerful ways of interpreting and disseminating groundwater quality information. However, with such power should come health warnings about the potential to mislead.[4] Style should never be a substitute for substance. The preparation of maps, which nowadays is almost a default GIS activity, should be carefully planned, considering presentation style, the psychology of perception, and the choice of background information (for example, geology, land use, pollution sources, surface water features, and so on).

The primary choice of presentation style is between showing point (that is, well or spring) information and interpolated surfaces. The essential precondition, however, for mapping is to establish the aquifer or hydrogeological unit for which data will be displayed. Point data may be displayed crossing geological boundaries provided that those boundaries are displayed as a background theme, but interpolated surfaces should ideally be calculated separately for each geological unit.

Point data are easy and relatively safe to display using a combination of colors and symbol styles and sizes, but the author should be aware of the biases that this can introduce. Bold colors, such as red, and exotic or large symbols attract the eye and are useful in helping the reader locate critical sites but may also exaggerate their spatial importance. Also, colors such as red carry a subliminal message of danger, whereas green or gray may have the opposite effect. Similar effects are achieved by making symbol size proportional to concentration; however, combining symbol size and color in the same map is best avoided. Traffic-light color systems are popular; however, red-green color blindness[5] reduces the effectiveness for some readers. For these readers, combining color and symbol style (for example, red triangles and green circles) is helpful. The message to the map creator is that the choice of colors and symbols (symbology) is not only a matter of aesthetics: Bias is not necessarily wrong, but unrecognized bias is dangerous.

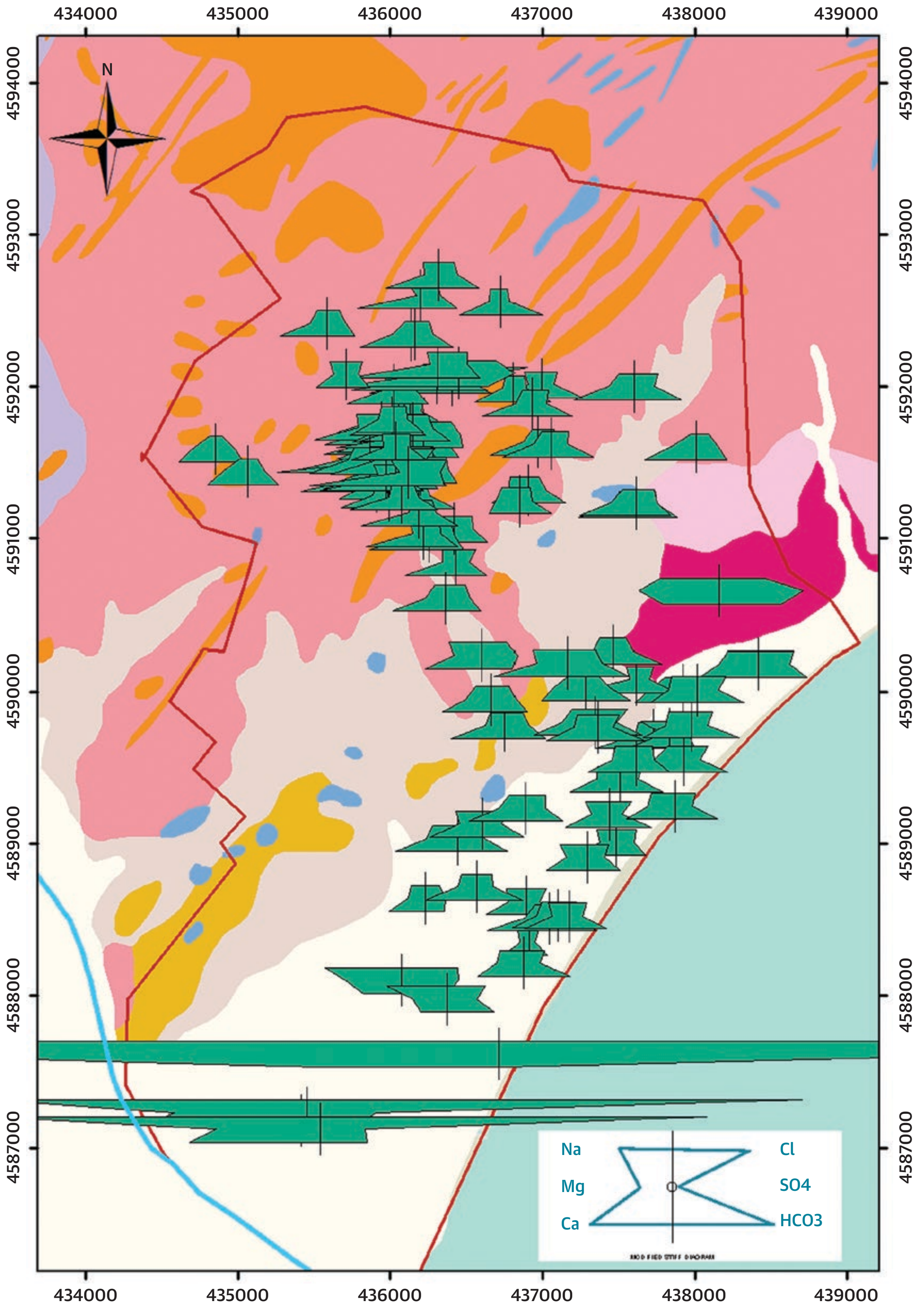
When the density of data points is high and large colored symbols are used, point maps can transition into a pseudointerpolated surface. True interpolated surface maps are based on calculation schemes, such as inverse distance weighted, nearest neighbors, and kriging methods (see, for example, Kitanidis 1997). The choice of method is important but often overemphasized in comparison to conceptualization and the preparation and presentation of data, and in any case, its importance diminishes as the density of points increases.

