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## Effects of human-induced alteration of groundwater flow on concentrations of naturally-occurring trace elements at water-supply wells

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### ABSTRACT

The effects of human-induced alteration of groundwater flow patterns on concentrations of naturally-occurring trace elements were examined in five hydrologically distinct aquifer systems in the USA. Although naturally occurring, these trace elements can exceed concentrations that are considered harmful to human health. The results show that pumping-induced hydraulic gradient changes and artificial connection of aquifers by well screens can mix chemically distinct groundwater. Chemical reactions between these mixed groundwaters and solid aquifer materials can result in the mobilization of trace elements such as U, As and Ra, with subsequent transport to water-supply wells. For example, in the High Plains aquifer near York, Nebraska, mixing of shallow, oxygenated, lower-pH water from an unconfined aquifer with deeper, confined, anoxic, higher-pH water is facilitated by wells screened across both aquifers. The resulting higher-O<sub>2</sub>, lower-pH mixed groundwater facilitated the mobilization of U from solid aquifer materials, and dissolved U concentrations were observed to increase significantly in nearby supply wells. Similar instances of trace element mobilization due to human-induced mixing of groundwaters were documented in: (1) the Floridan aquifer system near Tampa, Florida (As and U), (2) Paleozoic sedimentary aquifers in eastern Wisconsin (As), (3) the basin-fill aquifer underlying the California Central Valley near Modesto (U), and (4) Coastal Plain aquifers of New Jersey (Ra). Adverse water-quality impacts attributed to human activities are commonly assumed to be related solely to the release of the various anthropogenic contaminants to the environment. The results show that human activities including various land uses, well drilling, and pumping rates and volumes can adversely impact the quality of water in supply wells, when associated with naturally-occurring trace elements in aquifer materials. This occurs by causing subtle but significant changes in geochemistry and associated trace element mobilization as well as enhancing advective transport processes.

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### 1. Introduction

Since the discovery of As in groundwater in Bangladesh, numerous incidences of As-enrichment in groundwater used for drinking have been documented (Smedley, 2003). Recent studies predicting the occurrence of As worldwide suggest that As exceeding human-health benchmarks can be expected over large regions (Amini et al., 2008; Winkel et al., 2008). Still, there are situations (e.g., well-field scale) where mobilization of As or other trace elements is difficult or impossible to anticipate because the complexity of groundwater flow systems and the associated effects of water use are not well understood. Naturally-occurring trace elements can remain sequestered by geochemical conditions that minimize their solubility. If the geochemical balance of the natural system

is altered by activities such as groundwater withdrawal for water supply, these trace elements may be mobilized and the quality of the water supply compromised.

Design and construction of water-supply wells typically focuses on obtaining sufficient yields, often by installing wells across long vertical sections of an aquifer or aquifers, which results in the pumping of water of different recharge ages and chemistry. Unintended increases in solute concentrations and degradation of shallow-water quality often result as water is drawn quickly to depth by steep hydraulic gradients associated with pumping. Geochemical evaluation has been instrumental in describing these problems (Edmunds, 2009). Water-supply wells, because of differences not only in aquifers and associated subsurface processes but also in use and management practices, are not equally vulnerable to degradation of water quality even where trace element sources in the subsurface environment are similar (Eberts et al., 2005).

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The purpose of this paper is to document examples where human-induced flow-system changes have led to unexpected mobilization of naturally-occurring trace elements that, for drinking-water supply, may exceed concentrations of concern for human health. Results from five study sites across the USA provide useful examples of how flow-system changes can mobilize naturally-occurring trace elements and how, in many cases, the geochemical processes leading to these changes can be identified.

### 1.1. Anthropogenic contaminants and enrichments of trace elements in groundwater

Many types of contaminants are found in groundwater throughout the USA, but overall, exceedences of human-health benchmarks (HHBs) are generally rare. HHBs refer collectively to standards for water quality that relate to human health, such as Maximum Contaminant Levels (MCLs) and Lifetime Health Advisories (LHAs). Some contaminant groups are more prone to HHB exceedences than others. Groundwater data collected across the USA by the US Geological Survey (USGS) as part of its National Water Quality Assessment Program (NAWQA) indicate exceedences of HHBs for volatile organic compounds (VOCs) and pesticides in less than 3% of several thousand samples (Gilliom et al., 2006; Zogorski et al., 2006). Up to about 12% of samples, predominantly from agricultural land-use monitoring wells, exceed HHBs for NO<sub>3</sub> (Dubrovsky et al., 2010). However, at least one trace element exceeded its HHB in about 27% of samples (Table 1), and exceedences were consistently high in water from all study areas. This finding suggests that trace elements are more widespread than other contaminant groups in groundwater and that concentrations of trace elements above HHBs may be controlled by factors other than those commonly associated with anthropogenic compounds. Trace elements occurred more frequently than anthropogenic contaminants in national studies of public and private well-water quality (DeSimone, 2009; DeSimone et al., 2009; Focazio et al., 2006), with concentrations of As, U and Pb each exceeding HHBs in more than 1% of samples. Mechanisms of release of trace ele-

ments, from both natural and anthropogenic sources, and ways in which trace elements make their way along the food chain to animals and humans are important factors in understanding the role of the environment in human health (National Academy of Sciences, 2009).

Well vulnerability to naturally-occurring trace elements depends in part on (1) the sources of these compounds near supply wells, (2) the physical properties of the aquifer (susceptibility) and/or the well, and (3) the biogeochemistry of the aquifer system (Focazio et al., 2002; Frind et al., 2006). Determining the contributing area to a well, or the land surface from which aquifer recharge is captured by the well (US Environmental Protection Agency, 1997), is an important part of determining well vulnerability. It is thought that by protecting the land in this area, contaminants captured by the well can be eliminated or reduced. The contributing area is proportional to the amount of water being withdrawn; thus, as pumping increases, the potential to capture contaminants also increases. Protecting the contributing area to a public-supply well (PSW) can reduce anthropogenic contamination, but it may not protect against potential mobilization of trace elements from the aquifer materials through which water flows to the well.

### 1.2. Enrichments of trace elements, pathways, and human factors

A geologic source in the aquifer system is the most fundamental risk factor for the potential mobilization of trace elements. The greater the concentration in the geologic source material, the smaller the overall fraction that needs to be mobilized before groundwater concentrations exceed HHBs. Aqueous concentrations of trace elements may be low for water flowing along original unaltered pathways (i.e., flow paths) within an aquifer. However, for supply wells (and other wells), water intercepted from along natural flow paths may be altered as a result of large changes in aquifer hydraulic gradient. These changes in hydraulic gradients are a function of pumping volume and aquifer hydraulic properties and may influence the quality of water withdrawn from the well. Human perturbation,

**Table 1**  
Percentage of selected US wells sampled for the National Water Quality Assessment program (NAWQA) during 1992–2003 for which one or more trace elements, VOCs, pesticides, or NO<sub>3</sub> exceeded human-health benchmarks, by primary water use and land use. (Bold where exceedences are greater than 10%. Modified from Gilliom et al., 2006; Zogorski et al., 2006; Dubrovsky et al., 2010; and G.C. Delzer, US Geological Survey, pers. comm., 2009. Major aquifers are regionally extensive groundwater supplies and include non-targeted land uses; but contributing areas to some wells may be dominated by one or more land-use types such as “urban” or “urban and mixed.”; –, no data).

Type of groundwater study	Public-supply wells		Domestic-supply wells		Observation wells	
	Number sampled	Percentage of samples exceeding benchmark	Number sampled	Percentage of samples exceeding benchmark	Number sampled	Percentage of samples exceeding benchmark
<i>Trace elements (including uranium but not other radionuclides)</i>						
Agricultural land use	–	–	402	9.5	904	<b>26.3</b>
Urban land use	9	<b>33.3</b>	17	<b>29.4</b>	740	<b>28.2</b>
Major aquifer	372	<b>12.1</b>	1896	<b>13.3</b>	188	<b>26.1</b>
Overall	382	<b>12.6</b>	2315	<b>12.7</b>	1832	<b>27.1</b>
<i>VOCs</i>						
Agricultural land use	–	–	69	<b>17.4</b>	199	2.5
Urban land use	–	–	–	–	750	1.5
Major aquifer	338	2.1	1545	0.32	111	0
Overall	340	2.1	1606	1.1	1060	1.5
<i>Pesticides</i>						
Agricultural land use	–	–	406	1.2	1005	1.1
Urban land use	9	<b>11</b>	17	<b>18</b>	835	4.4
Major aquifer	354	2	1933	0.5	453	2
Overall	364	2.2	2356	0.76	2293	2.5
<i>Nitrate</i>						
Agricultural land use	–	–	406	<b>22</b>	938	<b>20</b>
Urban land use	9	0	17	6	781	3
Major aquifer	374	2	1965	4	183	8
Overall	384	3	2388	7	1902	<b>12</b>

therefore, is capable of driving the mobilization of naturally-occurring trace elements.

Human perturbation induces alternate groundwater flow paths at various scales. These alternate or short-circuit pathways may arise from: (1) flow through breached confining layers (such as sinkholes through confined karst aquifer systems); (2) flow along fully penetrating well screens that connect otherwise separate aquifer systems, aquifers, aquifer units, or zones within an aquifer; (3) flow through artificial fracturing of an aquifer to increase yield; and (4) large-volume pumping or variable pumping that can create unnatural groundwater gradients. These factors can act to introduce trace elements directly through movement and mixing of water or indirectly by changing the geochemistry in the aquifer or well bore.

### 1.3. Geochemical processes and enrichments of trace elements

The theoretical effects of aquifer geochemistry on the mobility of trace elements are well understood (Drever, 1988; Hem, 1992). Primary geochemical factors that affect naturally-occurring trace element mobility in groundwater include: (1) pH, (2) the oxidation–reduction (redox) conditions, (3) the presence of ions that form soluble complexes with metals, (4) sorption processes and the effects of ion competition (for sorption sites), (5) evaporative concentration, and (6) mixing and dilution (Drever, 1988; Hem, 1992). Also important are advection, dispersion and diffusion (Drever, 1988).

In practice, however, the behavior of trace elements may be difficult to predict—especially when the naturally occurring system is altered—owing to the complex interplay of multiple controlling factors. Thermodynamic redox potential is an especially important consideration for most trace elements, many of which have multiple valence states with extreme differences in solubility. For example, As, Fe, Mn, and Mo commonly are more soluble under reducing conditions, whereas Cu, Pb, O, Se, U and Zn are often more soluble under oxic conditions. Redox potential can be directly measured in natural waters, but this measurement may be of limited utility

because groundwater is seldom at thermodynamic equilibrium and redox conditions may be controlled by multiple species and many redox couples (Lindberg and Runnells, 1984). Despite this limitation, factors that lead to trace element mobility are possible to evaluate at the supply-well level. Determining the redox condition of groundwater in natural and human-perturbed systems is an important, practical tool for hydrogeologists (Edmunds, 2009; McMahon et al., 2008b, 2009; McMahon and Chapelle, 2008).

