

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



Open-File Report 2023–1086

Cover. A center-pivot irrigation system pumps water from a well in Arizona.
Photograph by the U.S. Geological Survey.

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Edited by Anthony J. Tesoriero, Melinda L. Erickson, Christopher H. Conaway,
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Abstract

This report describes scientific gaps that limit our ability to predict water-quality effects on water availability for beneficial uses across the United States. Water-quality constituents considered in the report include salinity, geogenic constituents, contaminants of emerging concern, and nitrogen. For each constituent, there is a selection of scientific gaps, approaches, and outcomes to help guide portions of the U.S. Geological Survey Water Mission Area (<https://www.usgs.gov/mission-areas/water-resources>) research portfolio and other national research efforts.

Although the report is not comprehensive, and new issues are likely to emerge, it does provide an assessment of many of the major challenges and opportunities concerning water-quality effects on water availability for beneficial uses. Due to the changing nature of water-quality concerns, and to deal with issues not described in this report, it will be important to maintain broad-based expertise and flexibility to address the full spectrum of long-term water-quality issues facing the Nation's water resources.

Acknowledgments

The report was produced as a part of the National Gap Analysis of Water-Quality Understanding and Predictive Capabilities project for the U.S. Geological Survey (USGS). Barbara Bekins is gratefully acknowledged for co-leadership of this project. The authors would also like to thank the following reviewers for their insightful comments on the sections indicated: Allen Gellis, Lisa Lucas, Christine Rumsey, and Peter McMahon (salinity); Paul Stackelberg and Craig Brown (geogenics); Mark Dornblaser and Dana Kolpin (contaminants of emerging concern; and Jud Harvey (nitrogen). Advice and contributions on the salinity gap analysis vignette from Ted Stets, Melinda Erickson, Gretchen Oelsner, Joel Blomquist, Suzanne Paschke, Kelly Warner, and Yousif Kharaka are also gratefully acknowledged. The formatting contributions from contractor Tea Jackson-Strong, editing by Kathryn Pauls, illustration support by Kimber Petersen, and layout by Cory Hurd are also greatly appreciated.

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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)

Conversion Factors—Continued

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)	0.0000002	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 $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as $^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$.

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

AMCL	Alternative maximum contaminant level	Kow	octanol-water partitioning coefficient
ANRA	assimilatory nitrate reduction to ammonium	LNAPL	light non-aqueous phase liquids
ASR	aquifer storage recovery	LC-MS	liquid chromatography mass spectrometry
BGW	brackish groundwater	MAR	Managed aquifer recharge
BPA	bisphenol A	MCL	maximum contaminant level
BTEX	a group of volatile organic compounds: benzene, toluene, ethyl benzene, and xylenes	MTBE	methyl tertiary butyl ether
CCC	EPA criterion continuous concentration	PAH	polyaromatic hydrocarbon
CEC	contaminants of emerging concern	PCB	polychlorinated biphenyl
CFC	chlorofluorocarbon	PFAS	per- and polyfluoroalkyl substances
DBP	disinfection by-product	PFOA	perfluorooctanoic acid
DIC	dissolved inorganic carbon	PFOS	perfluorooctane sulfonic acid
DNRA	dissimilatory nitrate reduction to ammonium	PPCP	pharmaceutical and personal care products
DOC	dissolved organic carbon	PUMP	Predictive Understanding of Multiscale Processes
DoD	U.S. Department of Defense	PWS	public water supplies
DRBC	Delaware River Basin Commission	SAR	sodium adsorption ratio
EDC	endocrine disrupting chemical	SC	specific conductance
EDTA	ethylenediaminetetraacetic acid	TCA	1,1,1-trichloroethane
EPA	U.S. Environmental Protection Agency	TCE	trichloroethylene
FDA	U.S. Food and Drug Administration	TDS	total dissolved solids
GC-MS	gas chromatography/mass spectrometry	TP	transformation product
HAB	harmful algal bloom	UCMR	unregulated contaminant monitoring rule
ICP-MS	inductively coupled plasma mass spectrometry	USGCRP	U.S. Global Change Research Program
IWAA	Integrated Water Availability Assessment	USGS	U.S. Geological Survey
IWS	Integrated Water Science	VOC	volatile organic compounds
Koc	soil organic carbon partitioning coefficient	WMA	Water Resources Mission Area
		WWTP	wastewater treatment plant

Chapter A

Introduction to Water-Quality Limitations on Beneficial Uses of Water

By Melinda L. Erickson, Anthony J. Tesoriero, Larry B. Barber, Christopher H. Conaway, Kenneth Belitz, and John K. Böhlke

Purpose and Scope

An integrated water availability assessment for a region requires information about the demand for beneficial uses of water and an assessment of the water supply, which may be limited by the quality or quantity of water sources. Water quality may limit the beneficial use of a water source through natural processes, anthropogenic contamination, or environmental consequences of water use including treatment and return flow (fig. A1). For this report, “beneficial use” refers to human uses of a resource with emphasis on the benefits provided to individuals or to society, and “water use” refers to any human use of water resources. The predominant beneficial water use categories considered in this report are listed in table A1, including categories such as public supplies, domestic supplies, and irrigation. Water-quality considerations relevant to ecosystem services (benefits to people provided by ecosystems) are discussed separately in the companion Open-File Report “Knowledge Gaps and Opportunities in Water-Quality Drivers of Aquatic Ecosystem

Health” (Harvey and others, 2024). In combination, these two reports address selected water-quality research topics that could contribute to improved assessments and predictions of water availability for a broad spectrum of human and ecosystem needs.

This report describes some of the scientific gaps that limit our ability to predict water-quality effects on water availability for beneficial uses across the United States. The presentation is organized into chapters A through E, which focus on A, introduction, B, salinity, C, geogenic constituents, D, contaminants of emerging concern, and E, nitrogen (N). Each chapter contains a selection of scientific gaps, approaches, and outcomes that could help guide research efforts by the U.S. Geological Survey (USGS) Water Resources Mission Area (WMA, <https://www.usgs.gov/mission-areas/water-resources>), other mission areas, and other national research efforts. It is emphasized that these chapters are not comprehensive, and new issues are likely to emerge; thus, it will be important to maintain broad-based expertise and flexibility to comprehensively address the long-term water-quality issues facing the Nation’s water resources.

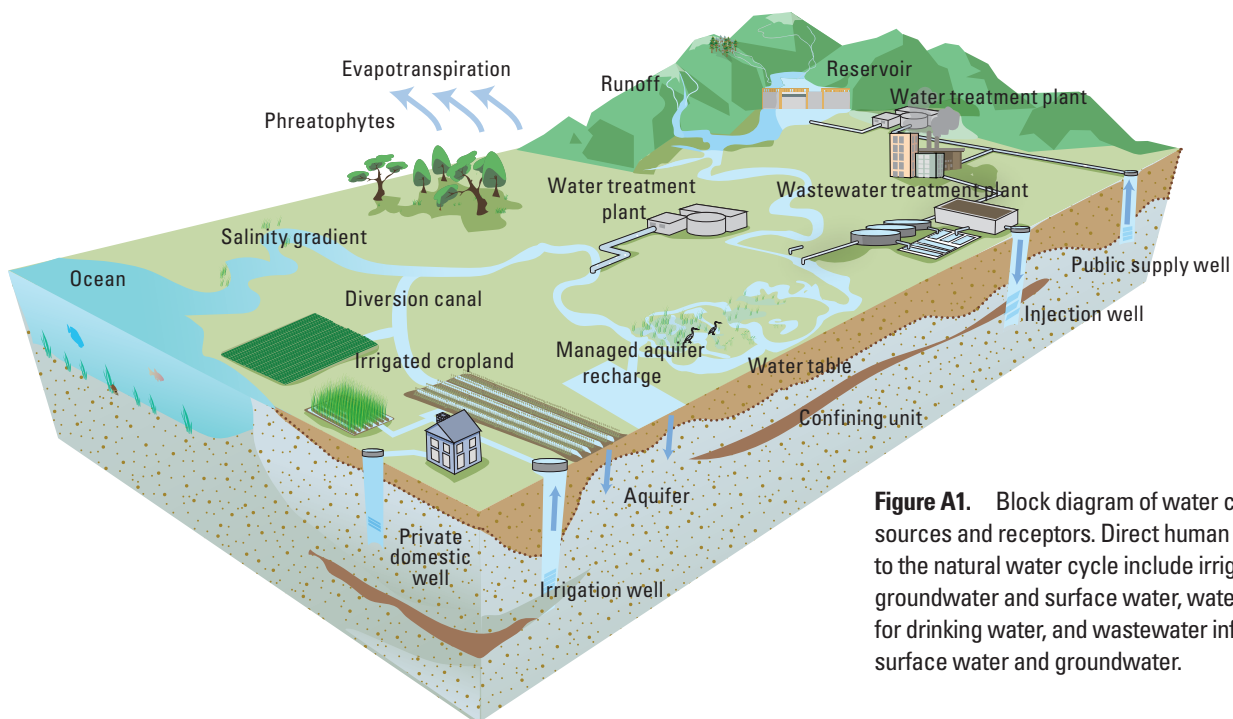


Figure A1. Block diagram of water cycle with sources and receptors. Direct human alterations to the natural water cycle include irrigation from groundwater and surface water, water withdrawal for drinking water, and wastewater inflow to surface water and groundwater.

Table A1. Common inflow water-quality limitations and outflow degradation for primary beneficial use categories in the United States. [TDS, total dissolved solids; PPCP, pharmaceutical and personal care product.]

Use category	Most common inflow water-quality limitations	Outflow water-quality degradation
Public Supply	Trace elements, radionuclides, TDS, nitrate, microbes, hydrocarbons	Nutrients, biogenic ¹ , PPCPs, trace elements, microbes
Domestic	Trace elements, radionuclides, TDS, nitrate, microbes	Nutrients, biogenic, PPCPs
Irrigation	Crop specific trace elements, boron, TDS	Nutrients, pesticides, adjuvants ² , geogenic
Livestock	Trace elements, nitrate, TDS, pH, alkalinity	Nutrients, biogenic, pharmaceutical, food additives
Aquaculture	Temperature, mercury, trace elements, ammonium	Nutrients, biogenic, biocides, antibiotics, growth promoters
Industrial	Widely variable depending on the industrial process	Trace elements, acids and bases, solvents, starting materials, waste materials, byproducts, products
Thermoelectric	pH, hardness, alkalinity, iron, hydrogen sulfide, sulfate, silica, and TDS	Temperature, complexing agents, scrubber wash down
Mining	Minimal	Metals, hydrocarbons, acidity
Oil and gas development	Hardness and concentrations of barium, boron, iron, sulfate, and TDS	TDS, hydrocarbons, naturally occurring radioactive material, metals

¹Such as endocrine disrupting compounds 17β-estradiol and estrone (see chapter D in this report “The Influence of Contaminants of Emerging Concern on Beneficial Uses of Water”).

²Such as additives to enhance pesticide activity.

Beneficial Water Uses and Water-Quality Requirements

In 2015, the cumulative water use for the United States was approximately 322 billion gallons per day (Ggal/d), with 74 percent coming from surface water sources (Dieter and others, 2018). The largest withdrawals were used for cooling of thermoelectric power plants (133 Ggal/d) and irrigation of agricultural crops (118 Ggal/d), followed by golf courses, parks, and other landscapes (Dieter and others, 2018). The pie chart in fig. A2 shows the percentage of United States water use by category. Consumptive uses prevent immediate return of some or all of the intake water, for example, with evapotranspiration from irrigation use, incorporation of water into the products in industrial use, and drinking by humans and livestock. Water that is not consumptively used (for example, thermoelectric power plant cooling) is returned to the hydrologic environment via direct or indirect discharge to groundwater or surface water, with potential subsequent effects on downgradient water quality.

Each beneficial use has its own specific water-quality requirements, as illustrated in table A1. As a result, the distribution and relative magnitude of various water-quality constituents will affect water availability in different ways, depending on intended use and treatment options (Pick, 2011; McMahon and others, 2016; U.S. Environmental Protection Agency [EPA], 2018). For example, drinking-water use requires considering a large list of geogenic (geologic-sourced) and anthropogenic (human-sourced) constituents, which may be toxic, interfere with treatment efficacy, or affect distribution systems (<https://www.epa.gov/awma/factsheets-water-quality-parameters>). Water use for irrigation requires considering boron (B), iron (Fe), and total dissolved solids (TDS) concentrations as well as the sodium (Na) abundance relative to magnesium (Mg) and calcium (Ca) (Wilcox, 1955). Water use for livestock requires considering the pH, alkalinity, and concentrations of sulfate

(SO₄²⁻) and TDS (<https://www.ndsu.edu/agriculture/extension/publications/livestock-water-quality>). Thermoelectric cooling water requires considering pH, hardness (Mg plus Ca concentration), and concentrations of alkalinity, Fe, hydrogen sulfide (H₂S), SO₄²⁻, silica (SiO₂), and TDS (Pan and others, 2018). Hardness and concentrations of barium (Ba), B, Fe, SO₄²⁻, and TDS may limit the effectiveness of water used for oil and gas development (McMahon and others, 2016; see chapter C in this report “Geogenic Water-Quality Effects on Beneficial Uses of Water”).

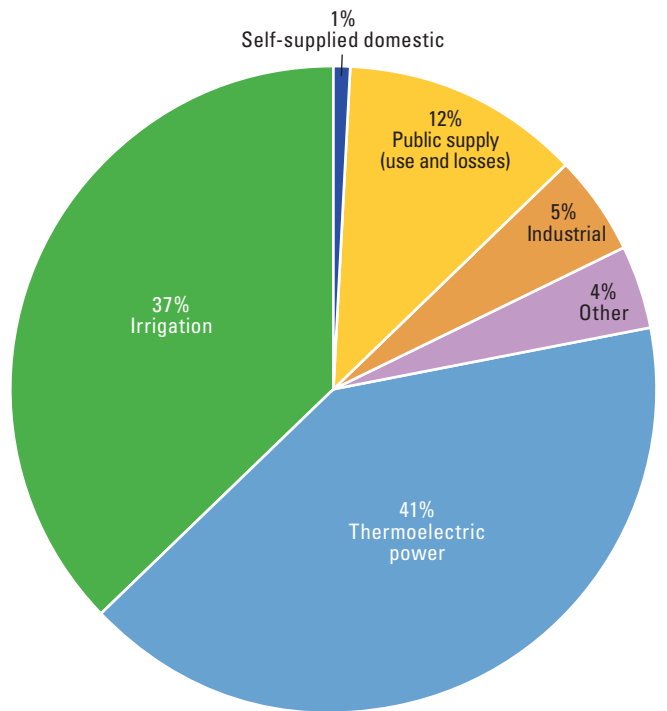


Figure A2. Pie chart of estimated percentage of United States water use per year by water-use category, based upon 2015 water use data obtained from Dieter and others (2018). %, percent.

Threats to Beneficial Uses of Water

Water availability depends on both water quantity and water quality (Evenson and others, 2013). Water availability limitations due to water quality can be caused by high concentrations of one or more categories of constituents. The following chapters of this report focus on salinity, geogenic constituents, contaminants of emerging concern (CEC), and nitrogen (N). These constituents are of concern for water quality because of their widespread sources, chemical properties and (or) toxicological effects. Salinity and salinization (see chapter B “Addressing Salinity Challenges to the Beneficial Uses of Water”) have long been leading water-quality issues in the United States and globally (Vengosh, 2014), and urban-influenced watersheds have a multi-decadal trend of increasing salinity on a continental scale (Kaushal and others, 2018; Stets and others, 2020). Elevated concentrations of geogenic constituents (see chapter C “Geogenic Water-Quality Effects on Beneficial Uses of Water”), which commonly occur naturally, are among the most prevalent water contaminants in the United States and globally (DeSimone, 2009; DeSimone and others, 2015; Hug and others, 2020; Shaji and others, 2021). Municipal wastewater, industrial products and waste, and agricultural practices and waste are primary sources of CECs affecting freshwater environments (see chapter D “The Influence of Contaminants of Emerging

Concern on Beneficial Uses of Water”). The CEC effects on beneficial uses are often more difficult to quantify than other constituent effects because of the uncertainty in their toxicity and acceptable threshold concentrations. Nitrate concentrations in groundwater and streams (see chapter E “Improving Predictions of Nitrogen Effects on Beneficial Uses of Water”) are typically greater in agricultural areas than in urban or undeveloped settings (Burov and others, 2010; Dubrovsky and others, 2010) and are a major global concern for both direct and indirect effects on water quality and use (Böhlke, 2002; Bijay-Singh and Craswell, 2021).

All of these constituents are relevant to public and domestic drinking water supplies, which are two of the primary beneficial use categories. Trace elements, radionuclides, and nitrate are the constituents most commonly found at high concentration exceeding a human health benchmark in groundwater sources supplying drinking water (DeSimone, 2009; DeSimone and others, 2015) (table A2). Arsenic (As) and nitrate are among the constituents most likely to exceed EPA maximum contaminant levels (MCLs) in public water supplies (Allaire and others, 2018). Both surface water (fig. A3A) and groundwater (fig. A3B) are used for public water supply. In substantial portions of the country, domestic well water is the dominant or only potable drinking water source available to an estimated 42.5 million users (fig. A3C) (Dieter and others, 2018). In many areas, a combination of both water sources is used for public supply (fig. A3D).

Table A2. Exceedances of drinking-water thresholds for selected constituents in public and domestic supply wells in the conterminous United States.

[%, percent; µg/L, microgram per liter; HBSL, health-based screening level (Norman and others, 2018); UCMR, unregulated contaminant monitoring rule (U.S. Environmental Protection Agency [EPA], 2016); pCi/L, picocuries per liter; MCL, maximum contaminant level (EPA, 2018); NA, not available; AMCL, alternative maximum contaminant level (EPA, 2018); mg/L-N, milligrams per liter as nitrogen.]

Constituent	Public supply wells ¹ (% high ²)	Domestic supply wells ³ (% high)	National/ Regional	Human health benchmark
Manganese	5	5	National	300 µg/L noncancer HBSL, UCMR
Arsenic	5	7	National	10 µg/L MCL
Lead-210/Polonium-210	4/1	2/5	National	NA (direct measure) ⁴ 15 pCi/L alpha radioactivity MCL (²¹⁰ Po) 50 pCi/L beta radioactivity MCL (²¹⁰ Pb)
Radium-226+Radium-228	3	2	Regional	5 pCi/L MCL
Radon-222	2	4	Regional	4,000 pCi/L (proposed AMCL)
Strontium	2	7	Regional	4,000 µg/L noncancer HBSL, UCMR
Iron	1	NA	National	4,000 µg/L noncancer HBSL
Nitrate	1	4	Regional	10 mg/L-N MCL
Uranium	1	2	Regional	30 µg/L MCL
Molybdenum	1	0.6	Regional	30 µg/L noncancer HBSL, UCMR
Cobalt	1	NA	Regional	2 µg/L noncancer HBSL, UCMR
Fluoride	1	1	Regional	4,000 µg/L MCL
Lithium	43	NA	National	10 µg/L noncancer HBSL
Lithium	4	NA	National	60 µg/L drinking water only threshold ⁵

¹Principal aquifers; public water system wells and equal-area assessment (Belitz and others, 2010, 2015, 2022), data in the U.S. Geological Survey (USGS) National Water Information System (USGS, 2021a).

²High-concentration exceeds a benchmark.

³Principal aquifers; domestic wells in networks, not equal area (DeSimone, 2009; DeSimone and others, 2015).

⁴Gross alpha and gross beta radioactivity measured.

⁵Assumes that 100% of exposure to lithium comes from drinking water (Lindsey and others, 2021).