Surface interpolation methods have become popular and can be applied in two main ways: either to calculate the most probable concentration or the probability of exceeding a concentration threshold, such as a drinking water standard. The former is more suitable for describing the nature of an aquifer, whereas the latter is better for characterizing public health risk. Other uncertainties in interpolating surfaces include the processing of nondetect values and mathematical transformation to approximate a normal distribution to prevent giving too much importance to a small number of extreme values. A general problem with interpolated maps is that because they are probabilistic, they risk disguising the ignorance in the gaps; hence deciding the maximum interpolation distance is important.[6] Given the underappreciated uncertainties in water quality maps, there is much to be said for providing two or more different presentations to emphasize that there is no single correct map.

Specialist software has the potential to calculate three-dimensional images of pollution plumes and to animate these images to show temporal changes and movement. The approach is most often applied to model output and can have a wow factor in presentations to influence decision making that may be disproportionate to its scientific validity.

A special type of mapping of groundwater quality is the Stiff diagram map (figure 11.1). The original Stiff diagram allows rapid visualization of both the absolute quantities and relative proportions of six major anions and cations in a single sample. Showing Stiff diagrams on a map makes it possible to show how the bulk composition of groundwater varies across a region.

**FIGURE 11.1.** **Example of Stiff Diagram Mapping**



*Source:* Reprinted from *Computers & Geosciences*, Vol. 70, Velasco et al. "GIS-Based Hydrogeochemical Analysis Tools (QUIMET)," 164–80, © 2014, with permission from Elsevier.

An example of how the sampling problem (chapter 5) can confound interpretations is shown in box 11.1. Here, interpolated maps of two surveys of arsenic in domestic wells made ten years apart suggest that groundwater contamination had dramatically decreased—but it is physically impossible, based on the volumes of water abstracted, that the bulk composition of groundwater had changed this much. This illusion arises because well users abandoned contaminated wells, switched to safe sources, or drilled new wells to different depths. The difference between the two maps actually reflects the effectiveness of mitigation in different areas. These maps show the distribution of arsenic in well water, not the distribution of arsenic in groundwater. To paraphrase George Box,[2] it may be said that "all water quality maps are biased but some are useful."

Plotting groundwater quality data on hydrogeological cross-sections is not done as often as it should because they are effective in explaining the essential three-dimensional nature of groundwater contamination. Conceptually, it is easier to interpret two separate two-dimensional presentations (that is, map

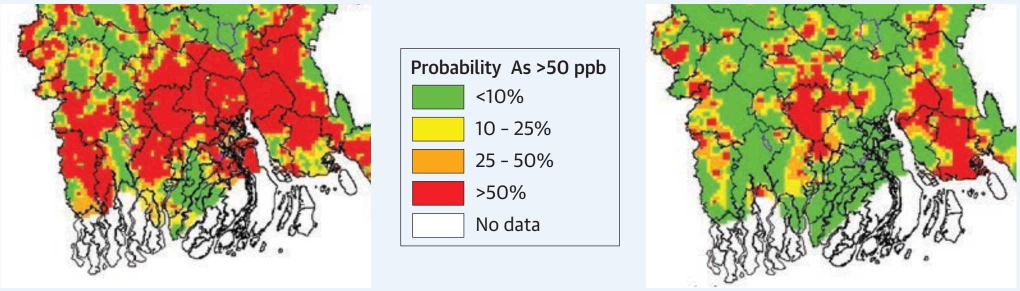
### BOX 11.1. How the Sampling Problem Can Bias Impressions of Groundwater Quality

The two surveys of arsenic in shallow handpumped wells in a thick alluvial aquifer were made ten years apart (map B11.1.1): the first when most people were unaware of arsenic contamination and the second after many well users had tried to avoid arsenic by switching or drilling new wells. Each map shows the probability of a well drilled randomly (in the top 150 meters) producing water with more than 50 ppb arsenic. The illusion that contamination had dramatically decreased occurs because our minds conflate the heterogenous quality of groundwater in an aquifer with the quality of water pumped from wells. Both maps are good descriptions of the quality of water being consumed at the time of the survey, but neither accurately describes the distribution of arsenic in the aquifers.

**MAP B11.1.1. Probability of Arsenic Contamination (>50 ppb) in Southern Bangladesh at Two Separate Time Periods**

**a. 1998-99**

**a. 2007-12**



*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).

and cross-section) than a single three-dimensional image.[8] Practically, it is much easier to access the skills to include water quality data in a two-dimensional GIS program than into a program that was probably created for borehole data management. Suitable software exists but is less readily accessible, can be expensive, and has fewer skilled users. When this is a constraint, analysts should not feel shy to rely on hand-drawn or not-to-scale computer-sketched sections. This is far superior to relying solely on map presentations.

