

Protecting Groundwater Quality in California

MANAGEMENT CONSIDERATIONS FOR AVOIDING NATURALLY OCCURRING AND EMERGING CONTAMINANTS

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1. Introduction

Protecting groundwater quality is an essential component of sustainable water management. However, active groundwater management often focuses on maintaining groundwater quantity – a target that does not always ensure groundwater quality goals are met. In fact, there are many ways in which both supply- and demand-side management actions can inadvertently impact groundwater quality. These impacts range from improving groundwater quality to unintentionally creating new groundwater quality problems. For example, the implementation of a managed aquifer recharge (MAR) project aimed to increase groundwater supplies can mobilize soil contaminants (e.g., nitrate) into the underlying groundwater. Similarly, water trading programs can alter the timing, magnitude, and spatial distribution of pumping, potentially resulting in changes to irrigation return flows and contaminant loading. Potential water quality impacts of management actions are particularly important to consider in the context of the Sustainable Groundwater Management Act (SGMA) (see Box 1). However, if management actions are planned in a holistic way that incorporates both water quantity and quality considerations, unintended contamination can be avoided, and in some cases, groundwater quality can even be improved.

The purpose of this document is to provide guidance to groundwater managers, consultants, and stakeholders on groundwater quality considerations associated with management actions and methods for preventing unintended groundwater contamination. Specifically, this document focuses on naturally occurring (or geogenic) contaminants (e.g., iron, manganese, arsenic, chromium, uranium, vanadium, and selenium) and other contaminants for which limited guidance currently exists (e.g., 1,2,3-trichloropropane (TCP) and per- and polyfluoroalkyl substances (PFASs)). We focus on these specific contaminants due to their prevalence in California, their impacts to human and ecosystem health, and the lack of existing guidance for addressing these types of contaminants. This document does not address groundwater contamination by nitrate and salts; nitrate and salts are only discussed in the context of their interactions with geogenic and emerging contaminants. While nitrate and salts threaten groundwater quality in many regions throughout California, there are already a number of helpful resources and regulatory programs available that are specifically aimed at addressing these contaminants.^{1,2,3,4}

Water Quality and the Sustainable Groundwater Management Act

The 2014 Sustainable Groundwater Management Act (SGMA) requires local agencies to achieve sustainable groundwater conditions within 20 years. SGMA defines sustainability as the avoidance of six "undesirable results" including: (1) declining groundwater levels, (2) reduction of groundwater storage, (3) seawater intrusion, (4) degraded water quality, (5) land subsidence, and (6) depletions of interconnected surface water.

Degraded water quality is unique from other undesirable results in that it can be caused or exacerbated by water management actions aimed to help achieve sustainability goals. For example, a managed aquifer recharge project can improve groundwater levels and groundwater storage, mitigate seawater intrusion and land subsidence, and provide benefits to interconnected surface waters (avoiding all other undesirable results). However, the same managed aquifer recharge project can also adversely impact groundwater quality by transporting or releasing contaminants into groundwater.

Briefly, geogenic contaminants are naturally abundant in Earth's soils and sediments and can be released to groundwater under certain geochemical and hydrological conditions. Emerging contaminants are contaminants that have not previously been identified as water quality concerns and pose a risk to human and ecosystem health. They are typically unregulated, but often expected to become regulated as research and awareness of their health impacts grows.

In this paper, we first present a set of key considerations for protecting water quality to set the context for why it is important to consider groundwater quality outcomes at the onset of initiating any new management action. We then describe geogenic and emerging contaminants and their importance to water management (Section 2), and then outline the main processes controlling groundwater quality as it relates to these contaminants (Section 3). Section 4 highlights management considerations and guidance for protecting groundwater quality during the planning and implementation of new management actions. Finally, Section 5 provides expanded summaries of key contaminants and the processes controlling their fate and transport.

Summary of key groundwater quality considerations

A summary of the key groundwater quality considerations discussed in Section 4 are briefly described here. If management actions are planned in a holistic way that incorporates both water quantity and quality considerations, unintended contamination can be avoided, and in some cases, groundwater quality can even be improved. Some key considerations include:

1. Careful site selection for both groundwater quantity and quality

Management actions can cause improvements or unintended impairments to water quality depending on the type of action and site conditions that existed prior to the action. For instance, if a management action is planned in an area with pristine drinking water wells and no current groundwater quality problems, a shift in geochemical and hydrological conditions can cause the release of geogenic contaminants and/or the introduction and/or migration of other contaminants. However, if a project is being considered in an aquifer with previous contamination, it is possible that the proposed management action can provide groundwater quality improvements. Careful consideration should be given to both the site suitability for the management action and its proximity to drinking water supplies.