In addition, redox conditions in the groundwater are often biologically mediated (McMahon and Chapelle, 2008; Oremland and Stoltz, 2005; Paschke, 2007; Peters and Burkert, 2008; Smedley and Kinniburgh, 2002; Thomas, 2007; Welch et al., 2006; Welch and Stollenwerk, 2003). Changes in redox conditions can occur naturally along a flow path, for example, as organic C is oxidized. Changes in redox conditions also can occur when primary aquifer water is mixed or replaced with geochemically distinct water. Because a small change can have substantial effect on trace element mobility, determining redox conditions and changes in those conditions can be useful in characterizing that mobility.

Small changes in other factors such as groundwater pH, ion exchange, and ion complexation all affect the mobility of trace elements. Changes in these factors may be initiated or enhanced by agricultural inputs and irrigation, which also can substantially change the major-ion composition of the groundwater (Böhlke et al., 2007; Dubrovsky et al., 1993; Fujii and Swain, 1995; Seiler et al., 2003; Szabo et al., 1997). Examples of common trace elements, the processes that affect their mobility and other controlling factors are listed in Table 2. The multiplicity of processes governing the occurrence and mobility of many trace elements implies that multiple modes of change in the geochemical environment may result in unexpected degradation of water quality.

## 2. Methods

Data and findings from previous studies of public and private drinking-water-supply wells in several hydrogeologic settings are

**Table 2**  
Common controlling or mobilizing processes for selected trace elements in ground water.

Trace element	Redox condition	Processes	Other controls	References
Arsenic	Oxic	Adsorption/desorption; sulfide oxidation; ion competition	High pH; high oxygen, high TDS, high sulfate	Robertson (1989), Price and Pichler (2006), and Scanlon et al. (2009)
	Reduced	Reductive dissolution; desorption	High pH	Hinkle and Polette (1999), Welch et al. (2000), Ayotte et al. (2003), Peters and Blum (2003), Welch and Stollenwerk (2003), Thomas (2007)
Chromium	Reduced	Adsorption/desorption/co-precipitation	High pH	Rai et al. (1989)
	Oxic	Adsorption/desorption	High pH	Stollenwerk and Grove (1985)
Molybdenum	Oxic/mixed	Adsorption/desorption	High pH desorption	Warner (2001) and Thomas (2007)
	Oxic/ mixed/ reduced	Carbonate dissolution and complexation; ion competition	High pH; high carbonate	Hodge et al. (1996)
Radium	Oxic	Desorption; competitive exchange	Low-pH; competition from additional H <sup>+</sup> (acidification/nitrification)	Szabo et al. (1997, 2005), and Focazio et al. (2001)
	Reduced (iron reduction)	Adsorption/desorption; reductive dissolution of iron oxides	Lack of sorption sites (iron oxide)	Szabo and Zapecza (1991)
	Oxic to reduced	Ion competition enhanced solubility; minor complexation	High TDS, high sulfate, and high pH	Sturchio et al. (2001)
	Reduced (sulfur reduction)	Sulfate reduction limits; co-precipitation	Sulfide and barium; high sulfate	Gilkeson et al. (1983)
Selenium	Oxic	Desorption; evaporation	High TDS, salinity, and pH	Dubrovsky et al. (1993), Fujii and Swain (1995), Seiler et al. (2003), and Böhlke et al. (2007)
Uranium	Oxic/mixed	Desorption; ion competition; complexation; evaporation; release from oxy-hydroxides; irrigation return flow	Presence of high bicarbonate, high alkalinity, nitrate	Fujii and Swain (1995), Ayotte et al. (2007), Katz et al. (2009), Landon et al. (2008), and Jurgens et al. (2009a)
	Oxic	Carbonate dissolution and complexation	High pH and carbonate	Langmuir (1978), Hodge et al. (1996), Katz et al. (2007), and Landon et al. (2008)

used in this paper to characterize the transport and capture of trace elements. Factors and processes that affect the transport of trace elements are then related to changes in the flow system as a result of human perturbation. The data and methods used in the selected studies are given in reports from each study, and information about the selection of the water-supply well(s), design and installation of the monitoring-well network, collection and analysis of water samples, quality assurance, and aquifer lithologies has been described previously. The supply wells include three PSWs in unconsolidated aquifer systems (California Central Valley, North Atlantic Coastal Plain, Glacial) (Jurgens et al., 2008; Landon et al., 2008; Szabo et al., 1997), one PSW in a carbonate aquifer (Upper Floridan) (Katz et al., 2007, 2009), and one research well designed to operate as a private-supply well in a sandstone aquifer (Gotkowitz et al., 2004; Schreiber et al., 2000, 2003). The study areas discussed are in Modesto, California, York, Nebraska, Tampa, Florida, eastern Wisconsin and New Jersey (Fig. 1).

### 2.1. Data used

For the studies considered, data collection was designed to allow for characterizing redox and reaction chemistry and to identify processes that alter the mobility of trace elements. Data-collection activities included: (1) depth-dependent sampling in the PSWs (integrated samples from various depths under pumping conditions) (Izbicki et al., 1999), (2) sampling of water from various depths in adjacent aquifers, (3) collection of aquifer-material samples, (4) collection of water geochemical data (such as redox indicators and pH), (5) collection of isotope tracer data (to identify sources of water and proportions of mixes), and (6) collection of bulk water samples (well discharge) over time.

In most of the studies, identification of redox conditions in conjunction with depth-dependent sample collection was an integral part of the analysis. The water-chemistry data collected from monitoring and supply wells included basic field measurements (pH, specific conductance, dissolved O<sub>2</sub>, turbidity and temperature), major ions, trace elements, nutrients, VOCs, pesticides, radionuclides, C and S isotopes, various age-dating isotopes, and some trace-element-speciation data.

### 2.2. Data analysis

Determination of the water chemistry and other data included use of standard graphical and non-parametric statistical methods (Helsel, 2005; Helsel and Hirsch, 1992; SAS Institute Inc., 2008). An Excel® program for determining inferred redox state based on commonly measured parameters (dissolved O<sub>2</sub>, NO<sub>3</sub>, Fe, Mn and SO<sub>4</sub>) was used to identify redox conditions in water samples (Jurgens et al., 2009b).

## 3. Human-induced flow-system alterations and trace element mobility

Trace elements occur in all five drinking-water-supply wells sampled and include As, U and Mn, but anthropogenic contaminants are also often present. Comparison of trace element concentrations and anthropogenic contaminants in water samples from these wells, along with other chemical data, information on apparent recharge ages, isotopic signatures, and aquifer-matrix chemistry, enables determination of the probable sources of the trace elements. In addition, possible processes and mechanisms of mobilization may be identified. In each system considered, pumping-induced change in hydraulic gradients moves water from one aquifer unit or flow path to another, resulting in mixing or displacement of water. As a result of this flow-system alteration, new geochemical

conditions develop that are in disequilibrium with aquifer materials.

### 3.1. Scales of pumping-induced movement and mixing

In any aquifer system, movement and mixing of waters can be expected as hydraulic gradients cause water to move along natural flow paths, such as across confining units or along fracture conduits. Human-induced gradients, however, are the inevitable result of the use of aquifers for water supply and can enhance trace element mobility by causing water of one geochemical regime to move into another, changing the ambient equilibrium. Differences in pH and redox of the water that moves into an aquifer unit can rapidly mobilize trace elements from the solid phase as mixing progresses. In some cases, movement of water into an aquifer unit is deliberate, as in aquifer storage and recovery (ASR), although the mobilization of trace elements is not; however, pretreatment of water for ASR can greatly reduce or prevent such mobility (Bell et al., 2009). Additionally, this mixing and mobilization can occur at various scales. The disequilibrium of the geochemical system may occur at the borehole scale (mixing of waters in a well bore) or local scale (movement or mixing of waters near a well) or may extend to the regional scale (large-scale movement of waters into adjacent aquifer units), where many wells are involved. Case studies illustrating effects of disequilibrium at various scales are considered next.

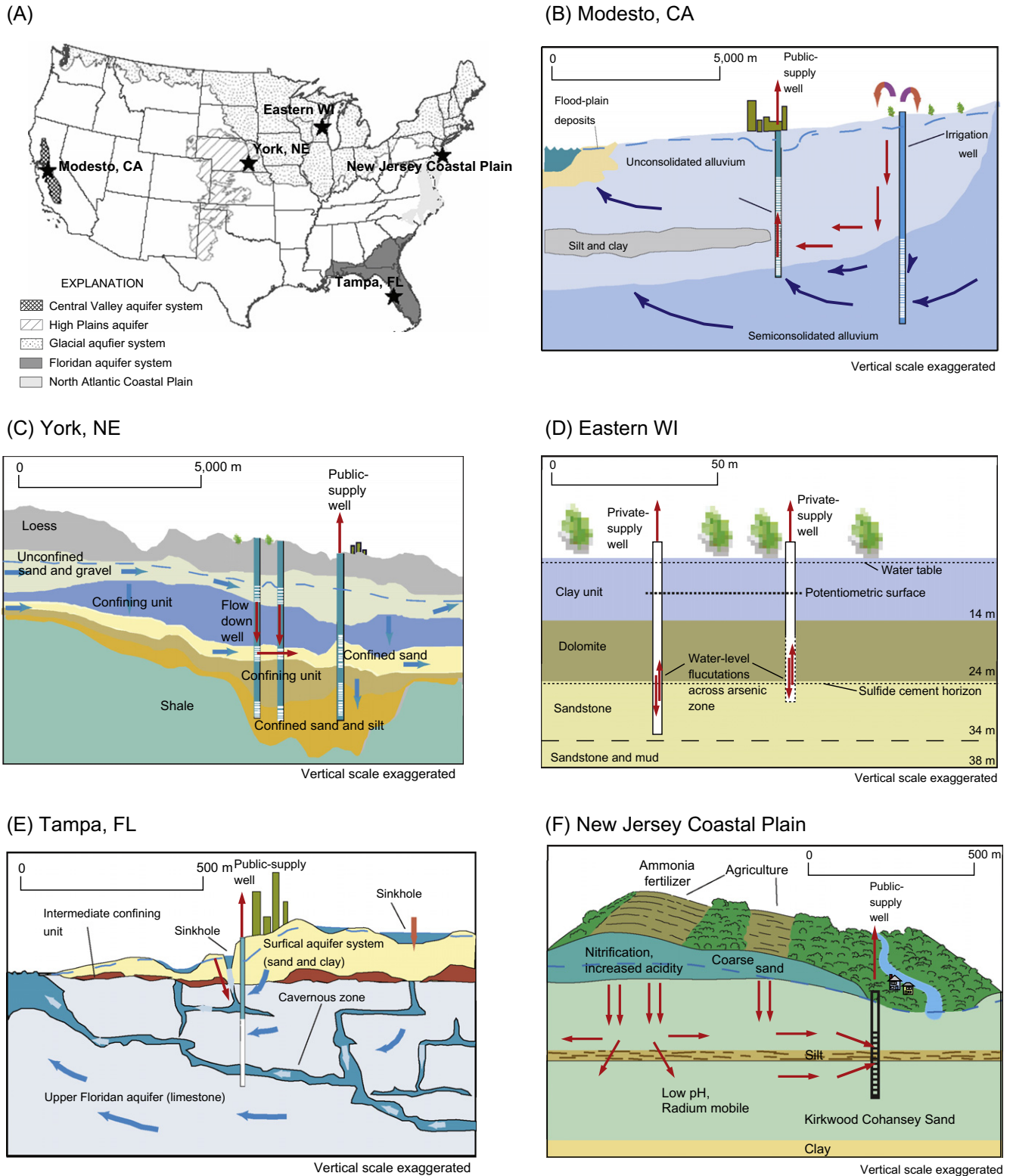
#### 3.1.1. Regional-scale changes

Changes in aquifer chemistry resulting from human activities can be evident at the regional scale (10<sup>0</sup>–10<sup>2</sup> km) as was found for the northern High Plains aquifer system near York, Nebraska. Groundwater flow is from NNW to ESE in this area and predominantly downward from a surficial unconfined aquifer, through a clayey silt confining unit, to an upper confined aquifer (McMahon et al., 2008a). (A second, lower zone of confined sand and silt is present in the area but is not discussed in this paper.) Much of the system near York is underlain by the Cretaceous Carlile Shale (Landon et al., 2008).