## Notes

1. For example, the famous Bangladesh arsenic case that went to the United Kingdom's House of Lords would have been avoided if the authors of the concerned report had explained the limitations of their survey—that is, what they had not analyzed for and its implications for policy (Attaran 2006).
2. This is similar to numerical dispersion in contaminant transport models. The interpolated horizontal profile of a chemical is based on concentration gradients, not flow rates and attenuation. This is an unavoidable constraint in GIS and does not prevent it being useful.
3. Many contaminant data sets are observed to follow a log-normal distribution, and normality is a requirement of many interpolation techniques, so the analysts may interpolate the logarithms of the concentrations and convert the output back to normal numbers after processing.
4. For a general discussion, see Monmonier 1991.
5. Red-green color blindness affects up to 8 percent of males and 0.5 percent of females of Northern European descent (Albrecht, 2010).
6. One practical solution is to select a "reasonable" distance in advance based on the conceptual model and field experience and then create a surface of zero and one values from radial buffers around the well locations. Multiplying this by the interpolated concentration surface will create blank areas, where it is not reasonable to infer a value. This detracts from the aesthetics of the map but creates a better psychological perception of certainty and uncertainty.
7. "All models are wrong but some models are useful" (that is, a useful fiction), see Box 1976.
8. It is practically difficult to display geological and chemical information in three-dimensional images, which are effective in showing plume shape but with the consequence that geological controls are not as easily revealed.

# Chapter 12
# Information Management

The study of groundwater quality is data intensive, so good information management is vital to water resources management. This section summarizes some principles for good groundwater quality information management, which are considered in terms of the following groups:

- Information policy
- IT infrastructure
- Information systems
- Data standards
- Scientific framework
- Human resources and logistics
- Feedback

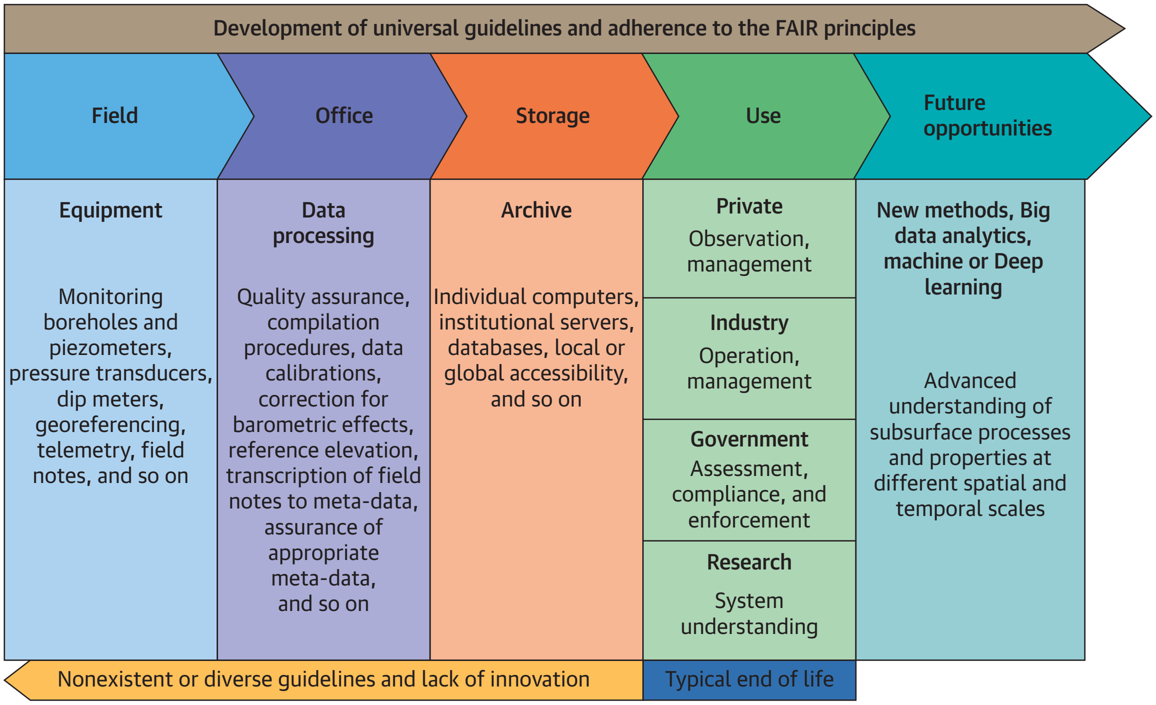
## Principles

Governments should establish an enabling information policy that, by default and as far as is practical, makes all data available easily and freely, following the FAIR principles: findable-accessible-interoperable-reusable (figure 12.1; Wilkinson et al. 2016). Free access to data supported by appropriate metadata should be seen as a public good, whereby maximum use of well-documented data will lead to better water resource decision making.[1] Thus, if the cost of collecting data has been paid by government or regulatory requirement, there is no economic justification for restricting access to the data. The main exception would be when a business has collected data as a commercial venture.

*IT infrastructure* is important in several domains. The first is in the collection of data through use of data loggers and telemetry, and in linking field and laboratory measurements using barcoding and smartphone technologies. The second is in the storage of digital information in databases and, more critically, in facilitating web-based access to large data sets and online processing to large numbers of users, which is a distinctly nontrivial activity.

*Information systems* comprise the visible interface between users and water data and their processing. These may include subsystems, such as a data collation and management back end, a user-facing front end, and specialized programs, such as laboratory information management systems. Water quality monitoring must be seamlessly integrated into environmental and water resources information systems. These systems may be developed in-house or from commercial vendors who can customize to the client's needs. The choice will depend heavily on the software development history of the agency.

**FIGURE 12.1. Overview of Groundwater Monitoring and Data Archiving**



*Source:* Adapted from Rau et al. 2020.
*Note:* FAIR = findable-accessible-interoperable-reusable.

In general, it is preferred to avoid including many data-processing functions inside the core information system, which should concentrate on the storage and delivery of validated data. Data analytics are better done through add-ins that allow selection of fit-for-purpose modules, are easy to upgrade, and encourage innovation from multiple users accessing a common database.

