

Geogenic Water-Quality Effects on Beneficial Uses of Water

By Melinda L. Erickson, Douglas B. Kent, John K. Böhlke, and Christopher H. Conaway

Chapter C of

Knowledge Gaps and Opportunities for Understanding Water-Quality Processes Affecting Water Availability for Beneficial Uses

Edited by Anthony J. Tesoriero, Melinda L. Erickson, Christopher H. Conaway, Elizabeth J. Tomaszewski, and Christopher T. Green

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	0.004047	square kilometer (km ²)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
gallon (gal)	3.785	liter (L)
billion gallons (Ggal)	3,785	cubic kilometer (km ³)
Flow rate		
gallon per day (gal/d)	0.003785	cubic meter per day (m ³ /d)
billion gallons per day (Ggal/d)	43.81	cubic meter per second (m ³ /s)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
Pressure		
atmosphere, standard (atm)	101.3	kilopascal (kPa)
Density		
pound per cubic foot (lb/ft ³)	0.01602	gram per cubic centimeter (g/cm ³)
pound per gallon (lb/gal)	0.1198	kilogram per liter (kg/L)
Energy		
kilowatthour (kWh)	3,600,000	joule (J)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)

International System of Units to U.S. customary units

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square kilometer (km ²)	247.1	acre
square kilometer (km ²)	0.3861	square mile (mi ²)
Volume		
liter (L)	0.2642	gallon (gal)
cubic centimeter (cm ³)	0.06102	cubic inch (in ³)
Flow rate		
liter per second (L/s)	0.2642	gallon per second (gal/s)
cubic kilometer per day (km ³ /d)	264.2	billion gallon per day (Ggal/d)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
Pressure		
kilopascal (kPa)	0.009869	atmosphere, standard (atm)
Density		
gram per cubic centimeter (g/cm ³)	62.4220	pound per cubic foot (lb/ft ³)
kilogram per liter (kg/L)	8.345	pound per gallon (lb/gal)
Energy		
joule (J)	0.000002	kilowatthour (kWh)
Radioactivity		
becquerel per liter (Bq/L)	27.027	picocurie per liter (pCi/L)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as °F = (1.8 × °C) + 32.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as °C = (°F – 32) / 1.8.

Supplemental Information

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Activities for radioactive constituents in water are given in picocuries per liter (pCi/L).

Abbreviations

BTEX	a group of volatile organic compounds: benzene, toluene, ethyl benzene, and xylenes
EPA	U.S. Environmental Protection Agency
HBSL	health-based screening level
IWS	Integrated Water Science
MAR	managed aquifer recharge
MCL	maximum contaminant level
SAR	sodium adsorption ratio
SC	specific conductance
TDS	total dissolved solids
USGS	U.S. Geological Survey
WMA	Water Resources Mission Area
WSS	Water Science Strategy

Chemical Symbols

Al	aluminum	N	nitrogen
As	arsenic	O	oxygen
Ba	barium	P	phosphorus
B	boron	Po	polonium
Ca	calcium	K	potassium
C	carbon	Ra	radium
Cl	chlorine	Rn	radon
Cr	chromium	Rb	rubidium
Cu	copper	Sm	samarium
F	fluorine	Se	selenium
H	hydrogen	Na	sodium
Fe	iron	Sr	strontium
Pb	lead	S	sulfur
Mg	magnesium	Th	thorium
Mn	manganese	U	uranium
Hg	mercury	V	vanadium
Ni	nickel	Zn	zinc

Chapter C

Geogenic Water-Quality Effects on Beneficial Uses of Water

By Melinda L. Erickson, Douglas B. Kent, John K. Böhlke, and Christopher H. Conaway

Purpose and Scope

This chapter is focused on identifying knowledge and data gaps, that if filled, could improve the ability to incorporate, model, and predict the effect of geogenic water-quality problems on intended beneficial uses. The gaps identified in this chapter are not intended to be comprehensive but are instead focused on key opportunities for the U.S. Geological Survey (USGS) Water Resources Mission Area (WMA, <https://www.usgs.gov/mission-areas/water-resources>). Geogenic constituent effects on ecosystems are not addressed in this chapter but are covered in the companion Open-File Report to this publication (Harvey and others, 2024) in their chapter C “Anthropogenic and Geogenic Contaminant Bioexposures Impacting Aquatic Ecosystems” and chapter E “Freshwater Salinization—An Expanding Impairment of Aquatic Ecosystem Health.”

Statement of the Problem

Water availability is dependent on both water quantity and water quality, as described in the 2013 USGS Water Science Strategy (WSS) (Evenson and others, 2013). Geogenic constituents, which are constituents related to geologic sources (although they can also have other sources), are among the most prevalent contaminants limiting water availability in the United States and globally. Geogenic constituents generally occur in groundwater due to geochemical conditions of water relative to the aquifer material. For example, concentrations of many constituents in the upper-crustal materials are sufficient so that dissolution of small fractions during water-rock interaction can cause concentrations of constituents to exceed a threshold for a beneficial use, as illustrated in table C1. Naturally occurring radioisotopes, including potassium-40 (^{40}K), rubidium-87 (^{87}Rb), samarium-147 (^{147}Sm), thorium isotopes (^{228}Th , ^{230}Th , ^{232}Th), uranium isotopes (^{234}U , ^{235}U , ^{238}U), polonium-210 (^{210}Po), lead-210 (^{210}Pb), radium-226 (^{226}Ra), and ^{228}Ra , are also present at levels that, if released, can exceed a threshold for a beneficial use (appendix C1, table C1.1). Geogenic constituents can also occur in surface water. Geogenic constituents may also occur due to environmental conditions such as an accumulation from atmospheric deposition in areas of arid climate or if redox or pH conditions in the aquifer facilitate the constituent to occur in a

more mobile state (appendix C1, fig C1.1). Many anthropogenic activities can exacerbate geogenic constituent mobilization.

As described in chapter A, water-quality requirements differ by beneficial use category (table A1). Drinking-water use requires consideration of total dissolved solids (TDS) concentration and a large list of geogenic constituents, which may be toxic, and (or) interfere with treatment efficacy or distribution system function. Water use for irrigation requires consideration of boron (B), iron (Fe), and TDS concentrations as well as the sodium (Na) abundance relative to magnesium (Mg) and calcium (Ca) (the sodium adsorption ratio [SAR]). Water use for livestock requires consideration of the pH, alkalinity, and concentrations of sulfate and TDS. Water use for cooling requires consideration of pH, hardness (sum of the concentrations of Mg and Ca), and concentrations of alkalinity, Fe, hydrogen sulfide, sulfate, silica, and TDS. Water use for oil and gas development requires considering hardness and concentrations of barium (Ba), B, Fe, sulfate, and TDS. The distributions and relative abundances of various water-quality parameters will affect water availability in different ways, depending on intended use and treatment options (McMahon and others, 2016a). Both surface water (fig. A3A) and groundwater (fig. A3B) are used for public water supply. In many areas both water sources are used for public supply (fig. A3D). In substantial portions of the country, domestic well water is the dominant or only potable drinking water source available (fig. A3C), estimated to serve 42.5 million people (Dieter and others, 2018).

There are many examples of how mobilized geogenic constituents can limit water availability in the United States, including existing and proposed USGS Integrated Water Science (IWS) Basins. In the Delaware River Basin, important concerns include geogenic metalloids and metals (arsenic [As], Fe, manganese [Mn], aluminum [Al]), radionuclides (radon-222 [^{222}Rn]), and saltwater intrusion into public and domestic supply wells (Scott and others, 2019). Along with sea-level rise, salt-water intrusion can mobilize geogenic constituents that are present in an aquifer matrix. In the Colorado River Basin, non-metals and metals from abandoned mines, including selenium (Se), mercury (Hg), U, and Rn, as well as geogenic nitrate are major threats to water availability (Spahr and others, 2000; Conaway and others, 2005; Naftz and others, 2008; Vengosh, 2014). The Illinois River Basin intensive study identified as major issues:

2 Water-Quality Processes Affecting Water Availability for Beneficial Uses

Table C1. Average abundance of selected geogenic elements in the upper crust, the equivalent pore-water concentration, human health benchmark, and the percent release to achieve exceedance.

[Avg., average; EPA MCL, U.S. Environmental Protection Agency maximum contaminant level; HBSL, health-based screening level; $\mu\text{mol}/\text{kg}$, micromole per kilogram; $\mu\text{mol}/\text{L}$, micromole per liter; —, human-health based benchmark or data are not available; g/cm^3 , gram per cubic centimeter; kg/L , kilogram per liter.]

Element ^a	Avg. crustal abundance ^b ($\mu\text{mol}/\text{kg}$)	Equivalent pore-water concentration ^c ($\mu\text{mol}/\text{L}$)	Human health benchmark ($\mu\text{mol}/\text{L}$ (mg/L))	Human health benchmark ^d	Percent release to achieve exceedance ^e
Antimony (Sb)	3.3	13	0.05 (0.006)	EPA MCL	0.4
Arsenic (As)	65	260	0.13 (0.01)	EPA MCL	0.05
Barium (Ba)	4,500	18,000	15 (2)	EPA MCL	0.08
Cadmium (Cd)	0.08	3.2	0.04 (0.005)	EPA MCL	1
Chlorine (Cl)	10,000	41,000	—	—	—
Chromium (Cr)	1,800	7,000	1.9 (0.1)	EPA MCL	0.03
Cobalt (Co)	290	1,200	0.03 (0.002)	HBSL	0.003
Copper (Cu)	440	1,800	20 (1.3)	EPA MCL	0.03
Fluoride (F)	29,000	120,000	210 (4)	EPA MCL	0.2
Iron (Fe)	7.0×10^5	2.8×10^6	72 (4)	HBSL	0.003
Lead (Pb)	82	330	0.07 (0.015)	EPA MCL	0.02
Lithium (Li)	3,000	12,000	1.4 (0.01)	HBSL	0.01
Manganese (Mn)	14,000	56,000	5.5 (0.3)	HBSL	0.01
Mercury (Hg)	0.25	0.99	0.01 (0.002)	MCL	1
Molybdenum (Mo)	11	46	0.31 (0.03)	HBSL	0.7
Nickel (Ni)	800	3,200	1.7 (0.1)	HBSL	0.05
Nitrogen (N)	5,900	24,000	—	—	—
Phosphorus (P)	21,000	84,000	—	—	—
Potassium (K)	420,000	1,700,000	—	—	—
Rubidium (Rb)	980	3,900	—	—	—
Selenium (Se)	1.1	4.5	0.6 (0.05)	EPA MCL	14
Strontium (Sr)	3,700	15,000	46 (4)	HBSL	0.3
Sulfur (S)	19,000	77,000	—	—	—
Thallium (Tl)	4.4	18	0.01 (0.002)	EPA MCL	0.06
Thorium (Th)	45	180	—	—	—
Uranium (U)	11	45	0.13 (0.03)	EPA MCL	0.3
Vanadium (V)	1,900	7,600	—	—	—
Zinc (Zn)	1,000	4,100	31 (2)	HBSL	0.8

^aSelected based on at least one known effect from a geogenic source and has an indirect effect on human health (for example, N, P), or has radioactive isotopes whose activities are sufficiently high to have potential effects on human health (table C1.1).

^bRudnick and Gao (2003).

^cEquivalent pore-water concentration is the average crustal abundance times a representative ratio of solids to pore volume in sediments, calculated by multiplying the sediment-bound concentration in column 2 by the bulk density of the sediments and dividing by the pore volume (Appelo and Postma, 2005, p. 84). A porosity of 0.4 and solid-phase density of $2.65\text{g}/\text{cm}^3$ were used for the purposes of these calculations, generating a ratio of solid to pore volume of 4 kg/L of pore volume. Assuming a lower porosity, such as 0.2 (for example, Appelo and Postma, 2005, p. 84), will yield higher porewater concentrations. On the other hand, concentrations are based on assuming complete release of each element, and, therefore, represent the maximum possible concentrations at a porosity of 0.4. The extent to which the element is released depends on its chemical form and reactivity with respect to the ambient groundwater composition.