The upper-confined-aquifer water is older than the water in the overlying unconfined aquifer and is geochemically distinct. The median pH of the unconfined-aquifer water is about 6.8 and of the upper-confined-aquifer water is 7.4 (Fig. 2A). The median dissolved-O<sub>2</sub> concentration is about 5 mg/L in the unconfined aquifer compared to about 0.1 mg/L (functionally anoxic) in the upper confined aquifer (Fig. 2B).

Withdrawals of groundwater for agriculture in this aquifer system account for more than 70% of total withdrawals, compared to about 2% for municipal wells (Maupin and Barber, 2005). Under pumping conditions, flow to irrigation wells, which are commonly screened across multiple aquifers, is generally from the aquifers to the wells; under low or non-pumping conditions, however, water flows from the unconfined aquifer, down the well bore, and out into the upper confined aquifer, short-circuiting the natural flow path. This geochemically distinct unconfined-aquifer water interacts with upper-confined-aquifer materials and is available for capture, such as at a PSW in York, Nebraska (Landon et al., 2008). This PSW is screened from 42.7 to 61 m below land surface, in the upper confined sand, but analysis of depth-dependent water samples suggests that unconfined-aquifer water can account for as much as 50% of the water in some zones of the well screen (Landon et al., 2008). Mixing of water in the borehole results in parameter values that are between or higher than those of the waters from individual end-member aquifers (Figs. 2A and B and 3). Large-volume agricultural withdrawals also may cause upward flow from the underlying Carlile Shale to the confined aquifer



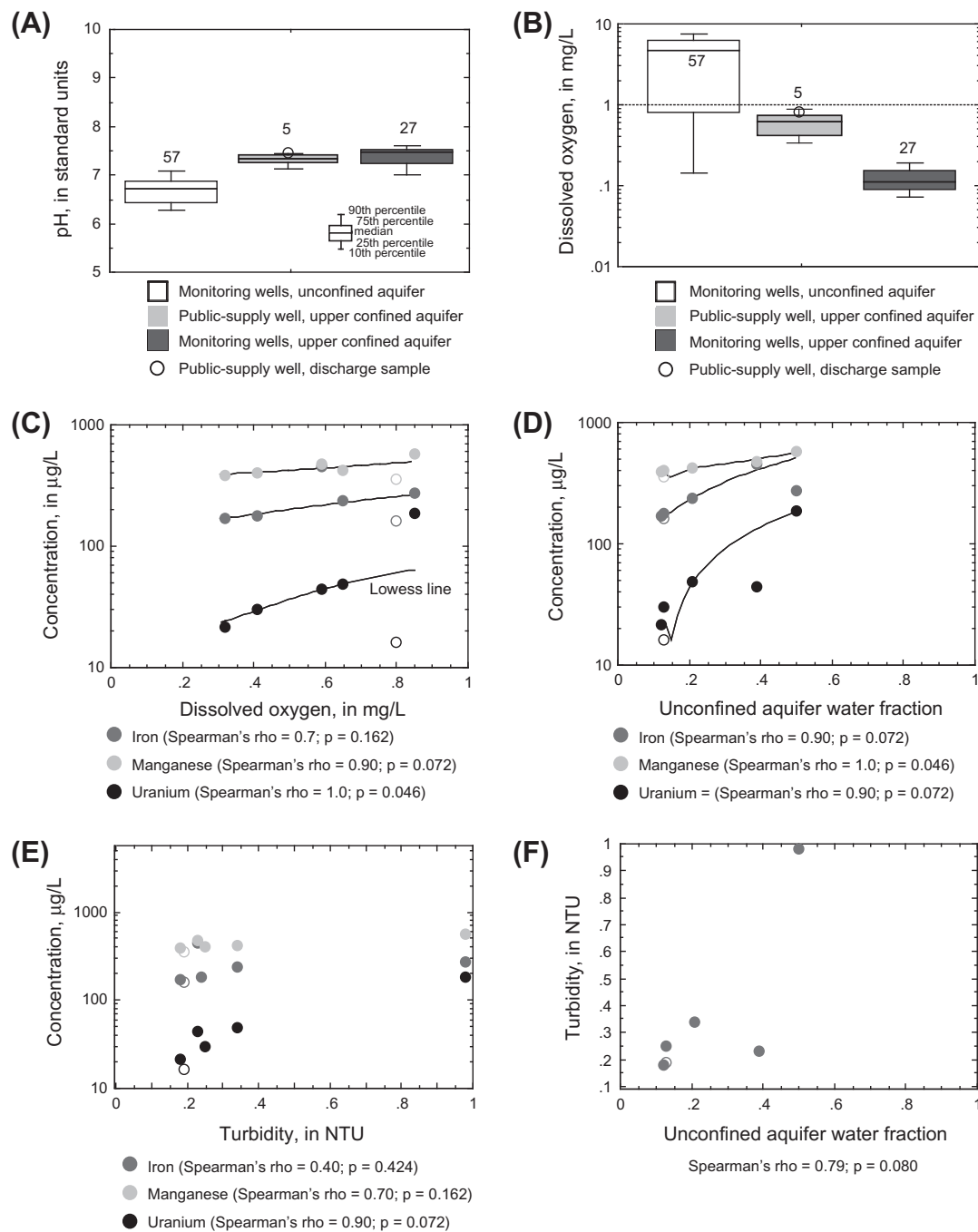


**Fig. 1.** (A) Location of study areas in the United States and schematics of the flow system in (B) Modesto, California; (C) York, Nebraska; (D) eastern Wisconsin; (E) Tampa, Florida; and (F) New Jersey Coastal Plain.

(McMahon, 2001) and may serve as an additional source of naturally-occurring trace elements.

Flow-model analysis indicates that leakage through multi-aquifer wells accounts for as much as 25% of the total flow from the unconfined to the confined part of the aquifer system (Clark et al., 2008; Landon et al., 2008) Although 25% of flow is itself a

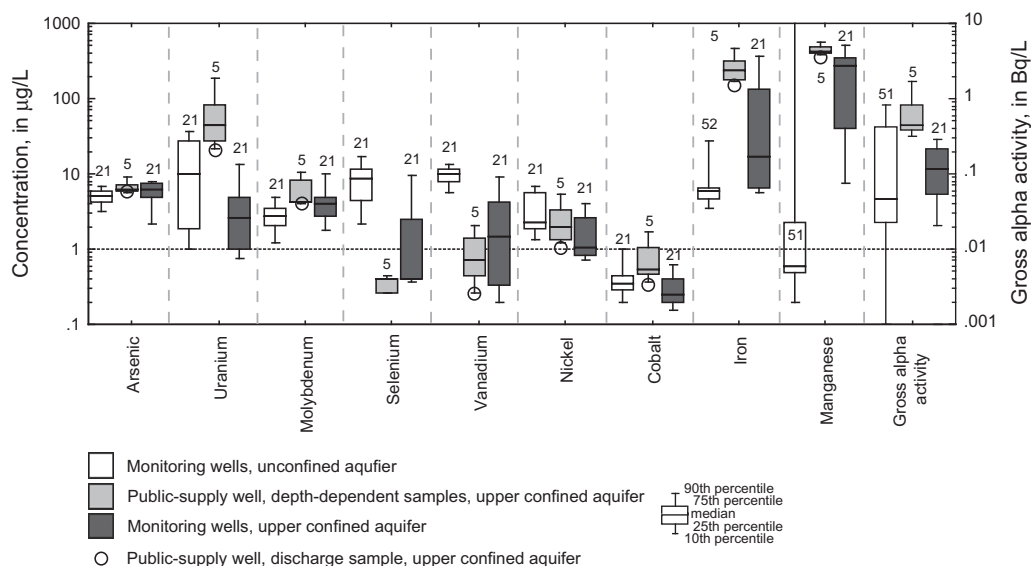
large percentage, this flow represents nearly all of the young low-pH, high-dissolved- $O_2$  water recharging the upper confined aquifer. In the mixed water from the depth-dependent PSW samples, U concentrations are highest in the samples with the highest dissolved  $O_2$ . Uranium concentrations also are highest in samples with the lowest pH, suggesting that the higher the proportion of



**Fig. 2.** Statistical distributions of (A) pH and (B) dissolved-oxygen concentrations in public-supply-well (PSW) and monitoring-well samples; iron, manganese, and uranium versus (C) dissolved oxygen, (D) unconfined-aquifer water fraction, and (E) turbidity; and (F) turbidity versus unconfined-aquifer water fraction in depth-dependent PSW samples in the High Plains aquifer, York, Nebraska. Open circles represent PSW discharge. The data indicate that PSW samples represent a mix of waters from the upper confined and unconfined aquifers. Number above box plots is the number of samples.

unconfined-aquifer water (which also is more oxidic), the more U in the samples. Dissolved Fe and Mn concentrations in the depth-dependent PSW samples also increased slightly as dissolved  $\text{O}_2$  increased (Fig. 2C), but these increases may have been caused by a slight decrease in pH of the same water. Oxygen-isotope data enabled the determination of the proportion of water from the unconfined aquifer and the confined aquifer in the depth-dependent samples (Landon et al., 2008). As expected from the dissolved- $\text{O}_2$  and pH data, concentrations of Fe, Mn and U also increased as the fraction of water captured by the PSW from the unconfined aquifer increased (Fig. 2D).