2. Characterization of current and anticipated geochemical and hydrological conditions

Understanding the current geochemical and hydrological conditions of a site is critical for both (1) identifying any existing water quality issues and (2) defining the existing conditions in order to avoid perturbations. If possible, avoiding any significant shifts in geochemical and hydrological conditions can help minimize the likelihood of causing or exacerbating contamination.

3. Development of a monitoring program

Anticipating potential changes in geochemical and hydrological conditions can help to inform a water quality monitoring program. For example,

certain contaminants are more likely to appear in groundwater when dissolved oxygen is introduced into an aquifer without previous exposure to oxygen. Based on the anticipated geochemical and hydrological shifts and site characterization, a list of the most likely contaminants can be determined. Monitoring programs should focus on these contaminants and on capturing critical geochemical and hydrological perturbations. Additionally, where possible, monitoring programs should be designed to allow sufficient response time between identification of water quality problems and arrival of contaminated water to users so that the problem can be addressed prior to reaching users.

4. Implementation of managed aquifer recharge projects

Managed aquifer recharge projects are the most likely management action to cause significant shifts in geochemical and/or hydrological conditions. Accordingly, such projects deserve special attention when evaluating potential water quality impacts. Recharging water, even clean water, into a previously uncontaminated aquifer can potentially alter the existing geochemistry and hydrology and subsequently cause the release of geogenic contaminants from soils and sediments. Specific considerations should be made for MAR projects including characterizing baseline aquifer geochemistry, the source recharge water chemistry and historical land use of the area selected for recharge. These considerations vary slightly depending on the type of MAR. A thorough understanding of the site-specific geochemical and hydrological conditions can inform the design of MAR projects that not only avoid new water quality problems, but also potentially offer water quality improvements.

5. Development of contingency plans

While precautions should be taken to avoid groundwater quality problems, a plan should be in place to address potential groundwater contamination events. This is particularly relevant if groundwater supplies are used for drinking water.

2. Geogenic and emerging contaminants

What are geogenic contaminants?

Geogenic contaminants are elements that naturally occur in Earth's soils and sediments. Some common geogenic contaminants include: iron, manganese, arsenic, chromium, uranium, vanadium, and selenium. These contaminants occur naturally in groundwater. Shifts in geochemical and hydrological conditions within an aquifer can cause new mobilization of these contaminants from primary minerals or release from soils and sediments into groundwater, where they pose a much larger risk to human and ecosystem health. Additionally, if groundwater is used for irrigation, these contaminants can threaten agricultural productivity.

Iron and manganese are only toxic at very high concentrations compared to the other geogenic contaminants discussed in this document; they are more commonly associated with taste and odor issues in water. However, iron and manganese are highly reactive in groundwater and can control the occurrence of other contaminants in an aquifer through their interactions with other contaminants. Arsenic, some forms of chromium, and uranium are toxic at very low (or trace) concentrations (on the order of micrograms per liter ($\mu\text{g/L}$)) and have both anthropogenic (man-made) and naturally occurring sources.

Naturally occurring contaminants have been increasingly associated with groundwater quality issues throughout California, particularly in the Central Valley. Vanadium is also increasingly being recognized as a groundwater contaminant, and health effects of vanadium exposure are actively being researched. While vanadium is currently not subject to enforceable regulation, it does have state drinking water Notification and Response Levels⁵, and it is anticipated to be considered for more formal regulation in the future.

Selenium toxicity is a greater threat to fish and waterfowl than human health, and notable issues of geogenic selenium exposure in waterfowl have occurred in the San Joaquin Valley as a result of irrigated agriculture drainage to wetlands.

Since the source of these contaminants is natural soils and sediments, which exist in spatially extensive layers and formations, contamination can occur over large areas. This potentially large scale and diffuse source

poses a significant and costly challenge for remediation once a contaminant has been released, emphasizing the importance of preventing their mobilization to groundwater.