*Data standards* are important in allowing diverse stakeholders to input and access data easily and without error. They should rigorously define core information on location, essential station attributes, and data specification while allowing maximum freedom for nonessential attributes. This is important for users seeking to access and combine data sets. Standards, including metadata specification, are vital for the efficient import of telemetry data and laboratory information.

A well-documented *scientific framework* should underpin the workings of the information systems. By explaining the objectives and metrics of the local water resources management scheme, the design of applications will be clearer.

Information management can work well only if the necessary *human resources* and logistic support are in place and require training for users and budgetary support for operation and maintenance of data collection systems, IT, and software services.

*Feedback* from users is vital for maintaining the effectiveness and growth of systems. This can be achieved by direct survey or questionnaires or through an online user forum and webinars. Active feedback and open debate will drive the useful development of information systems, improve the quality of data, and promote better analysis of data.

## Special Characteristics of Groundwater Quality Data

Worldwide, the shortage of groundwater quality data is widely bemoaned. In many countries, there is a tendency for the availability of data to be expressed in terms of what is collected through the routine monitoring programs of official agencies. However, this can massively underestimate the quantity of data available from ad hoc surveys and research studies. For instance, across the arsenic-affected countries of South and Southeast Asia, there are literally millions, if not tens of millions, of analyses that are not included in the official registers of data. The challenge therefore is to bring these data within the sphere of the total monitoring network (chapter 5), which requires a combination of information policy, data standards, and scientific framework that both enables and charges the network manager to locate and integrate these data. Such data may range in quality from semiqualitative field tests from blanket testing to high-quality research data and therefore demand clear descriptions in metadata and judgment in deciding how to use them. It is a mistake to reject out of hand large data sets that bring a spatial density of measurements that is usually unthinkable just because they do not meet certain QC requirements. It is merely a challenge of the imagination for the data analyst.

There is a disappointing tendency in some academic journals to not make data automatically available online. Agencies funding or participating in research should require the researchers to make their data available and offer the data sets to the relevant national agency.

## Emerging Trends in Groundwater Data Processing

In the twenty first century, advances in computing power and access to big data have opened new possibilities for data-driven and model-driven approaches that fall under headings such as artificial intelligence (AI), machine learning (ML), and deep learning (DL).[2] In other disciplines, they have given birth to stunning advances in voice recognition, medical image diagnosis, and autonomous vehicles. They have also given rise to much hype, false claims of new insight, and some unrealistic expectations. Applications in water resources have somewhat lagged other areas, but there is now a widespread anticipation of a blossoming field (for example, Bergen et al. 2019; Malakar et al. 2020; Shen 2018). Bergen et al. (2019) describe how ML can be divided into three categories of research:

- Automation to perform complex tasks not easily defined by explicit commands
- Inverse modeling to capture or approximate complex relationships
- Discovery of new and unexpected patterns or relationships

To date, applications to groundwater quality problems have been limited to predicting the distribution of arsenic, fluoride, and nitrate. This has shown promise but so far limited practical benefit (compared with non-ML techniques), particularly in studies that paid insufficient attention to the quality of the underlying data. In these relatively basic applications, one may distinguish between (a) the limited utility of using, say, arsenic to predict arsenic in areas already subjected to blanket testing compared with (b) using widely available data to predict arsenic in areas where it has not been tested for. The limited insights gained into arsenic and fluoride pollution, though useful as training exercises, may also be explained simply by the fact that they have been subject to active research for several decades. ML and DL may offer more by examining (a) less-studied trace contaminants, such as barium, chromium, molybdenum, and selenium and so on; (b) the complex links between groundwater contaminants and individual health outcomes; and (c) the many factors that contribute to determining the overall composition of groundwater.

In closing this look at the undoubted potential of ML and DL techniques, it must be cautioned that these are data-driven approaches and no amount of "fancy math" can compensate for fundamental deficiencies in the data sets, so it will be largely wasted effort to pursue such techniques except on data sets that are validated and representative.[3]

## Notes

1. And conversely, restricted access to data will lead to poor decision making.
2. A collection of advanced artificial neural network (ANN) techniques.
3. A well-balanced discussion of the opportunities and constraints of applying these new technologies can be found at https://www.bluefieldresearch.com/podcast/water-quality-in-the-cloud-with-neno-duplan/ (accessed July 21, 2021).

# References

Albrecht, M. 2010. "Color Blindness." *Nature Methods* 7 (775). https://doi.org/10.1038/nmeth1010-775a.

Alwathaf, Y., and B. Mansouri. 2011. "Assessment of Aquifer Vulnerability Based on GIS and ARCGIS Methods: A Case Study of the Sana'a Basin (Yemen)." *Journal of Water Resource and Protection* 3 (12): 845-55. doi:10.4236/jwarp.2011.312094.

Appelo, C. A. J., and D. Postma. 2005. *Geochemistry, Groundwater and Pollution*, 2nd ed. Rotterdam: Balkema.

ARGOSS (Assessing the Risk to Groundwater from On-Site Sanitation). 2001. "Guidelines for Assessing the Risk to Groundwater from On-Site Sanitation." NERC, British Geological Survey Commissioned Report, CR/01/142, United Kingdom.

Attaran, A. 2006. "Will Negligence Law Poison the Well of Foreign Aid? A Case Comment on: Binod Sutradhar v. Natural Environment Research Council." *Global Jurist Advances* 6 (1). doi:10.2202/1535-1661.1191.