Evidence for the movement of unconfined-aquifer water into the upper confined aquifer is reflected in the geochemical data. When water from the unconfined aquifer mixes with water from the upper confined aquifer (by short-circuiting through multi-aquifer wells) the resulting median dissolved- $\text{O}_2$  concentration increases to about 0.6 mg/L, as indicated by the depth-dependent PSW samples (Figs. 3 and 4C). This 6-fold increase in dissolved  $\text{O}_2$  may be enough to affect the mobility of some trace elements—particularly U, whose concentrations are higher in PSW samples (low  $\text{O}_2$  but not sub-oxic) than in samples from monitoring wells in the confined aquifer (reduced; sub-oxic) or the uncon-



**Fig. 3.** Box plots showing distribution of concentrations of selected trace elements and radionuclides in samples from public-supply and monitoring wells in unconfined and confined aquifers in the High Plains aquifer system near York, Nebraska.

finer aquifer (oxic). Thus, the PSW water samples may be thought of as having a “mixed” redox signal. Gross alpha activities (likely from U) also are highest in the PSW water. Concentrations of Mo, Co, Fe and Mn also are unexpectedly higher in the “mixed” PSW water than in samples from monitoring wells in either aquifer (Fig. 3).

The source of U and other trace elements in the PSW samples is unclear. One hypothesis, supported by U-isotope-ratio and turbidity data (Fig. 2E and F), is that transport of U on Fe- and Mn-hydroxide colloids from the unconfined aquifer occurs along the well bore of non-pumping, fully screened irrigation wells (short-circuit pathways) to the PSW screened in the confined aquifer (Landon et al., 2008). Uranium in the PSW water is isotopically similar to U in the unconfined-aquifer water and dissimilar to that in the confined-aquifer water (Table 3). Uranium-isotope ratios can be altered, however, especially with changes in redox conditions (Gilkerson and Cowart, 1987). Whatever the source, the important consideration is that U mobilization results from the changes in redox conditions and pH by the introduction of oxygenated, unconfined-aquifer water to the confined aquifer as a result of human-induced changes to the flow field.

### 3.1.2. Local-scale changes

At the well-field scale ( $10^{-2}$ – $10^0$  km) near Tampa, Florida, the screened interval of a large municipal PSW is open to the limestone and dolomite lithologies of the Upper Floridan aquifer. Intermittent sandy clay near the base of the overlying surficial sand unit functions as a semiconfining layer between the surficial aquifer system and the Upper Floridan aquifer (Katz et al., 2007, 2009; McMahan et al., 2008a,b). The Upper Floridan aquifer has natural conduit features, common in carbonate-rock aquifers, which allow water from the surficial aquifer to bypass the confining unit and flow downward to the Upper Floridan aquifer. Natural flow along these conduits can be enhanced by large withdrawals from the Upper Floridan aquifer.

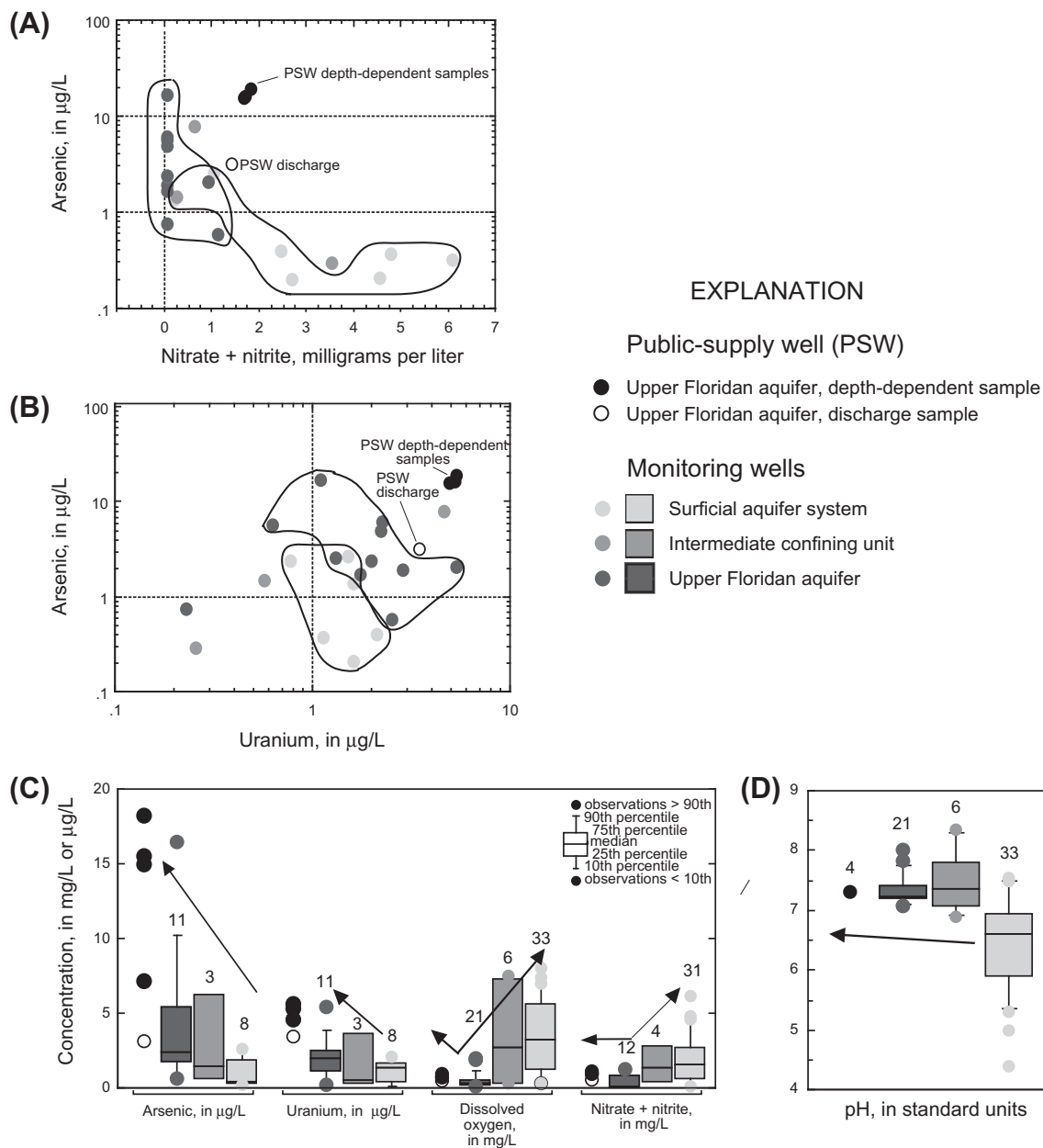
Under natural conditions, the water in the Upper Floridan aquifer shows little influence from the overlying surficial aquifer system (Fig. 4). Samples from monitoring wells in the Upper Floridan aquifer reflect this general confinement and are generally low in dissolved  $O_2$  (median <1 mg/L) and alkaline (median pH = 7.4) (Fig. 4C and D). Nitrate concentrations do not exceed

1 mg/L in monitoring wells in the Upper Floridan aquifer in the vicinity of the PSW (Fig. 4A and C) but are often greater than 2 mg/L in samples from monitoring wells in the surficial aquifer (Katz et al., 2007) (Fig. 4A and C).

Development of the Upper Floridan aquifer for water supply increases hydraulic gradients between the Upper Floridan aquifer and the surficial aquifer system, causing movement of oxic water from the surficial aquifer to the reducing Upper Floridan aquifer and, ultimately, the PSW. The PSW studied has an average pumping rate of about 2690 L/min, causing large downward gradients and resulting in discharge water that represents a mix of waters from both aquifers. Mixing models indicate that 40–70% of the water in the PSW comes from the Upper Floridan aquifer and about 30–60% comes from the surficial aquifer system (Katz et al., 2007, 2009). The fact that these percentages vary substantially may be related in part to the complexity of the karst features of the aquifer.

Chemistry of bulk water and depth-dependent water samples from the PSW in the Upper Floridan aquifer (collected at ambient conditions and at a pumping rate of 1320 L/m) suggest that differences in pumping rate can affect the redox conditions and concentrations of some contaminants (i.e.,  $NO_3$  and As (Table 4). Nitrate concentrations in depth-dependent samples collected from the PSW under non-pumping conditions were between 2 and 4 mg/L, whereas those in samples collected under pumping conditions were about 1.7–1.8 mg/L (Katz et al., 2007). Flowmeter tests indicate that flow in the borehole is downward during ambient conditions. The samples collected under non-pumping conditions are probably higher in  $NO_3$  because of downward movement of surficial aquifer system water along a transmissive zone that intersects the bottom part of the well (Table 4).

Arsenic concentrations, in contrast to  $NO_3$ , were generally greater in the depth-dependent samples collected under pumping conditions (15.3, 16.0 and 18.9  $\mu\text{g/L}$ ) than in those collected under non-pumping conditions (4.2 and 11.7  $\mu\text{g/L}$ ). This difference is consistent with the concept of low-As surficial aquifer system water with lower pH and higher dissolved  $O_2$  moving downward along a transmissive zone under ambient conditions (Fig. 4A and C; Table 4). Arsenic concentrations under pumping conditions, however, are similar to or higher than As concentrations in either aquifer or in the intermediate confining unit (Fig. 4C). The highest As concentration was measured in a sample from the bottom of the



**Fig. 4.** Relation of (A) arsenic and nitrite + nitrate and (B) arsenic and uranium, by well type and aquifer. Arsenic in the Upper Floridan aquifer is highest for public-well depth-dependent samples and co-occurs with nitrite + nitrate. Nitrite + nitrate, however, is generally low in the Upper Floridan aquifer (see graph C, monitoring wells) and high in the overlying surficial aquifer system (monitoring wells). Arrows pointing left on graph C indicate concentrations increasing with increased depth, whereas arrows to the right indicate increasing concentrations with decreasing depth. Pumping of the public-supply well captures water from the Upper Floridan and surficial aquifer system, resulting in a mix of water types and geochemical conditions. The relatively low dissolved oxygen (C) and high pH (D) in the Upper Floridan aquifer may help keep mobilized arsenic in solution. Number above box plots is the number of samples.

**Table 3**  
Uranium isotope ratios for water samples in unconfined and confined aquifers in York, Nebraska.

Well type	Setting	Well number	234U/238U
<i>Unconfined aquifer</i>			
Public-supply well	–	PSW	1.31
Urban monitoring	Shallow	FP1-63	1.27
Agricultural monitoring	Shallow	FP4-28	1.29
Agricultural monitoring	Deep	FP4-83	1.83
<i>Confined aquifer</i>			
Urban monitoring	Unmixed	FP1-147	1.62
Urban monitoring	Mixed	OFPS-157	1.67
Agricultural monitoring	Unmixed	FP4-168	2.38

well screen (49–53 m) (Table 4); As concentrations decreased slightly as more of the borehole (38–53 m) contributed to the discharge. This high-As zone is coincident with a high-flow zone identified by borehole geophysical investigations and is indicative of the presence of the Suwannee Limestone—known to contain abundant As-bearing pyrite (Katz et al., 2007; Price and Pichler, 2006). This pyrite-rich zone also had the highest concentrations of dissolved  $\text{O}_2$ ,  $\text{NO}_3^-$ ,  $^{222}\text{Rn}$ , atrazine, and trichloromethane, among other constituents, suggesting that the surficial aquifer system was the source of at least some of the water in the high-flow zone (Katz et al., 2007, 2009).

