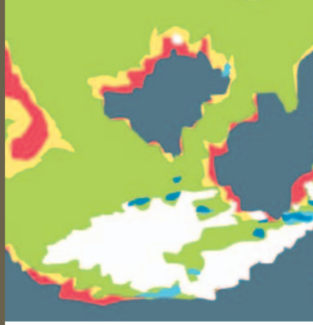

Hydrogeochemical Processes and Controls on Water Quality and Water Management

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The chemical constituents in water determine its potability, usability for agriculture and recreation, and interactions with biological systems. Anthropogenic processes have significantly influenced the geochemistry of water in many regions. Physical, chemical, and biological processes control the chemistry and chemical evolution of water in natural and contaminated systems. Advances in our ability to quantify these processes will improve our ability to manage our water resources, help us identify potential sources of contamination, and illuminate potential solutions to water-quality problems. Particularly impressive are the applications of chemical and isotopic tracers, which can track water movement and quantify water fluxes on the surface and in the subsurface. To better address societal needs, future advances will require a holistic approach to interpreting geochemical data.

Keywords: water resources, hydrogeochemistry, aqueous geochemistry, contaminants, isotopes, groundwater

INTRODUCTION

Hydrogeochemistry, a field combining hydrology and mineral/rock chemistry, is at the heart of many water resource issues for three reasons. First, chemicals and isotopes dissolved in water are excellent tracers for quantifying Earth's water reservoirs and the fluxes across reservoirs in the hydrologic cycle, both globally and locally (Fig. 1). Second, chemical knowledge is essential for understanding water-quality problems; for example, the concentrations and speciation of chemicals in water directly affect its potability and usability for agriculture and recreation. The deterioration of water quality can be either natural (geogenic) or human induced (anthropogenic). Third, possible modifications of hydrogeochemical processes that affect water quality are a key element in strategies for addressing future global warming and energy challenges.

One aspect of hydrogeochemistry concerns *water quantity and fluxes*. Hydrogeochemical data on water resources and fluxes are essential for sustainable management and for meeting human needs (see Table 1 in Oelkers et al. 2011 this issue, for water distribution in Earth's various reservoirs). Historically, studies of stable H and O isotopes have played a pivotal role in understanding the hydrologic cycle (Gat 1996). Ninety-eight percent of Earth's accessible freshwater reserves lie underground (as groundwater), but determining how much water can be "safely" extracted is challenging and controversial (Schwartz and Ibaraki 2011 this issue).

Geochemical tracers—such as Cl, the isotopes ^{14}C, ^{3}H, ^{36}Cl, ^{4}He, and ^{81}Kr, and the noble gases—have been used to estimate aquifer recharge rates and to determine groundwater ages (e.g. Phillips and Castro 2004). Trace gases and exotic isotopes have also allowed hydrogeochemists to use old water stored in aquifers as archives of paleoenvironmental information (Siegel 1991; Edmunds 2001). In recent years, we have recognized that submarine groundwater discharges into coastal oceans (Fig. 1), contributing 5–10% of freshwater inflows to oceans, as well as being a significant source of nutrients and pollutants for coastal ecosystems. These effusive fluxes to oceans are difficult to quantify with physical measurements, but geochemical tracers, such as the U/Th series radionuclides, prove to be effective tools (Swarzenski 2007).

Water quality refers generally to various chemical, physical, and biological characteristics. The required "quality" of water depends greatly on the purpose for which it is intended (e.g. drinking, swimming, or fishing), but it is mostly linked to drinking water standards (see Box 1). The connection between geochemistry and water quality is direct and obvious. The most important supplies of potable freshwater occur in the shallow subsurface. Accordingly, the geochemical processes that control the chemistry of freshwater bodies are closely coupled to microbiologic activities, climate forcing, atmospheric inputs, and physical transport processes.

The influence and importance of water quality on society are illustrated by the acute human health problems related to arsenic contamination of shallow wells in Bangladesh and southern India (Charlet and Polya 2006; Polya and Charlet 2009). High arsenic concentrations occur naturally in the sediments of the Ganges Delta, where arsenic compounds are adsorbed onto iron oxyhydroxide and

Box 1 EXAMPLES OF MAXIMUM CONTAMINANT LEVELS ALLOWED IN DRINKING WATER (MG L^{-1})

Chemicals	EU	WHO	USA	Primary Sources
arsenic	0.01	0.01	0.01	natural and industrial pollution
lead	0.01	0.01	0.015	plumbing, paints, fuels
nitrate	50	50	10 as N	agriculture
PCBs			0.0005	industrial products and wastes
Solids TDS*			500	natural

EU: European Union; WHO: World Health Organization; USA: US Environmental Protection Agency. * Secondary drinking water standard for total dissolved solids (TDS)

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sulfide minerals. Anthropogenic processes have led to the mobilization of the arsenic into shallow groundwater. Ninety percent of the local population use groundwater for drinking. As a result, about 21 million people are currently exposed to arsenic contamination and could suffer adverse health effects.