Ayers, R. S., and D. W. Westcott. 1994. "Water Quality for Agriculture." Food and Agriculture Organization (FAO), Irrigation and Drainage Paper 29, Rev. 1, Rome.

Bailey, R. T. 2017. "Review: Selenium Contamination, Fate, and Reactive Transport in Groundwater in Relation to Human Health." *Hydrogeology Journal* 25 (4): 1191-217. doi:10.1007/s10040-016-1506-8.

Barcelona, M. J., J. P. Gibb, J. A. Helfrich, and E. E. Garske. 1985. "Practical Guide for Ground Water Sampling." State Water Survey Publication 274 (EPA 600/S2-85-104), United States Environmental Protection Agency, Cincinnati, Ohio.

Barringer, J. L., Z. Szabo, and P. A. Reilly. 2013. "Occurrence and Mobility of Mercury in Groundwater." In *Current Perspectives in Contaminant Hydrology and Water Resources Sustainability*, edited by P. M. Bradley, 117-47. doi:10.5772/55487.

Bergen, K. J., P. A. Johnson, M. V. de Hoop, and G. C. Beroza. 2019. "Machine Learning for Data-Driven Discovery in Solid Earth Geoscience." *Science* 363 (6433). doi:10.1126/science.aau0323.

Box, G.E.P. 1976. "Science and Statistics." *Journal of the American Statistical Association* 71 (356): 791-9. doi:10.1080/01621459.1976.10480949.

Brassington. R. 2007. *Field Hydrogeology*, 3rd ed. Chichester: Wiley.

Brassington, F. C., and P. L. Younger. 2010. "A Proposed Framework for Hydrogeological Conceptual Modelling." *Water and Environment Journal* 24: 261-73.

Caldwell E.L, and L.W. Parr. 1937. "Ground Water Pollution and the Bored Hole Latrine." *Journal of Infectious Diseases* 61 (2): 148-183.

CGWB (Central Gound Water Board). 2020. "Uranium Occurrence in Shallow Aquifer in India." Department of Water Resources, River Development and Ganga Rejuvenation, Faridabad, India.

Chapelle, F. H. 2014. *Ground-water Microbiology and Geochemistry*, 2nd ed. Chichester: J. Wiley.

Chapman, P.M. 2007. "Determining When Contamination is Pollution - Weight of Evidence Determinations for Sediments and Effluents." *Environment International* 33 (4): 492-501.

Cherry, J. A., B. L. Parker, M. Einarson, S. W. Chapman, J. R. Meyer. 2015. Overview of Depth-Discrete Multilevel Groundwater Monitoring Technologies: Focus on Groundwater Monitoring in Areas of Oil and Gas Well Stimulation in California, Appendix 11, in "Recommendations on Model Criteria for Groundwater Sampling, Testing, and Monitoring of Oil and Gas Development in California" by B. Esser, H. Beller, S. Carroll, J. Cherry, J. Gillespie, R. Jackson, P. Jordan, V. Madrid, J. Morris, B. Parker, W. Stringfellow, C. Varadharajan, and A. Vengosh (2015), Lawrence Livermore National Laboratory.

Choudhury, I., K. M. Ahmed, M. Hasan, M. R. H. Mozumder, P. S. K. Knappett, T. Ellis, and A. van Geen. 2016. "Evidence for Elevated Levels of Arsenic in Public Wells of Bangladesh Due to Improper Installation." *Ground Water* 54 (6): 871-77.

CL:AIRE (Contaminated Land: Applications in Real Environments). 2008. "Principles and Practice for the Collection of Representative Groundwater Samples." Technical Bulletin 3, CL:AIRE. Haddenham, United Kingdom. www.claire.co.uk.

Damania, R., S. Desbureaux, A.-S. Rodella, J. Russ, and E. Zaveri. 2019. *Quality Unknown: The Invisible Water Crisis*. Washington, DC: World Bank. doi:10.1596/978-1-4648-1459-4.

EA (Environment Agency). 2003. “Guidance on Monitoring of Landfill Leachate, Groundwater and Surface Water.” EA, Bristol, United Kingdom. Accessed October 28, 2021. https://www.gov.uk/government/publications/monitoring-of-landfill-leachate-groundwater-and-surface-water-lftgn-02.

EA. 2019. “2021 River Basin Management Plans.” EA, Bristol, United Kingdom. Accessed October 28, 2021. https://consult.environment-agency.gov.uk/environment-and-business/challenges-and-choices/user_uploads/chemicals-in-the-water-environment-challenge-rbmp-2021-2.pdf

EAWAG (Swiss Federal Institute of Aquatic Science and Technology). 2015. *Geogenic Contamination Handbook: Addressing Arsenic and Fluoride in Drinking Water*, edited by C.A. Johnson and A. Bretzler. Dubendorf, Switzerland: EAWAG.

EGLE (Michigan Department of Environment, Great Lakes, and Energy). 2020. “Michigan Adopts Strict PFAS in Drinking Water Standards.” News Release, July 22. https://www.michigan.gov/egle/0,9429,7-135-3308_3323-534660--,00.html.

Enemark, T., L. J. M. Peeters, D. Mallants, and O. Batelaan. 2019. “Hydrogeological Conceptual Model Building and Testing: A Review.” *Journal of Hydrology.* 569: 310–29.