The As concentration (3.2  $\mu\text{g/L}$ ) measured during pumping of the full screened interval (38–53 m) with the PSW's turbine pump at 2650 L/m is consistently five times lower (more than 15  $\mu\text{g/L}$



**Table 4**

Concentrations of selected constituents in discharge water and depth-dependent groundwater samples from PSW TTP-4. (P, pumping; NP, non-pumping; E, value below laboratory reporting level but above method detection level.)

Site	Sample date	Depth interval (m)	Pumping rate (L/m)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	Dissolved oxygen (mg/L)	pH (standard units)	Nitrite (mg/L)	Nitrate (mg/L)	Arsenic ( $\mu\text{g}/\text{L}$ )	As(III) ( $\mu\text{g}/\text{L}$ )	As(V) ( $\mu\text{g}/\text{L}$ )
TTP-4-140-NP	10/27/04	43–53	0	577	0.8	7.3	0.039	2.3	11.7	E0.8	8.7
TTP-4-160-NP	10/27/04	49–53	0	537	0.8	7.3	0.011	3.6	4.2	<1	2.6
TTP-4-160-P	10/28/04	49–53	1320	567	1.0	7.3	0.035	1.8	18.9	E0.6	14.2
TTP-4-140-P	10/28/04	43–53	1320	586	0.6	7.3	0.02	1.7	16.0	2.1	10.7
TTP-4-125-P	10/28/04	38–53	1320	583	0.6	7.3	0.013	1.7	15.3	3.3	9.3
TTP-4-discharge	10/21/04	38–53	2650	606	0.5	7.3	0.008	1.4	3.2	1.5	E1.0

lower) than the concentration measured in water from the same interval during depth-dependent sampling at a lower pumping rate of 1320 L/m (Table 4). At first glance, this result appears to conflict with the capture of large volumes of water from the surficial aquifer and oxidation of pyrite in the high-flow zone. The composition of the well-discharge water under the high pumping rate (based on dissolved  $\text{O}_2$  and other chemistry) is closer to that of samples from other (non-Suwannee) parts of the Upper Floridan aquifer where As concentrations are generally low. One explanation for this observation is that incremental increases in the contribution of water from the surficial aquifer system to the PSW via short-circuit pathways may occur only until some maximum-inflow-capacity threshold is reached; as pumping increases, any additional water may come from the parts of the Upper Floridan aquifer (non-Suwannee) characterized by lower As concentrations as well as higher specific conductance, lower dissolved  $\text{O}_2$ , and lower  $\text{NO}_3^-$  concentrations.

The observation that As concentrations in the PSW are highest in water from the Suwannee Limestone part of the aquifer (49–53 m) and that water from this interval has a surficial aquifer system signature suggests that pyrite oxidation may be the mechanism leading to increased As concentrations in water from this zone. The pyrite is stable under anoxic conditions typical of the Upper Floridan aquifer, but rapid breakdown of the pyrite can occur under oxic conditions (Katz et al., 2009). In this way, As in the Upper Floridan aquifer sediments can be mobilized by the capture of low-pH, high-dissolved- $\text{O}_2$  (and high- $\text{NO}_3^-$ ) water from the surficial aquifer system. The dominant form of the As from the PSW is As(V), with As(III)/As(V) ratios ranging from 0.04 to 0.35, except for one sample in which the ratio was 1.5. Groundwater samples from monitoring wells completed in the Upper Floridan aquifer tend to have more As(III), consistent with generally reducing conditions in that system (Katz et al., 2009). The dominance of As(V) also is consistent with the oxidative release of As from aquifer materials. The mobilization of As may have other consequences that affect water quality in the area as the increasingly common practice of ASR is used to store water from the surficial aquifer system in the Upper Floridan aquifer (Price and Pichler, 2006), resulting in mixed water similar to that in the PSW.

### 3.1.3. Borehole-scale changes

At the borehole scale ( $\leq 10^{-3}$ – $10^{-2}$  km) in eastern Wisconsin, a study of wells in state databases indicated that As concentrations were highest in wells with static water levels near a regionally extensive sulfide-bearing unit. Arsenic concentrations in drinking-water wells in bedrock aquifers in eastern Wisconsin range as high as 12,000  $\mu\text{g}/\text{L}$  (Schreiber et al., 2003). In more than 20% of wells, As concentrations exceed 10  $\mu\text{g}/\text{L}$ ; in about 4%, concentrations exceed 50  $\mu\text{g}/\text{L}$  (Schreiber et al., 2003). Most wells are installed across the Ordovician Sinnipee Group, the St. Peter Sandstone, and the Prairie du Chien Group in the Fox River Valley. A sulfide cement horizon (SCH) lies below the Sinnipee Group and on top of the St. Peter Sandstone. Regional-scale analysis identified

geochemical factors that are related to elevated As concentrations in wells. These include, for wells with As >100  $\mu\text{g}/\text{L}$ , elevated concentrations of  $\text{SO}_4$ , Ni, Mn and Zn. Also for these wells, pH was generally low (median = 5) compared to the wells with lower or no As, for which median pHs were >7.5.

In wells with As >100  $\mu\text{g}/\text{L}$ , sulfide-mineral oxidation of the SCH was identified as the process that mobilizes As and leads to high concentrations in groundwater (Schreiber et al., 2003). Examination of  $\text{SO}_4$ -to-Fe molar ratios (about 2) and the correlation of the S isotopic signature of solid-phase samples (–6.05 for pyrite) and aqueous-phase samples (–6.48 for groundwater) from a high-As well support the oxidation hypothesis (Schreiber et al., 2003). Multiple mechanisms have been proposed for the pyrite oxidation. These include oxidation by  $\text{O}_2$  derived from: (1) regional recharge, (2) vertical leakage of oxygenated water, (3) regional dewatering and associated introduction of  $\text{O}_2$ , and (4) oxygenation of the borehole itself. In wells with static water levels at or below the SCH, the borehole acts as a direct conduit for movement of  $\text{O}_2$  in air into the borehole, where pyrite can be oxidized as cycles of air and water move past the SCH in response to routine pumping of the wells. Arsenic concentrations are highest when the static water levels in the well are within 15 m of the SCH, which supports the hypothesis that  $\text{O}_2$  in the borehole can reach the SCH and initiate sulfide-mineral oxidation (Gotkowitz et al., 2004). This model for oxidation implies that the source of the As is in or very near the borehole itself and that movement of water and air past the source is the mobilization mechanism directly related to human perturbation of the flow system.

A subsequent borehole-scale study designed to identify mechanisms for As mobility included the installation of a test well to simulate a low- to moderate-level As-bearing domestic well (Gotkowitz et al., 2004). Cores collected from the borehole showed that the SCH was present as a thin band between the Sinnipee Group and St. Peter Sandstone. Other sulfide minerals were present in the upper part of the St. Peter Sandstone and, like the SCH, had As concentrations as high as 500 mg/kg. The water in the well is derived primarily from the more permeable St. Peter Sandstone, which typically produces water low in As.

Sulfur isotopes from the rock core and from the water were similar, indicating that the source of the  $\text{SO}_4$  is likely sulfides in the rock. Sulfur odor noted during sampling indicated the presence of  $\text{SO}_4$ -reducing bacteria in the well bore. Although some sulfide oxidation is hypothesized to occur (generating  $\text{SO}_4$ ), other mechanisms for As release may be occurring and were investigated further.

A well-pumping experiment was designed to simulate domestic well use. Long periods between pumping allowed the well to become increasingly anoxic and resulted in higher As concentrations than when the well was pumped more frequently. A 17-day test during which the well was not pumped showed that As concentrations increased from 1.1  $\mu\text{g}/\text{L}$  on day 1 to 16  $\mu\text{g}/\text{L}$  at the end of the test. Iron concentrations also correspondingly increased with As concentrations; however,  $\text{SO}_4$  concentrations did not (Fig. 5). This

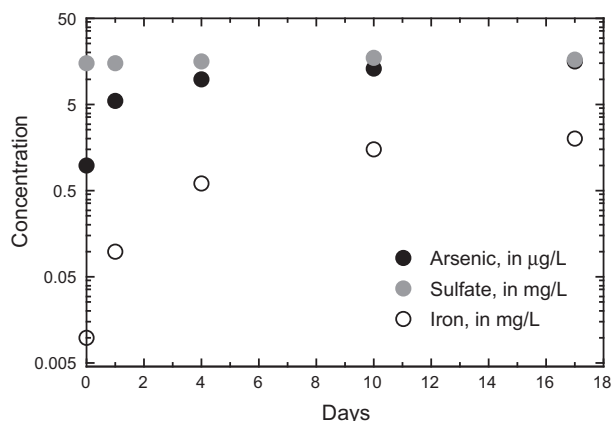


Fig. 5. Arsenic, iron, and sulfate concentration over time in the eastern Wisconsin test well during non pumping conditions. Arsenic and iron increase over time, whereas sulfate does not. (Modified from Gotkowitz et al., 2004.)

difference in concentration trends suggests that the release of As in this well is likely related to the reduced conditions in periods of no pumping. Under pumping conditions similar to domestic well use, concentrations of As varied but were all below current HHBs (Gotkowitz et al., 2004). Both sulfide oxidation and the reduction of As-bearing Fe hydroxides may have contributed to As mobility in this well, depending on water-use patterns. In either case, it is the change in redox in the borehole itself as a result of pumping (human perturbation) and pumping cycles that mobilizes As from the borehole or near-borehole rock and mineral surfaces, such as pyrite and Fe oxyhydroxide.

### 3.2. Ion complexation and competition

#### 3.2.1. Advection due to irrigation pumping in California

Withdrawals of water for irrigation of crops in the Central Valley account for about 2/3 of all groundwater withdrawals in California (Hutson et al., 2004; Maupin and Barber, 2005). Regional-scale pumping for irrigated agriculture in the San Joaquin Valley (southern Central Valley) near Modesto, California, has caused decreased hydraulic heads deep in the unconsolidated sand aquifer and increased heads in the upper part of the aquifer (Burow et al., 2008; Jurgens et al., 2008). One result is increased downward flow in the aquifer, causing young, upper-aquifer water to gradually be drawn deeper into the aquifer replacing older, deep water. Under natural conditions, the residence time and apparent age of the groundwater increases with depth, from  $10^1$  a near the water table to  $10^3$  a at depths >80 m below the water table (Jurgens et al., 2008). Irrigation wells, which capture water from various depths through long screens, produce water that represents a mix of groundwater of differing recharge ages (variable residence time). The irrigation water applied to the land surface becomes the primary source of recharge to the aquifer (Burow et al., 2004). PSWs in the area are constructed similarly to irrigation wells, with median depths about 85 m below land surface, and they also capture water of varying recharge ages (Burow et al., 2004). Transient tracer-concentration data measured at a PSW in Modesto indicate that the well produced a mix of young water (10–50 a old; 20%), intermediate-age water (50–100s a old; 55%), and old water (100s to >1000 a old; 25%); the mixture is presumed similar to that produced from the irrigation wells and applied at the land surface for irrigation (Jurgens et al., 2008).