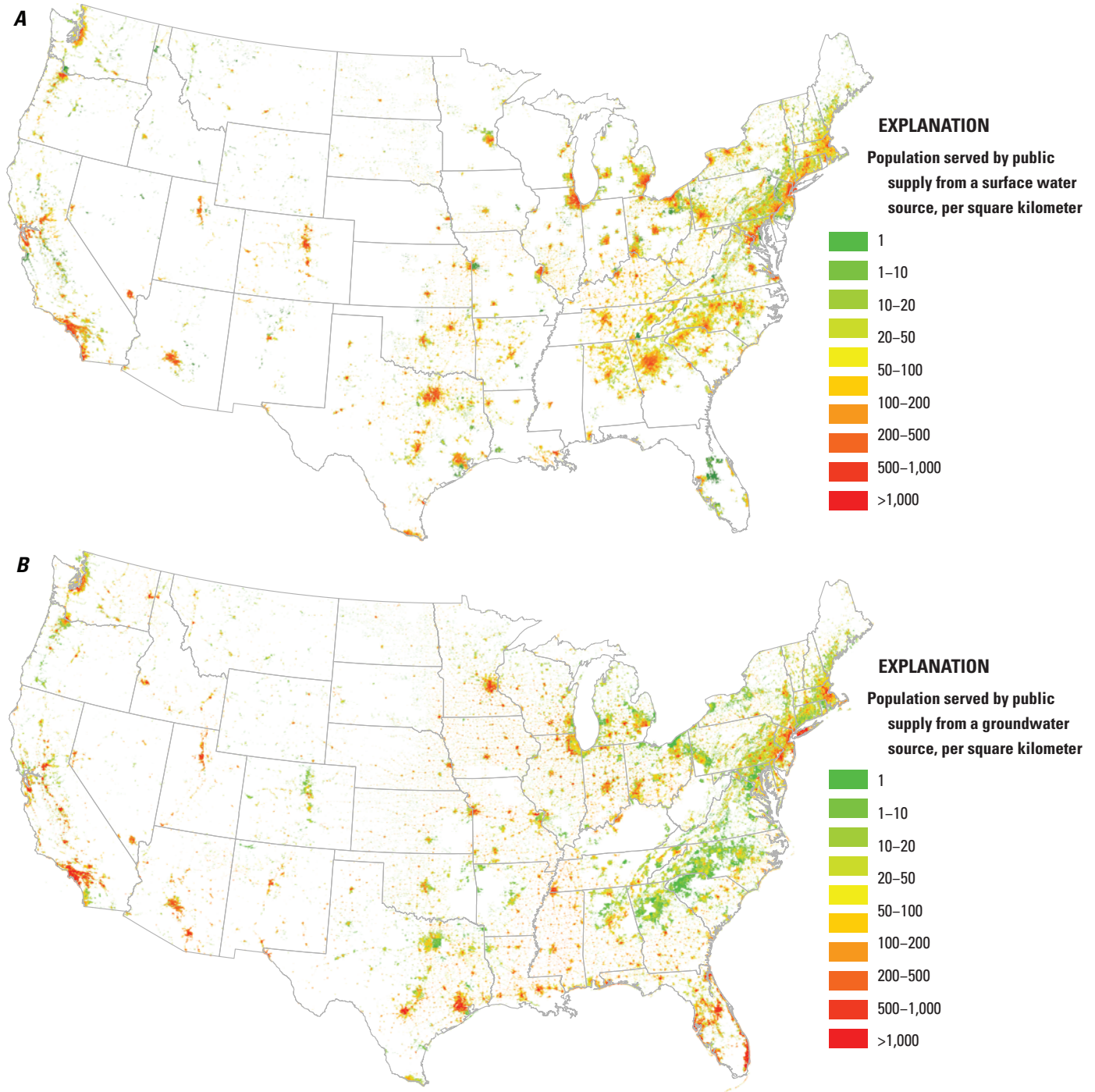


Figure A3. Maps of distribution of surface water and groundwater as sources of drinking water in the conterminous United States. *A*, Population served by a public supply from a surface-water source. *B*, Population served by a public supply from a groundwater source. *C*, Population served by a private (domestic) self-supplied groundwater source. *D*, Source of public supply: groundwater only, surface water only, or a mix of the two. Data from Johnson and others (2021).

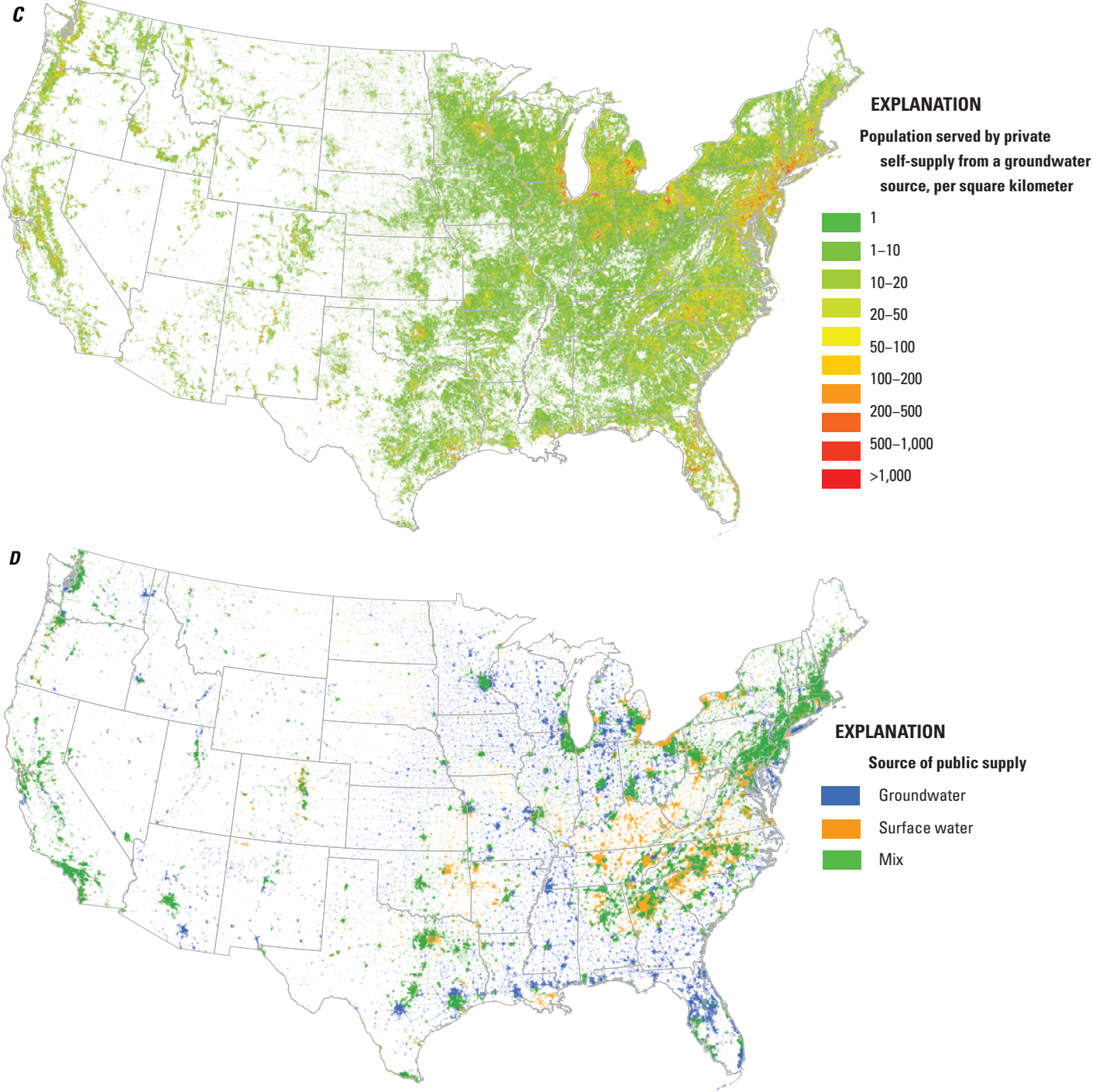


Figure A3.—Continued

There are many examples of water-quality concerns relating to water availability in the United States. For example, within the context of the USGS's Integrated Water Availability Assessment (IWAA) projects (<https://www.usgs.gov/mission-areas/water-resources/science/integrated-water-availability-assessments-iwaas>), selected drainage basins are being targeted for integrated water science studies to improve understanding of groundwater and surface water availability. USGS Integrated Water Science (IWS) basins are medium-sized watersheds (10,000–20,000 square miles [mi²]) that represent a wide range of environmental, hydrologic, and landscape settings and human stressors of water resources. Some water-quality issues related to the first three of those study basins are described below.

In the Delaware River Basin and underlying aquifers, salinity is a primary concern. Salinity affects water quality and availability (see chapter B) where, for example, (1) the marine salt wedge traveling up the Delaware River enters public surface water supply intakes at low flow, (2) sea level rise leads to saltwater intrusion in public water supply and domestic wells, and (3) road salt contaminates freshwater systems (Meyer and others, 2020; USGS, 2021b). Geogenic metals (Fe, manganese [Mn], aluminum [Al]) and radionuclides radon-222 [²²²Rn] and polonium-210 [²¹⁰Po]) are also a concern in groundwater in this basin (Scott and others, 2019; Szabo and others, 2020).

In the streams and aquifers of the Upper Colorado River Basin, selenium (Se), mercury (Hg), uranium (U), ²²²Rn, and geogenic nitrate limit water availability (Spahr and others, 2000; Conaway and others, 2005; Naftz and others, 2008; Vengosh, 2014). Salinity also poses a major challenge to water use, with estimated costs of hundreds of millions of dollars per year due to decreased crop yields, increased water treatment, degraded river health, clogged pipes, and damaged equipment (Vengosh, 2014). Mining waste contamination threatens water quality, particularly from increased acidity due to the weathering of exposed sulfide minerals, which mobilizes metals such as As, lead (Pb), cadmium (Cd), zinc (Zn), and copper (Cu).

The Illinois River Basin water resources are challenged by an overabundance of N and phosphorus (P) and harmful algal blooms that can result from excessive nutrient loads from urban and agricultural sources (Leland and Porter, 2000; Panno and others, 2008). Land-application of dredge sediment from the Chicago area (upper basin) to agricultural areas (lower basin) is redistributing metals and industrial chemicals that may contaminate water resources (Warner and others, 2003; Warner and Ayotte, 2015; Erickson and others, 2019; Szabo and others, 2020). High concentrations of nitrate, As, and radionuclides in the major aquifers in this basin (Mahomet, Glasford, glacial, and Cambrian-Ordovician system) also limit water availability (Groschen and others, 2001).

To assess, predict, and manage long-term risks to water availability in these, and other IWS basins, it is essential to understand sources, movement, and transformations of both natural and anthropogenic water-quality constituents throughout the combined natural and anthropogenic water cycle.

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Chapter B

Addressing Salinity Challenges to the Beneficial Uses of Water

By Christopher H. Conaway, Nancy T. Baker, and John K. Böhlke

Purpose and Scope

This chapter is focused on identifying knowledge and data gaps, that if filled, could improve predictions of the effects salinity has on the beneficial uses of water resources. 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>). Salinity effects on ecosystems are not addressed in this chapter but are covered in chapter E of Harvey and others (2024), “Knowledge Gaps in Salinity Drivers of Aquatic Ecosystem,” the companion Open-File Report to this publication.

Statement of the Problem

Salinity and salinization have long been leading water-quality issues nationally and globally. Salinity, defined here as the sum of dissolved salts (Anning, 2011), is a primary limitation to the beneficial use—and sometimes reuse—of water for drinking, irrigation, livestock, power generation, and oil, gas, and mineral resource extraction (McMahon and others, 2016). Salinity is an increasing challenge for water availability assessment and prediction for several reasons, including (1) readily accessible freshwater resources are threatened by increasing salinity, with more rapid increases occurring in recent decades (Kaushal and others, 2018a, b; Lindsey and others, 2018; Stets and others, 2020); and (2) there is increasing demand for alternative water resources such as brackish and saline groundwater, but the distribution, quantity, and quality of those resources are not well known (Stanton and others, 2017).

Whereas salinity may be composed of a range of dissolved salts in various concentrations—for example, calcium (Ca), chloride (Cl), magnesium (Mg), potassium (K), and sulfate (SO_4)—salinity in seawater is predominantly from sodium (Na) and Cl. Porewater or groundwater can range from fresh to highly saline. These waters are sometime classified based on their major cation and anion chemistry into water types such as sodium-bicarbonate type, calcium sulfate type, and sodium chloride type (Stanton and others, 2017). The major chemical composition varies as a result of

processes such as evaporation, water-rock interactions, human modifications, and mixing of different water types, including mixing with deep groundwaters that contain relict seawater or brine (Kharaka and Hanor, 2014).

Freshwaters are being salinized rapidly in all human-dominated land use types (fig. B1). Rapid salinity increases can alter biodiversity, mobilize sediment-bound contaminants, and increase lead (Pb) contamination of drinking water, but these and other effects are not well integrated into current paradigms of water management (Stets and others, 2020). Increasing major ion concentrations from pollution, human-accelerated weathering, and saltwater intrusion contribute to multiple stressors such as changing ionic strength and pH and mobilization of chemical mixtures resulting in the freshwater salinization syndrome (Kaushal and others, 2018b; (Kaushal and others, 2021). Furthermore, salt pollution can enter groundwaters, which can become dominant stream-water sources at baseflow and thereby affect biota during low-flow times of the year when they may be most sensitive to fluctuations in water quality (Stets and others, 2020). Extensive monitoring has increased our understanding of the spatial and temporal patterns of elevated salinity in rivers and streams; however, there are major gaps in our understanding of the relative contributions of human activities and other drivers, spatial and temporal patterns in groundwater, ecological and human consequences, and the effects of climate change on salinity. The U.S. Environmental Protection Agency (EPA) considers most dissolved salts associated with salinity to be nuisance chemicals and has established non-mandatory secondary standards as guidelines to assist public water systems in managing drinking water for aesthetic considerations, such as taste, color, and odor (<https://www.epa.gov/sdwa/secondary-drinking-water-standards-guidance- nuisance-chemicals>). In recognition that some combinations of these salts can cause life-threatening corrosion and mobilization of Pb and copper (Cu) in plumbing systems, the EPA developed technical recommendations for optimal corrosion control treatment evaluation (EPA, 2016). As the effects from freshwater salinization become more recognized and the processes better understood, it is possible that future guidelines and criteria will be developed to prevent and mitigate these threats. The results of freshwater salinization may be compounded if projections of increasing surface water and groundwater demand coupled with projected effects of climate change are realized (Stanton and others, 2017; Stets and others, 2020).

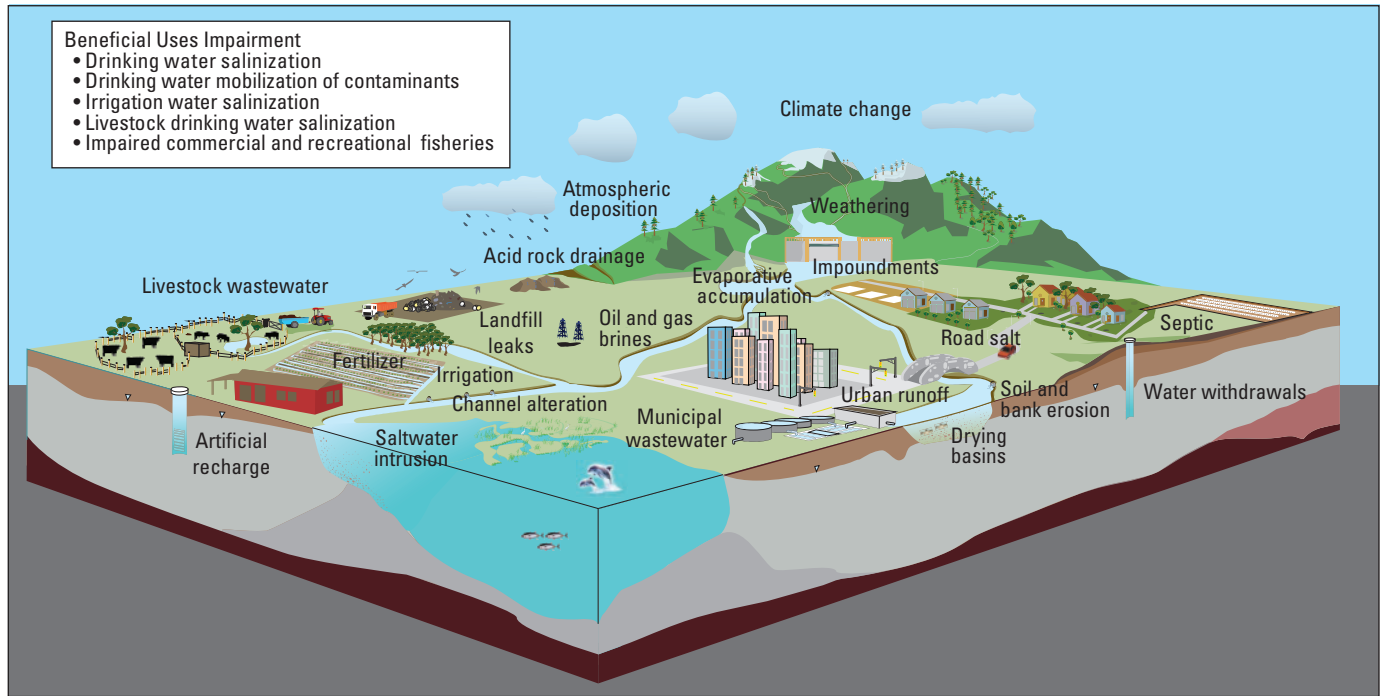


Figure B1. Diagram of sources and drivers of salinization that impair beneficial uses of water resources in the United States.

Status of Knowledge and Capabilities

Salinity and salinization have long been leading water-quality issues in the United States and globally (Vengosh, 2014). Some of the major issues related to salinization effects on beneficial uses of freshwater resources include corrosion issues and the safety of drinking water (corrosion of pipes) and infrastructure (corrosion of roads and bridges), elevated salts leaching essential elements from soil where saline water is applied to soils, and suitability for other agricultural purposes (Kaushal and others, 2018b; Stets and others, 2020). A recent analysis of USGS water-quality measurements made across the United States identified a multi-decadal trend of increasing salinity on a continental scale (Kaushal and others, 2018b; Stets and others, 2020), particularly in urban-influenced watersheds. Increases in alkalinity are also associated with salt pollution, although the environmental effects of alkalization have received comparatively less attention and are perhaps less well understood than those of salinity (Kaushal and others, 2018b). In addition, natural occurrences of deep saline groundwater can contaminate water-supply wells because of overpumping. Conversely, saline groundwater may be a useful resource in areas lacking freshwater resources, depending on the chemical composition of the saline groundwater, the types of water uses in those areas, and the viability of water-treatment options (McMahon and others, 2016; Stanton and others, 2017).

The predominant sources of salinity are well known. Sources and causes of observed salinity changes include: (1) anthropogenic inputs of salt such as road salt, wastewater, water treatment, brine disposal, and agricultural runoff; (2) acceleration of natural weathering or water-rock interaction via acid rain, fertilizers, and acid-mine drainage; and (3) weathering of construction and manufacturing materials such as cement, lime, and concrete (Kaushal and others, 2018b). Some of the anthropogenic practices and environmental factors driving changes in salinity include climate change (for example, timing and amount of precipitation related to various kinds of runoff or chemical weathering), changes in water use (for example, surface water diversion, groundwater withdrawal, irrigation), changes in land use and land cover, and sea-level rise (seawater intrusion).