BIOGEOCHEMICAL PROCESSES AND FRESHWATER CHEMISTRY

The abundance and temporal-spatial distributions of chemicals and isotopes in freshwater are a result of the various hydrogeochemical processes occurring in the hydrologic cycle (FIG. 1).

Atmospheric Mass Inputs

Rainwater is chemically altered as it falls through the atmosphere. Rainwater dissolves and incorporates sea salt aerosols as well as sulfate, ammonium, and nitrate from natural and human sources such as power plants, automobile exhaust, smelters, and agriculture. Rainwater also equilibrates with atmospheric CO_2, which has a partial pressure of $10^{-3.4}$ bar, giving unpolluted rainwater a pH of around 5–6. This water can also be chemically altered as it reacts with dry particulate aerosols on the ground accumulated between precipitation events.

Processes at the Earth's Surface and in the Recharge Zone

The chemistry of most surface water and shallow groundwater is the result of water–rock–gas interactions. Water evaporation concentrates solutes and may lead to the crystallization of minerals such as calcite and gypsum. The combination of evaporation and mineral precipitation can lead to high Na^+, Cl^-, and/or SO_4^{2-} concentrations. Soil gases commonly have partial CO_2 pressures of $10^{-2.5}$ to $10^{-1.5}$ bar because of root respiration and organic matter decay. Water percolation through organic-rich soil can, therefore, further lower pH, leading to mineral dissolution. Weathering reactions in the soil zone include the dissolution of unstable silicates, ion exchange reactions, and clay mineral precipitation. Carbonate and sulfate mineral dissolution/precipitation and ion exchange reactions are fast, and water commonly establishes equilibrium with these minerals and mineral surfaces. In contrast, silicate mineral dissolution in nature is controlled by slow kinetics, and the precipitation of secondary clay minerals is an even more sluggish process.

TABLE 1 COMMON RANGES OF SOLUTE CONCENTRATIONS IN UNPOLLUTED FRESHWATER§

Element	Range (mmol L^{-1})	Sources
Na^+	0.1–2	Feldspar, rock salt, atmosphere, cation exchange
K^+	0.01–0.2	Feldspar, mica
Mg^{2+}	0.05–2	Dolomite, serpentine, pyroxene, amphibole, olivine, mica
Ca^{2+}	0.05–5	Carbonate, gypsum, feldspar, pyroxene, amphibole
Cl^-	0.05–2	Rock salt, atmosphere
HCO_3^-	0–5	Carbonates, atmosphere
SO_4^{2-}	0.01–5	Atmosphere, gypsum, sulfide
NO_3^-	0.001–0.2	Atmosphere, organic matter
H_4SiO_4	0.02–1	Silicates

§ After Appelo and Postma (2005)

These processes control the chemistry of potable surface water and shallow groundwater, which leads to waters commonly containing Ca^{2+}, Na^+, Mg^{2+}, K^+, HCO_3^-, Cl^-, SO_4^{2-}, and H_4SiO_4 as the major solutes. TABLE 1 summarizes common concentration ranges and sources of these constituents.

Redox Processes

Redox (oxidation and reduction) processes exert significant controls on freshwater chemistry, especially on the major elements O, C, S, N, and Fe and on trace contaminants such as U and As. Redox reactions involve electron transfer and result in valence changes. Globally, the driver of almost all redox reactions near the Earth's surface is photosynthesis. With few exceptions, the ultimate oxidant is O_2 and the ultimate reductant is organic matter. The redox condition of a hydrologic system is thus commonly determined by the supply of organic matter on the one hand and the supply of O_2 and other electron acceptors, such as sulfate and ferric iron, on the other.