Groundwater redox conditions are generally oxic throughout, although the lowest concentrations of dissolved  $O_2$  are in the deepest part of the aquifer (2.2 to 3.0 mg/L). Uranium in samples from

monitoring wells ranged from 0.24 to 45.3 µg/L; in depth-dependent PSW samples, concentrations ranged from 3.2 to 35.8 µg/L. Sediments in the aquifer are derived in part from granitic rocks of the Sierra Nevada Mountains that were transported during the Pleistocene and Holocene Epochs. The weathered granitic rocks are the likely source of As and U in the sediment (Jurgens et al., 2008).

Labile U concentrations, determined from leaching experiments of aquifer sediments, increased with depth (Spearman's rho = 0.75,  $p < 0.03$ ), which was interpreted as an indication that U has been partially leached from near-surface sediments and that intermediate and deep sediments have not yet experienced leaching. Concentrations of U in water samples were strongly correlated with alkalinity (Spearman's rho = 0.94,  $p < 0.001$ ), which is dominantly  $HCO_3^-$  and Ca (Spearman's rho = 0.96,  $p < 0.001$ ). These correlations suggest that U adsorbed onto aquifer sediments is mobilized by ion competition and (or) forms stable complexes with Ca- $HCO_3^-$  ion pairs and/or  $HCO_3^-$  (Hodge et al., 1996; Langmuir, 1978). Currently, alkalinity concentrations are lower at depths greater than 50 m below land surface than at shallow depths (Fig. 6A). This more dilute geochemical condition inhibits desorption of U and the formation of U complexes at depth. Accordingly, depth-dependent sampling of the PSW shows that U concentrations are highest in the shallowest, most alkaline water captured by the well and that U and  $HCO_3^-$  concentrations generally decrease with depth (Fig. 6B). The long-term trend controlling water quality in this part of the aquifer system is the continued downward migration of shallow alkaline water to the intermediate and deep parts of the aquifer, acceler-

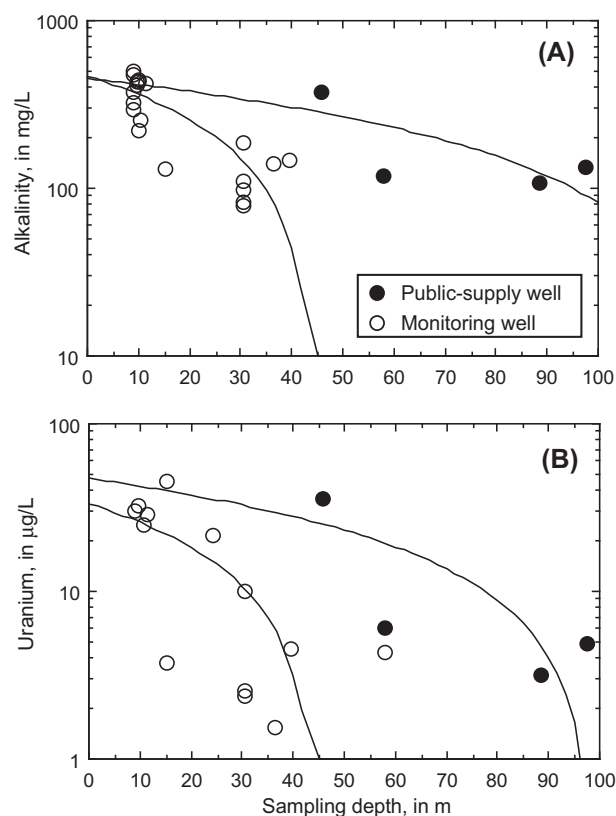


Fig. 6. (A) Alkalinity and (B) uranium concentrations versus sampling depth in the unconsolidated sand and gravel aquifer near Modesto, California. Public-supply-well data represent depth-integrated samples while pumping with the existing well pump. The uranium concentration in a well-discharge sample was 11.2 µg/L. The data indicate that alkalinity and uranium are related to depth of sample collection and suggest that alkalinity, particularly bicarbonate, may control uranium mobility by complexation.

**Table 5**

Percentage of public-supply wells in the eastern San Joaquin Valley producing water with uranium activities exceeding California drinking-water limits, 1990–2006 (Jurgens et al., 2009a) [Bq/L, becquerels/L; pCi/L, picocuries/L].

Time period	Number of wells	Median uranium concentration, Bq/L (pCi/L)	Percent of wells with uranium >0.74 Bq/L (20 pCi/L)
1990–1998	556	0.1332 (3.6)	6.8
1998–2006	610	0.1554 (4.2)	9.2

ated by large-volume pumping (Burow et al., 2008; Jurgens et al., 2009a). With the passage of time and continued heavy pumping, the larger volumes of oxic and alkaline water captured by the PSW will come in contact with a larger fraction of the deeper, U-rich sediment (Jurgens et al., 2008). The result could be progressively higher overall U concentrations in the discharge from the PSW.

The vulnerability of the aquifer system and PSWs to increasing concentrations of U in the future is clear from analysis of current water-quality data and from trend modeling that was done for the PSW in Modesto (Burow et al., 2008; Jurgens et al., 2009a). The percentage of other PSWs in the San Joaquin Valley with concentrations of U >0.74 becquerels (Bq)/L (20 picocuries (pCi)/L) also has increased over time (Table 5). The capture of higher alkalinity groundwater by the PSW is expected to increase over time and will depend in part on the amount of irrigation. At the land surface, the applied irrigation water becomes concentrated in HCO<sub>3</sub> and Ca as increases in partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in soil cause increased dissolution of minerals and the irrigation water then recharges the aquifer (Jurgens et al., 2008). Evaporation of irrigation water also may contribute to increases in HCO<sub>3</sub> (Jurgens et al., 2009a). The concentration of U is high in PSWs under both agricultural and urban land, suggesting that advection of alkaline water to the wells can occur beneath either type of land use (Burow et al., 2008).

In this aquifer, HCO<sub>3</sub> concentration (a major component of the alkalinity) is closely correlated with U concentration (Spearman's rho = 0.74;  $p < 0.0001$ ). On the basis of this relationship, an alkalinity of approximately 450 mg/L as CaCO<sub>3</sub> corresponds with a U concentration of about 30 µg/L. If alkalinity loads to the water table remain constant in the near future, the concentration of alkalinity in the PSW will increase gradually to near 450 mg/L, and thus concentrations of U would be expected to gradually increase to near 30 µg/L over the next 100–200 a (Burow et al., 2008). The downward migration of high-U water may even be accelerated in areas where the rate of recharge to the water table is highest. Pumping, the application of irrigation water to the land surface, the role of increased pCO<sub>2</sub> in mineral dissolution, the evaporative concentration, and the associated increase in alkalinity act in concert to mobilize U (by desorption and complexation) and move it downward in the aquifer at an increased rate.

### 3.2.2. Advection due to pumping near agricultural areas in New Jersey

Alteration of chemistry along flow paths and the complex mixing process within high-yield PSWs can be observed even in thin

aquifer systems. In a study in the Atlantic Coastal Plain of southern New Jersey, PSWs screened in the generally thin (<50 m), unconfined Kirkwood–Cohansey aquifer system commonly capture acidic, oxic, NO<sub>3</sub>- and Cl-laden water with moderate dissolved-solids content (75–200 mg/L) (Szabo et al., 1997). The PSWs also capture elevated concentrations of Ra that exceed the HHB of 0.185 Bq/L (5 pCi/L) for combined Ra (the sum of <sup>226</sup>Ra and <sup>228</sup>Ra). The aquifer material is composed primarily of highly permeable quartzose sand that is low in radioactive minerals and radionuclide concentrations. Median concentrations of both <sup>226</sup>Ra and <sup>228</sup>Ra were about 0.148 Bq/g (0.4 pCi/g) in aquifer core samples (Szabo et al., 1997), much lower than in most immature sands and typical rocks; hence, the presence of the elevated concentrations of Ra was unexpected.

Concentrations of combined Ra in water samples from 33% (56) of 170 wells (39 public-supply, 56 domestic, and 75 monitoring wells) exceeded the HHB (Table 6). Concentrations of combined Ra ranged from <0.0407 to 1.11 Bq/L (<1.1–30 pCi/L), with an overall median of 0.1406 Bq/L (3.8 pCi/L). Concentrations of <sup>226</sup>Ra and <sup>228</sup>Ra were significantly correlated (Spearman's rho = 0.70). The median ratio of the concentrations of <sup>228</sup>Ra to <sup>226</sup>Ra in the water was 1.06, almost identical to the 1:1 ratio in the sands that make up the aquifer system, indicating that the naturally occurring radioactive materials are the likely source of the dissolved Ra. These data indicate that despite low concentrations of Ra in aquifer materials, geochemical reactions result in high concentrations of Ra in water.

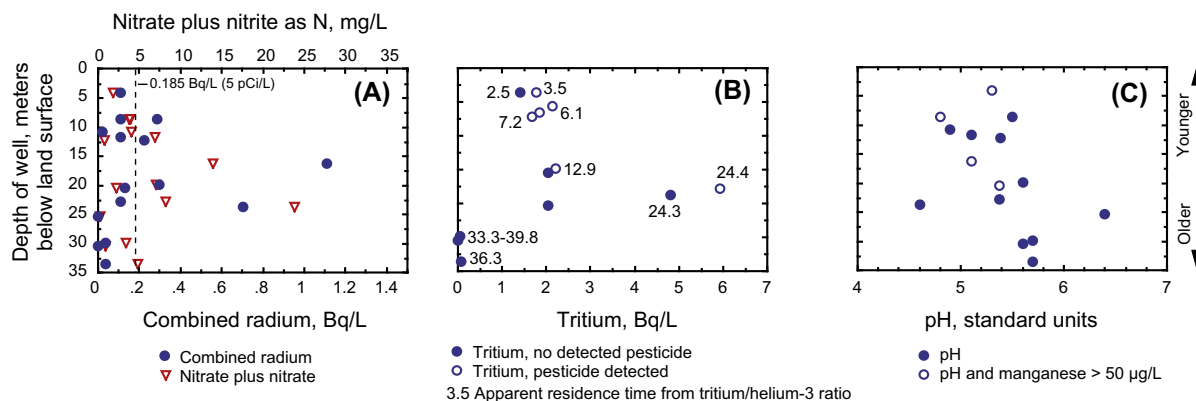
Wells containing water in which concentrations of combined Ra were greater than the 0.185 Bq/L (5 pCi/L) HHB typically were found where groundwater was acidic (pH < 5) and where NO<sub>3</sub> concentrations generally exceeded 5 mg/L. Of the 56 water samples in which the concentration of total Ra exceeded 0.185 Bq/L (5 pCi/L), 34 (61%) had a pH < 4.8. Of 63 samples with a NO<sub>3</sub> concentration >5 mg/L, 41 (65%) had Ra concentrations >0.185 Bq/L (5 pCi/L).