Watershed chemical transport is increasingly dominated by novel combinations of constituents (“chemical cocktails”) because human activities greatly enhance elemental concentrations, increasing the probability for biogeochemical interactions and shared transport along hydrologic flowpaths (Kaushal and others, 2021). Interactions with chemical cocktails can produce environmental effects greater than the sum of individual parts, however, the causes and consequences of water-quality problems often focus on one or a few constituents and do not consider potential interactions. Increases in chemical cocktails linked with salinization (for example, hydrogen $[H^+]$, Ca^{2+} , Mg^{2+} , Na^+ , and Cl^-) influence acid-base status of fresh waters and can affect

mobilization of other chemical cocktails such as those associated with brownification (increase in brown color caused mainly by dissolved humic matter) or eutrophication. In addition, these ions tend to be eluted from soil and sediment exchange sites and can be rapidly flushed in a primary pulse if they have accumulated in near surface environments from urban road salts, agricultural liming, and natural or human accelerated weathering. Significant quantities of these ions are also commonly located deeper in soil profiles leading to transport through the subsurface and eventual accumulation in groundwater and (or) discharge to streams (Kaushal and others, 2018a).

There are many examples of how salinity has affected water quality in the United States, including existing and proposed IWS basins. In the Delaware River Basin, salinity is a concern where (1) the marine salt wedge travels up the Delaware River and enters public water supply intakes at low flow, (2) sea level rise leads to saltwater intrusion into public water supply and domestic wells, and (3) road salt contaminates fresh-water systems. In the Upper Colorado River Basin salinity, caused by irrigated agriculture and by natural and human accelerated weathering of saline geologic formations, is a major threat to water use (Kenney and others, 2009). Damages across the entire Colorado River Basin are estimated to exceed hundreds of million dollars per year due to decreased crop yields, increased water treatment costs, degraded river health, clogged pipes, and damaged equipment (Vengosh,

2014). In the Illinois River Basin, sources of elevated salinity in streams and groundwater resources include road salt and brine in the Cambrian–Ordovician aquifers.

Gap Analysis and Approaches

Research needs related to salinity in surface water and groundwater were identified by reviewing the results, discussion, and conclusion of recent major works (Stanton and others, 2017; Kaushal and others, 2018b; Kang and others, 2020; Moore and others, 2020; Stets and others, 2020) and by discussions with USGS Water Enterprise researchers focused on salinity in IWS basins and nationwide. We divided core research areas into four main gap categories with detailed descriptions of each area presented in the following sections along with a summary in table B1:

1. Identifying salinity sources and drivers,
2. Predicting and understanding trends in freshwater salinization,
3. Improving assessments of brackish water resources, and
4. Identifying the components of salinity and their effect on contaminant mobility.

Table B1. Summary table for salinity gap analysis for understanding water-quality processes affecting water availability for beneficial uses in the United States.

Topic	Knowledge Gap	Importance	Proposed Approaches
Identifying salinity sources and drivers	Ability to distinguish various salinity sources and multiple transport pathways from sources to receptors.	Essential for model prediction, resource management, and remediation.	Watershed or aquifer mass balance approaches combined with flow modeling to better understand the interactions between surface water, the unsaturated zone, and groundwater. Development and application of geochemical and isotopic tools for identifying sources.
Predicting and understanding trends in freshwater salinization	Understanding of hourly, seasonal, and long-term changes in sources, peaks, and trends of salinization.	To extrapolate salinity measurements and models over a wide range of hydrologic and climate variables and gradients and time scales, including direct and indirect human effects.	Monitoring salinity with high-frequency sampling sensors. Develop long-term continuous data. Conduct studies in areas where human activities cause redistribution of salts or saline water.
Improving assessments of brackish water resources	Improved knowledge of availability and sustainability of groundwater and saline water resources.	Demand for freshwater is increasing as water quality is degrading and some regions are becoming more arid.	Refine knowledge of the distribution of brackish groundwater resources. Refine knowledge of the sustainable use and (or) treatment of brackish groundwater resources. Conduct research related to water treatment and desalination technologies and limitations.
Identifying the components of salinity and their effect on contaminant mobility	Ability to predict how saline water chemistry affects beneficial uses, mobilization of contaminants, and compatibility with water treatment technologies.	Different major ion ratios have different properties related to corrosion, scaling, or water treatment processes that may affect drinking water infrastructure. Ion ratios in irrigation water can affect soil fertility or have undesirable effects on the chemistry of agricultural return water.	Survey of data on major ion ratios and trace elements related to salinity in fresh and brackish water systems. Develop predictive models for geochemical water type in groundwater based on local geologic, hydrologic, and climatic conditions.

Gap 1. Identifying Salinity Sources and Drivers

Although the primary sources of salts driving freshwater salinization are known, the relative contributions—especially on a temporal scale—of these sources is a knowledge gap in many areas (for example, the contribution of road salt to groundwater and release to streams in areas where there is a low-flow pulse of Cl during non-winter months). Also, the contribution and chemical nature of groundwater as a saline input to surface water is an important avenue of study (Anning, 2011; Rumsey and others, 2017; Stets and others, 2020).

Salinization and the Storage of Salts in the Environment

Salt from atmospheric deposition, naturally occurring deposits of saline minerals, evaporation of surface water, or anthropogenic salinity sources can accumulate in the unsaturated zone and later be flushed downward or laterally (in the presence of low permeability strata) to the saturated zone. The flushing can be caused by changes in land use such as removing vegetation or changing vegetation type (for example, natural to cropland), or changes in hydrologic budget through increased rainfall and (or) snowfall, irrigation, or even sea-level rise. Storage and flushing of salinity are well-documented in dryland environments (Vengosh, 2014), but less so in urban areas or basins with anthropogenic salinization (Lax and Peterson, 2009). To quantitatively address “salinity storage” in target basins, the balance of saline inputs and outputs and storage should be addressed, and processes moving salinity from land surface to lakes, rivers, and streams, or through the unsaturated zone to groundwater in urban, suburban, and regions of anthropogenic salinization should be characterized. Deliverables for projects could include mass balance of salinity in a region, identification of important zones of salt accumulation (in both the unsaturated zone and groundwater), an understanding of steady-state chloride concentration in groundwater for current and predicted salinization, and an understanding of processes controlling movement of salinity from land surface through the unsaturated zone to groundwater or discharge to streams.

Evaluation of Sources of Salinity

Determining the salinity sources affecting beneficial uses is an essential component in water-quality management and prediction. When there are multiple sources of salinity to a system, the integration of multiple chemical and isotopic analyses is required to distinguish between these sources (Vengosh, 2014). Common tracers for salinity sources include chemical ratios (for example, Na/Cl, Br/Cl, B/Cl, Ca/Cl, SO₄/Cl) and isotopic ratios (for example, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in H₂O, $\delta^{11}\text{B}$, $\delta^{34}\text{S}$, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in SO₄, $^{36}\text{Cl}/^{35}\text{Cl}$, $^{129}\text{I}/^{127}\text{I}$, and $^{87}\text{Sr}/^{86}\text{Sr}$). To quantitatively attribute sources of salinity to water-quality observations and predictions in target basins, projects could apply these geochemical modeling tools when data are available. This work is also applicable and

relevant to seawater intrusion and saltwater displacement in coastal aquifers. Deliverables for projects could include identification of the best combination or integration of tracers in these systems, a compilation of available data, and include potential tracers for reuse water. When data are not available, collection of new data or development of models may be warranted to better distinguish various salinity sources and multiple transport pathways from sources to receptors.

Gap 2. Predicting and Understanding Trends in Freshwater Salinization

One of the major gaps in understanding salinization and its effects is the influence of seasonal, interannual, and long-term changes and drivers (Kaushal and others, 2021). The most important drivers on these temporal scales are climate change, landscape and water use change, hydrologic characteristics of the underlying aquifer, and sea level rise. Climate driven changes include reduction in precipitation and increases in aridity. Other long-term changes contributing to salinization include increasing urbanization and water use, converting forests to agricultural land, and in some cases afforestation of grasslands which draws water from shallow groundwater leaving its salt load in the unsaturated zone (Vengosh, 2014). Seasonal and long-term salinity fluctuations can be important because changes in salinity can affect the suitability of water for agriculture or can mobilize health-related contaminants (Vengosh, 2014; Stets and others, 2020; Kaushal and others, 2021). Better understanding of these short-term and long-term drivers can allow us to better predict and manage salinity in the future. Consequently, integrated water availability studies could be improved by additional process-oriented research related to the following issues (among others).

Climate Factors

How are seasonal or interannual salinity trends in rivers and lakes affected by climatic fluctuations, such as storm events, droughts, and snow events? Climate change is an underlying part of many of the issues related to freshwater salinization. Here we focus predominantly on temporal changes that have effects on landscape-scale or over major geochemical processes. For example, changes in precipitation, phase, amount, and timing can affect the relative importance of salinity sources, such as groundwater inputs or agricultural water returns. Antecedent conditions and how climatic fluctuations interact with variable conditions on the landscape can alter the response of salinity to a given climatic event. During drought conditions, salt may accumulate in the subsurface over many years and as a region transitions to a wet period, accumulated salts are flushed; however, little is known about the timing and magnitude of these events. Climatic fluctuations can also affect groundwater and surface water interactions over time (Kløve and others, 2014), which may be an important consideration for salinity transport in some regions. In another example, freeze-thaw episodes followed by

intense winter rainstorms can cause episodic salinization lasting from hours to days after snowstorms in response to road salting, triggering mobilization of different chemical cocktails and shifting acid-base status (Haq and others, 2018).

Hydrologic Characteristics of the Aquifer

In the Upper Colorado River Basin, climate driven changes in baseflow may increase dissolved solids loading and reverse the long-term dissolved solids decline observed in streams throughout the twentieth century (Miller and others, 2021; Rumsey and others, 2021). In some groundwater systems, the lag time between the start of a land-use practice and arrival of contaminants in deep parts of aquifers can be long. Therefore, hydrologic characteristics of aquifers are also important factors with respect to temporal change. Some of the limitations regarding the availability of this sort of data related to aquifer storage and transmissivity are outlined for brackish water resources in Stanton and others (2017), which is described in the section “Gap 3. Improving Assessments of Brackish Water Resources,” but filling those data gaps may also apply here, particularly in the case of compiling additional data from multiple sources that provide estimates of needed parameters (for example, porosity, permeability, and storage coefficients).

Land and Water Use Change

In areas of major water diversion or where beneficial uses will be affected by salinization, how is salinity affected by withdrawals and hydrology? Climate change, increasing population, and increasing power generation are all drivers of water scarcity. How land and surface water is managed to address that scarcity and how that management can alter water quality is a consideration that we focus on here. Water diversions or interbasin transfers are a major tool in addressing water availability in areas of increasing water scarcity. Droughts are increasing in frequency and severity in many areas (Williams and others, 2020) resulting in decreased flow and volume in streams and increased saline groundwater inputs leading to increased salinity due to reduced dilution and concentration of mass (Mosley, 2015). Droughts are associated with increases in lake and reservoir salinity as a result of reduced outflows and evapoconcentration (Mosley, 2015). Land use and landscape changes and drought can negatively affect salinity in a region, while implementing land management practices such as improving irrigation systems, recovery of vegetation and soil condition, and construction of reservoirs may substantially affect how salinity is transported to streams (Rumsey and others, 2021). Migration of the salt front upstream during droughts in estuaries has also been reported (McAnaly and Pritchard, 1997). Release of water from impoundments during periods of low flow can be used to prevent upstream movement of saltwater. The Delaware River Basin Commission (DRBC) Flexible Flow Management Plan is an agreement between New York City (which transfers a large amount of water outside of the watershed) and the DRBC to maintain sufficient flows during periods of low flow in the Delaware River to prevent upstream

migration of the salt front which threatens water supply intakes in Philadelphia and other communities (DRBC, 2020).

Sea-Level Rise

Effects from coastal flooding and inundation, exacerbated by sea-level rise and population growth in coastal regions, are expected to increase in upcoming decades (Strauss and others, 2012). Flooding and storm surges inundate lands trapping saline water in depressions and soils in areas previously not exposed to saltwater. Along coastal wetlands, saltwater is seeping further inland through soils causing woodlands to die and be replaced with more salt-tolerant shrubs and grasses threatening wildlife, ecosystems and local farms and forestry businesses. Increasing sea-level rise and storm surge can drive salt water up coastal rivers placing water supply intakes at risk. In addition, lateral encroachment of seawater along coastal areas combined with excessive groundwater pumping can reduce freshwater flow toward coastal areas and cause saltwater to be drawn toward freshwater zones in coastal aquifers decreasing freshwater storage and potentially making the resource unsuitable for use or increasing the cost of desalinization.

Approaches for Predicting and Understanding Trends

To evaluate seasonal, interannual, and long-term trends, continuous sensors allow salinity to be monitored frequently, preferably across a range of land use types and precipitation patterns (rain, snow, snow melt, arid, humid, urban, agriculture). Continuous sensors typically measure specific conductance (SC) which can then be used as a proxy for chloride concentrations. Because the relation between SC and chloride concentrations varies by region, these high-frequency data will need to be combined with new approaches to modeling and links to other geochemical data (McCleskey and others, 2012; Kaushal and others, 2021) to fully understand temporal variability and drivers of salinity change. Establishing relations between SC, chloride, and other constituents may be more difficult to achieve for groundwater than for surface water because groundwater-quality data are usually sparser. Increased groundwater-quality data collection with special consideration for areas where groundwater discharges to surface water may greatly improve our understanding of salinity trends in different hydrologic compartments. Short to long-term changes in drivers should also consider shifts in relative contributions of mixing water (seawater, stormwater, urban sources, groundwater, and so forth) or water-rock interaction (as water is displaced or water tables rise or fall) and the resulting changes in water quality. Deliverables for this work could be high-frequency sampled salinity data for target basins that can be used to better understand and predict natural and human-accelerated salinization on short-term to decadal scales, and an interpretation of the chemical and physical processes driving these changes.

Gap 3. Improving Assessments of Brackish Water Resources

The increasing reliance on brackish water resources seems a certainty in the face of decreasing water supply and deteriorating water quality (Vengosh, 2014). Because of the importance of brackish water as a groundwater resource, Stanton and others (2017) proposed next steps and identified data gaps in an expanded effort to understand the distribution and chemistry of brackish groundwater (BGW) resources in the United States. Their gap identification was distributed into five categories: (1) “Occurrence and Distribution of Brackish Groundwater,” (2) “Hydrogeologic Characterization,” (3) “Geochemistry,” (4) “Brackish Groundwater Use,” and (5) “Sustainability.” Specific recommendations in these categories that are most related to USGS water-quality process research are in the categories of “Geochemistry” and “Sustainability.” Their primary recommendations related to geochemistry include: (1) complete a more thorough review and compilation of existing geochemistry data that are not readily accessible in digital format, and (2) explore links between geochemistry, required water treatment, and potential end users with the aid of geochemical modeling and simulations. Stanton and others (2017, p. 144) primary recommendations related to sustainability are to do the following:

Assess BGW sustainability with use of appropriate tools (models to simulate water movement and transport) to quantify the response (flow and chemistry) of a principal aquifer to extraction of BGW. Numerical models, groundwater age dating, and time-series water-quality sampling would aid in understanding effects of development, such as the alteration of hydraulic properties because of changes in water chemistry; effects on geochemistry of the inflow of more mineralized or fresher water into the reservoir (for example, mobilization of other unwanted constituents); possibility for subsidence; and whether or not BGW resources are renewable at a timescale of human use.

Based on our review and the recommendations of Stanton and others (2017), we identify the next steps and data gaps to understand the distribution and chemistry of BGW resources in the United States.

Refining Knowledge of the Distribution of Brackish Groundwater Resources

The recent USGS national brackish groundwater resource assessment (Stanton and others, 2017) estimated the distribution of saline and brackish groundwater in the United States by using a compiled database of chemistry data from wells. Results of that study could be refined and extended in several different ways. For example: ensuing research to address the recommendations of Stanton and others (2017) could include a more thorough review and compilation of existing geochemistry data and the addition of geophysical data, such as existing surface geophysical

surveys and borehole logs, to refine spatial resolution. Borehole logs of electrical properties could provide improved resolution of the depths and shapes of salinity gradients that are needed for delineating boundaries and determining actual volumes of fresh, brackish, and saline groundwater (Williams and others, 2013; Stephens and others, 2019). Borehole logs also could be used to refine the distribution of geologic features that control the distribution of groundwater salinity, potentially leading to improved interpolation models.

Refining Knowledge of the Sustainable Use of Brackish Groundwater Resources

Understanding the sustainable use of BGW resources is an essential area of research. This includes efforts to refine the distribution of hydrogeologic properties affecting the sustainable use of brackish and saline groundwater. Sustainability of deep groundwater resources depends on hydrogeologic properties such as porosity, permeability, recharge, discharge, confinement, and connection with adjacent aquifers. The subsurface distribution of such properties could be refined with three-dimensional (3-D) geologic maps, borehole descriptions, well yields, and pump tests. Research on sustainability of use also includes efforts to investigate temporal salinity variations in existing chemical data from wells. The previous national-scale BGW study (Stanton and others, 2017) focused on spatial variations by selecting single analyses from each well. Further analysis of the data could determine if there are trends in some wells indicating responses to pumping, seawater intrusion, anthropogenic contamination, or other processes. Predictions of BGW trends and sustainability could be improved with additional knowledge of groundwater ages and flow velocities. Such information could be obtained by using groundwater models calibrated with analyses of environmental tracers of groundwater chemical and isotopic age ranging from decades to more than one million years. Further work on sustainability includes incorporating brackish and saline groundwater within regional integrated water availability assessments for multiple uses. Local water availability and water needs commonly are not well matched and may require multiple water sources with a range of salinities that need to be integrated and combined with various treatment and distribution options. Water use sustainability could be improved by comprehensive collaborative (interagency) regional investigations of potable and non-potable groundwater and surface water resources in context with various use requirements and treatment options.

Water Treatment and Essential Research on Desalination

Desalination or other water treatments are a technical solution to freshwater scarcity, but there are essential research needs in the creation of this new fresh water (Vengosh 2014; Ahdab and Lienhard, 2021). Research in this category includes the need to develop geochemical modeling tools to assist water treatment and planning. Variability in the chemical composition

of brackish and saline water resources affects the evaluation of water treatment needs and the design and energy requirements of treatment processes (McMahon and others, 2016; Ahdab and others, 2018). Geochemical modeling software could facilitate such work, with reference to the natural distribution of geochemical conditions. Geochemical modeling could also support water-quality models through the prediction of the chemical compositions of desalinated water and brine wastewaters and their return to the environment. Forensic tools described above could assist in evaluating the fate of these “anthropogenic” waters in the environment (Vengosh, 2014). There is also a need to evaluate the distribution of potentially valuable byproducts associated with desalination processes. Desalination facilities can include processes that recover valuable commodities from the waste stream. Geochemical databases could be evaluated for the distribution of metals and other potentially useful constituents in non-potable waters. California Energy Commission’s Energy Research and Development Division is investigating the potential for co-production of power and lithium carbonate (used in electric vehicle batteries), from geothermal brines like those found in the Salton Sea (Ventura and others, 2020).