The redox reaction sequence is determined by the relative Eh (oxidation potential) values of the redox reactions; an example of a reaction sequence is given in TABLE 2. When organic matter is added to a closed aqueous system, O_2 reduction occurs first, followed by NO_3^- reduction, and then, in order, MnO_2, $Fe(OH)_3$, and SO_4^{2-} reduction. Such a sequence can be monitored by the disappearance of O_2, NO_3^-, and SO_4^{2-}, and by an increase in NO_2^-, $N_2(g)$, Mn^{2+},

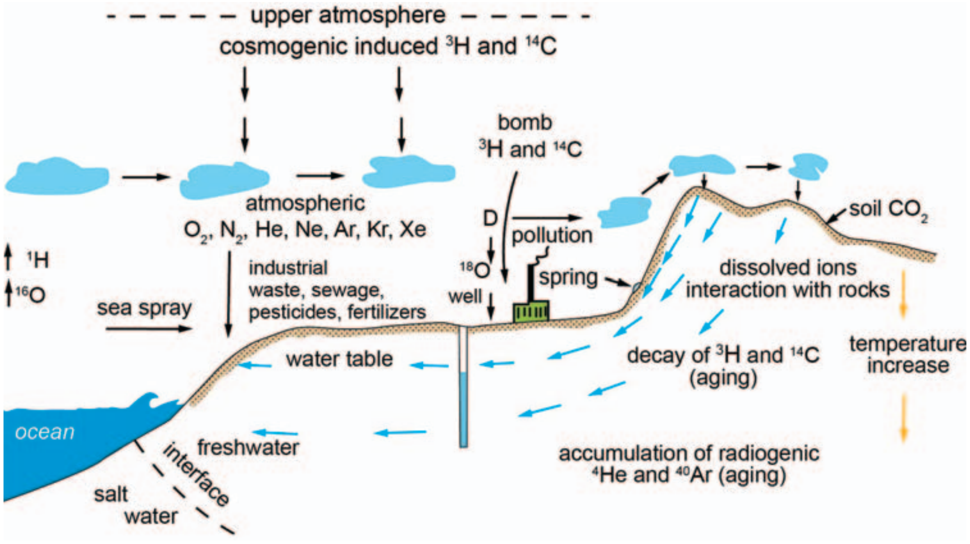


FIGURE 1 Mass sources and chemical processes in the hydrologic cycle. From left to right, ocean water evaporates and the moisture is enriched with ^1H and ^{16}O. Atmospheric water dissolves cosmogenic ^{14}C, ^{36}Cl, and ^3H, equilibrates with O_2, N_2, CO_2, and noble gases, and dissolves sea salts and industrial pollutants. Water condenses and precipitates, producing rain and snow enriched in ^2H and ^{18}O. Once on the ground, rainwater dissolves dry-deposit aerosols. As water enters the soil, it dissolves CO_2 from organic matter decay, and the acidified water dissolves carbonates and weathers silicate minerals. Underground and isolated from the atmosphere, ^{14}C and ^3H decay with time, permitting estimates of groundwater ages. Fresh groundwater in the coastal area interacts with salt water. Large withdrawals of freshwater from the subsurface can cause encroachment of salt water from the ocean. AFTER MAZOR (1991), REPRINTED WITH PERMISSION FROM DEKKER

TABLE 2 SEQUENCE OF REDOX PROCESSES, OR REDOX LADDER, AT PH 7 AND 25 °C IN A NATURAL SYSTEM[§]

Reactions	Eh (V)	Assumptions
$O_2(g) + 4H^+ + 4e^- = 2H_2O$	0.816	$P_{O_2} = 0.2$ bar
$NO_3^- + 6H^+ + 5e^- = ½ N_2(g) + 3H_2O$	0.713	$[NO_3^-] = 10^{-3}$ M, $P_{N2} =$ 0.8 bar
MnO_2 (pyrolusite) $+ 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	0.544	$[Mn^{2+}] = 10^{-4.74}$ M
$NO_3^- + 2H^+ + 6e^- = NO_2^- + H_2O$	0.431	$[NO_3^-] = [NO_2^-]$
$NO_2^- + 8H^+ + 6e^- = NH_4^+ + 2H_2O$	0.340	$[NO_2^-] = [NH_4^+]$
$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O$	0.014	$[Fe^{2+}] = 10^{-4.75}$ M
$SO_4^{2-} + 10H^+ + 8e^- = H_2S(aq) + 4H_2O$	-0.217	$[SO_4^{2-}] = [H_2S]$
$HCO_3^- + 9H^+ + 8e^- = CH_4(aq) + 3H_2O$	-0.260	$[HCO_3^-] = [CH_4]$