^dEPA MCL, EPA (2018). HBSL, Norman and others (2018).

^eThe percent of the geogenic element that, if released, would cause an exceedance of the human-health-based benchmark.

As, Mn, radionuclides, and salinity in the major drinking-water aquifers (Mahomet, Glasford, glacial, and Cambrian–Ordovician) as well as application of Chicago area (upper basin) dredge sediment to agricultural areas (lower basin), redistributing metals and industrial chemicals (Warner and others, 2003; Warner and Ayotte, 2015; Erickson and others, 2019; Szabo and others, 2020).

This chapter highlights some of the most important issues related to geogenic constituents that can limit water availability in current IWS Basins and elsewhere in the Nation. The chapter includes descriptions of vital gaps in methods, approaches, and process understanding related to addressing these issues.

Status of Knowledge and Capabilities

Major water-quality issues related to geogenic constituents are summarized in table C2. The broad categories of the most significant issues based on current understanding include the following:

1. Geogenic constituent sources and distribution processes,
2. Geogenic constituent risk,
3. Anthropogenic activity effects on geogenic constituent distribution, and
4. Climate change effects on geogenic constituent distribution.

Geogenic Constituent Sources and Distribution Processes

Geogenic constituents can also have anthropogenic sources and can be mobilized by both natural and anthropogenic processes (see “Gap 1. Geogenic Constituent Sources and Distribution Processes” section of this chapter). Many geogenic constituents commonly occur in groundwater and surface water because of natural processes such as soil leaching and rock weathering. For example, natural weathering reactions drive mass transfer of As from sulfide minerals or U from oxides and aluminosilicate minerals to Fe oxyhydroxide coatings on mineral-grain surfaces, from which they can be mobilized (fig. C1.1) (Smedley and Kinniburgh, 2002; Ayotte and others, 2007). However, As contamination can result from the manufacture and application of chemicals used for agriculture and in meat production (Arai and others, 2003; O’Day and others, 2004) and U contamination can result from disposal of waste from nuclear weapons manufacture or activities related to the nuclear fuel cycle (Zachara and others, 2013). Chromate and perchlorate are also produced both naturally and industrially (Dasgupta and others, 2006; Hausladen and others, 2018). Geochemical and isotopic analyses can be used to distinguish natural versus

What are Geogenic Constituents?

We define geogenic water-quality constituents as any chemical or isotope that has a natural source (for example, soil leaching, water-rock interaction, atmospheric deposition). Many geogenic constituents are, however, also manufactured or concentrated by humans. Although geogenic constituents commonly occur in water because of natural processes, their distribution and concentration can be affected by human activities (for example, mining, dispersal of mineral products, irrigation, pumping practices). Effects of human activities can be direct (for example, application of fertilizers on the land surface) or indirect (for example, alteration of geochemical or hydrologic conditions, which in turn affects constituent solubility or mobility).

To understand geogenic constituent distributions, we must distinguish between at least three source categories: (1) natural sources distributed by natural processes; (2) natural sources distributed by human activities; and (3) artificial sources distributed by natural processes or human activities. These categories can overlap and change, creating ongoing challenges. Understanding the distribution of geogenic water-quality constituents is crucial for evaluating water availability and beneficial use, establishing practical regulations, and optimizing remediation or treatment strategies.

anthropogenic sources, as well as natural versus anthropogenic distribution processes (McMahon and Böhlke, 2006; Manning and others, 2015; Hatzinger and others, 2018).

Geogenic Constituent Risk

Geogenic constituents, as compared to anthropogenic constituents, are more commonly found at high concentrations (the word “high” is used herein to refer to concentrations exceeding a human health benchmark) in groundwater sources supplying drinking water (DeSimone, 2009; DeSimone and others, 2015) (table A2). Arsenic, for example, is among the most common constituents to cause a public water system violation (Allaire and others, 2018, Foster and others, 2019). To understand the distributions of geogenic constituents, we can consider three generalized categories of sources: (1) natural sources distributed by natural processes (for example, As contamination in glacial aquifers in the upper Midwest [Erickson and Barnes, 2005]); (2) natural sources distributed by human activities (for example, As contamination in bedrock aquifers due to water table drawdown in Wisconsin [Gotkowitz and others, 2004]); and (3) artificial sources distributed by natural processes or human activities (for example, heavy metal contamination from mining or contamination from leaks and spills of oil and gas production

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Table C2. Summary table for geogenic constituent gap analysis for understanding water-quality processes affecting water availability for beneficial uses in the United States.

[TDS, total dissolved solids; CO₂, carbon dioxide.]

Topic	Knowledge Gap	Importance	Proposed approaches
Geogenic constituent sources and distribution processes	Methods to distinguish naturally occurring sources or distribution processes from anthropogenic sources or distribution processes	Crucial for development of appropriate models, regulations, remediation strategies, responses, or other management tools.	Develop and deploy new chemical and isotopic analytical forensic methods; conduct field and laboratory experiments, and augment thermodynamic databases, to improve parameterization for advanced geochemical models; apply new machine-learning modeling methods.
Geogenic constituent risk	Ability to quantify, model, map occurrence, and map risk from constituent mixtures and complex distribution patterns	To provide more comprehensive assessments of geogenic limitations on water availability for multiple uses (beyond constituent-by-constituent exceedance probabilities), a key step toward more appropriate methods, models, and strategies to manage/optimize water resources and to quantify human exposure risk.	Use existing data, advanced statistical tools, and geochemical modeling tools to assess and predict co-occurrence and toxicity of geogenic constituents, delineate regional background concentrations, determine crucial geochemical (for example, redox, pH, TDS) boundaries, and quantify risk to vulnerable populations.
Anthropogenic activity effects on geogenic constituent distribution	Knowledge of groundwater availability and sustainability in conditions of enhanced constituent mobilization and redistribution from irrigation, managed aquifer recharge, pumping, and chemical inputs from agriculture, landfills, wastewater releases, organic chemical spills, oil/gas production, and mining	Water use demands are increasing, and human-induced exacerbation of water availability problems from high concentrations of geogenic constituents are poorly understood. Crucial for development of appropriate methods, models, strategies, and other management tools to anticipate, quantify, and respond.	Coordinate with stakeholders to plan field and laboratory studies to quantify effects of specific human activities on occurrence, fate, transport of constituents; develop hydrologic and biogeochemical models that incorporate human activities to predict potential water-quality limitations to beneficial use.
Climate change effects on geogenic constituent distribution	Understanding of processes and parameters is needed to develop the ability to predict how climate change will directly or indirectly affect beneficial uses due to redistribution or mobilization of constituents.	To anticipate and mitigate climate-related limitations on water availability for intended beneficial use	Develop basic understanding or conceptual models for the effects of climate change (flood inundation frequency and extent, extended drought conditions, sea level change and inundation) and how the changes redistribute or change mobility of geogenic constituents either directly or indirectly; conduct field studies of water-quality responses to water table changes, pumping, water mixing, CO ₂ sequestration, and other climate-related activities.

wastes [Fashola and others, 2016; Cozzarelli and others, 2021]). In many settings, these general source categories can overlap or change. These source categories can lead to geogenic constituent occurrence in water resources that range from widespread areas of risk due to chronic exposure to localized areas of risk due to acute exposure. They can also lead to the occurrence of complex mixtures of constituents that could increase substantially the risk associated with beneficial uses. These issues are documented, and gaps related to them are discussed in the section “Gap 2. Geogenic Constituent Risk” in this chapter.

Anthropogenic Activity Effects on Geogenic Constituent Distribution

High concentrations of geogenic constituents in drinking water can result from natural conditions in the aquifers, human activities such as irrigation, pumping, and managed aquifer recharge, all of which can change geochemical, biogeochemical and hydrogeologic conditions to enhance constituent mobilization (Erickson and Barnes, 2006; McMahon and others, 2006; Ayotte and others, 2015; Rosen and others, 2019; Tesoriero and others, 2019; Degnan and others, 2020). Point sources

of geogenic constituents from ongoing or former mining and fossil fuel extraction activities, for example, can result in very high concentrations locally. The effects on mobility of geogenic constituents based on aquifer geochemistry are well recognized (illustrated in fig. C1.1), including: (1) redox conditions, (2) pH, (3) sorption processes and ion competition for sorption sites, (4) formation of soluble complexes, (5) evaporative concentration, and (6) mixing and dilution (Hem, 1985; Drever, 1988; Welch and others, 2000; Böhlke, 2002; Stollenwerk, 2003; Appelo and Postma, 2005; McMahon and others, 2016; Jurgens and others, 2019; Yuan and others, 2021). Human activities can alter all these conditions in various ways. For example, recharge of landfill leachates and some types of wastewater can introduce large amounts of organic carbon or other electron donors, which can reduce iron oxyhydroxides and As(V) to As(III), promoting arsenic mobilization (Welch and others, 2000) in otherwise oxic aquifers (fig. C1.1). Conversely, increased recharge of electron acceptors such as agricultural nitrate and dissolved oxygen can cause enhanced oxidation of reduced phases such as pyrite, mobilizing chalcophile elements like As and Se in otherwise anoxic aquifers (fig. C1.1) (Fakhreddine and others, 2021).

Climate Change Effects on Geogenic Constituent Distribution

Projected effects of climate change in the United States include warmer air temperatures, regionally and seasonally varying changes in precipitation and streamflow, increased frequency and intensity of floods and droughts, and sea-level rise affecting coastal regions (Wuebbles and others, 2017). Coastal rivers, estuaries, and aquifers may undergo increased saltwater intrusion due to rising sea level, storm surges, and hydrological changes (Paul and others, 2019). The geologic materials in aquifer systems are a substantial source of geogenic contaminants, and these contaminants (for example, Mn, As) are susceptible to mobilization by changes in temperature, pH, or redox condition all of which may be influenced by changes in recharge temperature and recharge geochemistry (Riedel, 2019). Groundwater is an important source of drinking water supply, irrigation supply, and baseflow to streams and rivers, so the effect of climate change on the quantity and quality of the groundwater system must be considered in conjunction with the other parts of the hydrologic cycle (Aizebeokhai and others, 2017; Amanambu and others, 2020). Reduced groundwater recharge from precipitation pattern changes could lead to longer residence times in aquifers; increased residence time allows greater water-rock interaction, which can lead to increased salinity (Hem, 1985; Kayane, 1997). Increased recharge can also result in increased groundwater salinity due to increased flushing of salts from the unsaturated zone (Sugita and Nakane, 2007). Leaching of the large reservoirs of nitrate, perchlorate, and other salts that accumulated by natural processes in arid areas may be especially problematic (Walvoord and others, 2003; Rao and others, 2007; Graham and others, 2008; Jackson and others, 2015). Sea-level rise is expected to increase saltwater intrusion in coastal areas and volcanic islands (Vengosh, 2014) and to increase up-stream advancement of salt wedges in coastal rivers (Hurdle, 2020).

Capabilities

The USGS has a long history of contributions to understanding the sources, transport, and transformations of geogenic constituents in water, for example:

- Developing chemical and isotopic tools for determining sources of solutes and processes influencing transformations and mobility.
- Carrying out laboratory characterizations and experiments to understand properties of natural materials that influence transformations and mobility of geogenic constituents.
- Carrying out field-scale experiments and studies that elucidate the important controls on transformations and mobility of geogenic constituents.
- Carrying out field-scale measurements required to characterize flow systems, an essential component to understanding movement of anthropogenic and geogenic constituents.

The continued application of these capabilities will help to address the crucial gaps in assessing the effects of geogenic constituents on water availability.