Gap 4. Identifying the Components of Salinity and Their Effect on Contaminant Mobility

Whereas high salinity water tends to be predominantly NaCl-type water, brackish water occurs in a range of geochemical types such as sodium bicarbonate, calcium sulfate, Na, Cl, and mixed (Stanton and others, 2017). Much of the work on the environmental effects of salinization has focused on Na and Cl; but different components of salinity—Na, Mg, barium (Ba), bicarbonate (HCO_3^-), sulfate, and silica—are recognized to limit the beneficial uses of water in different ways (Vengosh, 2014; McMahon and others, 2016). Examples include: (1) groundwater saturated with barite can cause scaling problems when water is used or treated; (2) different major ion ratios have different properties related to corrosion that may affect drinking water infrastructure; and (3) ion ratios in irrigation water can affect soil fertility or have undesirable effects on the chemistry of agricultural return water. A survey of the importance and availability of data on major ion ratios (for example, Cl and SO_4^{2-} , Na and K, and Cl and HCO_3^-) related to salinity in freshwater systems would be beneficial for understanding the effects of salinization. In addition, predictive models for geochemical water type in groundwater based on local geologic, hydrologic, and climatic conditions could be applied more widely. There is also an important link between salinization and the mobilization of health-based contaminants (Vengosh, 2014). Consequently, a vital area of research in salinity is the evaluation and geochemical modeling of chemical composition of saline water and associated contaminants (see the geogenic section of this report, chapter C “Geogenic Water-Quality Effects on Beneficial Uses”). Examples of this kind of research include:

- The prediction of major ion ratios and effects on beneficial uses via corrosion, mobilization of contaminants, and suitability for use.
- An examination of the role of salinity in the prediction of health-related geogenic constituents (for example, fluorine [F], arsenic [As], selenium [Se], boron [B], and radium [Ra])
- Inclusion in models of prediction of water types based on geochemical processes (for example, base cation exchange, freshening, generation of dissolved inorganic carbon (DIC) by oxidation of organic matter).

Expected Outcomes

The significance of data gaps with regards to addressing the challenge of salinization and assessing groundwater resources is captured in three quotes from USGS research papers that we present here. From Stets and others (2020, p. 4336):

“... increasing salinity negatively affects biodiversity, mobilizes sediment-bound contaminants, and increases lead contamination of drinking water, but the effects are not well integrated into current paradigms of water management...”

and on p. 4241:

“... Water-quality regulations and best management practices designed to address the problems of excess nutrients and sediments in surface waters are not adequate to curtail the growing problem of salinization, which is driven by different sources. More research is needed to understand how increases in salinity, and in specific major ion concentrations, might be affecting aquatic ecology and ecosystem services. Regular, broad, large-scale studies are crucial to provide appropriate context of the largest changes in water quality and can serve as a basis for up-to-date research and decision-making to respond appropriately to the most important threats facing water supplies for human and ecological well-being.”

Stanton and others (2017, p. 6) note that:

“Future water demand is projected to heighten the stress on groundwater resources...this increased water demand coupled with projected climate change could produce moderate to extreme risk to water-supply sustainability for most of the United States...To ensure the water security of the Nation, untapped water sources may need to be developed in some areas. Brackish is a nontraditional water source that may offer a partial solution to current and future water challenges.”

The research gaps discussed are crucial areas of research in an emerging national problem, which is comparable in scale to acid rain, eutrophication, loss of biodiversity, and other

mainstream environmental issues (Kaushal and others, 2021). Essential in developing a management approach for salinization and increasing water scarcity, the following are needed to identify the next generation of research and management topics: (1) the development of regional mass balance and forensic tools to identify salinity sources and drivers, (2) deployment of high-frequency sampling sensors to improve trend assessments, (3) refining knowledge of the distribution and chemistry of brackish groundwater, and (4) developing geochemical modeling approaches for the examination of the components of salinity and mobilization of contaminants.

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Chapter C

Geogenic Water-Quality Effects on Beneficial Uses of Water

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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:

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; $\mu\text{mol/kg}$, micromole per kilogram; $\mu\text{mol/L}$, 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 ($\mu\text{mol/kg}$)	Equivalent pore-water concentration ^c ($\mu\text{mol/L}$)	Human health benchmark ($\mu\text{mol/L}$ (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 g/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

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 (Teeple, 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; μmol/kg, micromole per kilogram; Bq/kg, becquerel per kilogram; Bq/L, becquerel per liter; β β, double beta decay; β⁺β⁺, 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	<i>t</i> _{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)
Primordial							
¹³⁰ Ba ^e	β ⁺ β ⁺	1×10 ²¹	6.9×10 ⁻²²	5.0	6.5×10 ⁻¹¹	2.6×10 ⁻¹⁰	2 ^f
¹³² Ba ^e	β ⁺ β ⁺	>3×10 ²⁰	<2.3×10 ⁻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	β β	5.6×10 ¹⁹	1.2×10 ⁻²⁰	1,200	2.9×10 ⁻⁷	1.2×10 ⁻⁶	2 ^f
¹¹³ Cd ^j	β	8.0×10 ¹⁵	8.6×10 ⁻¹⁷	0.0098	1.6×10 ⁻⁸	6.4×10 ⁻⁸	2 ^f
¹¹⁶ Cd ^j	β β	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	β β	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	β β	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	β β	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	β β	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}	β β	2.3×10 ²⁴	3.1×10 ⁻²⁵	1.4	8.2×10 ⁻¹⁵	3.3×10 ⁻¹⁴	2 ^f
¹³⁰ Te ^{aa}	β β	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}	β β	2.2×10 ²¹	3.2×10 ⁻²²	—	—	—	—
⁹⁶ Zr ^{ag}	β β	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 ($\mu\text{mol/kg}$)	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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 10^6 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} $\mu\text{mol/kg}$ (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} $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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} $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/kg}$ (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 $\mu\text{mol/L}$, 30 $\mu\text{g U/L}$, 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,

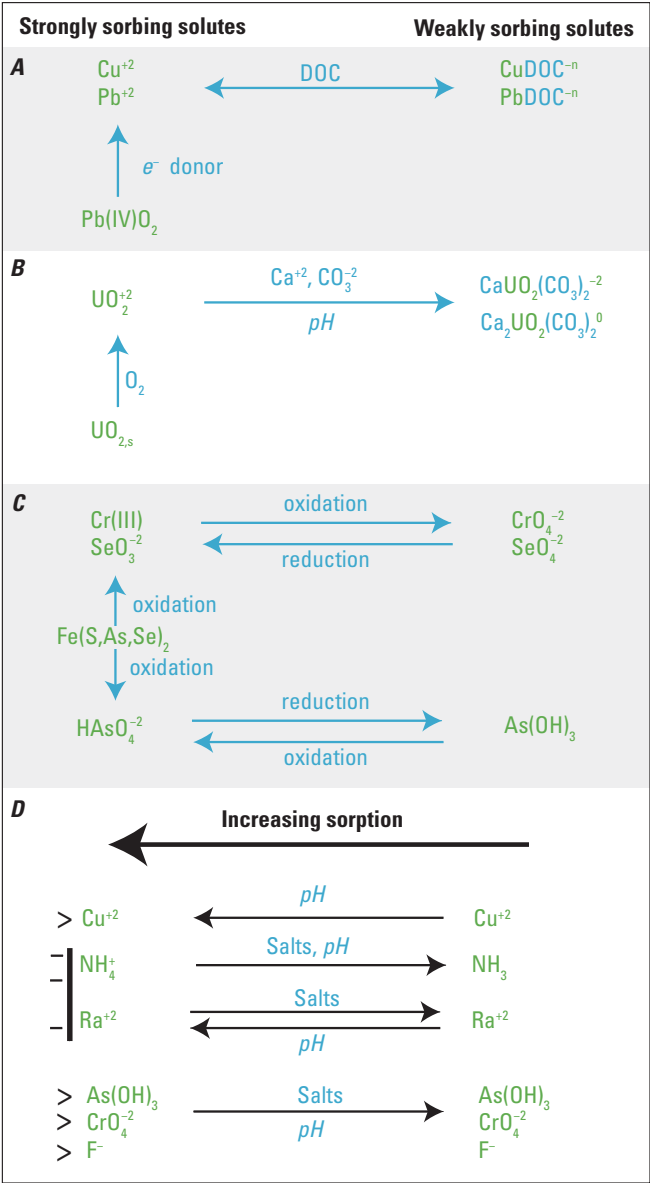


Figure C1.1. Schematic diagram of factors affecting mobilization and sorption of geogenic constituents: *A*, formation of weakly sorbing dissolved organic carbon complexes; *B*, formation of weakly sorbing inorganic complexes, such as with aqueous carbonate species favored at alkaline pH values; *C*, 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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Chapter D

The Influence of Contaminants of Emerging Concern on Beneficial Uses of Water

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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 effects of contaminants of emerging concern (CECs) on intended beneficial uses of water. 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>). CEC's 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 Affecting Aquatic Ecosystems."

Statement of Problem

What is a contaminant of emerging concern (CEC)? There is no single consensus, definition, or static list of CECs (Diamond and Burton, 2021). A CEC list must be dynamic, as new chemicals are continuously developed, produced, and detected with analytical advancements (Murray and others, 2010). The U.S. Department of Defense (DoD) definition includes the criteria: (1) presents a potential human health or environmental risk, and (2) has new or changing toxicity estimates or environmental regulatory standards (DoD, 2019). Based on the criteria, CECs include both new chemicals that little is known about, and legacy chemicals with renewed attention due to new information about occurrence or health effects. For example, in the case of legacy contaminants, new science shows that reactions of legacy pesticide and petroleum hydrocarbons can result in contamination by both the parent compounds and transformation products (Bekins and others, 2016; Mahler and others, 2021). Similarly, per- and polyfluoroalkyl substances (PFAS) have existed for decades but it is only recently that their many pathways to natural waters and their consequent widespread occurrence and potential health risk have been recognized (Ahrens and Bundschuh, 2014; Guelfo and Adamson, 2018; Sunderland and others, 2019; Ankley and others, 2021). In addition, improved analytical detection limits for CECs have led to recognition of more widespread

occurrence across the Nation and awareness of the potential risk to environmental and human health caused by chemicals that are biologically active by design (Barber, 2014). Thus, the definition of CECs results in a mix of chemicals that changes with time and understanding (Barber, 2014). Determining the environmental fates and toxic effects of individual CECs can be challenging because they often occur as complex mixtures with complex effects (Kolpin and others, 2002; Barber, 2013; Bradley and others, 2016; Masoner and others, 2019; Battaglin and others, 2020). Treated wastewater is one of the largest sources of water with complex mixtures of CECs. In water-stressed areas there is a growing need for better understanding of the environmental fate and biological effects of CECs for de facto water reuse for drinking water and for sustainable ecosystem health in those streams with high percentages of total flow coming from accumulated wastewater discharge.

We have identified three specific gaps in CEC research and knowledge: (1) wastewater reuse and anthropogenic return flow relationships to water quality, (2) point-source sites and legacy contaminants, and (3) transformation products as CECs. Transformation products (TPs) are molecules formed from the original contaminant by metabolism, biotransformation, and (or) chemical reactions with light and (or) other chemical species. This list is not intended to be comprehensive but rather to highlight opportunities to address gaps in knowledge as they relate to current USGS priorities. We first address the status of knowledge and capabilities in relation to CECs as a class of contaminants. Each of the three gaps is then discussed in detail, with a statement of problem, status of knowledge, and suggested approaches. We conclude with a summary of outcomes for the USGS.

Status of Knowledge and Capabilities

CECs can be considered from a chemical and a microbial perspective (Cozzarelli and others, 1995; Johnson and others, 2002); however, in this document we only address chemical contaminants when discussing CECs. The sources of CECs are as varied as the contaminants themselves, ranging from municipal wastewater to septic tanks to agricultural run-off to chemical spills. Downstream water quality is known to be degraded by treated municipal wastewater discharge (Kolpin and others, 2002;

Barber, 2014; Bradley and others, 2016; Bradley and others, 2017; Gallen and others, 2018; Battaglin and others, 2020), industrial contaminants from wastewater discharge and chemical spills (Squillace and others, 1996; Landmeyer and others, 1998; Akob and others, 2016; Zhang and others, 2016; Cozzarelli and others, 2021), and return flows from agricultural practices (Kolpin and others, 2002; Murray and others, 2010; Salimi and others, 2017; Woodward and others, 2018, 2019). USGS scientists can prioritize investigations into the ever-increasing suites of new CECs, their sources and exposure pathways, and their effects on potential downstream water uses, by focusing on complex mixtures of contaminants coming from predominant source types. Three broad categories of sources related to water use discussed here are: (1) municipal wastewater, (2) industrial waste and products, and (3) agricultural practices and waste (table D1). Within each of these categories are classes of contaminants that have various uses, occurrence, and toxicity. Although new classes of contaminants and new contaminants themselves are always being identified, the examples in the following discussion highlight the wide range of contaminant chemistry that should be considered.

Municipal Wastewater and Return Flows

Wastewaters are a main source of CECs to freshwater environments (Glassmeyer and others, 2005; Fork and others, 2021), with the loads in surface water being more highly characterized compared to the loads in groundwater (Lapworth and others, 2012). A broad class of contaminants ubiquitously found in municipal wastewater effluents is pharmaceuticals and personal care products (PPCPs). Compounds such as

pharmaceuticals and food products are rarely completely metabolized, leading to excretion primarily through urine and subsequent concentration in wastewater (Murray and others, 2010; Salimi and others, 2017). Some organic compounds considered PPCPs include analgesics, non-steroidal anti-inflammatory drugs, antihyperlipidemics, antihyperglycemics, antimicrobials, surfactants, synthetic hormones, fragrances, insect repellents, and stimulants (table D1) (Murray and others, 2010; Salimi and others, 2017). PPCPs have a wide range of polarities and octanol-water partitioning coefficient (K_{ow}) values affecting their partitioning in the water column and in organisms, ranging from polar compounds that are highly water soluble to hydrophobic/lipophilic compounds more likely to partition into sediments and bioaccumulate in aquatic organisms. Some of the lipophilic compounds enable them to easily enter the food chain and propagate toxic effects throughout an ecosystem (Gramatica and others, 2016). A subclass of PPCP compounds is endocrine disrupting chemicals (EDCs), which alter functions of the endocrine system and interfere with synthesis, metabolism, binding, or cellular responses to natural estrogens (Salimi and others, 2017). Many EDCs make their way into sewage collection systems from domestic and commercial activities and are not completely removed by wastewater treatment plants (WWTPs), resulting in their discharge into streams. Some of these EDCs are biogenic (for example, 17 β -estradiol and estrone), others are synthetically designed to affect biological systems like pharmaceuticals (for example, 17 α -ethinylestradiol and metformin) or pesticides (for example, endosulfan and atrazine), while other consumer chemicals inadvertently cause endocrine disruption (for example, alkylphenols, bisphenol A [BPA], phthalate esters,

Water Contaminants

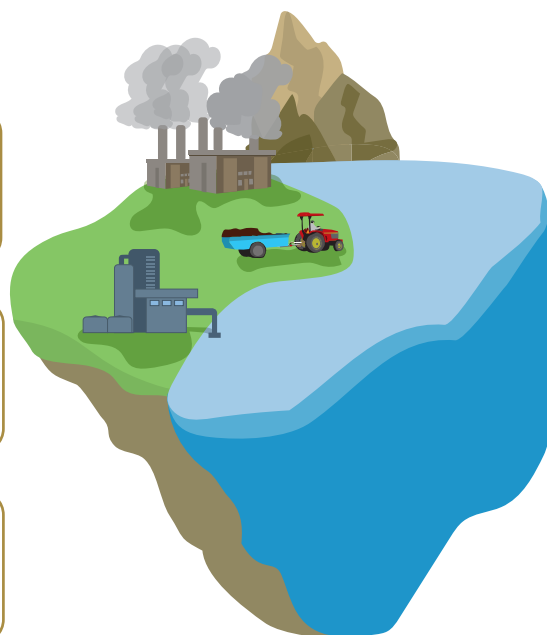
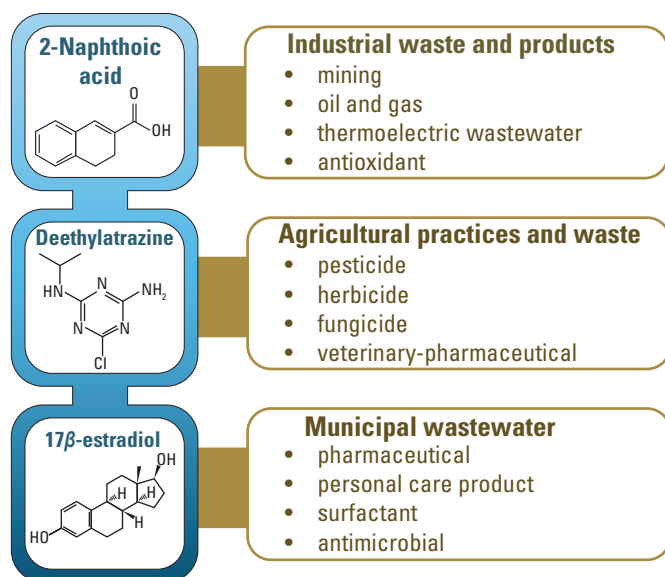


Figure D1. Diagram showing the three broad sources of contaminants of emerging concern (CECs) discussed in the text: (1) municipal wastewater, (2) industrial waste and products, and (3) agricultural practices and waste. Some key example contaminants from these sources are shown: 17 β -estradiol, 2-naphthoic acid, and deethylatrazine.

Table D1. Contaminant sources and classes in relation to water use in the United States. Uses of the compound classes as well as specific examples are shown, based on Salimi and others (2017).