§ After Langmuir (1997)

e^- = electrons; Eh is in volts (V); square brackets = molar (M) concentration; P = partial pressure

Fe^{2+}, H_2S, and CH_4 in water. This sequence has been observed in vertical profiles of eutrophic lakes, marine sediments, and aquifers, although it generally does not manifest itself in idealized or complete form. Redox zonation corresponds to successive dominance of different microbes that use different metabolic pathways according to the decreasing energy available from the reduction reaction (Chapelle 2000). In aquifers, redox zones can develop over hundreds of meters to several kilometers, as waters evolve along flow systems. Groundwater impacted by organic contaminants can also exhibit zonation. FIGURE 2 shows redox zoning developed from the leakage of landfill leachate into an aquifer; the zones are delineated based on the redox characteristics of the water. Generally, complete separation of zonation is not observed in groundwater, and various redox couples, as well as their respective microbial groups, may overlap.

Redox reactions affect water quality in many ways. For example, microbially mediated oxidation of pyrite and other sulfide minerals produces acid mine drainage, which has contaminated thousands of mountain streams around the world. The mobility of trace contaminants can depend on their redox state, as is the case for uranium. Hexavalent uranium (UO_2^{2+}) is mobile, particularly when complexed with bicarbonate. The reduction of U^{6+} to U^{4+} typically results in the precipitation of uraninite (UO_2), which immobilizes the uranium. This chemical reaction has been exploited in the bioremediation of uranium-contaminated groundwater. For example, in Oak Ridge, Tennessee, USA, where groundwater was contaminated by the disposal of uranium and nitrate wastes resulting from weapons production, the injection of nutrients (organic compounds) into aquifers stimulates microbial activity, which sequentially reduces O_2, NO_3^-, Fe^{3+}, SO_4^{2-}, and UO_2^{2+} (Istok et al. 2010).

Adsorption Processes

Adsorption to mineral surfaces, rather than mineral solubility, is the process that generally controls the concentration of most contaminants (e.g. F^-, As^{3+}, As^{5+}, Pb^{2+}, and UO_2^{2+}) that are present at the parts per million to parts per billion level in aquifers, soils, and sediments. Porous media in the subsurface have large mineral surface areas. Fe and Mn oxyhydroxides commonly play a major role in element adsorption; although they constitute a minor fraction of the bulk rock, soil, or sediment, their large surface areas and high reactivities make them efficient scavengers of trace metals and radionuclides. The fate and cycling of trace elements are, therefore, closely tied to the redox cycles of Fe and Mn. For example, arsenic release from iron mineral surfaces to groundwater in Bangladesh is thought to result from microbial reduction of iron minerals and subsequent desorption of arsenic (Neumann et al. 2010).

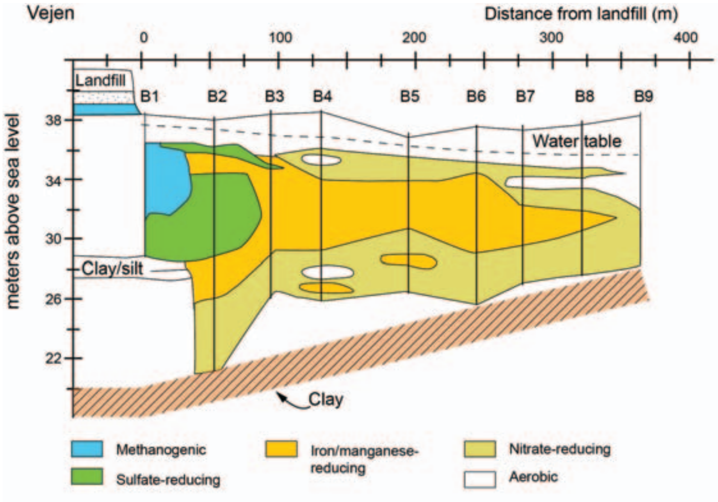


FIGURE 2 Redox zones characterized by water chemistry were developed in a sandy aquifer contaminated by organic contaminants leaking from the Vejen Landfill in Denmark (upper left). Groundwater flows from left to right, and the zonation is complicated by the distribution of NO_3^- and SO_4^{2-} in the mobile phase (water) and Fe and Mn oxyhydroxides in the immobile phases (aquifer matrix). B1 to B9 denote boreholes. AFTER LYNGKILDE AND CHRISTENSEN (1992), REPRINTED WITH PERMISSION FROM ELSEVIER