Protection of groundwater quality requires managing aquifers so that geochemical and hydrological conditions are unlikely to cause contaminants to be released from soils and sediments into groundwater. These conditions are specific to each contaminant, can sometimes be contradictory (i.e., what is good for one is bad for another), and are further complicated by the complex interactions between contaminants and other water quality parameters.

Importantly, geogenic contaminants of concern occur in most groundwater at very low concentrations due to the ubiquity of many of these natural elements in the earth's crust – the materials and sediments derived from those rocks through which groundwater flows. Some of these elements are essential nutrients (e.g., some forms of chromium, selenium, iron, and manganese) and are important to human health. However, at contaminant-specific, higher concentration thresholds these geogenic elements become contaminants in drinking water or other beneficial uses of water and begin to pose a risk to human and ecosystem health.

What are emerging contaminants?

Emerging contaminants are contaminants that have not previously been identified or have only recently been identified as a water quality concern. Emerging contaminants often do not have established regulatory standards. Emerging contaminants may pose a risk to human and ecosystem health, though these risks may not be well understood.

Notably, vanadium is an emerging contaminant as it has no current regulation. Since it is also a geogenic contaminant, we include it in the discussion of other geogenic contaminants that behave similarly in the environment. We also discuss considerations related to 1,2,3-trichloropropane (TCP) and per- and polyfluoroalkyl substances (PFASs) which are both anthropogenic contaminants. PFASs have anthropogenic (man-made) sources and are currently unregulated. Similarly, TCP remained unregulated until 2017. We consider TCP an emerging contaminant despite its recent regulation because there remains a need for research and guidance to address TCP contamination in groundwater.

Anthropogenic contaminants can be *point source contaminants*, meaning they have specific, identifiable sources, or *nonpoint contaminants*, which originate from diffuse sources (e.g., runoff from large agricultural areas containing elevated concentrations of pesticides). TCP has both agricultural and industrial sources and can fall under either category. TCP is highly persistent in groundwater and is toxic at extremely low concentrations (on the order of nanograms per liter (ng/L)). It is important to prevent inadvertently placing new wells in areas with TCP contamination. Additionally, a disturbance to a groundwater aquifer can transport TCP into previously uncontaminated wells within the aquifer.

3. Factors controlling groundwater quality

Groundwater quality is controlled by the geology of an area, historic land use, and the resulting geochemical and hydrological conditions within the aquifer. While the geology and historic land use cannot be changed, management can significantly impact geochemical and hydrological conditions. Knowing the historic land use of a given region can help determine possible anthropogenic sources of contaminants. For example, the use of certain soil fumigants introduced TCP into groundwater at specific sites (see Section 5.8). Here, we provide an overview of relevant geological information related to the occurrence of geogenic contaminants. We also describe key geochemical and hydrological processes as they relate to overall groundwater quality.

3.1 Geology

The geology of an area determines which types of earth materials (minerals and organic material that make up soils and sediments) are present in an aquifer. Different sediment types have distinct chemical properties and concentrations of geogenic contaminants. While groundwater quality will ultimately be determined by how these particles respond to the geochemical and hydrological conditions in the aquifer, an understanding of the underlying and regional geology will provide some insight into which geogenic contaminants may be more problematic than others in a given region. During rock weathering, geogenic contaminants are deposited within the soils and sediments that compose groundwater aquifers.