[NSAID, Nonsteroidal anti-inflammatory drug; PFAS, poly- and perfluoroalkyl substances; EDTA, ethylenediaminetetraacetic acid; NTA, nitrotriacetic acid; DEET, N,N-diethyl-meta-tolamide; THMs, trihalomethanes; HANs, haloacetonitriles; HAAs, haloacetic acids; NDMAN-nitrosodimethylamine; AHTN, acetylhexamethyltetrahydronaphthalene; HHCb, hexahydrohexamethylcyclopentabenzopyran; PCBs, polychlorinated biphenyls]

Compound Class	Use	Examples
Municipal wastewater		
Analgesics	Pain reliever	Acetaminophen and acetylsalicylic acid
NSAIDs	Anti-inflammatory	Naproxen, ibuprofen, ketoprofen
Antiepileptic drugs	Treat seizure disorders	Carbamazepine and primidone
Antidepressants	Treat depression/anxiety	Fluoxetine, desvenlafaxine, venlafaxine
Antihyperglycemics	Diabetes control	Metformin, glyburide, sitagliptin
Antihyperlipidemics	Lipid regulators	Gemfibrozil, clofibrilic acid
Antimicrobials	Antibiotics and disinfection	Sulfamethoxazole, sulfamethazine, erythromycin, tetracycline, triclosan
Antioxidants, flame retardants, plasticizers	Plastic and resin products	Bisphenol A, bisphenol F, diethyl phthalate, tris-(2-chloroethyl) phosphate, tris-(dichloroisopropyl)phosphate
Surfactants	Detergents, water and stain resistance	Nonylphenols, octylphenols, PFAS
Chelating agents	Metal ion sequestration, water softener, solubilization	EDTA, NTA
Natural and synthetic hormones	Hormone modulation	17 β -estradiol, estrone, 17 α -ethinylestradiol
Insect repellent and insecticides	Pest control for fleas, ticks, roaches, white flies for pets, golf courses, turf	Fipronil, pyriprole, DEET
Herbicide	Herbicides for urban residential environments	Pendimethalin, glyphosate, dacthal
Disinfection by-products	Unwanted by-products of disinfection of drinking water and wastewater effluent	THMs, HANs, HAAs, NDMA
Other	Fragrances, stimulants, UV inhibitors	AHTN, HHCb, acetophenone, caffeine
Industrial products and waste		
Halogen-containing flame retardants	Flame retardants and aqueous film forming foam (AFFF)	Polybrominated diphenylethers, PFAS
Halogen-containing organic compounds	Heat transfer fluids and lubricants	PCBs
Antioxidants, plasticizers, flame retardants	Plastic and resin products	Bisphenol A, bisphenol F, diethyl phthalate, tris-(2-chloroethyl) phosphate, tributylphosphate
Oil and gas waste	Additives, fracking fluids, degreasers, hydrocarbons	Methyl-tertiary-butyl ether, ethylene dibromide, trichloroethane, 1,4-dioxane, polyaromatic hydrocarbons, methane
Industrial by-products	Chemical and plastics manufacturing	Dioxins, microplastics, 1,4-dioxane, PFAS
Alkylphenols	Household industrial products	Nonylphenol and octylphenol
Mining extractants	Mining and milling of natural resources	Trioctylamine, EDTA
Anti-corrosives	Aircrafts, dishwasher detergents, thermoelectric power	Benzotriazole and tolyltriazole
Agriculture practices and waste		
Carbamates	Herbicides, insecticides, fungicide	Carbendazim, benomyl and carbaryl
Chloroacetanilides	Preemergent herbicides	Metolachlor, alachlor
Chlorophenoxy acids	Herbicides	Bentazone, triclopyr
Organochlorines	Insecticides	DDT, dieldrin, endrin, endosulfan
Organophosphates	Insecticides	Diazinon, malathion, chlorpyrifos, tebufospyr
Phenylpyrazole	Insecticide	Fipronil
Pyrethroids	Insecticides	Bifenthrin, cypermethrin
Triazines	Herbicides	Atrazine, cyanazine, simazine
Triazine	Insecticide control of aphids and white flies	Pymetrozine
Neonicotinoids	Insecticides	Imidacloprid, clothianidin, thiacloprid, thiamethoxam
Fungicides	Fungicides	Azoxystrobin, boscalid, fluxapyroxad, metalaxyl, metconazole, myclobutanil, trifloxystrobin
Other prevalent herbicides	Herbicides	Phenylurea, isoproturon
Other prevalent insecticides	Insecticides	Propargite
Plant sterols	Phytoestrogenic effects	Daidzein, coumestrol, equol, biochanin A
Veterinary pharmaceuticals	Confined animal feeding operations	Bacitracin, arsenic acid, erythromycin, chlortetracycline

and polychlorinated biphenyls) due to chemical structure similarities with estrogen or other natural hormones (Roy and others, 2009; Barber and others, 2012; Barber and others, 2015). Many PPCP compounds undergo biodegradation or oxidation during wastewater treatment producing TPs that are potentially more harmful than their respective parent compounds (Roberts and others, 2016; Eriksson and others, 2017). Furthermore, rising populations and water scarcity (especially in the arid southwestern United States) have led to greater proportions of treated wastewater being reused intentionally or incidentally to supplement drinking water sources and other beneficial water uses (National Research Council, 1998; Rice and others, 2013; Rice and Westerhoff, 2015; Abbott and others, 2019). Therefore, there is increasing concern for the occurrence and adverse effects of the anthropogenically introduced CECs that enter water bodies. When this water is treated as drinking water, additional concerns arise regarding the production of toxic disinfection by-products (DBPs) like trihalomethanes, haloacetonitriles, haloacetic acids, and N-nitrosodimethylamine, which are formed when disinfectants (chlorine, chloramine, ozone) react with naturally occurring organic matter (Richardson and others, 2007; Weisman and others, 2019; Weisman and others, 2021).

It also is important to understand the lesser-known water-quality effects from mining, thermoelectric power plant cooling, and aquaculture water being used and returned to the hydrologic environment via direct and indirect discharges. There are fewer studies investigating the water-quality effects of return flows coming from storm water drainage, aquaculture, and agricultural biosolids applications, which create complex chemical mixtures of pesticides, fertilizers, pharmaceuticals and PPCPs, all exposing aquatic organisms to impaired water quality, potentially at critical life stages or habitats (Australian and New Zealand Environment and Conservation Council [ANZECC] and Agriculture and Resource Management Council of Australia and New Zealand [ARMCANZ], 2000; Nowell and others, 2014; Nowell and others, 2018; Masoner and others, 2019).

Industrial Products and Waste

The production of goods and materials used in modern urban environments involves the use of a variety of chemicals that can have deleterious effects on water quality. Industrial organic chemicals used in manufacturing and production processes include antioxidants, flame retardants, surfactants, perfluorates, phenols, phthalates, triazoles and others (table D1) (Murray and others, 2010). Antioxidants toxic to aquatic organisms, such as butylated hydroxyanisole and butylated hydroxytoluene, are used in the production of rubber, petroleum products or to preserve food (Kolpin and others, 2002). Per- and polyfluoroalkyl substances are used extensively in firefighting efforts at military bases and airports (for example, perfluorooctane sulfonic acid, aka PFOS), while a multitude of other PFAS compounds, such as perfluorooctanoic acid (PFOA) and other perfluoroalkanoic acids, are widely used in consumer products for their non-stick properties, water resistance, and stain resistance (Navarro and

others, 2016; Suthersan and others, 2016; Zhang and others, 2016). These compounds are increasingly important for water resource managers due to our growing understanding of toxicity effects and prevalence (Clara and others, 2009; Sunderland and others, 2019; Ankley and others, 2021; MacGillivray, 2021), as they are ubiquitously found in municipal and industrial wastewater effluents and biosolids (Zhang and others, 2016; Eriksson and others, 2017; Gallen and others, 2018), landfill leachates (Lang and others, 2017), and even agricultural sources (Kolpin and others, 2021). Phenols are commonly found in epoxy resins and plastics and some compounds, such as nonylphenol and BPA, are considered endocrine disrupters (Murray and others, 2010). Most phthalate esters tend towards hydrophobicity, but low molecular weight phthalates such as dimethyl phthalate and diethyl phthalate used as solvents in PPCPs and insecticides, and time released pharmaceuticals are more soluble, thus contributing to widespread detection of these compounds in the aquatic environment (Murray and others, 2010).

In addition to the manufacturing of materials and goods, industries at the intersection of anthropogenic activity and the natural environment, such as oil and gas production and mining, can contribute to the input of contaminants into water bodies of concern. Contaminants of concern for oil and gas exploration and production activities, including spills and waste disposal sites, are both inorganic and organic in nature. For example, in North Dakota, the number of oil and gas waste-fluid releases has been increasing from 2008–2015, often due to pipeline leaks or spills during transfer from storage tanks (Cozzarelli and others, 2021). These oil and gas wastes contain contaminants such as salinity, barium (Ba), strontium (Sr) and trace hydrocarbons, some of which were detected 2.5 years (yrs) after a spill and up to 7.2 kilometers (km) downstream (Cozzarelli and others, 2021). Similarly, downstream from an oil and gas waste facility in West Virginia, waters contain elevated specific conductivity, chloride (Cl⁻), and radium (Ra) (Akob and others, 2016). Another oil and gas persistent contaminant stemming from leaking underground storage tanks is methyl tertiary butyl ether (MTBE), which was added to gasoline in the United States beginning in the mid-1980s and by the early 1990s was the second most frequently detected volatile organic compound in shallow urban groundwater (Squillace and others, 1996). Microbial degradation rates of MTBE are relatively slow compared to other gasoline components (Landmeyer and others, 1998), and thus can remain an issue at some spill sites long after its use has been discontinued.

Mining waste contamination concerns are typically focused on heavy metals, which are classified as CECs, and improvements in analytical techniques allow for detection of lower concentrations that previously went unnoticed. In the Upper Colorado River Basin, heavy metals such as lead (Pb), cadmium (Cd), zinc (Zn), arsenic (As), and copper (Cu) from mining activities threaten water quality. Silver mining in the Gunnison National Forest at the Standard Mine site, about 7 km west of the town of Crested Butte, for example, has led to heavy metal contamination of soil, ground, and surface waters (Nash, 2002). Deposition of heavy metals into nearby Elk Creek has also caused contamination of Coal Creek and other downstream water bodies (Nash, 2002). Mining contaminants are not only an issue due to the transport of these constituents

to vulnerable water bodies, but also because biogeochemical conditions change along a flow path and may be different in the receiving water body. Factors such as pH, redox conditions, salinity, total suspended solids, and microbial communities vary spatially, and influence metal contaminant speciation, toxicity, and bioavailability. The effects of anthropogenic extractants and chelating agents, such as trioctylamine and ethylenediaminetetraacetic acid (EDTA), used during extraction and milling processes are largely ignored in the public literature, although their aquatic concentrations are high enough to influence shifts in geochemical speciation and bioavailability of in-stream metals. Therefore, to best assess long-term water risk management of Integrated Water Science (IWS) basins, it is essential that sources of contamination are identified, and that contaminant chemistry in receiving water bodies is understood.

Agricultural Practices and Waste

The production of agricultural products (that is, foodstuffs, cotton, hemp, turf, livestock) is another example where anthropogenic activity intersects with the natural environment and contributes CECs to the aquatic environment. Agriculture is vital for human survival but runoff and (or) waste from agricultural practices can introduce CECs, such as pesticides, veterinary pharmaceuticals, nitrification inhibitors, surfactants, and estrogenic hormones to water bodies (Kolpin and others, 2002; Murray and others, 2010; Salimi and others, 2017; Woodward and others, 2018; Woodward and others, 2019). Pesticides can be further classified as herbicides, insecticides, fungicides, rodenticides, and miticides, all of which are designed to control weeds, pests, and fungi via prevention, destruction, or repulsion to enhance food production (de Souza and others, 2020). It is estimated that 10 percent of pesticides applied to soil reaches non-target areas, an amount that is enhanced if it rains shortly after application (Schulz, 2004). Although few pesticides have been officially classified as persistent organic pollutants as of 2020, many fall into this category in that they are persistent, toxic, and demonstrate long-range environmental transport (de Souza and others, 2020).

The occurrence and synergistic biological effects of most pesticides and their TPs are not fully understood, especially in the context of responses to changes in flow conditions or timing of applications (Murray and others, 2010; Nowell and others, 2014; Nowell and others, 2018; Norman and others, 2020; Mahler and others, 2021). A fair amount of literature can be found discussing the concentrations and water-quality effects of specific pesticide chemicals (that is, insecticide, herbicide, or fungicide) as they enter the freshwater environment following irrigation or storm runoff events (Stone and others, 2014; McKnight and others, 2015; Miller and others, 2020). For example, atrazine is an herbicide that historically has been widely spread on soybean and corn crops across large areas (de Souza and others, 2020). With approximately 80 million pounds applied annually, atrazine is the most common pesticide contaminant of ground and surface water in the United States and has a half-life of a year or more (Solomon and others, 1996). It has been widely detected in Europe despite a ban in 2003 (de Souza and others, 2020). This compound

is considered an endocrine disruptor, as demonstrated by demasculinization (chemical castration) and complete feminization in adult male frogs following environmental exposure (Hayes and others, 2006a, 2006b, 2010). Other triazine herbicides such as cyanazine and simazine have similar chemical structures and modes of action but have not been studied as thoroughly. In general, the effects of pesticides on endocrine disruption are not well known, particularly when TPs are also considered.

Agricultural chemical inputs to water bodies can be found throughout the United States. General agricultural practices can contribute to harmful algal blooms (HABs) in the Illinois River Basin. On a broader scale, the use of pesticides across the United States has been linked to the growth of HABs (Harris and Smith, 2016; Stackpoole and others, 2021). Therefore, manufacturing, processing, storage, and use of agricultural chemicals are potential sources of contamination for organic contaminants such as pesticides in basins where agricultural land use is prevalent. Finally, spills and pesticide handling and mixing facilities should also be considered as potential sources of agricultural CECs (Haack and others, 2015).

Gap Analysis and Approaches

Gap 1. Wastewater Reuse and Anthropogenic Return Flow Relations to Water Quality

Knowledge Gaps

Key knowledge gaps involve water-quality degradation effects associated with various water use categories (table D2). The major knowledge gaps in understanding the contaminant and water-quality relationships between water use, reuse, and sustainability of high-quality water resources are:

1. Water-quality requirements and effects of the various water use categories and associated water-quality degradation effects (described later in this section).
2. The major drivers and mechanistic processes controlling exposure pathways and adverse effects to human and aquatic organism health as noted in the companion Open-File Report to this publication, their chapter C “Anthropogenic and Geogenic Contaminant Bioexposures Affecting Aquatic Ecosystems” (Harvey and others, 2024).
3. Wastewater discharge and other anthropogenic return flows with their associated chemical loads (for nutrients, geogenics, and CECs) need to be quantitatively incorporated into predictive hydrologic and solute transport models.
4. The transference from source water of intake to different receiving water of return flow.

The USGS can seek ways to better characterize what the water-quality needs are for some of the important water use categories, especially in relationship to salinity or currently

Table D2. Summary table for contaminants of emerging concern gap analysis for beneficial water use in the United States.

[CEC, contaminants of emerging concern; WWTP, wastewater treatment plant; IWS, Integrated Water Science; TP, transformation product; USGS, U.S. Geological Survey.]

Topic	Knowledge Gap	Importance	Proposed Approaches	References
Wastewater reuse and anthropogenic return flow relationship to water quality.	Determination of output degradation effects from consumptive use on water quality and CEC fate, as well as corresponding assessment of the effect of CEC input to water bodies of concern	Anthropogenic water use-and-loss effects on CEC concentrations could lead to adverse water-quality and biological effects. Water-quality needs from dominant water use categories are unclear, especially in relationship to currently unregulated CEC.	Field and laboratory-based studies of CEC fate in relation to landscape use and WWTP. Compilation of a water use requirements database to identify critical water-quality study needs.	Kolpin and others, 2002; Rice and Westerhoff, 2015; Barber and others, 2019; Weisman and others, 2019.
Legacy point sources	Identification of legacy point source sites near IWS basins and corresponding hydrogeochemical and geophysical processes and parameters affecting CEC transport and fate	Legacy point sources and corresponding flow paths to IWS basins could be introducing CECs with detrimental water-quality effects	Collaboration with local and State stakeholders to locate point sources of interests. Geochemical water-quality analysis and collaboration with geophysicists to understand systems.	Lapworth and others, 2012; Akob and others, 2016; Cozzarelli and others, 2021.
TPs of CECs	Ability to measure TP concentrations in water bodies of concern and better understand TP biogeochemistry	TPs may be more soluble, toxic, and concentrated compared to parent compounds but are currently not measured. Biogeochemical behavior is understudied.	Development of methods to better quantify TPs of interest and assess toxicity in collaboration with the USGS Ecosystems Mission Area. Assessment of sampling frequency and hydrogeological behavior.	Kolpin and others, 2004a; Barber, 2014; Bekins and others, 2016; Mahler and others, 2021.

unregulated CECs. It also would be useful to develop an assessment approach for determining gradations of water-quality requirements that can be universally applied to water use applications. A summary of known inflow water-quality suitability requirements for the nine USGS defined water use categories plus effects to aqueous ecosystem health, is provided in table A1 in chapter A of this report. Thermoelectric and mining uses typically have minimal water-quality requirements, whereas public water supply is highly regulated and maximum contaminant levels for biogenic and anthropogenic contaminants are strictly enforced. Some of the other water uses are difficult to succinctly summarize by category since many of the water-quality requirements are industry specific or process dependent, but a universally applied water-quality requirement scheme could be useful.

There is an even larger gap in our knowledge of the water-quality degradation that occurs when anthropogenically used water is returned to natural waters (Rice and Westerhoff, 2017). Consumptive use of water occurs when an anthropogenic activity draws from available water supplies within a basin and returns only a portion or none of the withdrawn water to the basin. Water might be lost to evaporation (for example, thermoelectric cooling or reservoir storage), evapotranspiration (for example, agriculture and landscaping), or incorporation into a product, such as a

beverage, and shipped out of the basin (Dieter and others, 2018). Approximately 97 percent of the 133 billion gallons per day (Ggal/d) withdrawn for United States thermoelectric power in 2015 was returned to natural waters (Dieter and others, 2018). The addition of thermal energy (temperature increases), salinity (evaporative concentration), and specific contaminants, such as corrosion inhibitors and antimicrobial chemicals, to the returned water could have dramatic effects on downstream water quality and warrants further investigations. Concerns include thermal pollution of sensitive riparian ecosystems that may be located where cooling water outflows are returned to surface waters. For water uses like crop irrigation, with high consumptive use, concentration effects on the return flow can raise concerns for water-quality degradation. Of the 118 Ggal/d of groundwater and surface water and the 0.669 Ggal/d of reclaimed wastewater used for irrigation in the United States in 2015, it is estimated that 62 percent was consumed through evaporation, evapotranspiration, or incorporation into the irrigated crops (Dieter and others, 2018). The estimated 38 percent of irrigation water returned to natural waters will carry the load of agricultural chemicals used, flush geogenic constituents from the soils, and have concentration effects, all leading to potentially unacceptable levels of salinity, toxic metals, or anthropogenic contaminants with adverse biological effects.

Approaches to Fill Knowledge Gaps

To assess the effects of intentional or incidental wastewater and return-flow water reuse, and address the gaps discussed above, the following approaches are suggested. A systematic review of the nine water use categories is suggested to prioritize those uses with the greatest potential for causing water-quality degradation in critical water resources. This review also will identify the water return flow categories most suitable for reuse, along with barriers that hinder the incorporation of planned, purposeful water reuse into a community's water planning portfolio (U.S. Environmental Protection Agency [EPA], 2020). One framework for evaluating water reuse science is the National Water Reuse Action Plan (EPA, 2020), which provides useful data and lessons learned to advance the consideration of purposeful water reuse to improve the security, sustainability, and resilience of our Nation's water resources in the face of a changing climate. It would be useful to expand this framework to develop an assessment approach for determining gradations of water-quality effects of return flows based on type and compare those with established toxicity or water-quality benchmarks in combination with a universally applied water-quality requirement framework for each of the beneficial use categories.

Table D1 summarizes the well-known contamination sources and classes in relation to water use. Reviews of relevant documents and databases could be developed to prioritize lists of CECs to consider in IWS basins' investigations (Kolpin and others, 2002; Buxton and Kolpin, 2005; Nowell and others, 2014; Bradley and others, 2016, 2017; Hladik and others, 2016; Conley and others, 2017a, b; EPA, 2021a, b). This work aims to provide evaluations of water-quality assessments that could be improved or need more studies to better understand the occurrence, fate, and biological effects of CECs.

In compiling water-quality effects of the nine USGS defined water uses plus ecosystem health, we could develop a scheme that allows for cross comparison of the different water-quality or toxicity benchmark measurements used in different aspects of water assessment, such as maximum contaminant levels (MCLs) for drinking water versus aquatic life benchmarks used for aquatic organism health. The table of compiled water-quality benchmark values should be annotated with the: (1) definition of the benchmark concentration unit and description of what it means to have this benchmark value exceeded, (2) source type of the data, measured or predicted (for example, computational and modeled simulations), with citations, and (3) quality of the data with information on limitations, uncertainties, and underlying assumptions. This qualitative information will be important to data users when interpreting water quality data and trying to make water management decisions. The importance of knowing what is meant when exceedances are observed can be illustrated with the example of Canadian water-quality guidelines, which are intended to protect all forms of aquatic life during all stages of the aquatic life cycle and should not be exceeded at any time (<https://ccme.ca/en/current-activities/canadian-environmental-quality-guidelines>); in contrast, EPA's criterion continuous concentration (CCC) is a chronic exposure benchmark that applies to four-day average

concentrations, and is intended to protect 95 percent of aquatic species, and should not be exceeded more than once in three years. Moreover, important water management decisions should be made with a clear understanding of the quality of the data. For example, a sediment benchmark for aquatic life might be: (1) measured based on spiked sediment bioassays, (2) predicted from a measured toxicity value in water using the soil organic carbon partitioning coefficient (K_{oc}) and equilibrium partitioning theory, or (3) predicted based on K_{ow} only. The quality of the benchmark in these cases would decrease from (1) to (3).