Gap Analysis and Approaches

Our ability to simulate processes and to model, map, and predict geogenic constituent occurrence in water supplies is limited by some fundamental gaps in understanding. Some of the major issues related to geogenic constituents that can limit water availability are summarized in table C2. Some of the most critical gaps in addressing these issues will be described in detail in this section, but this chapter is not an exhaustive presentation of knowledge gaps. The narrative is organized around the following broad knowledge categories:

1. Geogenic constituent sources and distribution processes,
2. Geogenic constituent risk,
3. Anthropogenic activity effects on geogenic constituent distribution, and
4. Climate change effects on geogenic constituent distribution.

Gap 1. Geogenic Constituent Sources and Distribution Processes

A key gap to understanding constituent sources and distribution is the absence of adequate methods to distinguish naturally occurring sources or distribution processes from anthropogenic sources or distribution processes. This section will present examples of significant gaps related to geogenic constituent sources and distribution processes, and then approaches to fill the gaps.

Knowledge Gaps

Analytical Forensic Methods

Methods to separate the “people signal” from the “natural signal” (for example, natural background concentrations) are necessary because source and distribution processes fundamentally affect how to appropriately model, manage, regulate, or remediate a contamination problem. Many chemicals that occur naturally are also produced artificially for various purposes. For example, chromate is widely distributed in soils and groundwaters in some areas as a result of natural weathering of chromium (Cr)-bearing minerals, but chromate is also produced for industrial use and there are sites where high concentrations of chromate are a result of industrial waste disposal (Manning and others, 2015; Hausladen and others, 2018). Similarly, elevated perchlorate concentrations in public supply wells in some areas of the United States can be from at least three different sources: (1) synthetic perchlorate from industrial products; (2) natural perchlorate in imported nitrate fertilizer from the Atacama Desert; and (3) natural perchlorate accumulated locally from atmospheric deposition (Jackson and others, 2010; Hatzinger and others, 2018). Other constituents can also have both geologic or atmospheric sources and anthropogenic sources (for example, nitrate, ammonium, methane, Cd, Pb, copper [Cu], radioactive isotopes, and so forth.).

For some geogenic constituents, like ^{226}Ra and ^{228}Ra , it can be difficult to determine whether elevated concentrations are from sources of contamination or natural background. ^{226}Ra and ^{228}Ra are part of the ^{238}U and ^{232}Th decay series (table C1.1). Anthropogenic sources or mobilization of these isotopes can be identified by determining whether they are in secular equilibrium with their parent isotopes. Concentrations above the radioactive decay concentration are likely to result from anthropogenic sources or mobilization of Ra, such as inputs of wastewater from oil and gas production (Akob and others, 2016; Cozzarelli and others, 2017; Cozzarelli and others, 2021). Distinguishing between anthropogenic sources of geogenics, such as wastes from oil and gas development and legacy coal mining is a gap that requires further investigation (Chambers and others, 2015).

Advanced Geochemical Modeling

In addition to improved source attribution, it is also important to improve understanding of geochemical conditions and processes that control the chemical forms and mobility of geogenic constituents to model their distribution, co-occurrence, and movement. Some geogenics are more mobile in reduced conditions, others in more oxidized conditions. Geochemical modeling to understand and characterize the quantity of geogenic constituents that can be mobilized in response to changing chemical conditions requires field, lab, and theoretical data for mineral dissolution, oxidation-reduction reactions, sorption properties, and so forth. Better understanding of processes could lead to better modeling, which could lead to improved assessment and prediction at multiple scales.

Approaches to Fill Knowledge Gaps

Develop and Deploy New Chemical and Isotopic Analytical Forensic Methods

Measurements of stable isotope ratios can be used to distinguish sources of geogenic constituents (for example, rock weathering, atmospheric, synthetic) and track their movement through groundwater and surface water. For example, isotopic ratios of light elements such as hydrogen (H) and carbon (C) (for example, in carbon dioxide, methane, oil), nitrogen (N) (for example, in nitrate, ammonium, organic matter, and so forth), oxygen (O) (for example, in oxyanions such as nitrate, sulfate, phosphate, chlorate, perchlorate), sulfur (S), and chlorine (Cl) commonly vary depending on the source of the constituent and as a result of fractionation during transport and transformation reactions. Isotope ratios of heavier elements such as Fe, Cu, Pb, strontium (Sr), Hg, and Cr can provide similar information but have been used less extensively. Development of new analytical methods could include more constituents and elements, with better precision and accuracy, faster throughput, reduced cost, and exploration of new isotopic principles for resolving water-quality questions.

Several different types of isotopic analyses are in various stages of development, and some could be applied more extensively for environmental forensics and process studies of important geogenic constituents. For example, non-statistical isotopic distributions (isotopic “clumping”) in compounds such as methane and oxyanions including nitrate can potentially provide clues about their formation mechanisms and degradation processes (Ono and others, 2014; Hilkert and others, 2021). Non-mass-dependent isotopic variations in O, Hg, S, and other elements in various compounds can indicate their sources and transport processes (Thiemens, 2006; Jackson and others, 2008; Jackson and others, 2010; Bindeman and Pack, 2020; Tsui and others, 2020). Oxygen isotopic analyses of phosphate may be useful in some situations for understanding the sources and distribution of this important nutrient (Davies and others, 2014; Jaisi and Blake, 2014). High-precision isotopic measurements of heavy elements could be used more routinely for similar studies (Teng and others, 2017), and could also be combined with O isotopic analyses when in the form of oxyanions.

Augment Geochemical Modeling Capabilities and Thermodynamic Databases

Geochemical modeling, which combines theoretical principles and empirical data, is important for developing both conceptual understanding and quantitative predictions of water quality.

If constituents and alternative physical conditions were added to existing thermodynamic databases, geochemical modeling tools such as PHREEQC (Parkhurst and Appelo, 2013) could be used for more comprehensive process modeling and scenario testing. The current thermodynamic databases could be improved with more data for geochemical

modeling at temperatures higher or lower than 25 degrees Celsius (°C); for modeling solutions that are brackish or brines and not dilute solutions; for modeling in conditions other than 1 standard atmosphere (atm); and for additional chemical species and redox reactions that control solubility and mobility of geogenic constituents. In future climate and water scarcity conditions, modeling alternative physical settings could be decisive in evaluating scenarios.

Using more complete thermodynamic databases and isotopic composition information, geochemical and other modeling techniques could be used to apportion types of water, sources of water (Teepie, 2017), and source composition to appropriately simulate geogenic constituent mobilization risk. Salinity can mobilize geogenic constituents, so understanding the composition of the salinity (for example, solute chemistry and elemental ratios) can help identify the salinity source. Road salt, produced water, and saltwater intrusion are all examples of salinity sources directly or indirectly caused by human activities—but each source would require a different type of management strategy to reduce impact or risk.

Laboratory and Field Experiments to Identify and Quantify Controlling Processes and Parameters

Processes such as sorption, transformation, and biologic uptake can determine the persistence and distribution of contaminants in groundwater and surface water. Controlled experiments in laboratory and field settings are essential for discovering and quantifying such processes and parameters that need to be included in water-quality prediction models. Although lab experiments are relatively simple and controllable, they may not correspond to natural conditions. Experiments carried out in field settings may be more difficult, but they may reveal additional processes and more realistic rates that correspond more directly with environmental monitoring or modeling requirements.

Experiments using tracers enriched in specific stable (non-radioactive) isotopes (for example, ^{13}C , ^{15}N , ^{18}O , ^{34}S) can be especially useful for determining reaction parameters for constituents that participate in complex biogeochemical transformations by tracking both reactants and products. For example, field experiments with compounds enriched in the ^{15}N isotope can help resolve processes that simultaneously transport, produce, and consume various nitrogen compounds in streams and aquifers (Smith and others, 2004; Böhlke and others, 2006; Smith and others, 2015). Isotopic tracer experiments with compounds containing heavy metals can be used to determine processes and transport rates of those constituents (for example, using isotopically enriched metals or oxygen, depending on the compounds). Similarly, labeled organic compounds, dissolved gases, and other constituents can be tracked in carefully designed field experiments. Corroborative analysis of biologic communities and biomolecules in such experiments can improve understanding of biologic controls of constituent concentrations and mobilities.

Delineate Regional Background Concentrations

Existing data and tools could be used systematically to delineate regional background concentrations of selected geogenic constituents. An understanding of regional background concentrations and their dependence on geology and climate should provide important information about the “natural signal,” which can inform more effective and appropriate modeling tools, management strategies, and regulatory frameworks for geogenic constituents. These applications would require the compilation of existing data plus collection of new data, including solid-phase chemistry (and mineralogy).

Gap 2. Geogenic Constituent Risk

Although comprehensive understanding of geologic controls on water quality was highlighted as an objective in the 2013 USGS Water Science Strategy (Evenson and others, 2013), we have not yet characterized the national, spatial distributions of most geogenic constituents. Assessing the co-occurrence of geogenic constituents is a crucial step toward developing holistic approaches to manage and optimize water availability and to quantify human exposure risk. This section will present examples of significant gaps related to geogenic constituent distribution and risk, and then approaches to fill the gaps.

Knowledge Gaps

Co-Occurrence and Distribution Patterns

At present, there have not been many comprehensive attempts to quantify, model, and map the occurrence of mixtures of geogenic constituents, and we are unable to map exposure risks from constituents or constituent mixtures. We also lack complete understanding of background concentrations (concentrations present from geologic sources due to natural processes) and complex distribution patterns of geogenic constituents. A comprehensive analysis of constituent co-occurrence—mixtures of geogenic and other constituents at concentrations near or above human health benchmarks—has not yet been completed. Evaluations of mixtures of some organic constituents have been completed, but comprehensive assessments and evaluations of geogenic constituents are less common so little is known about potential combined effects. Geogenic constituents commonly co-exist, and their aggregated potential health effects may not be reflected in their individual regulatory exceedances.

Geogenic constituent mobility is substantially controlled by geochemical conditions, such as redox boundaries, for example, transitions from oxic to suboxic and anoxic conditions. Understanding and mapping these boundaries or transition zones requires understanding of three-dimensional hydrogeologic characteristics with relevant vertical resolution to reflect small-scale but important spatial heterogeneity.

Exposure Risk Assessments

Methods are improving for predicting the likelihood of high concentrations of geogenic constituents (for example, As, Mn, Fe, salinity, and so forth) in groundwater in drinking water aquifers (Ayotte and others, 2016; Rosecrans and others, 2017; Knierim and others, 2020; Erickson and others, 2021a; Erickson and others, 2021b; Stackelberg and others, 2021). However, few studies have quantified the risk of single or mixed constituents to overall populations or for population socioeconomic subgroups (rural population, median income, underserved communities, and so forth).

Enforceable drinking water standards are developed within a framework of balancing health risk, economics, and practical application. Some standards, therefore, are not comprehensive with respect to exposure risk reduction. Two examples are ^{210}Pb and ^{210}Po (Szabo and others, 2020), which are regulated indirectly through the gross beta-particle activity screening level and gross alpha-particle activity maximum contaminant level (MCL) rather than having individual MCLs. These regulatory screening levels are not protective for ^{210}Pb or ^{210}Po in drinking water based on lifetime fatal cancer risk levels (Seiler, 2016).

Approaches to Fill Knowledge Gaps

USGS has access to a large amount of existing water-quality data and related information, and it has built substantial scientific capabilities and expertise. Further analysis of existing data with advanced statistical tools including machine-learning methods, and targeted additional sampling could help address some key knowledge gaps.

Constituent Co-Occurrence and Mixture Analysis

Existing tools could be used by current scientists to analyze existing data on mixtures and co-occurrence of geogenic constituents. In addition to advanced statistical tools, geochemical modeling tools can also be employed to assess and predict co-occurrence of geogenic constituents that are related through their dependence on local or regional geochemical conditions (for example, geology, redox state, pH, and so forth). Specific groups of geogenic constituents, with or without co-existing anthropogenic constituents, could be identified by common occurrence and potentially related to common health effects at low individual concentrations.