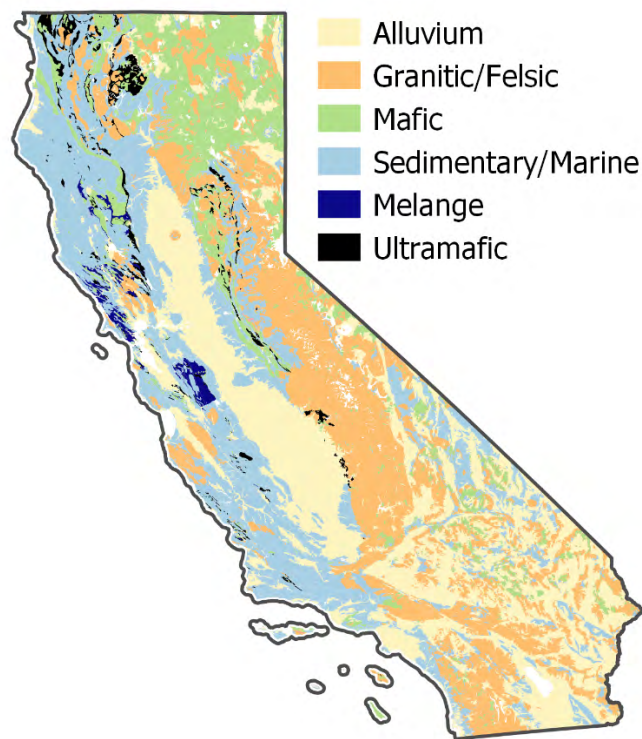


Figure 1: Map of relevant geologic features associated with various geogenic contaminants in California. Shales are included in the Sedimentary/Marine category. Map is adapted from the California Department of Conservation and California Geological Survey's geologic map of California (Jennings et al., 2010).

Figure 1 highlights key geologic features within California that are relevant to the geogenic contaminants discussed within this document. Following aluminum, iron and manganese are the second and third most abundant metal elements in Earth's crust, respectively. Therefore, they are found in high concentrations in soils and sediments and are ubiquitous within most geologic features especially in *mafic rocks*. Arsenic and uranium are found in higher abundance in granitic materials like those comprising the Sierra Nevada. The Sierra Nevada has weathered over time, leading to the deposition of sediments containing these elements within the Central Valley. Chromium is elevated in mafic and *ultramafic rocks*. Vanadium is also enriched in mafic rocks although generally not in ultramafic rocks. Both vanadium and selenium are also associated with the marine *shales* of the California Coast Range, with selenium particularly concentrated in the Southern Coast Range and in areas affected by hydrothermal fluids (naturally heated water found in the environment).

Continued rock and mineral weathering followed by alluvial (water) transport and deposition leads to the formation of soils and sediments that compose groundwater aquifers. While not all the aquifers in California are alluvial aquifers, they are the most relevant to the water management actions described here and we use them to introduce and describe concepts related to groundwater quality.

Most groundwater aquifers, including those comprised of alluvial sediments, are heterogeneous, meaning they have multiple discontinuous layers of different types of earth materials and sediments (Figure 2). These layers vary in both their chemical and physical properties. In general, shallow portions of an aquifer have higher amounts of dissolved oxygen (DO) in groundwater as they are closer to the surface and have likely been recharged more

recently, while deeper portions of an aquifer typically have older groundwater with limited DO concentrations.

The presence of oxygen and other substances affects the types of minerals and associated elements present in the aquifer. Portions of an aquifer with abundant dissolved oxygen (DO) tend to be rich in minerals like iron oxides (or rust particles/surfaces). Iron oxides are a critical mineral affecting the overall chemistry of groundwater and are discussed in Section 5.1. Deeper portions of an aquifer that typically have less abundant oxygen do not support the formation of iron oxides. Both the geochemical and physical heterogeneity of aquifers means that contaminant fate and transport can vary greatly throughout various zones of an aquifer, both vertically and laterally.