Ferguson, A. S., B. J. Mailloux, K. M. Ahmed, A. van Geen, L. D. McKay, and P. J. Culligan. 2011. “Hand-Pumps as Reservoirs for Microbial Contamination of Well Water.” *Journal of Water and Health* 90 (4): 708–17. doi: 10.2166/wh.2011.106

Fetter, C.W. (1993) Contaminant Hydrogeology. Macmillan Publishing Company. New York.

Fetter, C. W., T. Boving, and D. Kreamer. 2018. *Contaminant Hydrogeology*, 3rd ed. Waveland Press Inc. Long Grove, Illinois.

Frisbie, S. H., E. J. Mitchell, and B. Sarkar. 2015. “Urgent Need to Reevaluate the Latest World Health Organization Guidelines for Toxic Inorganic Substances in Drinking Water.” *Environmental Health* 14: 63. doi:10.1186/s12940-015-0050-7.

Gardner, M. 2012. “Improving the Interpretation of ‘Less Than’ Values in Environmental Monitoring.” *Water and Environment Journal* 26: 285–89. doi:10.1111/j.1747-6593.2011.00287.x

GW-MATE (Groundwater Management Advisory Team). 2006a. “Groundwater Monitoring Requirements for Managing Aquifer Response and Quality Threats.” Sustainable Groundwater Management Concepts and Tools, Briefing Note 9, GW-MATE, World Bank, Washington, DC.

GW-MATE. 2006b. “Natural Groundwater Quality Hazards: Avoiding Problems and Formulating Mitigation Strategies.” Sustainable Groundwater Management Concepts and Tools, Briefing Note 14, GW-MATE, World Bank, Washington, DC.

GW-MATE. 2009. A Hydrogeologic and Socioeconomic Evaluation of Community-based Groundwater Resource Management – The Case of Hivre Bazaar in Maharashtra-India. Case Profile Collection No 22. World Bank, Washington, DC.

Guo, H., W. Zhao, H. Li, W. Xiu, and J. Shen. 2018. “High Radionuclides in Groundwater of an Inland Basin from Northwest China: Origin and Fate.” *ACS Earth and Space Chemistry* 2 (11): 1137–44.

Gupta, S., and S. Banerjee. 2009. “Fluoride Accumulation in Paddy (Oryza Sativa) Irrigated with Fluoride Contaminated Groundwater in an Endemic Area of the Birbhum District, West Bengal.” *Fluoride* 42 (3): 224–27.

Gupta, S., and S. Banerjee. 2011. “Fluoride Accumulation in Crops and Vegetables and Dietary Intake in a Fluoride-Endemic Area of West Bengal.” *Fluoride* 44 (3): 153–57.

Handa, B.K. 1975. “Geochemistry and Genesis of Fluoride-Containing Ground Waters in India.” *Groundwater* 13: 275-281. doi:10.1111/j.1745-6584.1975.tb03086.x

Hashim, M. A., S. Mukhopadhyay, J. N. Sahu, and B. Sengupta. 2011. “Remediation Technologies for Heavy Metal Contaminated Groundwater.” *Journal of Environmental Management* 92 (10): 2355–88. doi:10.1016/j.jenvman.2011.06.009.

Hem, J.D. 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water*. 3rd Edition, US Geological Survey Water-Supply Paper 2254, University of Virginia, Charlottesville.

Hunter, J. 2011. “How Do We Know What We Know? Deming’s SoPK Part IV.” The Deming Files, *Process Excellence Network*, September 20. Accessed October 28, 2021. https://www.processexcellencenetwork.com/lean-six-sigma-business-performance/columns/an-introduction-to-deming-s-theory-of-knowledge-on.

ITRC (Interstate Technology and Regulatory Council). 2007. *Protocol for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater.* Washington, DC: ITRC Diffusion/Passive Sampler Team. www.itrcweb.org. Accessed October 28, 2021. https://connect.itrcweb.org/HigherLogic/System/DownloadDocumentFile.ashx?DocumentFileKey=a163426b-4043-4971-b488-e10650aa6e35

Jiao, J., and V. Post 2019. *Coastal Hydrogeology*. Cambridge, United Kingdom: Cambridge University Press

Kitanidis, P. K. 1997. *Introduction to Geostatistics: Applications in Hydrogeology*. Cambridge, United Kingdom: Cambridge University Press.

Kubier, A., R. T. Wilkin, and T. Pichler. 2019. "Cadmium in Soils and Groundwater: A Review." *Applied Geochemistry* 108: 104388.

Langmuir, D. 1997. Aqueous Environmental Geochemistry. Prentice Hall. Upper Saddle River, NJ.

Lewis, W. J., S. S. D. Foster, and B. S. Drasar. 1982. *The Risk of Groundwater Pollution by On-site Sanitation in Developing Countries.* International Reference Centre for Wastes Disposal, IRCWD-Report No. 01/82. Duebendorf, Switzerland.

Madhnure, P., P. N. Rao, K. M. Prasad, A. D. Rao, and J. S. Kumar. 2018. "Hydrochemical Evaluation of Fluoride-Rich Groundwater in Cherlapalli Watershed, a Fluorosis Endemic Area, Nalgonda District, Telangana State." In *Clean and Sustainable Groundwater in India*, edited by D. Saha, S. Marwaha, and A. Mukherjee. *Springer Hydrogeology 6:* 81-94. doi:10.1007/978-981-10-4552-3.

Malakar, P., S. Sarkar, A. Mukherjee, S. Bhanja, and A. Y. Sun. 2021. "Use of Machine Learning and Deep Learning Methods in Groundwater." In *Global Groundwater Source, Scarcity, Sustainability, Security, and Solutions*, edited by A. Mukherjee, B. R. Scanlon, and A. A. McKenzie, 545-57. Mahwah, NJ: Elsevier.