Evaluation of constituent mixtures would also contribute to characterizing water availability based on water-quality resource characteristic requirements. For example, water-quality requirements for irrigation may be less stringent than water-quality requirements for domestic drinking water supply. Comprehensive water-quality assessments can put water resources into the context of what is needed.

New Machine-Learning Applications and Modeling Methods

Big data and machine learning approaches have been applied to studies of impaired drinking water resources

including those affected by methane, salinity, Mn, and As (Knierim and others, 2020; Erickson and others, 2021b; Lombard and others, 2021a; Wen and others, 2021). Refinement of these models to better represent geogenic contaminant concentrations is an active area of research in USGS (Lombard and others, 2021a), and represents a key opportunity for the USGS. Lombard and others (2021a, p. 5019) specifically call out for the “development and inclusion of relevant predictor variables that represent geochemical mechanisms responsible for arsenic mobilization in groundwater such as pH and redox conditions.” Predictions of high As and Mn concentrations at relevant drinking water depths across the subcontinental-scale glacial aquifer system (Lombard and others, 2021b) illustrate the efficacy of developing models of the geochemical drivers of geogenic contaminant concentration (pH, Stackelberg and others, 2021; redox condition, Lombard and others, 2021a) and then using the models of drivers in developing a high-performing machine-learning groundwater contaminant model.

Delineate Crucial Geochemical Boundaries, Timescales, and Processes

Existing data, advanced statistical and geochemical modeling tools, and process understanding can be used to identify and delineate crucial geochemical boundaries in selected high-priority aquifers. This will require three-dimensional data for subsurface geology, including formation boundaries, rock types, mineralogy, geochemistry, and weathering history, as described in 2013 USGS Water Science Strategy (Evenson and others, 2013, see Goal 2, Objective 1). Geologic boundaries and structures are likely to control boundaries between water masses with different chemical characteristics. Mineralogy and geochemistry of aquifer solids are likely to control the distribution of geogenic constituent sources and concentrations. Within geologic units, groundwater flow patterns will affect gradients in water-quality constituents by various progressive reactions between water and rocks.

For important drinking water aquifers, there is a need to quantify to what extent geogenic constituents have been flushed through the sub-surface system. Climate data, chemistry and mineralogy of soils and aquifers, and other existing geochemical measures can be used to evaluate the number of pore volumes that have flowed through systems in the context of the geologic reservoir of geogenic constituents, for example in the humid east as compared to the arid west. There are timescale and process perspectives that must be considered. Additionally, even if the reservoirs of labile geogenic constituents have been flushed through a system, a change in conditions (for example, precipitation chemistry, input of anthropogenic chemicals, water level change or fluctuation, saltwater intrusion caused by sea-level rise in coastal areas), could cause formerly immobile geogenic constituents to be mobilized. As illustrated in table C1, mobilization of just a small fraction of a geogenic constituent reservoir can result in water-quality and water-availability problems. There are also important unknowns and

questions to be investigated about the role of surface chemistry in reestablishment of steady-state concentrations in aquifers in different settings.

Information about flushing factors and pore volumes to reach new steady-state conditions between aqueous solutions and aquifer material can help answer questions such as “How long are we going to face the problem?” and “What could happen to trigger a change away from a current steady-state?”

Quantify Risk to Vulnerable Populations

Several regional and national-scale drinking water-quality models have recently been published (Knierim and others, 2020; Erickson and others, 2021b; Ransom and others, 2021). These water-quality models, or new water-quality models that could be developed using existing information, could be used as a basis for predicting populations served by impaired drinking-water quality. A better understanding of human health risk could be formulated by building on these recent predictions of drinking-water quality. For example, constituent concentrations above a human health benchmark could be predicted for selected socioeconomic groups. Socioeconomic groups could include categories such as drinking water source (rural domestic well water) or median income, to explore factors driving the findings.

A systematic and comprehensive assessment of drinking water source-water would enhance understanding of human health risks. One example, discussed above, is whether human health risks from ^{210}Pb and ^{210}Po are adequately addressed by the current regulatory approach, especially in Gulf and Atlantic coastal aquifers, carbonate, and interior sandstone or carbonate aquifers.

Some effects of water quality on water availability may be indirect, for example when source-water chemistry can interact or interfere with treatment processes or distribution systems resulting in unintended consequences. Examples include production of potentially harmful organic compounds during chlorination of water sources containing dissolved organic compounds, or release of Pb by corrosion in water distribution systems. Such risks can be evaluated in various ways, including assessments of source-water characteristics, such as Pb solubility potential (Jurgens and others, 2019), and geochemical modeling to assess the consequences of mixing different waters on corrosivity, sorption/desorption, and mineral precipitation/dissolution.

Gap 3. Anthropogenic Activity Effects on Geogenic Constituent Distribution

Natural geochemical conditions can cause high concentration occurrence of geogenic constituents, which can in turn affect the availability of groundwater and surface water for beneficial uses. However, even where geogenic constituents have natural sources, their distributions and concentrations can be altered substantially by human activities such as irrigation, artificial recharge, pumping practices, oil and gas exploration and extraction, and many other activities.

Well vulnerability to geogenic constituents depends in part on: (1) the sources of geogenic constituents in proximity to water supply wells, (2) the physical properties of the aquifer and (or) the well, and (3) the biogeochemistry of the aquifer system (Focazio and others, 2002; Frind and others, 2006; Eberts and others, 2013). A geologic source in the aquifer system is the most fundamental risk factor for the potential mobilization of in-situ geogenic constituents. The traditional model of “source water protection” or “capture zone protection” is unlikely to fully protect groundwater supplies from geogenic constituents because these constituents are mobilized from within the geologic materials, not transported from surface sources. Many anthropogenic activities, however, can influence and alter the biogeochemistry of the aquifer system, potentially mobilizing or changing the distribution of geogenic constituents in the system. This section will present examples of significant knowledge gaps related to the effects of anthropogenic activities on geogenic constituent distribution, and then approaches to fill the gaps.

Knowledge Gaps

How Anthropogenic Activities Mobilize Geogenic Constituents

There are many unknowns about how the geochemistry of irrigation water or enhanced recharge rates mobilize, immobilize, or redistribute geogenic constituents. Enhanced recharge rates from water well pumping or irrigation return can flush accumulations of geogenic salts such as nitrate or perchlorate from the unsaturated zone (Rao and others, 2007; Scanlon and others, 2007; Scanlon and others, 2009). Elevated total salinity in these enhanced recharge situations also can release sorbed constituents like phosphorus (P), Ra, Sr, and so forth (Szabo and others, 1997; Stackelberg and others, 2018; Musgrove, 2021).

The chemistry of irrigation water or enhanced recharge can also mobilize geogenic constituents via oxidation of reduced phases driven by the introduction of nitrate or dissolved oxygen. Uranium can be mobilized in this way. Sulfate, As, and metals like Cu and Pb can be mobilized during enhanced sulfide-mineral oxidation. Geogenic constituents can also undergo bioaccumulation into food crops, for example, As can occur at concentrations of concern in rice (U.S. Food and Drug Administration, 2016) and perchlorate can be enriched in vegetables (Yu and others, 2004).

An influx of organic carbon or other electron donors can mobilize As, Mn, and other elements that are often stable under oxic conditions but mobilized under reducing conditions. Comprehensive maps of locations and geochemical composition of these types of anthropogenic carbon sources are not available. Examples include abandoned landfills (Degnan and Harte, 2013), petroleum leak or spill sites (Cozzarelli and others, 2016), wastewater disposal (domestic and larger septic systems) (Kent and Fox, 2004; Erickson and others, 2014; Elliott and others, 2018a), wastewater reuse for irrigation (Elliott and others, 2018b), and so forth. Despite the voluminous literature on As and Mn fate and transport, significant gaps remain in understanding

relationships between speciation and mobility of As, particularly in sulfidic environments (O'Day and others, 2004; Wilkin and others, 2019) and Mn, particularly the role of Mn(III) aqueous and sorbed species (Madison and others, 2013).

Human activities such as intensive groundwater pumping can result in groundwater level fluctuations or upwelling of groundwater that can mobilize or redistribute geogenic constituents. Flushing or redistribution of geogenic contaminants can result from human appropriation of water flows (Degnan and others, 2020; Lindsey and others, 2021; Minsley and others, 2021).

The development and extraction of both conventional and unconventional fossil energy sources and effects on beneficial uses of water resources is an active and highly visible research area (McMahon and others, 2018a; McMahon and others, 2019; McMahon and others, 2021a). The effects of oil spills and well stimulation for unconventional oil and gas production are at the forefront of this area of research (McMahon and others, 2018b; Kulongoski and McMahon, 2019). The effects of intentional and unintentional releases of oil and gas wastewater into the environment are also an important area of study (Wright and others, 2019; Rosecrans and others, 2021). Liquids (hydrocarbons and water) and gases move and behave differently in the subsurface. Also unknown is the composition of fracking fluids. Oil and gas wastewater is disposed via deep injection wells that may leak and via beneficial re-use applications such as deicing or irrigation of crops (Tasker and others, 2018; Redmon and others, 2021). Because water and contaminant transport through the vadose zone and groundwater is slow, it can be decades before contaminants are present in drinking water wells or in groundwater discharge (McMahon and others, 2017). The distribution of geogenic hydrocarbons and other organic contaminants mobilized by oil and gas resource extraction is also unknown (Morrill and others, 2013; McMahon and others, 2017).

Managed aquifer recharge (MAR) offers the opportunity to improve the quality of the injected water through filtration of pathogens, degradation of organics, sorption of trace elements, or precipitation of solids containing undesirable solutes; however, it can also be associated with unintended consequences. There are several typical types of MAR, including: river-bank filtration; surface-water spreading; aquifer storage and recovery; soil aquifer treatment (also known as stormwater infiltration or tertiary wastewater treatment by infiltration); infiltration basins; and aquifer storage, transfer, and recovery (Dillon, 2005). Aquifer storage and recovery could be an increasingly important means of impeding saltwater intrusion exacerbated by sea-level rise (Hussain and others, 2019). The interaction of fresh, oxygenated water into a salty aquifer can result in reactions with the native water and aquifer solids, including cation exchange, and mineral dissolution and precipitation. Geochemical modeling has been used to simulate hydrologic and geochemical effects of aquifer storage recovery in many coastal areas, including a carbonate and sand aquifer in South Carolina (Petkewich and others, 2004), iron-rich, carbonate-poor coastal plain aquifers in the New York City area (Brown and Misut, 2010), and several carbonate aquifers in southern Florida (Mirecki, 2006).

MAR types are expanding to include novel water sources and purposes, such as use of diverse sources of water (reclaimed wastewater or recycled wastewater); lower quality water (for example, treated wastewater from oil and gas development); injection of fresh water into brackish aquifers; and injection of water to store thermal energy. Injection of water that differs in composition from the ambient groundwater can, however, induce geochemical changes that degrade water quality due to mobilization of geogenic constituents. A recent survey shows that 26 percent of the MAR projects in the United States have been abandoned, with 21 percent of the wells abandoned because of water-quality problems caused by vanadium (V), Mn, Fe, nickel (Ni), zinc (Zn), As, fluorine (F), and U. Half of the wells were abandoned because of elevated As concentrations (Fakhreddine and others, 2021). Table C1 provides a summary of geologic abundance of selected elements, and the average upper-crustal abundance of each element serves as a proxy for the concentration in aquifer material; only a small fractional release from solid materials may be required to trigger a water-quality concern. For example, geologic materials have a range of As concentrations from 40 to 134 micromoles per kilogram ($\mu\text{mol/kg}$) dry weight. Assuming a porosity of 0.4 and solid-phase density of 2.65 grams per cubic centimeter (g/cm^3), the ratio of solids to porewater is 4.0 kilograms per liter (kg/L). If all the As bound to the geologic material was released, the dissolved concentration would be 160–540 micromoles per liter ($\mu\text{mol/L}$) (123–415 micrograms per liter [$\mu\text{g/L}$]), compared to the U.S. Environmental Protection Agency's (EPA's) drinking water standard of 0.13 $\mu\text{mol/L}$ (10 $\mu\text{g/L}$) (table C1).