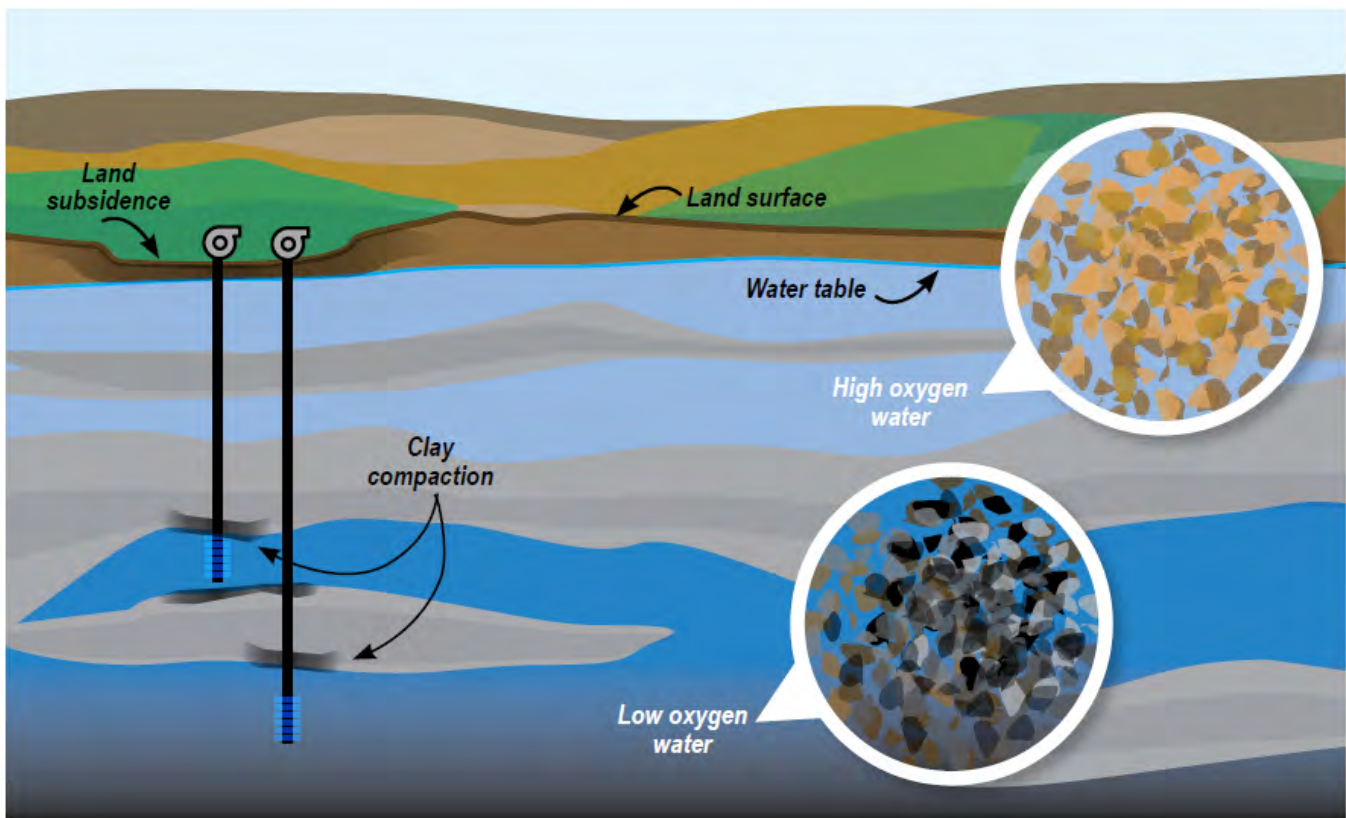


Figure 2: Generalized cross-section showing the physical and chemical heterogeneity of an alluvial groundwater aquifer system with interbedded clay layers. Shallower regions with higher oxygen abundance in groundwater tend to be enriched in minerals including orange-colored iron oxides while deeper regions with low oxygen content in groundwater tend to be enriched in darker-colored sulfide-bearing minerals. Additionally, activities like heavy pumping can compact clay layers affecting the physical (hydraulic) and chemical properties of the aquifer system.

3.2 Geochemistry

The fate and transport of contaminants depends on the geochemical reactions occurring within the aquifer system. The reactions of primary concern are those that occur at the interface between sediment materials and the surrounding groundwater. In general, contaminants are either incorporated into minerals, adsorbed to mineral surfaces, or dissolved in groundwater where they are transported by groundwater flow (Figure 3).

A contaminant that is dissolved in groundwater is considered mobile and is readily transported with the flow of groundwater. When contaminants are adsorbed to aquifer materials, they are no longer dissolved in groundwater. They can be transported when small particles (called colloids) move with the water; however, these particles are relatively easy to filter or settle out of water. In general, adsorption processes make groundwater contaminants relatively immobile unless a geochemical or hydrological trigger causes them to desorb from their host surface. Under some conditions, groundwater contaminants precipitate (form solids) and are removed from groundwater where they become immobile and remain on the aquifer solids.

Different contaminants have different levels of partitioning between the water and mineral surfaces (i.e., varying tendencies to adsorb to solids versus dissolve in groundwater) and are controlled by various chemical reactions. To avoid degrading water quality, management actions should promote geochemical conditions that favor maintaining contaminants on aquifer solids rather than geochemical conditions that release them

into groundwater, or those that ensure that any such mobilization is spatially limited such that it does not materially affect extracted groundwater quality. This is a technically challenging task as multiple contaminants co-occur within aquifer solids and have varying, sometimes opposite, geochemical conditions leading to release.