Municipal wastewater is a prime example of a complex chemical mixture of CECs that is often reused and the point source discharge of WWTPs allows for direct correlation between chemical loads and resulting stream concentrations. For these reasons, we suggest initially focusing on municipal and industrial WWTPs in future IWS basins for field and laboratory-based studies to address the interactive effects of complex mixtures of CECs and their TPs on water quality, similar to work done by USGS colleagues in Muddy Creek, Iowa (Zhi and others, 2020, 2021; Webb and others, 2021). Initial landscape assessments could be conducted to identify additional CEC sources, in addition to WWTPs, and would entail collaborations with local stakeholders. Subsequent investigations could be done to fill in other data gaps from other return flows from surrounding landscape uses (for example, agricultural) and anthropogenic activities (for example, thermoelectric). Measurements of specific CECs would depend on IWS basin needs and require state-of-the-science measurements using gas chromatography-tandem mass spectrometry (GC-MS/MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) techniques for organic contaminants and inductively coupled plasma-mass spectrometry (ICP-MS) and optical emission spectroscopy (ICP-OES) for toxic metals and trace element contaminants. In addition to targeted and unknown compound measurements, a combination of geochemical (for example, conductivity, pH, dissolved oxygen, nutrient concentrations) and hydrologic (for example, streamflow and flow velocity) measurements could be used to assess CEC sources, fate, and transport. These field measurements also would involve assessing water quality of surrounding natural waters in relation to WWTPs and other sources to determine the effects of reuse on water quality and aquatic organisms or risks to drinking water sources, building upon previous investigations of complex mixtures like those undertaken in Boulder Creek, Colorado, and Fourmile Creek, Iowa (Bradley and others, 2007; Barber and others, 2011; Barber and others, 2013; Zhi and others, 2020; Zhi and others, 2021). Once specific CECs in IWS basins are identified through field investigations, laboratory-based studies could be carried out to establish transformation rates, TPs, and potential health risks needed as input parameters for wastewater and hydrologic transport modeling of the complex mixtures.

Most of the organic and inorganic CECs cannot be monitored continuously, but instead require discrete sampling. As with the point-source legacy contaminants, the analyses require complex, labor-intensive, and relatively expensive (for example, GC-MS/MS and LC-MS/MS) techniques for organic contaminants. WMA could promote research-based development of new analyses

and remote sensing techniques for CEC assessments around the nation that could support stakeholder-driven decisions. The USGS Actionable and Strategic Integrated Science and Technology (ASSIST) projects in the Colorado River Basin are examples of interdisciplinary science and application of advanced techniques for complex stakeholder driven challenges. For example, recent proof-of-concept studies in the Colorado River Basin during 2022–2023 have tested and begun environmental validation procedures for the following advanced techniques: (1) novel Turner C6P fluorescence sensors with continuous remote readings of fluorescence measurements that can characterize organic water-quality constituents (including screening for risk of wastewater-driven CEC contamination), (2) in-stream solid-phase extraction samplers (“SPE-bots”) allowing enrichment of trace organic contaminants (that is, PFAS, PPCPs, EDCs, pesticides) for simplified sample processing and analysis in the lab, and (3) molecularly imprinted polymer-modified electrochemical sensors (MIPMECS) as an innovative technique for in-stream measurements of PFAS contaminants. Another approach is development and modification of analytical methods (likely mass-spectrometry techniques) to provide a rapid screening method for detecting priority CECs and proxies for hazardous aqueous chemicals coming from different sources, different chemical classes, and with different modes of action. This method would focus on limiting the total constituents analyzed and using important proxy chemicals to represent chemical classes and (or) source categories, along with incorporation of automated sampling and processing steps to reduce analytical costs and improve data delivery times, both of which can be limitations of existing CEC measurement techniques. These screening methods for CECs and relevant proxy constituents would provide essential and timely measurement data for calibration and ground-truthing of CEC hydrologic transport models. It would also help to identify water resources highly affected by CECs that warrant additional monitoring with more comprehensive water-quality analyses.

Gap 2. Legacy Point Source Sites of Contaminants of Emerging Concern

Knowledge Gaps

CECs in surface water and groundwater may migrate from a point source to a water body of interest. Point-source pollution originates from discrete locations and inputs into aquatic systems can be defined in a spatially discrete manner (Lapworth and others, 2012). Some point sources are the result of accidents such as oil or waste spills, while others may be the result of decades-long (legacy) anthropogenic activity such as landfills or WWTP effluent discharges. Many legacy landfills were constructed with little or no leachate controls systems, posing unquantified threats to local water bodies (Hepburn and others, 2019; Masoner and others, 2019). The scale of this threat depends on a variety of factors including leachate composition, distance from water bodies, and local geochemistry and geology (Masoner and others, 2014, 2016;

Stamps and others, 2016; Talalaj and Biedka, 2016; Hepburn and others, 2019). Just as varied as the types of point sources are the types of contaminants that stem from them, ranging from metals such as Pb, Zn, and Cd, to organic chemicals such as volatile organic compounds (VOCs,) polychlorinated biphenyls (PCBs), light non-aqueous phase liquids (LNAPLs), 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), creosote, phthalate esters, and a wide range of PPCPs (table D1). Geochemical parameters including salinity, pH, dissolved oxygen, and dissolved organic carbon as well as sediments have a distinct influence on the fate of legacy CECs in surrounding water bodies (Hepburn and others, 2019). These factors effect CEC degradation, transformation, transport, and bioavailability in receiving water bodies adjacent to a legacy point source. Furthermore, complex geological and geophysical characteristics, such as low-permeability sediments, may allow legacy point source sites to act as long-term sources of CECs (de Lambert and others, 2021).

The WMA initially identified three IWS basins for intensive study: (1) the Delaware River Basin, (2) the Illinois River Basin, and (3) the Upper Colorado River Basin. These basins are being monitored to understand distinct processes such as the effects of drought on water supply in the Delaware River Basin, cold-region snow and ice processes in the Upper Colorado River Basin, and nutrient contributions to HABs in the Illinois River Basin. Legacy point-source contamination has links to all these processes. For example, after a drought there will be less water available for diluting contaminant input from a point source (Kolpin and others, 2004b). In cold regions, snow and ice melt during spring may cause a surge of contaminant flow from mining waste during spring runoff. Finally, HABs are influenced by pesticides, as described above in the status of knowledge. Therefore, as intensive studies of the basins continue, it is important to consider the effect of legacy point-source contamination and associated CEC’s on water-quality processes to understand overall water body and ecosystem health.

Though there are many potential legacy point-source sites surrounding IWS basins and we discuss a few examples, this is by no means an exhaustive discussion. For example, there is a site of concern stemming from oil spills in Bridgeport, New Jersey, 2 miles south of the Delaware River (Hochreiter and Kozinski, 1985; Kozinski and others, 1990). This site housed oil waste from 1960–1981 and caused widespread damage to surrounding wetlands as early as the 1970s. The groundwater is contaminated with VOCs, PCBs, and LNAPLs and the underlying aquifer is a source of drinking water (Hochreiter and Kozinski, 1985; Kozinski and others, 1990). Another site within the Delaware River Basin is the Cinnaminson Township, New Jersey, where groundwater is contaminated with a suite of organic contaminants including TCE, benzene, cis-1-2, dichloroethane and vinyl chloride. Overall, oil refinery effluents and crude oil spills have affected the Delaware River and the Delaware Bay, though studies are currently limited (Hall and Burton, 2005; Habicht and others, 2015; Walker and others, 2016).

Many legacy point-source sites that may be affecting IWS basins involve contaminated groundwater from spills and improper disposal of commonly used solvents such as TCA and TCE, along with stabilizer chemicals such as 1,4-dioxane. Long-term exposure to 1,4-dioxane causes kidney and liver damage; acute exposure can result in death (Pollitt and others, 2019). Remediation efforts for TCA and TCE over the past 40 years were not designed to remove the very soluble 1,4-dioxane from contaminated groundwater sites, leaving a continued legacy CEC (Adamson and others, 2014). For example, in a study of greater than 2,000 California groundwater sites affected by chlorinated solvents, 76 percent had co-occurrence of 1,4-dioxane with TCA, many with 1,4-dioxane concentrations three orders of magnitude above the 0.67 micrograms per liter ($\mu\text{g/L}$) EPA drinking water standard (Adamson and others, 2014). Use of 1,4-dioxane as a solvent in consumer products is not regulated. Because 1,4-dioxane is recalcitrant to conventional wastewater and drinking water treatments there are significant numbers of drinking water sources potentially exposed as the result of wastewater discharges (Adamson and others, 2017; McElroy and others, 2019). Thus, 1,4-dioxane is an example of a legacy and current use CEC with substantial data gaps on occurrence, fate, and biological effects.

While the sites described here offer key examples of legacy point source contamination, it also is vital to consider lesser-known legacy point sources of CECs that are unique to the water body of interest. CECs at local point source sites will depend on a breadth of anthropogenic activities and proximity to urban areas (that is, manufacturing sites and landfills). Working with local stakeholders to identify these sources is an essential step toward tracking and predicting CEC fate.

Approaches to Fill Knowledge Gaps

To characterize the effects of legacy point source pollution, sites can first be identified in the IWS basins. Some potential legacy point source sites include municipal and industrial wastewater discharges, landfills, chemical spills, food processing plants, pharmaceutical manufacturing plants, and so forth; however, this is not a complete inventory. It is unclear exactly how many legacy point-source sites exist in these areas, with potentially poorly characterized sites that are contributing to surface and (or) groundwater contamination. Searches of national databases and collaborative efforts between the USGS and State and local agencies can help identify legacy point-source sites and assess the degree of water-quality impairment at these sites and the associated threat they may pose to IWS basins. Once identified, sites could be ranked based on threat to the basin in terms of CEC concentrations, toxicity, reactivity, and transformation potential.

Water-quality parameters at major legacy point-source sites of interest could be measured using data loggers, discrete samples, in-situ passive and continuous samplers, and other water-quality monitoring tools available to the USGS. Together, available discrete sample data and continuous information about pH, salinity, dissolved oxygen, and temperature would

provide a record of baseline geochemical conditions over time. With regards to CECs, there is an overarching lack of data and understanding as it relates to the sources, fate, and effects of these constituents. Initial characterization of aqueous geochemical parameters and CEC concentrations in relation to a known legacy point-source site would allow for relationships between these parameters and CEC fate to be established. Geochemical, surface-water, and groundwater modeling could then be leveraged with in-situ measurements to enhance predictive capabilities of CEC fate. However, it must be noted that CEC geochemical behavior is extremely complex and while this work could potentially improve predictions, it is not expected to be a one-size-fits-all understanding of CEC geochemistry.

In addition to measuring water quality at point-source sites, long-term measurements along groundwater and surface-water flow paths to water bodies within IWS basins could also be analyzed to better understand the role of water quality and aqueous geochemistry in contaminant fate and transport from legacy point source sites. Collaboration with geophysicists would allow for the use of electromagnetic and thermal imaging techniques that can be used to track the fate of plumes (Ball and others, 2020; Briggs and others, 2020). These data, along with physicochemical properties of the chemicals that control fate and transport, could be incorporated into hydrologic transport models that could be used to understand groundwater and surface water interactions in relation to points of discharge. These models could help to predict CEC behavior from point sources in current and future IWS basins and potentially help to assess risk to downstream aquatic organisms and (or) drinking water sources.

Direct measurements of contaminant concentrations (for example, gas chromatography with mass spectrometry [GC-MS], liquid chromatography with mass spectrometry [LC-MS], ICP-MS, and ion chromatography) and biological assessments (for example, field and lab bio-exposure experiments, tissue analysis of native aquatic species, cellular assays, genomic and transcriptomic technologies) from legacy point source sites and along flow paths in IWS basins will be an important aspect in assessing their effect. Many organic and inorganic CECs require discrete sampling and complicated analyses due to low concentrations and complex mixtures. The chemical structures of many CECs are not conducive to typical real-time monitoring equipment (for example, potentiometric, spectrophotometric, or fluorometric analyzers). By focusing initially on the primary processes of interest at each IWS basin (drought conditions in the Delaware River Basin, HABs in the Illinois River Basin, and snowmelt-driven processes in the Upper Colorado River Basin), CECs that affect each of these processes can be targeted. For example, in the Illinois River Basin, fertilizers and pesticides from legacy point sources such as chemical storage and (or) spills can be measured along flow paths and changes in concentration noted to discern their potential influence on HABs growth. Conversely, in the Upper Colorado River Basin, which is influenced by mining waste, it is logical to focus on metals and metalloids whose mobilization and aqueous concentrations

will be affected by snow and ice melts on a seasonal basis. These are just a few examples of potential target contaminants, allowing for room and flexibility to expand in new directions.

Gap 3. Transformation Products as Contaminants of Emerging Concern

Knowledge Gaps

Organic contaminant studies have focused primarily on the original compounds (that is, parent compounds) released into the environment. However, it has been recognized for decades that TPs of pesticides and consumer product chemicals may be more prevalent than the parent compounds in groundwater (Field and others, 1992a; Field and others, 1992b; Kolpin and others, 2000, 2004a; Bexfield and others, 2021; Fisher and others, 2021). Moreover, because occurrence of TPs is common in groundwater, baseflow is an important source of TPs to streams (Squillace and others, 1993). Notably, some TPs are more toxic than their parent compounds, as is the case for polyaromatic hydrocarbons (PAHs) (Knecht and others, 2013). For some compounds, such as triclosan, the TP methyl triclosan can be the predominant form found in surface water (Lindström and others, 2002). In a nationwide survey of contaminant mixtures in streams (Bradley and others, 2017), the most frequently detected compound was an insecticide TP (desulfinyl fipronil). In another national study, the TP desulfinyl fipronil was detected in over 90 percent of stormwater samples (Masoner and others, 2019). Thus, TPs of hydrocarbons (Bekins and others, 2016), pesticides (Mahler and others, 2021), and wastewater compounds (Barber, 2014) are ubiquitous in water, but their formation, persistence, and toxicity are poorly characterized. Gaining a better understanding of TPs is important for water assessments because overall toxicity of contaminants in water could be vastly underestimated if TPs are not also considered.

Recent examples in the literature illustrate how TPs are affecting United States water quality. For example, a TP of a tire antioxidant has been linked to Coho salmon (*Oncorhynchus kisutch*) mortality in the Pacific Northwest (Tian and others, 2021). The TPs of the insecticide fipronil are more stable than the parent compound and show ecological effects at much lower values than the EPA fipronil chronic invertebrate benchmarks (Miller and others, 2020). A major issue with TPs is that there are few health-based screening criteria. TPs may be more prevalent and present in higher concentrations than the parent compounds (Kolpin and others, 2000). In some cases, they are more soluble and polar than parent compounds and thus more mobile and persistent. Furthermore, they may be undetected because of a lack of standard methods (Mahler and others, 2021). Recognition of TP prevalence is growing as new methods are developed to identification and quantifications. USGS can now measure more than 100 pesticide TPs (Mahler and others, 2021). Recent results show that the frequency of sampling is very important for evaluating whether stream concentrations exceed aquatic benchmarks (Norman and others, 2020). Sampling strategy is also important, as

hydrologic-based sampling provides a better picture of pesticide concentrations in streams (Hladik and others, 2014).

Approaches to Fill Knowledge Gaps

A key approach needed for this work is to determine a sampling frequency strategy for transformation products of pesticides. It has been established that daily sampling reveals exceedances that are not apparent in weekly samples (Norman and others, 2020). Because daily samples may be impractical, research is needed to determine alternate approaches. Previously, sampling strategies based on hydrologic events have been successful (Hladik and others, 2014; Woodward and others, 2018; Hama and others, 2021). Future strategies may involve a combination of hydrologic event-based approaches, passive sampling devices, autosamplers or proxy methods.

More research on TP toxicity will facilitate development of meaningful screening criteria. Of the 116 pesticide transformation products measured by Mahler and others (2020), only one-quarter have an aquatic life benchmark. Often the toxicity of the parent compound is substituted for the TP, but this may be too high or low. Furthermore, the existing benchmarks may be for less sensitive species than are affected in the streams. In the case of petroleum hydrocarbons and PPCPs, very few toxicity benchmarks of parent compounds or TPs exist. Addressing this gap may involve working with toxicologists in the USGS Ecosystems Mission Area and other Federal, State, and local agencies.

In many cases, the reporting levels for TPs are higher than those for the parent compounds, leading to fewer detections. New methods that include more parent compound and TP pairs also are needed, as many potentially important compounds are not measured. Often the problem is a lack of available standards. Continued methods development on quantifying additional TPs and lowering existing reporting levels could be carried out by the USGS's National Water Quality Laboratory, the Organic Geochemistry Research Laboratory in Kansas, the Organic Chemistry Research Laboratory in Sacramento, and other USGS laboratories (<https://www.usgs.gov/science/laboratories>).

Often TPs are formed in groundwater and subsequently discharge to surface water (Squillace and others, 1993). Thus, TPs of pesticides are most concentrated in streams during baseflow (Mahler and others, 2021). In some cases, TPs of pesticides banned for a decade are still present in surface water suggesting long transit times in groundwater (McKnight and others, 2015; Mahler and others, 2021). Predicting the impact of TPs on water quality may require research relating to fossil fuel, pesticide, and PPCP use, parent compound and TP formation rates, transit times in groundwater, and rate of discharge to surface water. Improved methods for quantifying TP transport and transit times in groundwater is a cross-cutting issue affecting many contaminants including CECs, nutrients, geogenics, and salinity.

Concerns about the health effects of contaminant mixtures together with the impracticality of quantifying thousands of unregulated chemicals are motivating new toxicologic approaches. The goal of these new approaches is to discover which chemicals are of greatest concern (Diamond and Burton, 2021). Scientists

in the USGS Ecosystems Mission Area (<https://www.usgs.gov/mission-areas/ecosystems>) use exposure-effects-driven tools. These tools assess the biological effects of a mixture or an extracted portion of a mixture. If adverse effects are observed, then chemical analyses are used to identify which chemical(s) in the mixture are responsible. Collaborations among WMA and Ecosystems Mission Area scientists can foster use of these new toxicological approaches.

Expected Outcomes

The wide variety of CECs, their complex interactions, and the ever-expanding list of compounds make understanding their fate and prioritizing research an extremely challenging task. This document does not address every knowledge gap that exists with respect to CECs, nor does it offer what should be considered sole approaches. Instead, we propose to address some of the most pressing gaps in knowledge as they relate to current WMA priorities. The complexity of understanding and predicting the fate, geochemical drivers, water-quality effects, and biological effects associated with CECs can be addressed by interdisciplinary teams and inter-mission area and interagency collaborations. Below are some key outcomes anticipated from this work.

- Provide novel results necessary for improved modeling capabilities, create much needed databases, and begin to address the many gaps in literature related to CEC fate, sources, and effects.
- Assess water-quality requirements for the dominant water-use categories in relation to currently unregulated CECs. Update open-platform databases that can be used for improved modeling inputs.
- Compile a comparative assessment of water-quality effects of the nine water use categories using science-based toxicity and water-quality benchmarks, resulting in the identification of water management changes most influential for preserving water quality and advancing sustainable use of critical water resources. This could provide valuable information for modeling that can be used in predicting water quality.
- Compile comparative assessment criteria to identify the water return flow categories most suitable for reuse in a watershed or region, along with identification of local and national barriers that could hinder the incorporation of planned, purposeful water reuse into a community's water portfolio (National Research Council, 1998; Rice and others, 2013; Rice and Westerhoff, 2015; Abbott and others, 2019). The collected data could advance the consideration of purposeful water reuse to improve the security, sustainability, and resilience of our Nation's water resources in coordination with the EPA's National Water Reuse Action Plan online platform at <https://www.epa.gov/waterreuse/national-water-reuse-action-plan-online-platform> (EPA, 2020).

www.epa.gov/waterreuse/national-water-reuse-action-plan-online-platform (EPA, 2020).