McArthur, J. M., D. M. Banerjee, S. Sengupta, P. Ravenscroft, S. Klump, A. Sarkar, B. Disch and R. Kipfer. 2010. "Migration of As, and 3H/3He Ages, in Groundwater from West Bengal: Implications for Monitoring." *Water Research* 44: 4171-85.

McCleskey, R. B, D. K. Nordstrom, and A. S. Maest. 2004 "Preservation of Water Samples for Arsenic (III/V) Determinations: An Evaluation of the Literature and New Analytical Results." *Applied Geochemistry* 19 (7): 995-1009.

Mishan, E. J. 1974. "What Is the Optimal Level of Pollution?" *Journal of Political Economy* 82 (6): 1287-99.

Monmonier, M. 1991. *How to Lie with Maps,* 3rd ed. Chicago, United States: University of Chicago Press.

Moore, R. B., and W. W. Staubitz. 1984. *Distribution and Source of Barium in Ground Water at Cattaraugus Indian Reservation, Southwestern New York*. U.S. Geological Survey, Water-Resources Investigations Report 84-4129. New York. doi:10.3133/wri844129.

Nielsen, D. M., and G. L. Nielsen. 2006. *The Essential Handbook of Ground-water Sampling.* Boca Raton: CRC Press.

Oze, C., D. K. Bird, and S. Fendorf. 2007. "Genesis of Hexavalent Chromium from Natural Sources in Soil and Groundwater." *Proceedings of the National Academy of Sciences of the United States of America (PNAS)* 104 (16): 6544-49. doi: 10.1073/pnas.0701085104.

Parker, B. L., J. A. Cherry, and B. J. Swanson. 2006. "A Multilevel System for High-Resolution Monitoring in Rotosonic Boreholes." *Ground Water Monitoring and Remediation* 26 (4): 57-73.

Parker, L. V., and C. H. Clark. 2002. "Study of Five Discrete Interval-Type Groundwater Sampling Devices." Technical Report ERDC/CRREL TR-02-12, Washington, DC: Engineer Research and Development Center, U.S. Army Corps of Engineers.

Post, V., H. Kooi, and C. Simmons. 2007. "Using Hydraulic Head Measurements in Variable-Density Ground Water Flow Analyses." *Ground Water* 45 (6): 664-71.

Prager, J. C. 1998. *Environmental Contaminant Reference Databook*. Vol. 1-3. Wiley-Blackwell. New York.

Rau, G. C., M.O. Cuthbert, V.E.A. Post, D. Schweizer, R.I. Acworth, M.S. Andersen, P. Blum, E. Carrara, T.C. Rasmussen and S. Ge. 2020. "Future-Proofing Hydrogeology by Revising Groundwater Monitoring Practice." *Hydrogeology Journal* 28: 2963-69. doi:10.1007%2Fs10040-020-02242-7.

Ravenscroft, P., and J. M. McArthur. 2004. "Mechanism of Regional Enrichment of Groundwater by Boron: The Examples of Bangladesh and Michigan, USA." *Applied Geochemistry* 19 (9): 1413-30. https://doi.org/10.1016/j.apgeochem.2003.10.014.

Ravenscroft, P., Z.H. Mahmud, M.S. Islam, A.K.M.Z. Hosain, A. Zahid, G.C. Saha, A.H.M. Zulfiquar Ali, K. Islam, S. Cairncross, J.D. Clemens and M.S Islam. 2017. "The Public Health Significance of Latrines Discharging to Groundwater Used for Drinking." *Water Research Volume* 124: 192-201. doi:10.1016/j.watres.2017.07.049.

Ravenscroft, P., H. Brammer, and K. S. Richards. 2009. *Arsenic Pollution: A Global Synthesis.* Chichester: Wiley-Blackwell.

Riedel, T., and C. Kübeck. 2018. "Uranium in Groundwater: A Synopsis Based on a Large Hydrogeochemical Data Set." *Water Research* 129: 29-38.

Rushton, K. R. 2003. *Groundwater Hydrology: Conceptual and Computational Models*. Chichester: Wiley.

Rushton, K. R. 2009. "Recollections of an Inquiring Engineer." *Groundwater* 47 (5): 745-49.

Shen, C. 2018. "A Transdisciplinary Review of Deep Learning Research and Its Relevance for Water Resources Scientists." *Water Resources Research* 54 (11): 8558-93. doi:10.1029/2018WR022643.

Sherrod, L., W. Sauck, and D. D. Werkema. 2012. "A Low-Cost, In Situ Resistivity and Temperature Monitoring System." *Ground Water Monitoring and Remediation* 32 (2): 31-39.

Smedley, Pauline L., and David G. Kinniburgh. 2017. “Molybdenum in Natural Waters: A Review of Occurrence, Distributions and Controls.” *Applied Geochemistry* 84: 387-432. https://doi.org/10.1016/j.apgeochem.2017.05.008.

Smith A., E.O. Lingas, and M. Rahman. 2000. “Contamination of Drinking-Water by Arsenic in Bangladesh: A Public Health Emergency.” *Bulletin of the World Health Organization* 78 (9): 1093-103.

Solinst Canada Ltd. *Solinst Waterloo System*: Model 401 Data Sheet. Georgetown, Ontario Canada. Accessed October 28, 2021. https://solinst.com/products/data/401.pdf.