Much progress has been made in understanding adsorption processes. Fe and Mn oxyhydroxides and many other minerals have charged surfaces in aqueous solution, and their surfaces are neutralized when ions such as H^+ and metals are adsorbed. The adsorption of cations can be regarded as a competition between cations and H^+ for surface sites (Drever 1997). At low pH, cation adsorption is minimal (FIG. 3A). As the pH rises, there is a relatively

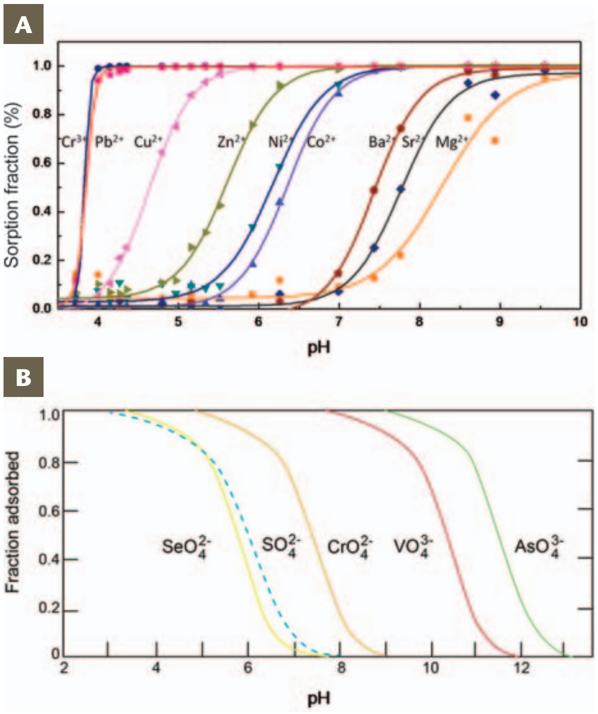


FIGURE 3 Adsorption of (**A**) metals and (**B**) anions onto the surface of ferrihydrite as a function of pH (the "sorption edges"). Metal sorption experiments were performed at ambient conditions, with 10 mmol L^{-1} $Fe(NO_3)_3$ in 10 mmol L^{-1} KNO_3 background solution, and metal concentrations of 1 ppm (Zhu et al. unpublished data). Anion edges in B are schematic. The exact locations of the edges will shift with different adsorbate/ferrihydrite ratios and background electrolyte solutions.

narrow pH range over which adsorption changes from near zero to essentially complete (Fig. 3a). These "adsorption edges" vary for different metals and shift according to different sorbate/sorbent ratios and background electrolyte concentrations. Anions compete with OH^- for adsorption sites, so their pH dependence is the opposite of cation adsorption (Fig. 3b). Anion adsorption is often complicated by changes in the speciation of the adsorbing element as pH changes.

Adsorption processes can explain why different metals have different mobilities in the environment, as shown in the Nickel Rim mine tailings site example, described in more detail below. However, modeling surface adsorption and trace element mobility in natural systems is a complex problem. The distribution of the adsorbents (Fe and Mn oxyhydroxides, organic matter, clays) in geological systems is spatially heterogeneous, and the Fe and Mn oxyhydroxides in the environment more often than not have different properties from those of the phases used in laboratory experiments. Reduction of Mn and Fe oxyhydroxides generally results in the release of adsorbed elements into water, as described above.

ANTHROPOGENIC INFLUENCES ON WATER QUALITY

Point-Source Contamination: The Nickel Rim Mine Tailings Impoundment, Sudbury, Canada

Inappropriate disposal of hazardous materials can lead to groundwater and surface water contamination. When originating from a single, well-defined source, such a contamination is referred to as a "point-source" contamination. The groundwater contamination from the Nickel Rim Ni–Cu mine tailings site near Sudbury, Canada (Johnson et al. 2000) is illustrative of thousands of point-source problems throughout the world.

The oxidation of sulfide minerals, principally pyrrhotite, has generated acidic waters with pH values as low as 2.1 and high concentrations of Fe (up to 9800 mg L^{-1}), SO_4^{2-} (24,000 mg L^{-1}), Al (1130 mg L^{-1}), Ni (688 mg L^{-1}), and other dissolved constituents (Johnson et al. 2000). Groundwater flow through the tailings is mainly horizontal, with velocities of 4–8 m y^{-1} (Fig. 4). As the acidic water flows, its chemistry evolves remarkably within a short distance. Distinct pH zones with values of around 3.0, 4.1, 5.6, and 6.7 are developed as the acidic water reacts with calcite and aluminosilicates in the tailings and is buffered by reactions with iron oxyhydroxides, aluminum hydroxide, siderite, and calcite, respectively (Fig. 4; see Box 2).