Geogenic constituent mobilization is controlled by the chemical forms of As and other constituents in geologic materials, the difference in geochemical conditions between injected water and ambient groundwater, and the resulting groundwater geochemical conditions. Without sampling and geochemical analyses, little would be known about the chemical forms of geogenic constituents in site-specific geologic materials. The very small percentage release to achieve exceedance in table C1 illustrates that there is substantial potential for geogenic elements to deteriorate the quality of the water introduced in MAR to the point where water cannot be put to its intended beneficial use. The extent to which each element will be released depends on its chemical forms in the sediments, contact between sediments and water introduced during MAR (controlled by hydrology), and potential for the chemical composition of the introduced water to induce release. For example, the dominant forms of As in sediments are pyrite and other sulfide minerals in anaerobic groundwater or a mix of pyrite and As(V) sorbed to hydrous ferric oxides and other reactive constituents in aerobic groundwater. Thus, water with oxygen and (or) nitrate introduced to anaerobic groundwater will mobilize As if hydrologic conditions are favorable for the introduced water to come into contact with pyrite and other sulfide minerals. Conversely, when anaerobic water with electron donors is introduced into an aerobic aquifer, As adsorbed to iron oxides may mobilize over time during MAR (fig. C1.1).

Approaches to Fill Knowledge Gaps

Field Studies Targeting the Effects of Anthropogenic Activities on Mobilizing Geogenic Constituents

Field studies of human effects could be planned and coordinated with stakeholders who are engaged in various practices to manage water supplies and transfers. Improved coordination between researchers and stakeholders could provide new opportunities to learn how well various water resource management efforts (for example, “best management practices”) actually work, and what sorts of unintended consequences may occur (see Strategic Action 12, in Evenson and others, 2013). Understanding and modeling the effects of human activities on water quality commonly rely on available data and literature, which may be incomplete or not directly relevant. Field studies that provide comprehensive information about water-quality responses to specific human activities are difficult to carry out, in part because they require advance planning and coordination, as well as long-term commitments in many cases.

Studies should begin before implementation of a targeted plan to manipulate water supplies and continue throughout and afterwards, to provide records suitable for trend and effect analysis. Empirical studies could be integrated with modeling studies, to provide feedback for adaptive modeling and data collection. Studies could be multi-disciplinary (for example, hydrology, chemistry, biology, microbiology) to provide a comprehensive way to monitor and explain water movement and water-quality changes. Studies would require various combinations of data gathering techniques including high-frequency monitoring with remote sensors (for example, temperature, specific conductance, pH, dissolved oxygen, dissolved organic matter, nitrate, and so forth), laboratory analyses of discrete samples (for example, chemistry, isotopes, biometrics), and remote sensing (for example, geophysics, land cover, lidar), among others. Additional topical research may be needed to investigate unexplained or poorly parameterized processes that affect system-wide modeling.

Studies that combine geochemical samples, geophysical surveys, geologic mapping, and hydrogeologic modeling have demonstrated the need for, and efficacy of, multidisciplinary and multiscale techniques to understand and model complex water resource problems. This includes transport of geogenic constituents from deeper groundwater flow through upwelling to drinking water aquifer depths (Gallegos and others, 2021; Minsley and others, 2021). It is also essential to carefully choose the sampling frequency for the purpose and question. Novel high-frequency sampled groundwater-quality measurements (Saraceno and others, 2018) can be used in combination with high-frequency sampled water level measurements and frequent (bi-monthly) discrete sampling of a comprehensive suite of water-quality parameters. The water-quality monitoring results can be combined with climate data and other information. Outcomes can include development of proxies for suites of contaminants, predictions of constituent speciation, understanding of mobilization drivers,

interconnectivity and responsiveness between layered aquifers, and numerous other applications relevant to development of predictive models or other management tools (Levitt and others, 2019; Musgrove and others, 2019; Degnan and others, 2020).

Quantifying and understanding groundwater-age distributions can elucidate geogenic constituent sources, anthropogenic stressor contributions to enhance mobilization, and mobilization mechanisms, thereby informing appropriate management responses (McMahon and others, 2015; Kingsbury and others, 2017; Stackelberg and others, 2018; Levitt and others, 2019; Musgrove and others, 2019; McMahon and others, 2021b). Chemical and isotopic analyses of field samples can identify sources of water and dissolved constituents in unconventional oil and gas produced water (Gallegos and others, 2021). Comprehensive field studies could evaluate sources of organic compounds (for example, methane, benzene) in groundwater to differentiate geogenic sources from anthropogenic sources; proper identification of source is imperative for selection and implementation of an appropriate management action (McMahon and others, 2016b, 2017, 2019; Wright and others, 2019).

Incorporate Human Activities into Hydrologic and (or) (Bio)Geochemical Models

For proposed MAR sites and designs—as well as other human activities—comprehensive a priori geochemical modeling and field studies could be carried out to quantify how the expanding use of MAR or other practices could affect water quality and intended beneficial use.

There are many hydrologic and geochemical unknowns associated with typical types of MAR, resulting in a high rate of facility abandonment. Improved understanding and comprehensive modeling of MAR practices could reveal unanticipated consequences related to coupled hydrologic and biogeochemical processes that can cause mobilization of geogenic constituents, which in turn can deteriorate water quality to the point where the water will not meet standards for its intended beneficial use.

Gap 4. Climate Change Effects on Geogenic Constituent Distribution

Knowledge Gaps

Evolving Effects of Geogenic Constituents Under Changing Climatic Conditions and Mitigation Strategies

Change in wet and dry cycles can result in constituent build-ups during dry or drought conditions followed by flushing of constituents through the system during wet or flood conditions (Nordstrom, 2009). The pattern and concentrations of fluxes of constituents would vary with changes in distribution and flushing patterns. Also, influx of carbon from expanded or more frequent flooding, or redistribution of geogenic constituents in

sediment repositories, could also change the mobilization and occurrence patterns of geogenic constituents. The effect of drought on geogenic constituent mobilization requires much additional understanding and study. Lombard and others (2021b) estimated that in drought conditions, an additional 1.4 million domestic well users would be using a groundwater source with As concentrations exceeding the EPA MCL—a 54 percent increase from the scenario in non-drought condition. Bondu and others (2016) describe how climate change, land use change, increased water well pumping, and water table declines could mobilize As via oxidation of arsenic-bearing sulfides in bedrock aquifers. Drought could substantially change the distribution of irrigation or irrigation source water in agricultural areas.

Sea-level rise is expected to affect water availability in coastal areas, but the effects are not well understood. Census data show that in 2017, 94.7 million people (29 percent of the United States population) lived in coastline counties (Cohen, 2019). Thus, understanding the effects of sea-level rise on beneficial uses of water is critically important. Vengosh (2014, p. 328–329) describes saltwater intrusion as “...one of the most widespread and important processes that degrades water-quality to levels exceeding acceptable drinking and irrigation standards.” Sea-level rise can be expected to accelerate saltwater intrusion in groundwater and to promote the up-stream advancement of the salt-water wedge in coastal rivers. In the Delaware River, upstream advancement of salt water may require moving the intake for the water supply of Philadelphia (Hurdle, 2020). Sodium and Mg are the dominant cations in seawater but saline groundwater affected by seawater intrusion is typically dominated by Ca owing to cation exchange reactions between the intruding sea water and sediments (Appelo and Postma, 2005). Calcium is potentially more reactive than Na, which may promote mobilization of geogenic constituents on exchange sites or sequester geogenic constituents if carbonate-mineral precipitation occurs. Inundation of coastal soils can lead to As mobilization, but the potential magnitude of the problem and effect on other geogenic constituents is unknown (LeMonte and others, 2017). Studies on Jeju Island, a volcanic island south of the Korean peninsula where groundwater management practices are similar to those used for the Hawaiian Islands, have shown that sea-water intrusion can occur up to 2.5 km inland owing to the permeability of the basaltic aquifer (Vengosh, 2014). Thus, the drinking and irrigation water on the Hawaiian and other volcanic islands may be particularly vulnerable to the effects from sea-level rise.

Carbon dioxide sequestration, which involves injection and storage of large volumes of carbon dioxide in deep formations, can have water-quality effects, but the extent of these effects is unknown. Injection of carbon dioxide causes a decrease in pH (Carroll and others, 2009; Wilkin and DiGiulio, 2010), which can threaten the integrity of the cap rock by dissolving cements, increasing dissolved salt concentrations, and increasing the concentrations of BTEX (a group of volatile organic compounds; benzene, toluene, ethyl benzene, and xylene) and other hydrophobic organic compounds (Kharaka and others, 2006). Decreases in pH can mobilize metal ions like Cu, Cd, and Pb, and increases in dissolved salt concentrations

can mobilize oxyanions like As (Kharaka and others, 2010). Whether mobilization of toxic inorganic and organic solutes will be far reaching (Zheng and others, 2012) or short-range and transient (Plampin and others, 2021) is unknown. Considering the potential for widespread application of deep injection of carbon dioxide for sequestration, understanding possible consequences is an important research area that needs to be addressed.

Approaches to Fill Knowledge Gaps

Wet and Dry Cycles

Improved understanding of the effects of spatial and temporal hydrologic variability can be gained from long-term studies where hydrologic and water-quality data are collected along a gradient of sites from the headwaters to lower parts of the watershed. Water-quality data would include geogenic constituents, particularly those generated during sulfide mineral weathering (for example, As, Cu, Se, Zn). Hydrologic data would include rainfall, groundwater levels, and streamflow along with water temperature and specific conductance in streams and dissolved oxygen in wells. Findings from an investigation of changes in water quality over time carried out in the upper Snake River watershed (Manning and others, 2013) suggest that the Upper Colorado River Basin would provide an excellent location for such a study in the semi-arid west. Companion studies could be conducted in humid areas and areas subject to flooding. Such studies can provide long-term datasets for examining long-term temporal and spatial trends and whether trends are linked to climate change, decadal oscillations, or both.

Sea-Level Rise

Approaches to understanding the effects of sea-level rise involve assessing vulnerability, understanding effects of sea-level rise on the mobility of geogenic constituents, and improving models for carrying out vulnerability assessments. The vulnerability assessments could be carried out for fresh-water intakes to advancing salt-water wedges in coastal rivers and for sea-water intrusion to groundwater in coastal aquifers. Concentrations and chemical forms of geogenic constituents in coastal soils and sediments could be characterized. Understanding the concentrations and chemical forms can identify the geogenic constituents most likely to be mobilized by sea-level rise. Laboratory and well-controlled field experiments of the effects of inundation on mobility of geogenic constituents are needed to develop and improve models used in vulnerability assessments. The Hawaiian and other islands rely on careful management of groundwater to maintain fresh water for beneficial uses. Management models can prove useful for assessing the effect of sea-level rise on maintaining fresh water for beneficial uses, but the effects of agricultural, industrial, and domestic return flows and discharges could also be considered carefully.

Carbon Dioxide Sequestration

Gaps in understanding water-quality effects of carbon dioxide sequestration could be addressed with a combination of field, modeling, and laboratory studies. Field studies could be carried out in coordination with carbon dioxide sequestration activities (Kharaka and others, 2006; Kharaka and others, 2010). Findings from such field studies can identify constituents with the greatest potential to affect water quality and spur improvements in models required to predict potential effects (Zheng and others, 2012; Plampin and others, 2021). Application of models to describe results of field investigations can identify processes and parameters for which improved understanding is needed. Processes and parameters needed to improve predictive modeling can be examined in laboratory and small-scale field experimental studies, which allow controls to be put in place that will allow specific sets of processes to be examined and parameters needed to describe those processes to be quantified.