- Identify principal legacy point-source sites and the corresponding CECs that pose some of the greatest threats to water quality and ecosystem health, specifically in IWS basins, which could further work in these basins and provide valuable information to local (State, county, city, and so forth) stakeholders.
- Characterize groundwater contaminant plumes from point-source sites in IWS basins and promote understanding of the hydrological and biogeochemical processes that contribute to plume mobilization. These data can be used to improve inputs in a variety of water-quality models and improve local stakeholder understanding of contaminant plumes needed for decision making.
- Expand, develop, and improve methods for foundational scientific activities through laboratory and field experiments for sample collection and detection of priority CECs, their TPs, and relevant proxy chemical indicators, which includes understanding the best sampling times and frequency related to hydrological parameters of a water body of concern.
- Improve toxicity benchmarks for a variety of unregulated CECs and TPs that should lead to improved predictions of water quality and suitability for different water use categories.

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Chapter E

Improving Predictions of Nitrogen Effects on Beneficial Uses of Water

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Purpose and Scope

This chapter is focused on identifying knowledge and data gaps, that if filled, would improve predictions of nitrogen (N) effects on beneficial uses of water resources. 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>). Nitrogen effects on ecosystems are not addressed directly in this chapter but are covered in the companion Open-File Report to this publication (Harvey and others, 2024) in their chapter B “Coupled Nutrient-Carbon Cycle Processes and Related Ecological-Flow Drivers.”

Statement of the Problem

Human activities have roughly doubled the amount of reactive N that enters the terrestrial biosphere since industrialization, with crop production by far the largest component of this increase (Smil, 1999). Even sharper increases in reactive N have been observed in developing countries in recent decades (Gu and others, 2015). With no imminently viable alternative to N fixed by the Haber-Bosch process, reactive N is expected to continue to increase in the next several decades to feed a growing population (Smil, 1999; Galloway and others, 2004). While increases in reactive N have been essential to feeding a rapidly growing world population, they have also led to negative environmental effects (Erisman and others, 2013), including degradation of drinking water supplies (Pennino and others, 2020), increasing human health concerns (Ward and others, 2018), nutrient enrichment of aquatic ecosystems (Boesch, 2002; Rabalais, 2002) and contributions to global climate change (Fagodiya and others, 2017; Thompson and others, 2019).

Nitrate is the form of reactive N that poses the greatest threat to beneficial uses, both in the United States and globally; nitrate is among the compounds most likely to exceed U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCLs) in public water supplies (PWS) (Allaire and others, 2018). Nitrate

concentrations exceeded MCLs in 1.3 percent of catchments containing groundwater or surface water PWS (Pennino and others, 2020). While nitrate MCL exceedances in surface-water supplied PWS are becoming rarer, groundwater-supplied PWS exceedances are increasing (Pennino and others, 2017). Assessments of groundwater sources of private domestic and public drinking water supplies also indicate that nitrate is one of the most common threats to drinking-water quality, with nitrate concentrations in groundwater exceeding the MCL in 4 percent and 2 percent of the private and public drinking water sources, respectively (DeSimone, 2009; Toccalino and others, 2010). The highest risk of an MCL exceedance in a groundwater PWS was found in areas with intensive cropland such as the Central Valley of California, Central Columbia Plateau in Washington, and the Great Plains; MCL exceedances in surface water were more common in the non-mountainous west and the southwest (Pennino and others, 2020). Shallow groundwater beneath agricultural areas poses the greatest risk, with over 20 percent of the wells in this environment exceeding the MCL in a nationwide survey (Burow and others, 2010). The human health effects may be more widespread than indicated by MCL exceedance frequency, as some epidemiological studies have indicated elevated risk of cancers and birth defects with ingestion of nitrate at concentrations below the MCL (Schullehner and others, 2018; Ward and others, 2018; Temkin and others, 2019; Mathewson and others, 2020).

Excess N has also resulted in adverse effects to ecosystems and various beneficial uses of surface water (streams, lakes, estuaries), with more than 40 percent of streams and rivers in the United States in poor condition with respect to nitrogen concentration (EPA, 2016). High total N concentrations are predicted for streams in many agricultural areas in the United States (Bellmore and others, 2018; Shen and others, 2020) and have been linked to many adverse effects, such as hypoxia, harmful and nuisance algal blooms, and species shifts leading to biodiversity loss (Davidson and others, 2011).

Although N concentrations in streams commonly are correlated with N applications to the land surface (Bellmore and others, 2018), such correlations are complicated by highly variable pathways, travel times, and transformations of N during transport from the land surface to streams (fig. E1).

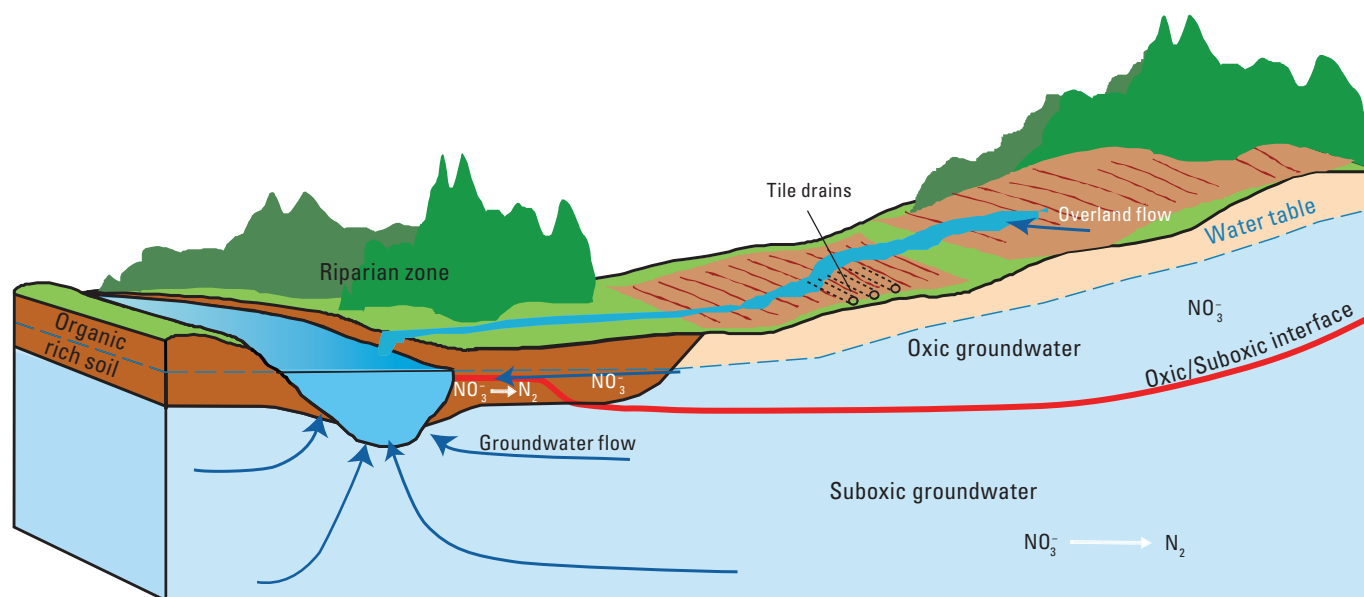


Figure E1. Block diagram showing nitrate (NO₃⁻) transport pathways from the land surface to groundwater and streams and areas of denitrification to nitrogen (N₂). Modified from Wherry and others (2021).

For example, agricultural nitrate can be delivered to streams rapidly and efficiently through surface runoff and tile drains (Tomer and others, 2010), but more slowly and commonly less efficiently (more attenuation) through deeper groundwater flow paths (Sanford and Pope, 2013). Nitrate can be attenuated further after being discharged into streams, rivers, lakes, wetlands, and estuaries (Seitzinger and others, 2006). The combined results of these processes cause much variability in the timing and magnitude of excess nitrate delivery to water supplies and N-sensitive ecosystems.

Other issues related to N transport and transformations include elevated groundwater concentrations of ammonium from landfills, wastewater disposal, and natural production in aquifers (Manning and Hutcheon, 2004; Cozzarelli and others, 2011). Emissions of gaseous forms of N to the atmosphere from soils, wetlands, and surface waters also can be problematic; for example, ammonia gas can be a source of excess N in atmospheric deposition (Tian and others, 2020), and nitrous oxide is a potent greenhouse gas (Pardo and others, 2011; Xu and others, 2019).

Status of Knowledge and Capabilities

Limitations on the beneficial uses of water due to high nitrate concentrations are commonly the result of human activities, especially those associated with agriculture and wastewater disposal (Pennino and others, 2020). Numerous studies have documented that nitrate concentrations in groundwater and streams typically are higher in agricultural areas than in urban or undeveloped settings (Burow and others, 2010; Dubrovsky and others, 2010). Conversely, nitrate concentrations in groundwater and streams in undeveloped settings typically are low and do not

exceed MCLs. Anthropogenic N inputs that can lead to nitrate contamination include fertilizer applications, animal waste infiltration (manure spreading, lagoons), wastewater disposal (including septic systems), enhanced biologic N fixation, and atmospheric deposition (van der Schans and others, 2009; Bellmore and others, 2018). While anthropogenic sources of N have increased dramatically since industrialization (Galloway and others, 2004), natural sources of nitrate also can affect water quality in some areas, especially in arid regions (Walvoord and others, 2003; Jackson and others, 2015; Linhoff and Lunzer, 2021). For example, nitrate concentrations in groundwater may be elevated where natural recharge rates are low and where long-term nitrate accumulations in soils are leached by flooding, irrigation, or artificial recharge. In addition, disturbance and drainage of organic-rich soils can cause enhanced N mineralization and oxidation to nitrate.

Nitrate is highly soluble and mobile in water, but it also can be highly reactive, depending on local conditions. Nitrate is produced biogeochemically by oxidation of reduced N in soils and other oxic environments, abiotically by commercial processes, and by photochemical reactions in the atmosphere. Nitrate is consumed by biologic uptake and microbial reduction to other N species. Denitrification has been suggested as a dominant process causing the loss of nitrate in groundwater (Böhlke and Denver, 1995; Tesoriero and others, 2000; Böhlke, 2002; Seitzinger and others, 2006; Green and others, 2008). Denitrification is inhibited by dissolved oxygen (O₂). As a result, high nitrate concentrations typically are limited to oxic portions of aquifers, and indicators of groundwater redox conditions are often good predictors of denitrification extent (Hinkle and Tesoriero, 2014). While denitrification has long been considered an important process for removing nitrate from groundwater, increasing attention has been given to other pathways such as assimilatory nitrate reduction to ammonium (ANRA), dissimilatory nitrate reduction to ammonium

(DNRA), and anaerobic ammonium oxidation (Henson and others, 2017). Recent studies suggest anaerobic ammonium oxidation (anammox) rates may rival or exceed denitrification in areas where fixed N persists and dissolved O_2 is depleted, such as wetlands and groundwater affected by wastewater (Smith and others, 2015; Li and others, 2021). Other forms of N include organic N compounds, ammonium and (or) ammonia, nitrite, nitrous oxide, and N_2 gas, all of which can be related to sources or sinks for nitrate and may also cause water-quality constraints (for example, ammonia toxicity, nitrous oxide as a greenhouse gas).

Although the major sources of excess N and processes affecting mobility are generally understood, the spatial distribution of elevated N concentrations, the processes that affect its fate and transport, and the timing of water-quality changes in response to changing inputs remain uncertain. Groundwater residence times are highly variable and range from less than a year to many thousands of years (Edmunds and others, 2002), and must be considered in order to accurately predict changes in water quality that result from changes in land use practices (Meals and others, 2010). Spatial and temporal variations in N sources and mobility must be understood and quantified at various scales to support accurate modeling and optimum management strategies. For example, some effects of timing are illustrated in the many studies indicating stable or increasing nitrate concentrations in water-supply wells and streams, despite decreasing N loading to the land surface (Sprague and others, 2011; Eberts and others, 2012; Sanford and Pope, 2013; Van Meter and Basu, 2015, 2017).

Gap Analysis and Approaches

Predictions of N effects on beneficial uses are limited by an inadequate quantitative understanding of N sources, pathways, and timing of N delivery from the landscape to wells and surface waters, and the distribution and effects of N transformations throughout the water cycle. Here, we identify three conceptual gaps (table E1) that represent areas where further scientific understanding and technical ability are needed to monitor and predict water quality related to the N cycle:

1. Nitrogen source identification and tracking,
2. Nitrogen transport pathways and transit times to streams and wells, and
3. Distribution and controls of the natural attenuation of nitrate.

Gap 1. Nitrogen Source Identification and Tracking

Knowledge Gaps

Although the major sources of excess N are generally understood, their distributions and relative effects on water quality locally remain uncertain. Watershed N management is increasingly being optimized by targeting specific areas for implementation of best management practices, which requires

improved spatial and temporal resolution of different source contributions. Evaluating the effectiveness of best management practices also requires predictions of the timing and reactivity of N during transport; these issues are addressed in knowledge gaps 2 and 3. Nitrate concentrations and fluxes in groundwater and surface water depend on N source strengths, aquifer recharge rates, discharge rates, and streamflows on multiple time scales. Improved quantitative understanding of N sources is needed for modeling and mitigation. For example, understanding changes in nitrate sources with changing streamflow may be requisite for managing nonpoint-source N pollution in an era of changing climate (Kaushal and others, 2011). Although temporally intensive monitoring programs provide quantitative information about watershed N yields and trends at selected stream sites, more spatially detailed data are needed to identify local source areas for high-resolution watershed modeling and for locating spatially targeted best management practices. One opportunity to improve our understanding is by relating spatially detailed data with landscape variables describing N sources using machine learning.

Isotopic data commonly are used to assess sources and processes affecting the distributions of nutrients and other contaminants in groundwater and surface water (Hinkle and others, 2007; Kaushal and others, 2011; Nikolenko and others, 2018; Matiatos and others, 2021). While the isotopic composition of N and O in nitrate can be related to its sources and sinks throughout the water cycle, there are important uncertainties in some of the widely held assumptions about how the isotopic data should be interpreted. For example, there is considerable uncertainty in the isotopic fractionation factors for major nitrate transformations, and temporal variation in the isotopic composition of nitrate may confound source identification (Loo and others, 2017; Boshers and others, 2019; Asamoto and others, 2021; Yu and others, 2021). Similar issues apply to other N species such as ammonium/ammonia, nitrous oxide, organic N, and N_2 gas, which must be included with nitrate in models of the physical and biogeochemical cycling of N.

Approaches to Fill Knowledge Gaps

Nitrate Isotopes—Metadata Analysis

A systematic national-scale compilation and evaluation of nitrate isotopic data along with ancillary data from multiple sources could provide new insights and guidance for incorporating isotope data into integrated water availability assessments and watershed water-quality modeling at local, regional, and national scales. One approach would be to compare existing nitrate isotopic data with predictions of nitrate concentrations and controlling factors from machine learning models (for example, Ransom and others, 2021) or with other selected sets of landscape variables. Metadata analyses could include readily available USGS datasets, external datasets, and targeted compilations of results from published local studies. Inclusion of data from selected local studies could help expand the scope of variation in environmental conditions (climate, geology, land use, and so forth) that would be targeted as explanatory variables.

Table E1. Summary of nitrogen gap analysis for understanding water-quality processes affecting water availability for beneficial uses in the United States.

[N, nitrogen; LPM, lumped parameter model]

Topic	Knowledge Gap	Importance	Proposed Approaches
Nitrogen source identification and tracking	Distribution and relative magnitude of various N sources are not known with sufficient spatial and temporal resolution.	Critical for the assessment, monitoring, and development of nutrient management strategies.	Improve analytical techniques and interpretive models for stable isotopes of nitrate and related constituents. Improve spatial resolution of nitrate data in small streams. Build new statistical models relating concentrations of nitrate and other constituents with sources and other landscape factors.
Nitrogen transport pathways and transit times to wells and surface waters	Transit times of nitrate delivery from the land surface to wells and surface waters are often not known or poorly constrained.	Accurate transit time characterizations have many uses, including predicting and assessing outcomes of management practices, developing nutrient budgets and trends, and estimating degradation rates.	Initiate basin-scale monitoring of tritium in surface water. Develop tritium in recharge and precipitation records. Create and maintain national-scale age-tracer synthesis dataset. Use more tracers with unique age ranges. Identify novel tracers. Incorporate multiple tracers in LPM and distributed parameter models.
Distribution and controls of natural attenuation of nitrate	Nitrate reduction processes and rates are highly variable and difficult to predict.	Critical for accurate prediction of groundwater vulnerability and vulnerability of streams to groundwater sources of N.	Discern reaction processes and rates using field studies, with a focus on surface-water and groundwater interfaces. Increase coordination of research with specific stakeholder actions. Perform large-scale machine-learning studies to delineate zones where nitrate transformations are expected.

Maps, plots, statistics, and machine learning methods (for example, boosted regression, random forest) could be used to relate nitrate isotope data to information about sample chemistry and environmental setting, such as climate, land use, geology, major ions, redox, and the isotopic composition of water. Machine learning modeling results, including variable importance measures and partial dependence plots would be used to identify key sources and transformations affecting nitrate isotope variations. In parallel, selected sample sets representing especially well-characterized, and widely varying, environmental conditions and (or) isotopic compositions could be used to answer specific questions and to assist with machine learning training and refinement.

Stable Isotopes—Improved Analytical Approaches

Past improvements in nitrate isotopic analytical techniques have increased the number of isotope ratios that can be evaluated ($\delta^{15}\text{N}$, followed by $\delta^{18}\text{O}$, followed by $\delta^{17}\text{O}$), decreased the necessary sample sizes (initially micromoles [μmol], now nanomoles [nmol]), and in some cases increased efficiency of sample preparation and analysis. Nonetheless, not all of these parameters are analyzed routinely in USGS programs, and the USGS cost per analysis for nitrate limits the accessibility of such data at regional and national scales. Additional analytical chemistry research to improve isotopic analytical methods (for example, incorporating laser spectroscopic methods or direct measurement of intact molecular species) could potentially reduce costs and turn-around times, while also providing more diverse kinds of isotopic information (Wassenaar and others, 2018; Hilkert

and others, 2021). Co-located isotopic analyses of other redox-sensitive compounds (for example, sulfide, sulfate, organic and inorganic carbon [C], ammonium) could be applied more routinely in studies designed to improve understanding of redox reactions and geologic controls on the distribution of nitrate. Development of such techniques could contribute to more informed applications of isotopic data in N monitoring, assessment, and modeling in aquifers and watersheds. In selected situations, new methods could be applied to archived samples from previous studies, or simultaneously to new samples and to archived samples to document trends that might be related to changing natural or anthropogenic factors. Preservation of sample archives could be a priority for these and many other potentially important applications.

Nitrate Intensive Spatial Surveys

Watershed N model calibrations commonly rely heavily on intensive monitoring data from selected stream sites. Such data provide defensible quantitative values of streamflow and constituent fluxes over time, useful for regional mass balance and long-term trend analyses. However, improvements in understanding and management likely will require more spatially distributed stream monitoring data to capture the effects of variations in land use, geology, and hydrology within a watershed. Because it is expensive to install quantitative monitoring sites at fine spatial resolution, there is a need to expand the acquisition of fine-scale distributed spatial data within stream networks during representative flow conditions (that is, synoptic sampling).

Simultaneously, watershed modeling approaches should be developed for relating these two data dimensions to each other (statistically or functionally), to produce higher resolution estimated datasets over both space and time. In addition, it may be possible to increase spatial resolution of groundwater data for nitrate and related constituents by increased assimilation of existing data, or new sampling and analyses, from domestic wells and other water-supply wells. Such larger estimated spatial-temporal datasets for nitrate, other constituents, and other relevant factors affecting nitrate sources, fate and transport could potentially provide more robust objectives for higher-resolution watershed models of N sources, transformations, and fluxes.