Box 2 REACTIONS AND PROCESSES AT THE NICKEL RIM TAILINGS IMPOUNDMENT

Microbially mediated oxidation of sulfide:
$Fe_{(1-x)}S$ (pyrrhotite) + $(2-0.5x)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + 2xH^+ + SO_4^{2-}$
or
$Fe_{(1-x)}S + \frac{1}{2}O_2 + 2H^+ \rightarrow (1-x)Fe^{2+} + S^o + H_2O$
$S^o + 3/2O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}$
Successive buffer reactions due to dissolution of carbonates:
pH ≈ 3: $Fe(OH)_3$ (ferrihydrite) + $3H^+ = Fe^{3+} + 3H_2O$
pH ≈ 4.1: $Al(OH)_3$ (gibbsite) + $3H^+ = Al^{3+} + 3H_2O$
pH ≈ 5.6: $FeCO_3$ (siderite) + $H^+ = Fe^{2+} + HCO_3^-$
pH ≈ 6.7: $CaCO_3$ (calcite) + $H^+ = Ca^{2+} + HCO_3^-$
Other chemical reactions:
Weathering of biotite, pyroxene, amphibole, and plagioclase in acidic water
Jarosite precipitation and decomposition
Gypsum precipitation

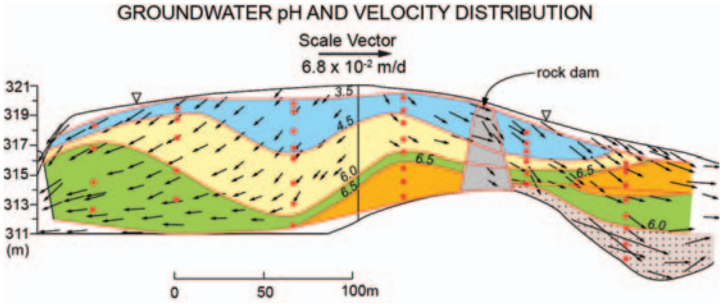


Figure 4 Distributions of pore water pH and simulated groundwater flow directions and velocities (shown by the oriented arrows of variable length) in a profile through the Nickel Rim mine tailings impoundment near Sudbury, Ontario, Canada. The red dots denote locations of pore water samples. The red lines show pH contours with pH values labeled above. The colored zones indicate zones of pH values controlled by successive buffer reactions (see Box 2). White: Fe oxyhydroxide, pH <3.5; blue: Al oxyhydroxide, pH 3.5–4.5; yellow and green: siderite and calcite, pH 4.5–6.0/6.5; and orange: calcite, pH > 6.5. Note that the vertical and horizontal scales are different. After Johnson et al. (2000), reprinted with permission from Elsevier

Concentrations of dissolved metals, such as Ni, Cr, and Co, are attenuated by coprecipitation with and adsorption onto Fe and Al hydroxides. Jarosite [e.g. $KFe_3(SO_4)_2(OH)_2$] and gypsum also precipitate, and their accumulation, together with iron oxyhydroxides in the oxidation zone, forms "hardpan" that cements the tailings.

This case illustrates the link between hydrogeochemistry and traditional mineralogy, petrology, and geochemistry: understanding the overall processes requires careful mineralogical characterization of the system and the buffer reactions that occur (see Zhu and Anderson 2002).

Worldwide, there are thousands of sites contaminated by mining wastes and mine tailings. While decommissioning and remediation have been going on for decades in developed countries, remediation of such sites in developing countries and emerging economies is just starting or has not yet begun. The recent disaster resulting from the breach of a bauxite residue impoundment in Hungary, which allowed 200 million gallons of sludge to flow through waterways and into the Danube River, is a harsh reminder of the potential magnitude of these problems (Bakhshi 2011). The incident caused 9 deaths and injuries to 122 people. The sludge had a pH of 13 and extinguished most life in local rivers.

Non-Point-Source Contamination of Lake Taihu, China

Contamination of groundwater and surface water can also originate from non–point sources. These problems are often directly related to the application of fertilizers and pesticides, urban runoff, or waste disposal in and around large cities (Johnston et al. 2011 this issue). Of particular concern are macronutrients (e.g. NO_3^- and PO_4^{3-}) and agrochemicals (e.g. herbicides and insecticides).