There is a need to develop basic understanding or conceptual models for the effects of climate change (flood inundation frequency and extent, extended drought conditions, sea level change and inundation) and how the changes redistribute or change mobility of geogenic constituents. For example, in semi-arid climates (Upper Colorado River Basin and San Joaquin Valley in California), climate-change-driven drought will drive decreases in the water table elevation both directly, owing to lower precipitation and higher evapotranspiration, and indirectly, owing to increased pumping of groundwater for irrigation and other beneficial uses (Alley and others, 1999). Questions include whether sulfide-rich sediments will be exposed to oxygen, increasing sulfide-mineral oxidation rates, which, in turn, will drive decreases in pH mobilizing toxic metal ions like Cu and Pb and oxyanions like As.

Expected Outcomes

Numerous publications document point and non-point sources of geogenic constituents, which are ubiquitous across the nation. Most importantly, geogenic constituents at high concentrations can limit or threaten water availability for numerous beneficial uses. Specific processes and drivers that mobilize geogenic constituents, including mobilization by anthropogenic activities such as agriculture and groundwater pumping, are not understood well enough to model and map effectively. Completion of the outlined activities as part of the current IWS basin activities will add knowledge and capabilities applicable to water availability understanding in the study basins—and to other basins.

Specific results from completing these activities would include the following:

- Expertise and methods to distinguish naturally occurring sources or distribution process from anthropogenic sources or distribution processes. Distinguishing natural from anthropogenic sources and processes is crucial for the development of appropriate models, regulations based on

sound science, remediation strategies, responses, or other management tools for geogenic constituents.

- The ability to quantify, model, map occurrence, and map risk from constituent mixtures and complex distribution patterns. These can provide more comprehensive assessments of geogenic limitations on water availability for multiple uses (beyond constituent-by-constituent exceedance probabilities), which is a key step toward developing more appropriate methods, models, and strategies to manage/optimize water resources and to quantify human exposure risk.
- Knowledge of groundwater availability and sustainability in conditions of enhanced constituent mobilization and redistribution from irrigation, managed aquifer recharge, pumping, and chemical inputs from agriculture, landfills, wastewater releases, organic chemical spills, oil and gas production, and mining. As water use demands increase, we can strive to understand how human activities exacerbate water availability problems from high concentrations of geogenic constituents. This understanding is fundamental for development of appropriate methods, models, strategies, and other management tools to anticipate, quantify, and respond to water availability needs.
- Understanding of processes and parameters can facilitate predictions of how climate change will directly or indirectly affect beneficial uses due to redistribution or mobilization of constituents. We should be able to better anticipate and mitigate climate-related limitations on water availability for intended beneficial use.

Outcomes from this research can provide the basis for incorporating the effects of geogenic constituents on water resource assessment. Improved understanding can improve matching resource-water quality with the water-quality needs of specific beneficial uses, and identifying what is affecting or limiting required uses. The new knowledge can also allow for more effective management of groundwater and surface water resources, and for planning needed treatment or blending strategies to meet beneficial use water-quality requirements.

There are limitations inherent in this report, which is focused on a selection of important scientific knowledge gaps and suggested approaches for improving understanding that are relevant to current and potential USGS directions and capabilities. Success in these areas will depend on maintaining capabilities for water-quality research in topics such as chemistry, geochemistry, microbiology, hydrology, geology, geochronology, and modeling large datasets. Development of next-generation forensic tools, and other chemical and isotopic approaches for field and laboratory studies will require expanding research laboratory methods beyond current analytical schedules. Analysis of the effects of water management will depend on our ability to coordinate with stakeholders and to support long-term studies—before, during, and after implementation. Although this chapter touches on a variety of information needs required to understand and predict how

geogenic constituents impact water availability, it is incomplete. Additional issues exist, and new ones will emerge, so it will be important to maintain broad-based expertise and flexibility to remain nimble.

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Appendix C1. Additional Information Related to Geogenic Constituents in Water

Glossary

activity Rate of decay of a radioactive isotope, typically expressed as becquerels or curies. The activity equals the number of radionuclides times the decay constant ($a_i = N_i \lambda_i$, where a_i is the activity, N_i is the number of radionuclides of type i , and λ_i is the decay constant of radionuclide i).

alpha decay (α) The mode of radioactive decay where an alpha particle, containing two protons and two neutrons, is released from the nucleus of a radioactive isotope. Alpha decay generates a new element with an atomic number and nominal atomic mass two units and four units, respectively, less than the parent radioactive isotope.

becquerel (Bq) The unit for activity in the International System of Units (SI), (Newell and Tiesinga, 2019). One becquerel equals one disintegration per second (s^{-1}).

beta decay (β) The mode of radioactive decay where a beta particle (a high-energy electron) is released from the nucleus of a radioactive isotope. Beta decay generates a new element with the same nominal atomic mass and an atomic number one unit higher than the parent radioactive isotope.

cosmogenic radioisotope Cosmogenic radioisotopes are created by interactions between cosmic radiation and elements in the atmosphere, hydrosphere, or lithosphere. Examples include tritium (^3H), beryllium-10 (^{10}Be), carbon-14 (^{14}C), chlorine-36 (^{36}Cl). Cosmogenic radioisotopes are unlikely to occur at activities high enough to affect water availability. Anthropogenic sources, such as atmospheric testing of nuclear weapons and spills or leaks of radioactive wastes, are the most likely sources that can affect water availability.

curie (Ci) The traditional unit for activity. One curie equals 3.7×10^{10} Bq. Originally the curie was defined as the activity of one gram (g) of radium-226 (^{226}Ra), but the decay constant of ^{226}Ra was subsequently revised so that definition no longer applies.

daughter (radioactive isotope) A radioactive isotope generated by radioactive decay of one or more other, generally heavier, radioactive isotopes. A radioactive isotope that produces the daughter radioisotope is called the “parent” radioisotope. For examples, see parent (radioactive isotope).

decay constant (λ_i) The rate constant in the radioactive decay equation: $N_i, t / N_{i,0} = e^{-\lambda_i t}$, where N_i, t is the number of radionuclides at time t and $N_{i,0}$ is the initial number of radionuclides. The decay constant is often expressed in per year (yr^{-1}), but it is often difficult to ascertain whether the reported value is consistent with the SI definition of year (Newell and Tiesinga, 2019). The SI unit for the decay constant is per second (s^{-1}) (Newell and Tiesinga, 2019).

dose equivalent, or equivalent dose (rem, millirem, or sievert [Sv]) A measure of the energy from ionizing radiation deposited in tissues. The traditional unit is the rem; the SI unit is the sievert.

electron capture (EC) The mode of radioactive decay where an electron, typically an electron from a shell close to the nucleus (core electron), is captured by the nucleus of a radioactive isotope. EC is accompanied by the release X-rays and, in some cases, by electrons similar in energy to X-rays (Auger electrons).

gamma ray (γ) High-energy electromagnetic radiation that typically accompanies radioactive decay via alpha, beta, positron, or EC decay. Gamma decay does not change either the atomic number or nominal atomic mass of the original radioactive isotope.

gross alpha Sum of activities of all alpha-emitting radioisotopes in a sample. The maximum contaminant level (MCL) for gross alpha in drinking water established by the U.S. Environmental Protection Agency (EPA) is 0.6 becquerel per liter (Bq/L), which equals 15 picocuries per liter (pCi/L) (EPA, 2018).

gross beta The sum of activities of all beta-emitting radioactive isotopes in a sample. The MCL for gross beta in drinking water established by the EPA is the activity that yields a dose equivalent of 4 millirems per year. The MCL is based on calculations of the energy from beta and gamma emissions from 179 anthropogenic radioisotopes along with risk assessment estimates based on exposure to drinking water (EPA, 2002).

half-life ($t_{1/2}$) The time required for half of the radionuclides initially present to decay away. Although the half-life is often expressed in years for convenience, it is often difficult to ascertain whether values are consistent with the SI definition of the year (Newell and Tiesinga, 2019). $t_{i,1/2} = \ln(2) / \lambda_i$, where λ_i is the decay constant of radioisotope i .

millirem One millirem is equal to one thousandth of a rem.

parent (radioactive isotope) A radioactive isotope that decays to produce other (daughter) isotopes that may be either stable or radioactive isotopes. For example, uranium-238 (^{238}U) decays through four intermediate radioactive isotopes to produce ^{226}Ra , which decays to radon-222 (^{222}Rn), which decays through two intermediates to lead-210 (^{210}Pb), which decays through an intermediate to polonium-210 (^{210}Po), which decays to stable ^{206}Pb . So, ^{238}U is the parent to the daughter radioisotopes ^{226}Ra , ^{222}Rn , ^{210}Pb , and ^{210}Po . ^{226}Ra can be considered both parent and daughter.

primordial radioisotopes Primordial radioisotopes have half-lives that are long enough compared to the age of the earth that substantial fractions of the isotopes present after the formation of the earth remain.

positron decay (β^+) The mode of radioactive decay where a positron particle (a high-energy anti-electron) is released from the nucleus of a radioactive isotope following electron capture. Positron decay generates a new element with the same nominal

atomic mass and an atomic number one unit lower than the original radioactive isotope.

rem The rem is the traditional unit for dose equivalent, which is a measure of the energy from ionizing radiation deposited in tissues. One rem is equal to 0.01 joules per kilogram (J/kg) of tissue. The SI unit for dose equivalent is the sievert.

secular equilibrium A situation where a steady state has been achieved so that the activity of a daughter radioisotope is essentially equal to the activity of the parent radioisotope. In other words, the daughter radioisotope is being produced at essentially the same rate as it is decaying away. Secular equilibrium can only occur when the half-life of the daughter radioisotope is less than that of the parent radioisotope. It is considered to occur after passage of time equivalent to several (for example, five) half-lives of the daughter. At secular equilibrium, $N_D / N_P = \lambda_P / \lambda_D = t_{1/2,D} / t_{1/2,P}$, where N is the number of radioactive nuclides and the subscripts D and P refer to the daughter and parent, respectively.

SI (unit) The International System of Units, also known as the modern metric system (Newell and Tiesinga, 2019).

sievert (Sv) The SI unit for dose equivalent. One Sv is equal to 1 J/kg of tissue. 1 Sv=100 rem.

trigger level The gross beta activity above which further investigation is required to determine whether activities in drinking water exceed the MCL. The trigger level established by the EPA is 2 Bq/L, which equals 50 pCi/L ($\text{pCi}=10^{-12}\text{ Ci}$).

year (unit of time) The SI definition of the year is based on the tropical year for 1900, from which the length of time corresponding to the second has been defined (Newell and Tiesinga, 2019): 365.2422 days.

Table C1.1. Primordial radioisotopes and daughters, their half-lives, decay constants, abundance in upper crustal materials, equivalent porewater activities, and, for comparison, human-health benchmark activities.

[Decay modes and half-lives from the NUBASE2020 evaluated nuclear data library (Kondev and others, 2021). Half-lives in the NUBASE2020 library are reported using the SI definition of year (see glossary). More than thirty additional isotopes are listed in the library as stable but with one or more references in the peer-reviewed literature that report half-lives for the isotopes. These are not included in this compilation. For the purpose of calculating activities from concentrations, decay constants in years were converted to seconds using the SI definition of the second: 31,556,925.97 per year (Newell and Tiesinga, 2019). Daughters belonging to the uranium-235 (²³⁵U), uranium-238 (²³⁸U), and thorium-232 (²³²Th) decay chains are color-coded red, blue, and green, respectively. Radioisotopes that are not color-coded decay directly to isotopes considered stable. $t_{1/2}$, half-life; λ , decay constant; $\mu\text{mol/kg}$, micromole per kilogram; Bq/kg, becquerel per kilogram; Bq/L, becquerel per liter; $\beta\beta$, double beta decay; $\beta^+\beta^+$, double positron decay; α , alpha decay; MCL, maximum contaminant level established by the U.S. Environmental Protection Agency (EPA, 2002); mrem/yr, millirems per year; pCi/L, picocuries per liter; %, percent; SI, International System of Units; —, no data.]