Spiegelhalter, D. 2018. *The Art of Statistics.* London: Pelican Books.

Stumm, F., and M. D. Como. 2017. “Delineation of Salt Water Intrusion through Use of Electromagnetic-Induction Logging: A Case Study in Southern Manhattan Island, New York.” *Water* 9: 631. doi:10.3390/w9090631. Available at: www.mdpi.com/journal/water.

Sundaram, B., A. Feitz, P. de Caritat, A. Plazinska, R. Brodie, J. Coram, and T. Ransley. 2009. *Groundwater Sampling and Analysis - A Field Guide.* Geoscience Australia, Record 2009/27.

The Open University. 2006. *Water and Well-Being. S250 Science in Context*. United Kingdom.

UNICEF and WHO. 2018. “Arsenic Primer: Guidance on the Investigation & Mitigation of Arsenic Contamination.” UNICEF, New York.

UNIDO (United Nations Industrial Development Organization). 2016. “Identification Assessment and Prioritization of Pollution Hot Spots.” UNIDO. Vienna.

USEPA (United States Environmental Protection Agency). 1996. “Ambient Ground Water Quality Monitoring Cost Analysis.” EPA 816-R-97-013. USEPA, Washington, DC.

Velasco, V., I. Tubau, E. Vázquez-Suñè, R. Gogu, D. Gaitanaru, M. Alcaraz, A. Serrano-Juan, D. Fernàndez-Garcia, T. Garrido, J. Fraile, and X. Sanchez-Vila. 2014. “GIS-Based Hydrogeochemical Analysis Tools (QUIMET).” *Computers and Geosciences* 70: 164–80. doi:10.1016/j.cageo.2014.04.013.

Vroblesky, D. A. 2001. *User’s Guide for Polyethylene-Based Passive Diffusion Bag Samplers to Obtain Volatile Organic Compound Concentrations in Wells.* U.S. Geological Survey, Water-Resources Investigations Report 01-4060. Columbia, South Carolina. Accessed October 28, 2021. https://connect.itrcweb.org/HigherLogic/System/DownloadDocumentFile.ashx?DocumentFileKey=1092f110-9f2e-4534-b6a0-157f479038ae

Ward, M. H., R.R. Jones, J. D. Brender, T.M. De Kok, P.J. Weyer, B.T. Nolan, C. M. Villanueva, and S.G. Van Breda. 2018. “Drinking Water Nitrate and Human Health: An Updated Review.” *International Journal of Environmental Research and Public Health* 15 (7): 1557. doi:10.3390/ijerph15071557.

Wasserman, G. A., X. Liu, F. Parvez, H. Ahsan, D. Levy, P. Factor-Litvak, J. Kline, A. v. Geen, V. Slavkovich, N. J. LoIacono, Z. Cheng, Y. Zheng and J. H. Graziano. 2006. “Water Manganese Exposure and Children’s Intellectual Function in Araihazar, Bangladesh.” *Environmental Health Perspectives* 114 (1): 124-29. doi:10.1289/ehp.8030.

Weight, W. D. 2008. *Hydrogeology Field Manual,* 2nd ed. New York: McGraw-Hill.

Weiss, F. T., M. Leuzinger, C. Zurbrügg, and R. I. L. Eggen. 2016. Chemical Pollution in Low and Middle-Income Countries. EAWAG (Swiss Federal Institute of Aquatic Science and Technology). Dübendorf, Switzerland.

WHO (World Health Organization). 2018. National chemicals registers and inventories: benefits and approaches to development. WHO, Copenhagen. Accessed October 28, 2021. https://www.euro.who.int/__data/assets/pdf_file/0018/361701/9789289052948-eng.pdf

World Bank. 2010. “Deep Wells and Prudence: Towards Pragmatic Action for Addressing Groundwater Overexploitation in India.” World Bank, Washington, DC.

Wilkinson, M. D., M. Dumontier, I. J. Aalbersberg, G. Appleton, M. Axton, A. Baak, N. Blomberg, J.-W. Boiten, L. Bonino da Silva Santos, P. E. Bourne, J. Bouwman, A. J. Brookes, T. Clark, M. Crosas, I. Dillo, O. Dumon, S. Edmunds, C. T. Evelo, R. Finkers, A. Gonzalez-Beltran, A. J. G. Gray, P. Groth, C. Goble, J. S. Grethe, J. Heringa, P. A. C. ‘t Hoen, R. Hooft, T. Kuhn, R. Kok, J. Kok, S. J. Lusher, M. E. Martone, A. Mons, A. L. Packer, B. Persson, P. Rocca-Serra, M. Roos, R. van Schaik, S.-A. Sansone, E. Schultes, T. Sengstag, T. Slater, G. Strawn, M. A. Swertz, M. Thompson, J. van der Lei, E. van Mulligen, J. Velterop, A. Waagmeester, P. Wittenburg, K. Wolstencroft, J. Zhao, and B. Mons. 2016. “The FAIR Guiding Principles for Scientific Data Management and Stewardship.” *Scientific Data* 3: 160018. doi:10.1038/sdata.2016.18.

Williams, A. J., J. C. Lambert, K. Thayer, and J. C. M. Dorne. 2021. “Sourcing Data on Chemical Properties and Hazard Data from the US-EPA CompTox Chemicals Dashboard: A Practical Guide for Human Risk Assessment.” *Environment International* 154: 106566. doi:10.1016/j.envint.2021.106566.

GWSP
GLOBAL WATER
SECURITY & SANITATION
PARTNERSHIP

WORLD BANK GROUP

W21038