Approaches described above could be implemented selectively at various scales within Integrated Water Science (IWS) basins. For example, sampling could begin soon for isotopic analyses of water, nitrate, and possibly other constituents, in the Illinois River Basin, where complex spatial and temporal patterns of nitrate discharge are related to multiple sources and variable reactivity (Böhlke and others, 2009; Lin and others, 2019). Sampling could be targeted to maximize the value of the data for distinguishing urban, agricultural, and atmospheric nitrate sources, and to resolve groundwater and surface water nitrate attenuation patterns, all of which vary at inter-annual, seasonal, and event-related time scales. Some types of samples (for example, for stable isotopic analyses of water and nitrate) can be preserved and archived for later analysis. Isotopic analyses of archived samples can be done selectively, to maximize cost-effectiveness.

To improve understanding of watershed heterogeneity (to complement temporal records and monitoring stations), fine-scale spatial (synoptic) sampling and analyses could be employed in selected small watersheds within the Illinois River Basin. Detailed synoptic sampling networks should overlap with selected continuous monitoring sites and focus on representative small subwatersheds (for example, USGS watershed hydrologic unit codes HUC10 or HUC12) that are likely to exhibit distinctive patterns of flow and nutrient concentrations related to local land use and other conditions (for example, agricultural versus urban, tile-drained versus naturally well-drained aquifers). Data from small subwatersheds could reveal the diversity of system responses that coalesce into the mixed source and transport signals at larger stream monitoring sites.

Gap 2. Nitrogen Transport Pathways and Transit Times to Streams and Wells

Knowledge Gaps

There is persistent uncertainty in defining the travel times of the various flow paths that deliver nitrate to wells and surface waters (streams, lakes, coastal waters). This has resulted in poor estimates of nitrate concentrations in wells and streams from event to decadal time scales. For example, the age distribution of groundwater discharging to streams is poorly understood and may cause unexpected mismatches between changes in N management on the land surface and changes in N concentrations in streams

(Böhlke, 2002; Sprague and others, 2011; Van Meter and Basu, 2017; Basu and others 2022). This gap in understanding has limited the ability to predict changes in nitrate concentrations in streams that result from changes made to N management practices. The same gap also limits predictions of nitrate concentration trends in water-supply wells, which depend on groundwater age distributions within aquifers, the positions of the wells within the aquifers, and the history of nitrate concentrations in recharge (Eberts and others, 2012; Eberts and others, 2013). Nitrate trends in wells and streams are affected further by the distribution of nitrate reduction along groundwater and surface-water flow paths, as discussed in the section knowledge gap 3, “Distribution and Controls of Natural Attenuation of Nitrate” of this chapter.

Hydrograph separation and watershed models such as SPARROW (SPATIally Referenced Regression On Watershed attribute, <https://www.usgs.gov/mission-areas/water-resources/science/everything-you-need-know-about-sparrow>) have estimated the pathways and sources of N inputs to streams (Alexander and others, 2008; Miller and others, 2017; Husic and others, 2019). Increases in the amount of high-frequency nutrient monitoring data have expanded the use of these techniques. Estimating lag times between when nutrients are applied to the land surface and when nutrient effects are fully observed in streams has been more challenging and addressed with several modeling approaches (Vero and others, 2018). A seasonally dynamic version of SPARROW has recently been developed that includes time-varying storage effects (Schmadel and others, 2021).

Groundwater dating with chemical and isotopic environmental tracers can provide important information about aquifer recharge and sustainability, and the progress of contaminants in the subsurface; however, improvements are needed, especially for applications to groundwater discharge to wells and surface water bodies such as streams, lakes, and estuaries. Because of mixing from dispersion in the aquifer or from pumping into long screened wells, samples from wells contain mixtures of groundwater with many different ages. Age mixtures may be especially complex in surface waters receiving groundwater discharge because groundwater, soil water, and runoff can contribute varying proportions to the total discharge, each with its own mixed age distribution, and those mixtures can change on various time scales in response to changing hydrologic conditions in the watershed. Tracer measurements in surface waters will reflect those complex mixtures and, in addition, some tracers will be affected by gas-exchange with the atmosphere.

Vadose zone transit times are another major gap, as most groundwater age tracers only account for travel time since a water sample has been isolated from the atmosphere (that is, time of recharge to the aquifer). In fact, vadose zone storage can be a substantial source of nitrate globally (Ascott and others, 2017), with travel times through the vadose zone comprising a significant portion of the overall travel time in some cases (Green and others, 2018). Vadose zone time lags may be decades or longer (McMahon and others, 2006; Fenton and others, 2011; Wang and others, 2012; Wang and others, 2013), requiring their consideration for accurate prediction and assessment of nutrient best management practices (Ascott and others, 2021). Comprehensive evaluation of N storage and release trends also should include

masses and residence times of soil organic N, which contribute to nitrate runoff and infiltration over a range of time scales (Sebilo and others, 2013; Van Meter and others, 2016).

The majority of the work done to develop constituent transit times with tracers has focused on relatively local landscape and aquifer settings, and there are limited resources for integrating tracer data on a larger scale (Michel and others, 2018; Green and others, 2021). Compilations of tracer concentrations and associated site and project metadata, interpretive values, and citations are not readily available (either for the United States or on a global scale). As a result, synoptic assessments must start from scratch and often must make assumptions about the validity of input data, hydrogeologic setting, and other parameters. Approaches for interpreting tracer data on a synoptic scale are poorly developed and there is need for further research and data for developing multi-aquifer, regional and national scale investigations (McMahon and others, 2011; Visser and others, 2016; Lindsey and others, 2019; Zell and Sanford, 2020). Additionally, there are few examples of national groundwater transport and chemistry models that use tracer data, and considerable further development is needed to obtain national-scale modeling ability that captures the tracer results at a given site.

Approaches to Fill Knowledge Gaps

The time that water spends traveling in the subsurface is fundamental to understanding a watershed's response to changes at the land surface (for example, anthropogenic inputs). The distribution of transit times in a watershed describes how water and solutes are retained and released, which in turn affects biogeochemical cycling and contaminant persistence (McGuire and McDonnell, 2006; Sprenger and others, 2019). Several approaches are suggested that will improve assessments of the timing and delivery of nitrate to wells and streams.

Multi-Tracer Studies in Integrated Water Science Basins

The IWS basins provide excellent opportunities to address this important issue. Specifically, supplementing the existing sampling strategy to include environmental tracers at multiple scales could advance our understanding of transit times and provide valuable calibration targets for models. For example, transit time distributions in groundwater discharge could be compared to time lags estimated by seasonally dynamic SPARROW watershed models and may help quantify travel times of pathways defined by hydrograph separation models. Hydrograph separation models often define a slow flow component but are typically not able to quantify the travel time for this component (Miller and others, 2017). Transit time distributions may be useful for evaluating delayed responses to best management practices designed to reduce N loads to streams, as well as for identifying seasonal and climate related variations in nitrate sources and loads. Proposed analytes would include tritium (^3H), stable isotopes of water, dissolved gases, and various other chemical constituents. Tracer measurements in surface waters will reflect the complex mixtures of the many flow paths that deliver

water and solutes to a stream, as well as potential modifications within a stream corridor. In general, such complexities require simultaneous measurements of multiple tracers with contrasting input signals, combined with hydrogeologic insight and mathematical formulations to evaluate the age distributions.

Dissolved gases, tritium, stable isotopes of water and other chemical constituents have been used to determine groundwater transit times through catchments from recharge to discharge. For example, combined analyses of major dissolved gases and environmental gas tracers in streams can be used to estimate mean groundwater transit times through catchments during base flow conditions where streams undergo large diurnal temperature shifts and where relative rates of groundwater discharge and air-water exchange are favorable (Sanford and others, 2015). The recent stabilization of the tritium deposition rate presents the opportunity to establish the mean age of base flow in streams with a small number of samples (Morgenstern and others, 2010; Stewart and Morgenstern, 2016). For example, collection of tritium samples at intervals of 2 to 3 years may allow for the effective discrimination between different possible age solutions (Gallart and others, 2016). Recently, it has been demonstrated that tritium and stable hydrogen (H) and O isotopes of stream water can be used to constrain varying groundwater residence times contributing to streamflow over a range of flow conditions (Cartwright and others, 2020; Rodriguez and others, 2021). Concentrations of major ions and other constituents may also provide important information on transit times of stream base flow where steady rates of chemical weathering of aquifer material occur. Correlations between sodium (Na), calcium (Ca) and silica (SiO_2) and groundwater age have been used to estimate the mean residence time of base flow (Burns and others, 2003) and groundwater (Tesoriero and others, 2005). Fluoride (F^-) and chloride (Cl^-) were among the most important variables for predicting groundwater age in a recent study (Green and others, 2021) and may also hold promise for estimating residence times of groundwater contributing to streams. Vadose zone transit times should also be assessed using process-based unsaturated zone modeling techniques with suitable tracer data for calibration; these results can be combined with groundwater transport modeling results to estimate overall lag times (Wang and others, 2013; Green and others, 2018).

Geophysical approaches can add additional information to transit time assessments by providing details of aquifer structure, density, and locations of discharge into surface water (Lane and others, 2016). These approaches are powerful when combined with age-tracer related information for relating the spatial occurrence of nitrate discharge areas with mean transit time and (or) transit time distributions of the discharge. Data and interpretive models for multiple tracers generally will be needed to resolve age distributions in mixtures of younger and older water, which may or may not have simple or smooth functions (Green and others, 2010; Jurgens and others, 2012; Green and others, 2014; Green and others, 2016; Sprenger and others, 2019). This is particularly true in heterogeneous aquifers and many groundwater discharge areas, especially where seasonal and event-related

variations in flow and nitrate concentration need to be addressed (Rinaldo and others, 2015).

Development and Increased Use of Additional Tracers

Transit times of nitrate in groundwater are often determined using groundwater age tracers. Atmospheric tracers capable of determining the age of young water (less than 100 years), such as chlorofluorocarbons (CFCs), tritium-helium (^3H -He) and sulfur hexafluoride (SF_6), have been especially useful for estimating transit times, as some of the major changes in anthropogenic N loading have overlapped the period spanned by the atmospheric histories of these tracers (Böhlke and Denver, 1995; Böhlke, 2002; Puckett and others, 2011). This approach remains powerful, and there are likely further opportunities to refine and extend groundwater transit time determinations as additional age tracers become available. Recent advances in noble gas radioisotope sampling and detection methods have made sampling for krypton-85 (^{85}Kr), argon-39 (^{39}Ar), and ^{81}Kr more accessible (Aeschbach-Hertig, 2014; Lu and others, 2014). These tracers can resolve ages ranging from modern to millions of years. Argon-39 can be used for dating water between 70 and 1,000 yrs old, while both ^{39}Ar and ^{81}Kr can help refine dates from carbon-14 (^{14}C) dating when carbonate systems deviate from equilibrium (Seltzer and others, 2021). Krypton-85 is valuable for resolving decade-scale transit times for groundwater with reducing conditions, which is crucial as these conditions can transform CFC tracers, rendering them useless (Gröning and others, 2006). There are other modern tracer candidates such as perfluorocarbons (CF_4 , C_2F_6 , C_4F_8 , and others), minor CFCs (CFC-13, CFC-114, CFC-115, and others) and halons (H-1211, H-1301) that may also be used to determine nitrate transit times in groundwater, providing more accuracy and mixing information than the current suite of age tracers (Beyer and others, 2014; Haase and Busenberg, 2014; Bartyzel and Rozanski, 2016; Beyer and others, 2017).

Some new possibilities may exist to date groundwater by measuring abundances of artificial chemicals or chemical structures that have been manufactured and applied on the landscape over time. For example, a change in the chiral form of a manufactured pesticide is being investigated as an indicator of the age distribution of groundwater discharge to streams in agricultural areas with high nitrate loads (Rice and others, 2016). In principle, such tracers could be combined with other tracers with different input histories to resolve various types of age-distribution models in groundwater and surface water (Jurgens and others, 2012; Rinaldo and others, 2015).

Improving the Understanding of Tritium Deposition and Recharge

Refinements in our understanding of tritium deposition rates and recharge mechanisms could result in increased accuracy of all tritium-based approaches. Currently the best understanding of tritium deposition is a gridded approach based on data collected mostly in the 1970s and 1980s. The current model of the tritium input function (Michel and others, 2018) could be refined by

adding recently collected data and by establishing a modern precipitation monitoring program. Notably, seasonal variability of tritium in precipitation, recharge, and discharge is not constrained with high precision, and contributions of non-atmospheric tritium to groundwater discharge (for example, from landfills and other sources) are not well documented. Extrapolation methods used to establish the tritium input function lose accuracy if seasonal and temporal trends in tritium are not captured; this loss in accuracy then propagates to other empirical and interpreted values such as recharge rates and transit times (Li and Si, 2008). Additionally, by studying tritium deposition and recharge, the fundamental atmospheric processes that govern tritium creation might be better understood, with the ultimate goal that they could be modeled directly (Tadros and others, 2014; Palcsu and others, 2018).

Gap 3. Distribution and Controls of Natural Attenuation of Nitrate

Knowledge Gaps

The rates and dominant pathways of nitrate reduction have been determined at the field scale but are rarely understood at regional or larger scales. Denitrification is a well-studied process but its occurrence in groundwater is dependent on redox gradients that are not well defined spatially. Redox gradients in groundwater can have a significant effect on both the fate and lag times of nitrate transported from the landscape to groundwater and streams (Tesoriero and others, 2021). While recent advances using machine learning and statistical techniques have improved predictions of redox conditions in aquifers (Tesoriero and others, 2015, 2017; Close and others, 2016; Knoll and others, 2020), regional and larger scale redox assessments have often been compromised by limited information on geology, mineralogy, and geochemistry over a range of depths and spatial scales in the subsurface (Koch and others, 2019). In addition, the distribution and relative importance of other nitrate reduction processes (for example, anammox, DNRA, ANRA) that affect watershed N mass balance modeling are not known.

Nitrate reduction rates and pathways near groundwater discharge sites are likely to be spatially and temporally more complex than those in upgradient regions within aquifers, requiring more detailed parameterizations of near-stream hydrogeology and biogeochemistry. For example, agricultural or septic-system nitrate transmitted through surficial aquifers in oxic groundwater may encounter reducing conditions locally in riparian lowlands near streams (Hill, 2018), or complex and variable flow and mixing relations with reduced saline groundwater near coastal shorelines (Santos and others, 2021). Further reactions occur after groundwater discharges into surface water, where nitrate production and loss result from biologic activity in the water column, benthos, or hyporheic zone. As a result, net nitrate removal efficiencies and discharge fluxes between groundwater and surface

water interfaces have large uncertainties. Resolving these complexities and scaling their results for watershed models are persistent problems requiring multiple approaches.

Approaches to Fill Knowledge Gaps

Multi-Disciplinary Studies in Integrated Water Science Basins

Multi-disciplinary targeted field studies could determine nitrate reduction rates and pathways and provide a comprehensive evaluation of sources, transport, and transformation. Focus should be placed on the spatial and temporal variability and factors controlling nitrate reduction rates and pathways in groundwater discharge areas and other areas where variable fluxes and sharp redox gradients are expected. Comprehensive investigations should include detailed characterizations of the hydrogeology and biogeochemistry of watersheds, calling on the multi-tracer transit time approaches discussed above and (or) coordinating with larger collocated tracer studies as appropriate. Analyses could include groundwater dating, isotopes, microbial communities and activities, geophysics, continuous sensing of physical and chemical parameters, and intensive monitoring of harmful algal blooms (HABs). Such studies would be particularly useful for documenting effects of deliberate human actions such as land use change, best management practices, drainage, irrigation, fertigation, and water re-use. Suitable study sites could be selected based on nitrate risk assessments for both groundwater (for example, machine learning models) and surface water (for example, SPARROW) developed using existing data. Data from synoptic surveys of N loads using mobile sensors could also support site selection. Studies to document changes related to specific human activities would need to be coordinated with stakeholders and other Federal, State, and local agencies, and they would need to be relatively long-term (pre- and post-change), iterative, and with modeling built in. Ideally, study sites and approaches could be selected to maximize the scientific return from existing stakeholder investments in a basin.

Predicting Redox Conditions and Nitrate Inputs to Streams Using Machine Learning

Machine learning methods could be used to relate explanatory variables to measured concentrations of redox-sensitive constituents and predict redox conditions across the Nation. Multiple redox-sensitive constituents (for example, dissolved O₂, iron [Fe], manganese [Mn]) would be modeled. Explanatory variables could include those describing hydrology, soil chemistry, geology, and land use. Developing a three-dimensional (3-D) framework of subsurface geology, reactivity, and geochemistry from existing data could improve predictions of redox conditions in groundwater and identify data gaps that are limiting the accuracy of these predictions. For example, it will be important to understand the distribution and reactivity of electron donor phases that promote O₂ and nitrate reduction. Model predictions could be generated from regional to national scales. Temporal changes in redox interfaces could be evaluated where redox-sensitive species data are available over multidecadal time

periods and in other areas using vertical flux modeling (Liao and others, 2012). Machine learning predictions of redox conditions in groundwater could be used to delineate nitrate reduction zones for process-based models or used as an explanatory variable for statistical or machine learning models that predict base flow nitrate concentrations in streams (Wherry and others, 2021).

Expected Outcomes

A meta-analysis of nitrate isotope data could provide a much-needed framework for identifying nitrate sources and transformation both for WMA studies as well as those in the broader scientific and water resource communities. A large data set of nitrate isotope and ancillary data could provide an unprecedented opportunity to characterize factors that lead to changes in nitrate isotope ratios. Improved techniques and wider application for isotopic analyses of other N species such as ammonium and N gas, as well as other related redox-sensitive constituents, also could permit more integrated studies of nitrogen transport and transformations.

Improved multiple tracer-based transit time information for vadose zones and saturated zones could enable better predictions of water-quality conditions and trends in groundwater and surface water, particularly in relation to recent changes in nutrient management practices. Much of the current understanding of nutrient loading to surface water is based on statistical regression of flow-concentration relationships and does not readily yield an understanding of the nutrient reservoirs. Tracer-based transit times could provide information that is crucial for determining functional relationships between climate conditions, nutrient input, hydrology, and water quality. Residence times can be used to develop and validate models of nutrient transport, transformation, and loss, resulting in actionable information that indicates where large reservoirs and long flow paths of nutrients exist and provides insight into how changing nutrient application on the landscape will propagate in hydrologic systems.

Multidisciplinary studies in intensively monitored watersheds could produce needed information for evaluating nutrient management strategies, particularly when natural attenuation assessments are coupled with the transit time work. Synoptic studies of N transformations at IWS basins could provide detailed information on how N pathways to groundwater and streams vary as a function of hydrology (including stream order), geology and land use. This information could improve both statistical and process-based modeling predictions of N loading. Identifying nitrate transit times requires identifying the pathways that contain nitrate through an assessment of natural attenuation and identifying the transit times of these pathways using tracers and (or) modeling. Specifically, identifying reaction rates and transit times could inform modeling efforts in the intensively studied basins by identifying the lag times of nitrate pathways through non-reactive zones. Identifying nitrate reduction zones will aid nutrient management strategies; strategies that route water and solutes through these nitrate reduction zones will yield better results.

To scale these findings up, machine learning models could produce 3-D national- and regional-scale estimates of redox conditions in groundwater. These models could predict the depth below the water table at which a redox interface would be encountered and could provide insight on the temporal migration of these interfaces. These interfaces could delineate where redox transformations would be expected, important input for both process-based and statistical water-quality models. These interfaces will be useful both for predicting groundwater susceptibility to nitrate and nitrate concentrations in base flow.

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