Nuclide	Decay mode	$t_{1/2}$ (years)	λ (years ⁻¹)	Abundance ^a ($\mu\text{mol/kg}$)	Activity ^b (Bq/kg)	Equivalent porewater ^c activity (Bq/L)	Human health benchmark (Bq/L ^d)
Primordial							
¹³⁰ Ba ^e	$\beta^+\beta^+$	1×10^{21}	6.9×10^{-22}	5.0	6.5×10^{-11}	2.6×10^{-10}	2 ^f
¹³² Ba ^e	$\beta^+\beta^+$	$>3 \times 10^{20}$	$<2.3 \times 10^{-21}$	4.5	2.0×10^{-10}	7.9×10^{-10}	2 ^f
²⁰⁹ Bi ^g	α	2.0×10^{19}	3.5×10^{-20}	0.17	1.1×10^{-10}	4.5×10^{-10}	0.6 ^h
⁴⁸ Ca ⁱ	$\beta\beta$	5.6×10^{19}	1.2×10^{-20}	1,200	2.9×10^{-7}	1.2×10^{-6}	2 ^f
¹¹³ Cd ^d	β	8.0×10^{15}	8.6×10^{-17}	0.0098	1.6×10^{-8}	6.4×10^{-8}	2 ^f
¹¹⁶ Cd ^d	$\beta\beta$	2.7×10^{19}	2.6×10^{-20}	0.0060	3.0×10^{-12}	1.2×10^{-11}	2 ^f
¹⁵¹ Eu ^k	α	4.6×10^{18}	1.5×10^{-19}	3.2	9.1×10^{-9}	3.6×10^{-8}	0.6 ^h
¹⁵² Gd ^l	α	1.1×10^{14}	6.4×10^{-15}	0.051	6.2×10^{-6}	2.5×10^{-5}	0.6 ^h
⁷⁶ Ge ^m	$\beta\beta$	1.9×10^{24}	3.7×10^{-25}	1.5	1.1×10^{-14}	4.2×10^{-14}	2 ^f
¹⁷⁴ Hf ⁿ	α	2.0×10^{15}	3.5×10^{-16}	0.048	3.2×10^{-7}	1.3×10^{-6}	0.6 ^h
¹¹⁵ In ^o	β	4.4×10^{14}	1.6×10^{-15}	0.47	1.4×10^{-5}	5.6×10^{-5}	11 ^f
⁴⁰ K ^p	β^f	1.2×10^9	5.6×10^{-10}	49	520	2,100	2 ^f
¹³⁸ La ^q	β^+	1.0×10^{11}	6.7×10^{-12}	0.19	0.025	0.10	2 ^f
¹⁷⁶ Lu ^r	β	3.7×10^{10}	1.9×10^{-11}	0.047	0.017	0.067	2 ^f
¹⁰⁰ Mo ^s	$\beta\beta$	7.1×10^{18}	9.8×10^{-20}	1.1	2.0×10^{-9}	8.0×10^{-9}	2 ^h
¹⁴⁴ Nd ^t	α	2.3×10^{15}	3.0×10^{-16}	45	2.6×10^{-4}	0.0010	0.6 ^h
¹⁵⁰ Nd ^t	$\beta\beta$	9.3×10^{18}	7.5×10^{-20}	11	1.5×10^{-8}	6.1×10^{-8}	2 ^h
¹⁸⁴ Os ^u	α	1.1×10^{13}	6.2×10^{-14}	3.2×10^{-8}	3.8×10^{-11}	1.5×10^{-10}	0.6 ^h
¹⁸⁶ Os ^u	α	2.0×10^{15}	3.5×10^{-16}	2.5×10^{-6}	1.7×10^{-11}	6.7×10^{-11}	0.6 ^h
¹⁹⁰ Pt ^v	α	4.8×10^{11}	1.4×10^{-12}	3.4×10^{-7}	9.2×10^{-9}	3.7×10^{-8}	0.6 ^h
⁸⁷ Rb ^w	β	5.0×10^{10}	1.4×10^{-11}	270	73	290	11 ^f
¹⁸⁷ Re ^x	β	4.2×10^{10}	1.7×10^{-11}	0.0007	0.00022	0.0009	330 ^f
⁸² Se ^y	$\beta\beta$	8.8×10^{19}	7.9×10^{-21}	0.10	1.5×10^{-11}	5.9×10^{-11}	2 ^f
¹⁴⁷ Sm ^z	α	1.1×10^{11}	6.5×10^{-12}	4.7	0.58	2.3	0.6 ^h
¹⁴⁸ Sm ^z	α	6.3×10^{15}	1.1×10^{-16}	3.5	7.3×10^{-6}	2.9×10^{-5}	0.6 ^h
¹²⁸ Te ^{aa}	$\beta\beta$	2.3×10^{24}	3.1×10^{-25}	1.4	8.2×10^{-15}	3.3×10^{-14}	2 ^f
¹³⁰ Te ^{aa}	$\beta\beta$	7.9×10^{20}	8.8×10^{-22}	1.5	2.5×10^{-11}	1.0×10^{-10}	2 ^f
²³² Th ^{ab}	α	1.4×10^{10}	5.0×10^{-11}	45	42	170	0.6 ^h
²³⁵ U ^{ac}	α	7.0×10^8	9.8×10^{-10}	0.079	1.5	6.0	0.4
²³⁸ U ^{ac}	α	4.5×10^9	1.6×10^{-10}	11	32	130	0.4
⁵⁰ V ^{ad}	β^+	2.7×10^{17}	2.6×10^{-18}	4.8	2.3×10^{-7}	9.3×10^{-7}	2 ^f
¹⁸⁰ W ^{ae}	α	1.6×10^{18}	4.4×10^{-19}	0.012	1.0×10^{-10}	4.0×10^{-10}	0.6 ^h
¹³⁶ Xe ^{af}	$\beta\beta$	2.2×10^{21}	3.2×10^{-22}	—	—	—	—
⁹⁶ Zr ^{ag}	$\beta\beta$	2.3×10^{19}	3.0×10^{-20}	59	3.3×10^{-8}	1.3×10^{-7}	2 ^f
Daughter							
²²⁷ Ac ^{ah}	β	21.8	0.032	2.5×10^{-9}	1.5	6.0	2 ^f
²¹⁰ Pb	β	22.2	0.031	5.4×10^{-8}	32	130	2 ^f
²³¹ Pa	α	32,650	2.1×10^{-5}	3.7×10^{-6}	1.5	6.0	0.6 ^h
²¹⁰ Po	α	0.379	1.8	9.3×10^{-10}	32	130	0.6 ^h
²²² Rn	α	0.010	66	—	—	—	— ^{af}
²²⁶ Ra	α	1,600	4.3×10^{-4}	3.9×10^{-6}	32	130	0.7 ^{ai}
²²⁸ Ra	β	5.75	0.12	1.8×10^{-8}	42	170	0.7 ^{ai}
²²⁸ Th	α	1.91	0.36	6.1×10^{-9}	42	170	0.6 ^h

Table C1.1.—Continued

Nuclide	Decay mode	$t_{1/2}$ (years)	λ (years ⁻¹)	Abundance ^a (μmol/kg)	Activity ^b (Bq/kg)	Equivalent porewater ^c activity (Bq/L)	Human health benchmark (Bq/L ^d)
²³⁰ Th	α	75,400	9.2×10^{-6}	1.8×10^{-4}	32	130	0.6 ^j
²³⁴ Th	β	0.066	10.5	1.6×10^{-10}	32	130	2 ^f
²³⁴ U	α	246,000	2.8×10^{-6}	6.0×10^{-4}	32	130	0.4 ^{ac}

^aThe abundance of primordial isotopes was calculated from the corresponding elemental abundance (table C1 or, for elements not included in table C1, as reported in the footnotes) and the mole fraction for the isotope (Holden and others, 2018). None of the isotopes in this table was affected by the recent revisions to ranges in isotope abundances in Prohaska and others (2022). The abundance of daughters was calculated assuming secular equilibrium with the corresponding primordial parent using the equation in the Glossary under “secular equilibrium.”

^bThe abundance in column 5 was converted to activity as described in the Glossary under “activity.”

^cThe equivalent activity in porewater was calculated assuming instantaneous release of the specific activity in the sediments as described in table C1.

^dWhere there are potential effects on water availability from chemical toxicity of the element corresponding to the radioisotope, they are presented in table C1. For all other elements in this table, risks associated with radiological health hazards exceed those from toxicity of the element, as far as is currently known.

^eThe average abundance of barium (Ba) in the upper crust is reported in table C1. The mole fractions of ¹³⁰Ba and ¹³²Ba are 0.0011 and 0.001, respectively (Holden and others, 2018). Kondev and others (2021) list both isotopes as stable but cite literature that reports the half-lives and modes of decay shown here. Prohaska and others (2021), which includes many of the same authors as Kondev and others (2021), report the same half-lives as those included in the table.

^fThe human health benchmark for positron and beta emitters is the MCL for gross beta plus gamma activity, which is expressed as a dose-equivalent of 4 mrem/yr based on risk of cancer. See the Glossary for definitions of dose equivalent and millirems. The relationship between mrem/yr and Bq/L varies with the energy of the beta-gamma emissions of the isotope and assumptions about human exposure. EPA reports the equivalent activities in drinking water for a few isotopes in the table (¹¹⁵In, ⁸⁷Rb and ¹⁸⁷Re), and these were used as the human health benchmark for those isotopes (EPA, 2002). For other beta-emitters, the trigger level of 2 Bq/L (50 pCi/L) was used for the human-health benchmark. Exceedance of this activity triggers further investigation to determine if the MCL is exceeded.

^gThe average abundance of bismuth (Bi) in the upper crust is estimated to be 0.17 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ²⁰⁹Bi in naturally occurring Bi is 1 (Holden and others, 2018).

^hThe human-health benchmark for alpha emitters other than uranium (U) isotopes and radium-226 (²²⁶Ra) is the MCL for gross alpha (0.56 Bq/L, 15 pCi/L).

ⁱThe average abundance of calcium (Ca) in the upper crust is estimated to be 6.5×10^5 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ⁴⁸Ca in naturally occurring Ca is 0.00187 (Holden and others, 2018).

^jThe average abundance of cadmium (Cd) in the upper crust is reported in table C1. The mole fractions of ¹¹³Cd and ¹¹⁶Cd are 0.12227 and 0.07512, respectively (Holden and others, 2018).

^kThe average abundance of europium (Eu) in the upper crust is estimated to be 6.6 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹⁵¹Eu in naturally occurring Eu is 0.4781 (Holden and others, 2018).

^lThe average abundance of gadolinium (Gd) in the upper crust is estimated to be 25 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹⁵²Gd in naturally occurring Gd is 0.0020 (Holden and others, 2018). Not included in the compilation of radioactive isotopes that can drive variations in the atomic weight of Gd (Holden and others, 2018; Prohaska and others, 2021).

^mThe average abundance of germanium (Ge) in the upper crust is estimated to be 19 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ⁷⁶Ge in naturally occurring Ge is 0.0775 (Holden and others, 2018).

ⁿThe average abundance of hafnium (Hf) in the upper crust is estimated to be 30 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹⁷⁴Hf is 0.0016 (Holden and others, 2018).

^oThe average abundance of indium (In) in the upper crust is estimated to be 0.49 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹¹⁵In is 0.95719 (Holden and others, 2018).

^pThe average abundance of potassium (K) in the upper crust is reported in table C1. The mole fraction of ⁴⁰K is 0.000117 (Holden and others, 2018).