Concentrations of dissolved NO<sub>3</sub> (Fig. 7A) and Mg, and to a lesser extent Ca, like those of Ra, were significantly greater at the shallow and medium depths than near the base of the aquifer. Tritium/<sup>3</sup>He ratios at depths of about 25 m below land surface corresponded to water recharged about 25–30 a ago (Szabo et al., 1996) (Fig. 7B). Water from shallow and medium depths (3 to 20 m below land surface) contained water with the least <sup>3</sup>He and shortest residence time, as short as 2 a just below the water table at about 3 m depth. Waters near the base of the aquifer were recharged 35 to more than 40 a ago (Fig. 7B) and were still generally oxic, indicating little denitrification. As precipitation recharged the aquifer sys-

**Table 6**

Well type and median depth to open interval, percentage of wells in agricultural areas, and median nitrate concentration in water from wells in the Kirkwood–Cohansey system, southern New Jersey, 1988–1996 (Bq/L, Becquerels/L; pCi/L, picocuries/L).

Well type (and number sampled)	Median depth to top of well screen (meters below land surface)	Percentage of wells in agricultural areas	Median concentration of nitrate plus nitrite (mg/L)	Median concentration of combined Ra (Ra-226 plus Ra-228) Bq/L (pCi/L)	Percentage of wells for which combined Ra exceeds 0.185 Bq/L (5 pCi/L)
Public-supply (39)	28.3	38	2.8	0.1369 (3.7)	21
Domestic (56)	19.2	81	5.95	0.1443 (3.9)	43
Monitoring (75)	15.2	67	3.8	0.1406 (3.8)	32



**Fig. 7.** (A) Concentration of combined radium and nitrite + nitrate, (B) concentration of tritium, apparent residence time estimated from tritium/helium-3 ratio, and presence or absence of pesticide compounds, and (C) pH and manganese concentrations as a function of depth in sample of water from nested observation wells in the Kirkwood–Cohansey aquifer system, New Jersey Coastal Plain, 1991.

tem 40 or more years ago, before the time of peak fertilizer use, the acidic water was slowly neutralized by the chemical reactions of natural weathering, as indicated by increases in pH with depth in water from the nested wells (Fig. 7C). The increase in pH with depth, generally associated with the increase in groundwater residence time, corresponded roughly with the lowest concentrations of dissolved Ra,  $\text{NO}_3$  and Mg among the samples.

Leaching of N and Ca plus Mg from agricultural chemicals (fertilizer, lime) applied abundantly to cropland may increase dissolved-solids and divalent-cation concentrations, but it may also decrease pH because nitrification releases  $\text{H}^+$  ions. Mobility of the naturally occurring Ra is also enhanced by decreased sorption/exchange resulting from increasing competition with  $\text{H}^+$  as well as divalent Ca and Mg (Szabo et al., 1997). Cation exchange and adsorption onto Mn or Fe hydroxides might limit Ra concentrations at near-neutral pH values at depth in the aquifer, but these processes are inefficient in the acidic waters at shallow depths. Concentrations of Mn were commonly high (near or  $>50 \mu\text{g/L}$ ) in the shallow Ra-bearing waters, indicating that Mn hydroxides, extremely sorptive of Ra from solution (Moore and Reid, 1973), might be undergoing dissolution because they are unstable in the low-pH waters (Fig. 7C).

The HHB for total Ra was exceeded less frequently in water from PSWs (21%) than in water from domestic wells (43%) or monitoring wells (32%) (Table 6). The domestic and monitoring wells with short screened intervals were mostly in agricultural areas where fertilizer and soil-amendment use was highest and  $\text{NO}_3$  concentrations in groundwater also were highest (Table 6). Because PSWs pump large volumes of water and have long screened intervals, they mix water from large zones of contribution with a variety of land uses and also from a variety of depths within the aquifer. This mixed water still contained measurable Ra concentrations that commonly are high relative to the HHB. Despite their location near agricultural areas, the PSWs can draw in water recently recharged through the nearby agricultural soils and laden with  $\text{NO}_3$  and Ra. A much broader mixture of anthropogenic contaminants, such as pesticides and VOCs, was detected in the PSWs than in the monitoring wells, a trend consistent with the larger zone of contribution for the PSWs (Stackelberg et al., 2001).

The introduction of one contaminant ( $\text{NO}_3$ ) into the aquifer and its enhanced transport due to PSW pumping leads to slight decreases in groundwater pH, that, in turn, changed the equilibrium between the groundwater and the aquifer materials and promoted the release of Ra and Mn from the aquifer sediment. Thus, the induced downward migration of shallow, acidic,  $\text{NO}_3$ -laden ground-

water replacing or mixing with slightly more alkaline and more reduced groundwater caused more widespread increased Ra mobility than was the case in the absence of the large withdrawals.

#### 4. Implications for operation of water-supply wells

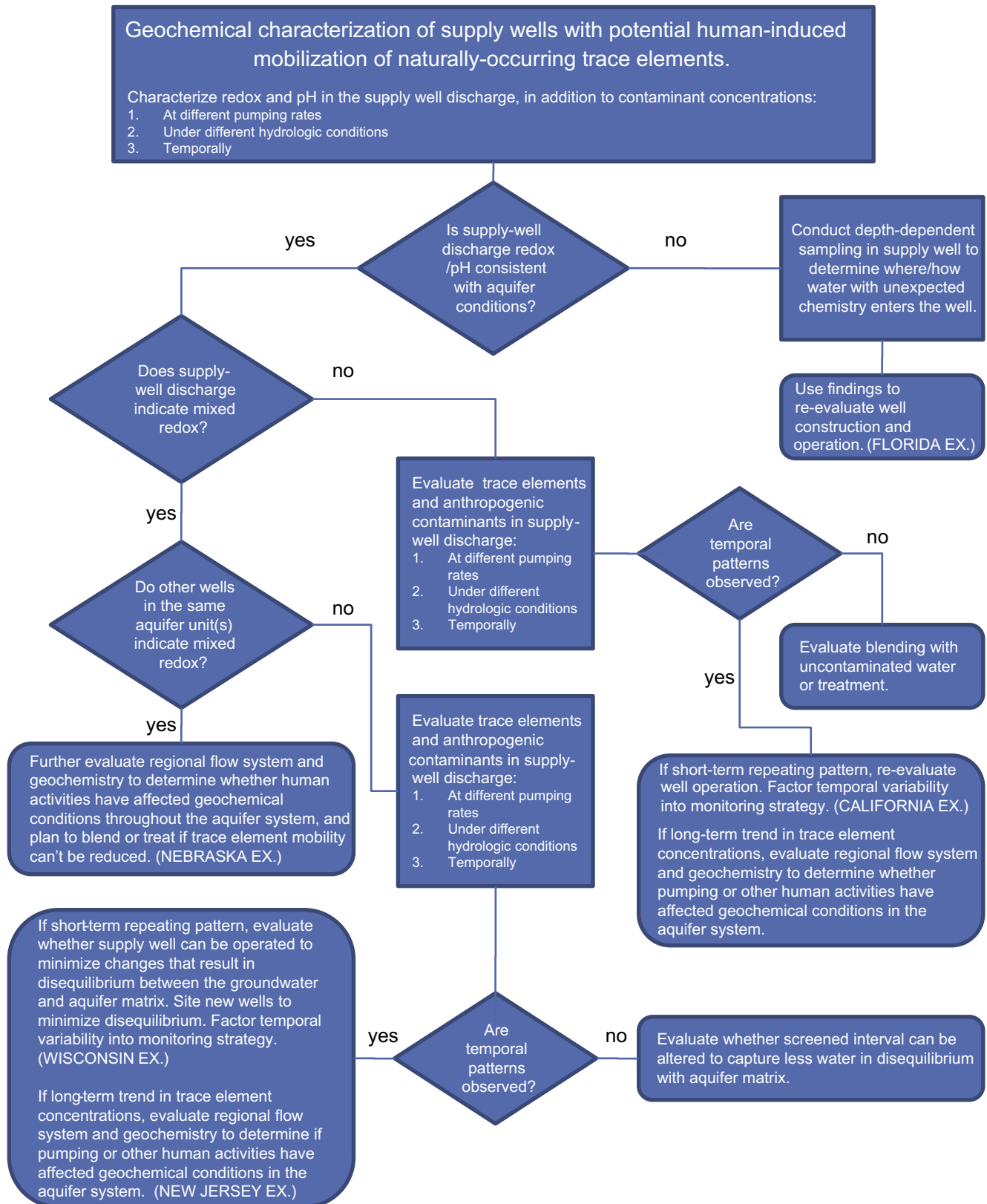
The movement and mixing of waters caused by water-supply well operation can result in changes in geochemistry (redox, ion exchange, ion complexation, dilution, or pH, among others). Often, combinations of these factors operate simultaneously and result in unexpected mobility of naturally-occurring trace elements. These human-induced changes are brought about by pumping stresses at individual supply wells (local mixing at or near the well), but more widespread pumping stresses (such as for irrigation) can affect the geochemical equilibrium of the groundwater system on a regional scale. Also, land application of chemicals superimposed on large, widespread groundwater withdrawals can act in concert to mobilize trace elements. In the case of Ra in groundwater of the Coastal Plain of New Jersey, it is the combination of the generation of low-pH and ion competition from agriculturally based  $\text{NO}_3$  and cations plus large-scale pumping that draws the affected waters through the aquifer toward PSWs. These changes ultimately lead to widespread mobilization of Ra by reducing the available sorption sites on the quartzose aquifer solids (Szabo et al., 1997). In the case of U in groundwater of the San Joaquin Valley, it is increases in alkalinity and in cations from agriculturally based activities (resulting in ion-exchange and U complexation), along with large-scale pumping, that lead to mobilization of U (Jurgens et al., 2008). In other instances, the addition of  $\text{NO}_3$  to the system can provide electron acceptors that can enhance rates of oxidation of minerals (perhaps sulfides) in the aquifer matrix and lead to increased concentrations of associated trace elements in the groundwater (Böhlke, 2002). Nitrate may be an alternative oxidant even in the Florida example.