The problems resulting from non-point-source as well as point-source contamination can be illustrated using the example of Lake Taihu (Fig. 5a), the third-largest freshwater lake in China. The lake has an area of about 2340 km^2 and an average depth of about 1.9 m; some 40 million people live in the lake's 36,500 km^2 basin. The lake is the main source of drinking water for Wuxi and neighboring cities. The area contributes 14% of China's gross national product. In the summer of 2007, the two million residents of Wuxi found odorous water coming from their taps. Volatile sulfide chemicals, including methyl thiols, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide, were the source of the odor. These contaminants originated from the decomposition of a massive cyanobacterial bloom caused by the eutrophication (SEE BOX 3) of Lake Taihu (Zhang et al. 2010).

The 2007 crisis at Lake Taihu illustrates how stresses associated with eutrophication can push an aquatic system beyond the tipping point, with severe consequences (see Prepas and Chartette 2005 for a discussion of eutrophication problems worldwide). The excessive loading (input) of nutrients to Lake Taihu comes from point sources such as untreated domestic sewage effluents and from non–point sources like the intensively fertilized agricultural lands around the lake and urban runoff. High nutrient input to the lake and warm temperatures created conditions promoting phytoplankton blooms (FIG. 5B). Nitrogen stable isotope studies show that riverine N inputs in winter are influenced by the discharge of human sewage into rivers and the lake (Townsend-Small et al. 2007). In spring, however, wastewater inputs to the lake are matched by fertilizers, atmospheric contributions, and/or N_2-fixation sources. During the rainy season, rainwater NO_3^- concentrations are high and isotopically enriched compared to other potential sources, indicating that rain may be a significant or even dominant source of N to the lake at that time of the year.

The International Lake Environment Committee, in cooperation with the United Nations Environment Program, undertook a survey of 217 lakes worldwide and found that 54% of lakes in Asia are eutrophic, compared to 41% in South America and 28% in Africa (Jørgensen 2001). The greatest water-quality problems are found in countries with large populations but scarce financial resources. The regulation of nutrients to protect drinking water supplies is urgently needed (see Johnston et al. 2011).

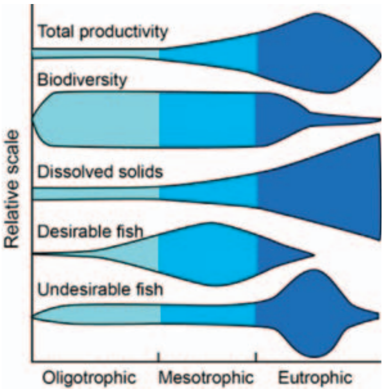
NEW OPPORTUNITIES AND CHALLENGES FOR HYDROGEOCHEMISTRY

Progress in hydrogeochemical research has produced major insights into both natural and anthropogenically impacted hydrologic systems. While we will not presume to predict where the next areas of innovation and discovery will be, we will mention a few areas presenting new opportunities and challenges.

Box 3 TROPHIC STATES OF LAKES AND RIVERS

Oligotrophic	waters with a low supply of nutrients and low organic production
Mesotrophic	waters with a moderate supply of nutrients and moderate organic production
Eutrophic	waters with a high supply of nutrients and hence a rich organic production

Changes of characteristics of lakes with various degrees of eutrophication:



Effects of Global Warming

Rising temperatures, the loss of glaciers and ice caps, the increasing scale and frequency of flood events, and rising sea levels due to global warming have important implications for water resources (IPCC 2007). For example, rising sea levels can increase saltwater intrusion into coastal aquifers (FIG. 1) and decrease the amount of freshwater available in coastal regions, where a large proportion of the world's population lives. Changes in precipitation, flow, and temperature can also significantly alter water chemistry in rivers, thereby affecting aquatic ecosystems. Increased temperature also affects in-lake chemical processes (IPCC 2007). Climate change will affect groundwater recharge rates and groundwater depth. However, as IPCC (2007) points out, knowledge of current groundwater conditions is poor, which hinders our ability to quantify the impact of climate change on groundwater resources.