^q⁴⁰K exhibits branched decay: 89% decaying to ⁴⁰Ca by beta decay and 11% to argon-40 (⁴⁰Ar) by EC.

^rThe average abundance of lanthanum (La) in the upper crust is estimated to be 220 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹³⁸La is 0.000881 (Holden and others, 2018). Positron decay accounts for 65.5 percent and beta decay for 34.5 percent of the radioactive decay of ¹³⁸La.

^sThe average abundance of lutetium (Lu) in the upper crust is estimated to be 1.8 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹⁷⁶Lu is 0.02599 (Holden and others, 2018).

^tThe average abundance of molybdenum (Mo) in the upper crust is reported in table C1. The mole fraction of ¹⁰⁰Mo is 0.09744 (Holden and others, 2018).

^uThe average abundance of neodymium (Nd) in the upper crust is estimated to be 190 μmol/kg (Rudnick and Gao, 2003). The mole fractions of ¹⁴⁴Nd and ¹⁵⁰Nd are 0.23798 and 0.05638, respectively (Holden and others, 2018). ¹⁴⁴Nd is a daughter of samarium-148 (¹⁴⁸Sm), but given that the half-life of ¹⁴⁴Nd is on the order of 10⁶ times the age of the Earth they are not in secular equilibrium and their activities can be considered to be independent of one another.

^vThe average abundance of osmium (Os) in the upper crust is estimated to be 1.6×10^{-4} μmol/kg (Rudnick and Gao, 2003). The mole fractions of ¹⁸⁴Os and ¹⁸⁶Os are 0.0002 and 0.0159, respectively (Holden and others, 2018).

^wThe average abundance of platinum (Pt) in the upper crust is estimated to be 2.8×10^{-3} μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹⁹³Pt is 0.00012 (Holden and others, 2018).

^xThe average abundance of rubidium (Rb) in the upper crust is estimated to be 980 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ⁸⁷Rb is 0.2783 (Holden and others, 2018).

^yThe average abundance of rhenium (Re) in the upper crust is estimated to be 1.1×10^{-3} μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹⁸⁷Re is 0.6260 (Holden and others, 2018).

^zThe average abundance of selenium (Se) in the upper crust is reported in table C1. The mole fraction of ⁸²Se is 0.0882 (Holden and others, 2018).

^{aa}The average abundance of samarium (Sm) in the upper crust is estimated to be 31 μmol/kg (Rudnick and Gao, 2003). The mole fractions of ¹⁴⁷Sm and ¹⁴⁸Sm are 0.1500 and 0.1125, respectively (Holden and others, 2018).

^{ab}The average abundance of tellurium (Te) in the upper crust is estimated to be 4.4 μmol/kg (Goldfarb and others, 2017). The mole fractions of ¹²⁸Te and ¹³⁰Te are 0.3174 and 0.3408, respectively (Holden and others, 2018).

^{ac}The average abundance of thorium in the upper crust is estimated to be 45 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ²³²Th is 0.9998 (Holden and others, 2018).

^{ad}The average abundance of uranium in the upper crust is reported in table C1. The mole fractions of ²³⁵U and ²³⁸U are 0.007204 and 0.992742, respectively (Holden and others, 2018). Human-health benchmark activities for uranium isotopes were calculated from the MCL for uranium (0.13 μmol/L, 30 μg U/L, table C1).

Table C1.1.—Footnote continued

^{ad}The average abundance of vanadium (V) in the upper crust is reported in table C1. The mole fraction of ⁵⁰V is 0.0025 (Holden and others, 2018).

^{ae}The average abundance of tungsten (W) in the upper crust is estimated to be 10 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ¹⁸⁰W is 0.0012 (Holden and others, 2018).

^{af}As inert gases, hazards associated with xenon (Xe) and radon (Rn) are from inhalation rather than consumption of water.

^{ag}The average abundance of zirconium (Zr) in the upper crust is estimated to be 2,100 μmol/kg (Rudnick and Gao, 2003). The mole fraction of ⁹⁶Zr is 0.028 (Holden and others, 2018).

^{ah}Beta and alpha decay account for 98.62 and 1.38 ± 0.36 percent, respectively.

^{ai}Human-health benchmark activities were calculated from the MCL for ²²⁶Ra plus ²²⁸Ra (0.7 Bq/L, 20 pCi/L).

Geogenic constituent mobilization often occurs as the result of changes in local chemical conditions that promote mineral dissolution or desorption. Sorption here refers to the association of one or more chemical species with moieties at or near the boundary between an inorganic or organic solid phase and a solution. The dominant sorption mechanisms are surface complexation (Davis and Kent, 1990) and ion exchange (Helferich, 1962).

As depicted in figure C1.1A, free metal ions like copper (Cu⁺²) and lead (Pb⁺²) sorb extensively to sediments. They can be mobilized by formation of weakly sorbing aqueous complexes with geogenic ligands, like dissolved organic carbon (DOC) (Soeder and Miller, 2003), or anthropogenic ligands like ethylenediaminetetraacetic acid (EDTA) (Davis and others, 2000; Jardine and others, 2002). Lead oxide in pipes can be reductively dissolved by geogenic constituents, like natural organic matter, manganese(II) (Mn[II]), and iron(II) (Fe[II]) (Shi and Stone, 2009). These processes contribute to the potential for exceedance of the drinking water standard for Pb (Jurgens and others, 2019).

As depicted in figure C1.1B, uranium(VI) (U[VI]) exists in aqueous solution as the uranium oxyanion UO₂⁺², which sorbs strongly to sediment grains. Uranium(VI) can be mobilized by formation of weakly sorbing Ca-U(VI)-CO₃⁻² aqueous species, which are favored by increasing pH, calcium (Ca⁺²), and carbonate concentrations (Stoliker and others, 2011; Stoliker and others, 2013; Ma and others, 2014). Uranium(VI) is generated by oxidation of uraninite (UO_{2[s]}) (Campbell and others, 2011) and, more slowly, by U(IV) released during weathering of aluminosilicate minerals.

As depicted in figure C1.1C, oxidation-reduction reactions can result in mobilization or immobilization of redox-reactive geogenic constituents. Some chalcophiles, like copper (Cu) and lead (Pb), can be incorporated into aluminosilicate minerals but others, like arsenic (As), selenium (Se), and molybdenum (Mo, not shown), occur almost exclusively in sulfide minerals. These elements, plus geogenic sulfate, are released during oxidation of pyrite and other sulfide minerals during natural weathering or anthropogenically enhanced weathering driven by, for example,

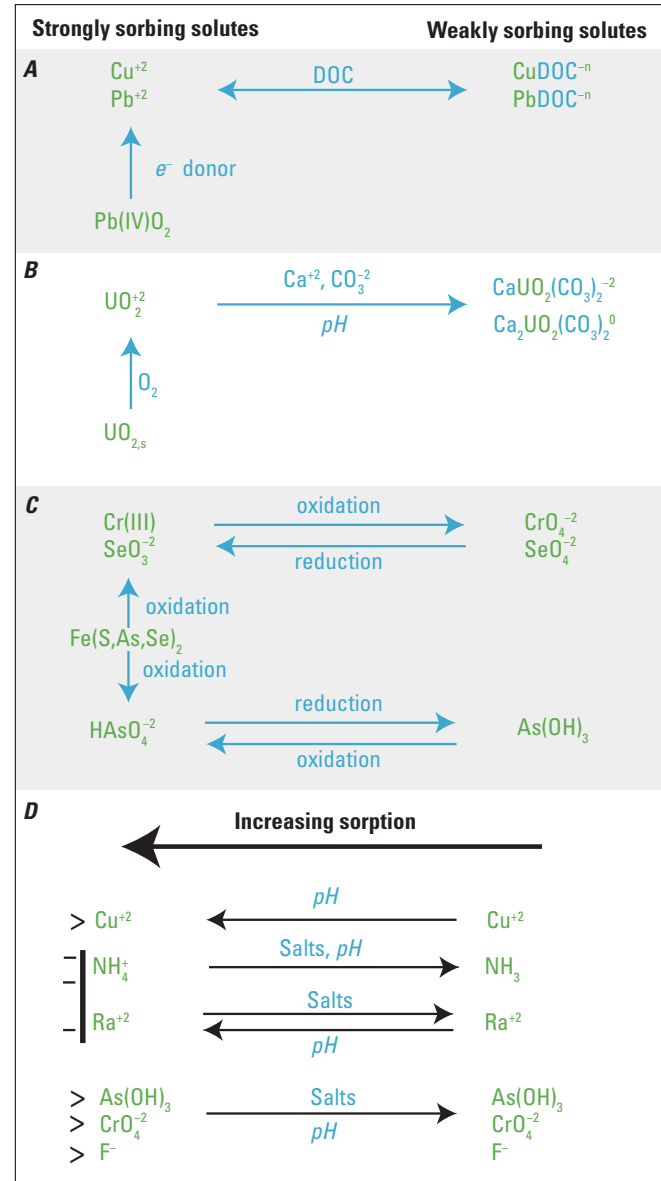


Figure C1.1. Schematic diagram of factors affecting mobilization and sorption of geogenic constituents: A, formation of weakly sorbing dissolved organic carbon complexes; B, formation of weakly sorbing inorganic complexes, such as with aqueous carbonate species favored at alkaline pH values; C, oxidation-reduction reactions; D, changes in salinity and pH; “-” represents a negatively charged surface, and “>” represents surface complexes. As, arsenic; Ca, calcium; Cd, cadmium; Cr, chromium; Cu, copper; DOC, dissolved organic carbon; e⁻, electron; F, fluorine; Fe, iron; H, hydrogen; N, nitrogen; O, oxygen; Pb, lead; Ra, radium; S, sulfur; Se, selenium; U, uranium.

fertilizer application (Postma and others, 1991; Böhlke, 2002; Böhlke and others, 2002), managed aquifer recharge (Fakhreddine and others, 2021), or in-situ leaching of uranium (Bullock and Parnell, 2017). Thus, sulfide-mineral weathering results in mass transfer of these elements from within the sulfide mineral structure to surfaces of iron Fe(III) oxyhydroxides, where they

can be mobilized under favorable chemical conditions. Oxidation-reduction reactions transform As between strongly sorbing As(V) and more weakly sorbing As(III); and Se between strongly sorbing Se(IV) and weakly sorbing Se(VI), which profoundly affects the mobility of As and Se (Hayes and others, 1988; Höhn and others, 2006; Postma and others, 2007). Reduction of chromium(VI) (Cr[VI]) to Cr(III) by Fe(II) or other electron donors (reductants) results in immobilization (Friedly and others, 1995) and oxidation of Cr(III) to Cr(VI) by electron acceptors (oxidants) can mobilize geogenic Cr (Robertson, 1975; Chung and others, 2001).

As depicted in figure C1.1D, the extent to which metal ions like Cu^{+2} , cadmium (Cd^{+2}), and Pb^{+2} sorb to mineral grains in sediments increases with increasing pH (arrows pointing in same direction) owing to the formation of surface complexes that displace hydrogen (H^+) ions from sorption sites (Davis and Kent, 1990; Dzombak and Morel, 1990). In contrast, the extent to which anions like fluorine (F^-) and many oxyanions like Cr(VI), As(V), As(III), and Se(VI) sorb decreases with increasing pH and dissolved salt concentrations (arrows pointing in opposite directions) (Davis and Kent, 1990; Dzombak and Morel, 1990; Kent and others, 1994, 1995; Davis and others, 2000). The extent to which geogenic constituents like Ra^{+2} and NH_4^+ bind to cation exchangers decreases with increasing dissolved salt concentration (Gonneea and others, 2013; Cozzarelli and others, 2017). Radium sorption on cation exchangers increases with increasing pH owing to the formation of surface complexes (Sajih and others, 2014; Missana and others, 2017) but NH_4^+ is expected to desorb as pH values increase owing to the conversion of NH_4^+ to NH_3 .

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