An example from the United Kingdom provides an argument for the role of geochemical evaluation in water-resource decisions. In this example, geochemistry serves as criterion for the siting of PSWs whereby a natural redox boundary conducive to denitrification must be within the presumed zone of capture of the new well downgradient from the zone of  $\text{NO}_3$  contamination (Edmunds, 2009). The implication is that conducting monitoring programs at the appropriate scale and complexity to reflect the information needs for management of the quality of the water supply will enhance the effectiveness of water-management decisions.



High concentrations of naturally-occurring trace elements can occur in well water at any scale of capture zone (i.e., proportional to the pumping rate), and, therefore, the design of a monitoring strategy to collect the information necessary for successful identification of water quality concerns related to human health is, in

part, scale dependent. The degree of mixing of waters captured by a well is related to the pumping rate of that well and to the aquifer hydraulics. In a simple case, a small community supply well in a highly transmissive sand aquifer results in little displacement or mixing of waters, and simple monitoring might determine



**Fig. 8.** Flow chart for evaluation of human-induced flow-field changes and the potential for mobility of trace elements at a water-supply well.

the potential effect on water quality. If, however, the same aquifer were considered for large-volume withdrawals, or if there were other large withdrawals nearby (e.g., for irrigation), the possibility of extra-borehole geochemical disequilibrium would increase and characterization might require additional (regional-scale and depth-dependent) monitoring.

## 5. Discussion

Considering the sources of waters in the mixture reaching a PSW and the nature of aquifer materials from which the various waters are derived is important to understanding the chemistry of the bulk supply-well water. However, it is not enough to sample for water quality parameters of interest in the main aquifer and in the potential contributing aquifers; groundwater and aquifer-material geochemistry, pH, and redox conditions (or surrogates thereof) also are vital measurements because substantial quantities of naturally-occurring trace elements may not be present in the aqueous phase in the contributing aquifers but may be mobilized by the movement or replacement of water with water of a different geochemical condition. The water captured by the supply well may, therefore, be more degraded than the water in any given aquifer contributing to the mix.

A practical solution to address this “scale-of-monitoring” issue is to begin with characterization of the potential for the water captured by a supply well to represent a mix of waters with contrasting geochemical conditions (Fig. 8). A practical approach is to first determine the geochemical condition (including redox status) of the water in existing supply wells or monitoring wells (Fig. 8). Methods for inferring redox state on the basis of whether values of easily measured parameters (dissolved O<sub>2</sub>, NO<sub>3</sub>, Fe, Mn, SO<sub>4</sub> and H<sub>2</sub>S) are above or below “threshold values” are documented (Chapelle et al., 2009; McMahon and Chapelle, 2008), and a computer program to apply these methods is available (Jurgens et al., 2009b). In some cases, the input data required may already be available. Even a simple determination of redox state, such as “oxic,” “mixed,” or “anoxic,” would help in characterizing the geochemical status of captured water and to guide the next steps in determining a monitoring strategy (Fig. 8). Also, pH and specific conductance are readily measurable in the field.

Characterization of water samples from supply wells described in this study indicates that the waters can have a redox signature that is oxic (Florida, California), anoxic (Nebraska), or mixed (Nebraska, New Jersey) (Table 7). The redox character at the supply well might differ from the redox character interpreted for the aquifer

from water samples from monitoring wells, providing likely evidence of mixing. For example, concentrations of dissolved O<sub>2</sub> were slightly greater than the threshold value of 0.5 mg/L and resulted in a “mixed” characterization for most (depth-dependent) samples from the York, Nebraska, PSW in the generally anoxic upper confined aquifer.

The flow chart in Fig. 8 is a framework that illustrates the process of using easily obtained information on redox, pH, and other geochemical conditions to guide evaluation of the conditions encountered in a supply-well discharge. Starting at the diamond at the top of the flow chart, the discharge from the York supply well is generally consistent with known aquifer conditions in which the PSW is located (i.e., anoxic conditions), and the decision is to move to the left on the flow chart. Further evaluation of the supply-well discharge indicates that some mixing of aquifer waters is occurring. Additionally, data from the monitoring wells in the upper confined aquifer indicate that part of the aquifer has mixed or oxic conditions and part is anoxic, suggesting that the PSW screen spans a redox boundary or that short-circuit flow paths have enabled water from the surficial aquifer to flow into the upper confined aquifer (Fig. 8). This information leads to the decision to further evaluate regional flow and geochemistry to assess whether the PSW is affected by a larger-scale human-induced perturbation of aquifer. In the case of the York, Nebraska, PSW, regional-scale leakage between aquifer units through multi-aquifer wells contributes to trace element mobility.

Similarly, the redox condition of the New Jersey PSW, which captures generally oxic and NO<sub>3</sub>-rich water from shallow depths, is “mixed” by using the criteria of this classification scheme, largely because of the presence of Fe above the threshold concentration of 100 µg/L (Table 7). In this relatively thin coastal aquifer, the “mixed” characterization at the PSW may be related to mixing of Fe-rich water from a thin reducing zone at the base of the aquifer (Szabo et al., 1997), where neither O<sub>2</sub> or NO<sub>3</sub> was abundant (Fig. 7), but that is below the depth of shallow monitoring wells and domestic wells. In both examples (Nebraska and New Jersey), the inferred redox condition suggests that water captured by the PSWs is a mix of waters with differing geochemical signatures. In New Jersey, however, the monitoring-well data do not indicate that large-scale mixed redox conditions are occurring outside the PSW; thus, the flow chart leads to evaluation of temporal trends (Fig. 8) and, in this case, long-term trends were identified where pumping drives agricultural chemicals downward in the aquifer and the resulting geochemical changes (especially in pH) affect Ra solubility.

**Table 7**  
Inferred oxidation–reduction conditions for selected samples from water-supply wells (Depth refers to the depth of sample collection and represents an upwardly integrated sample in response to pumping near the top of the well; “All” indicates the sample was collected from the discharge of the pump; –, no data; sulfide in mg/L).

Supply-well location	Depth (m)	Threshold values <sup>a</sup>						Inferred redox		
		Dissolved O <sub>2</sub> 0.5 mg/L	NO <sub>3</sub> <sup>-</sup> (as nitrogen) 0.5 mg/L	Mn <sup>2+</sup> 50 µg/L	Fe <sup>2+</sup> 100 µg/L	SO <sub>4</sub> <sup>2-</sup> 0.5 mg/L	Sulfide none	Redox category	Redox process	
Tampa, FL	All	0.5	1.40	1.8	6	116	0.03	Oxic	O2	
	43	1	1.80	2	3	103	–	Oxic	O2	
	49	0.6	1.70	2.2	5	106	0.008	Oxic	O2	
	38	0.6	1.70	1.7	9	107	–	Oxic	O2	
Modesto, CA	All	4.6	7.23	0.1	1	28.3	–	Oxic	O2	
South-western, NJ	All	7.5	4.6	24	120	1.0	–	Mixed (oxic-anoxic)	O2-Fe(III)/SO4	
York, NE	All	0.8	0.18	356	163	45.2	–	Mixed (oxic-anoxic)	O2-Fe(III)/SO4	
	42.7	0.3	0.16	387	169	48.9	–	Anoxic	Fe(III)/SO4	
	45.7	0.4	0.15	400	179	53.0	0.03	Mixed (anoxic)	Fe(III)-SO4	
	48.8	0.7	0.19	419	238	67.4	–	Mixed (oxic-anoxic)	O2-Fe(III)/SO4	
	51.8	0.9	0.47	571	277	151	0.001	Mixed (oxic-anoxic)	O2-Fe(III)	
	61.0	0.6	0.15	474	455	107	0.008	Mixed (oxic-anoxic)	O2-Fe(III)	

<sup>a</sup> See McMahon and Chapelle (2008) and Jurgens et al. (2009a) for description of criteria for application of thresholds to infer redox.

The threshold values for redox parameters that are relevant for the determination of mixed redox conditions (Table 7) may differ for different aquifers and cannot necessarily be applied uniformly without considering the regional geochemistry. For example, using the thresholds without modification for samples from the Tampa, Florida, well leads to characterization of the waters as “oxic” (Table 7). However, closer inspection reveals that there is little dissolved  $O_2$  (0.5–1 mg/L), indicating anoxic conditions, and yet a substantial amount of  $NO_3$  is present (>1 mg/L), indicating sub-oxic conditions. Also,  $H_2S$  is detected in some samples, indicating a reduced source of S, such as sulfide minerals, or actual  $SO_4$  reduction. Absence of  $NO_3$  and concentrations of dissolved  $O_2$  lower than 0.5 mg/L in monitoring-well-water samples from the Floridian aquifer in which the PSW is completed indicates that a reservoir of anoxic water is present and that mixing with  $O_2$ - and  $NO_3$ -bearing water is occurring near, at, or in the PSW (Table 7; Fig. 4c). Mobilization of naturally-occurring As was the result. Thus, the composition of the PSW discharge water is generally consistent with that of the Upper Floridian aquifer water; but there is an indication that the mix of discharge water contains some surficial aquifer system water. This mixed condition leads to the right at the top of the flow chart, indicating that depth-dependent sampling may identify the source of the inconsistent water type that is captured by the PSW (Fig. 8).

In each of the cases described above, it can be broadly stated that in the unperturbed system, the waters become increasingly anoxic with depth and/or residence time along flow paths, but either short-circuiting or shortened travel times caused by the high-volume pumping result in a mixture of  $O_2$ - and  $NO_3$ -bearing water with waters that are far more anoxic (Fe- or  $SO_4$ -reducing) and the consequent assignment of the “mixed” redox category for the supply well. The utility of the redox characterization is that it provides a simple quantitative measure that can be used as a basis for the next steps in understanding the potential for trace element mobility in water from the supply wells. The assignment of the “mixed” redox category for a PSW indicates mixing is occurring and may also cause other substantial compositional changes that may further chemical disequilibrium and make trace element mobilization more likely, thereby indicating that a more comprehensive monitoring approach may be needed (Fig. 8).

Sampling under different pumping rates, depth-dependent sampling, solid-phase chemical analysis, geochemical modeling, or isotope tracer sampling (to determine recharge age and flow path) also might be considered (Fig. 8). For any supply well that appears to have “mixed” redox conditions, sampling under varied pumping or hydrologic conditions would be a useful next step, where both trace element data and redox information are collected (Fig. 8). The results of this analysis may be enough for understanding the system, or they may point toward the need for additional data collection or geochemical modeling. Tracking changes in redox conditions over time can be a key consideration for determining whether trace element mobility is likely in the future, perhaps when a critical redox threshold is reached, again providing guidance for the type and frequency of monitoring needed. Changes in the concentration of surficial anthropogenic contaminants—primarily  $NO_3$ , but also organic compounds—were a useful indicator of changing geochemistry in four of the cases presented (California, Florida, Nebraska and New Jersey). Other associated hydrogeologic and landscape factors such as large-scale withdrawals, large changes in land use, and regional water use can be evaluated to help guide geochemical data collection or development of flow and geochemical models.

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