Emerging Economies and Developing Countries

Knowledge in hydrogeochemistry has proven to be critical in the environmental remediation of contaminated waters in developed countries. However, these advances are only beginning to be exploited in emerging economies and developing countries. The case of Lake Taihu and the arsenic epidemic in Bangladesh and southern India, described above, illustrate the potential magnitude of water-quality problems. In China, remediation strategies for surface waters and groundwaters contaminated by mining and manufacturing activities are currently being contemplated. We can expect a future surge of research and remedial activities in countries like China, India,

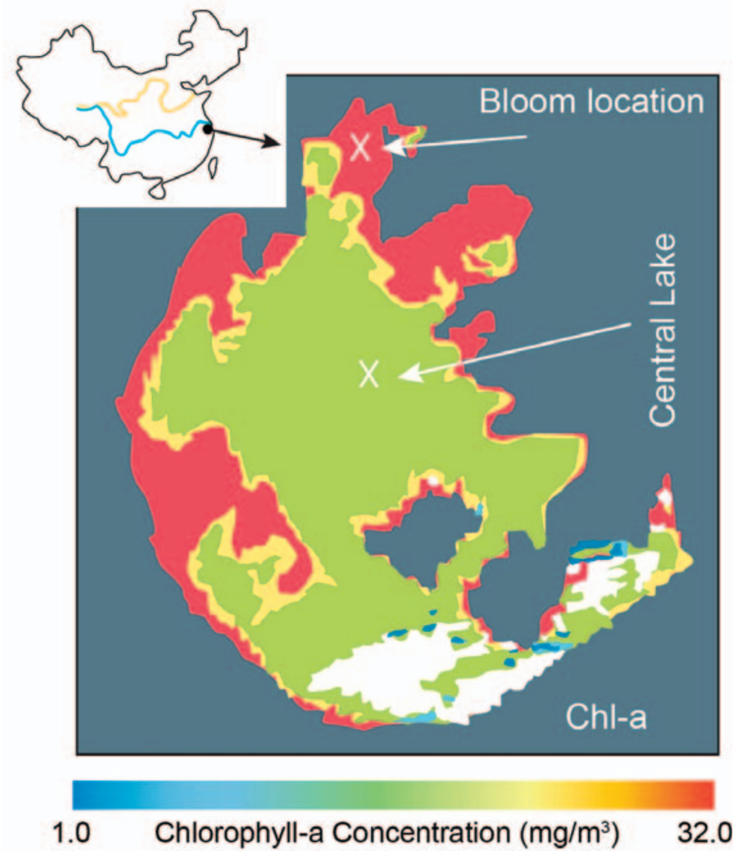


FIGURE 5 Lake Taihu is located in the Yangtze River delta in eastern China. The lake has experienced high nutrient loading from illegal industrial discharges, domestic waste water, aquaculture, and agriculture, especially from rivers to the north and west. Data from the moderate-resolution imaging spectrometer (MODIS) was useful in estimating chlorophyll-*a* concentrations, which are indicative of the extent of algal blooms. MODIFIED FROM WANG AND SHI 2008

Korea, South Africa, and Brazil. As "necessity is the mother of invention," we can expect more innovations and discoveries in addressing water-quality issues.

Future Anthropogenic Threats to Our Water Supply: Alternative Energy and Climate-Mitigation Strategies

Hydrogeochemistry is a critical aspect in society's search for "solutions" to energy- and water-resource problems. For example, storing excess surface water in the subsurface, a process known as *aquifer storage and recovery*, has emerged as an increasingly attractive water-management strategy for a warming climate (NRC 2008a). However, injected water can potentially react with the host rock and release toxic metals, such as As, Fe, Mn, U, and Ni, into the recharged (and eventually recovered) waters. First-generation biofuels will increase the use of fertilizers and pesticides, which could significantly increase non-point-source contamination of surface water and groundwater (NRC 2008b). Geological carbon sequestration is likely to become a key strategy to reduce carbon emissions by injecting CO_2 into deep subsurface geological formations (IPCC 2005). However, the buoyant CO_2 may escape via preferred pathways, such as unplugged or poorly sealed abandoned wells or fractures, and reach a shallow aquifer that is a source of drinking water. The dissolution of CO_2 into potable water decreases its pH and potentially liberates toxic metals (Little and Jackson 2010). Clearly, each of these factors can adversely affect water quality and supply; the consequences of each risk need to be considered before altering hydrogeochemical systems in order to help resolve other societal problems.

In short, to make hydrogeochemistry a truly useful tool for solving society's urgent water-resource challenges, a holistic approach to interpreting geochemical data must be taken. Being "holistic" means that we understand that the observed distribution of constituents and isotopes in water is the result of a complicated set of interrelated geochemical, physical, and biological processes and variable climate forcing. Significant advances and an expansion of the field are to be expected if we embrace the challenges of water management for a thirsty world.

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