Examples of the types of geochemical conditions that can control contaminant retention and release include **reduction-oxidation (redox)**, *pH* (a measure of acidity), and *solubility* (ability to dissolve in water). Redox and pH refer to the state of the groundwater while solubility refers to properties of different substances found in both an aquifer's materials and groundwater. Below is a brief overview of redox, pH, and solubility as they relate to contaminant release. While the ionic strength and hardness of water can also influence its reactivity, these tend to be less concerning than shifts in redox and pH.

3.2.1 Redox reactions

Redox reactions are reactions that involve the transfer of electrons (particles with negative charge) from one substance to another. The *oxidation state* of a substance is a measure of how many electrons it has gained or lost relative to its elemental state (its pure, uncharged, and unreacted state). *Reduction* is a gain of electrons resulting in a decrease in oxidation state. Conversely, *oxidation* is a loss of electrons resulting in an increase in oxidation state. Substances gain or lose electrons by reacting with other substances. Dissolved oxygen (DO) is involved in many redox reactions and is a strong *oxidant* (it causes the oxidation of another substance, meaning it strips them of electrons).

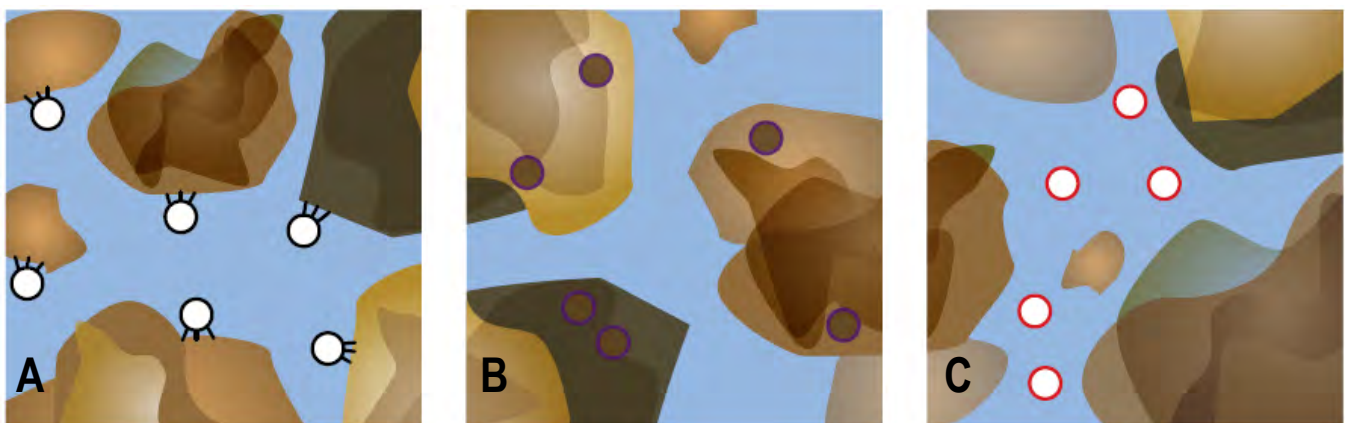


Figure 3: Contaminants in groundwater aquifers can either be (A) adsorbed to aquifer particles, (B) incorporated into aquifer particles, or (C) released to the surrounding groundwater.

Most geogenic contaminants are redox active, meaning that they are commonly found in more than one oxidation state, and each of these states may have different mobility and toxicity. For example, chromium in the environment can be found in both a trivalent (+3) oxidation state and in a hexavalent (+6) oxidation state. Trivalent chromium, Cr(III), is considered a micronutrient in human nutrition and is relatively immobile due to its low solubility and propensity to adsorb on aquifer minerals.

Generally, when oxygen is abundant, substances are more likely to be present in their more oxidized form.

By contrast, hexavalent chromium, Cr(VI), binds poorly to aquifer solids and is thus mobile in groundwater. It is also toxic to humans (at concentrations greater than 0.02 µg/L according to the Public Health Goal (PHG), see Section 5). Changes in redox conditions in an aquifer can cause trivalent chromium, Cr(III), to turn into the toxic, mobile hexavalent chromium, Cr(VI), and vice versa. Therefore, it is critical to understand the redox conditions in an aquifer and how management actions can cause redox conditions to shift. Even a small change in redox condition can have a large impact on contaminant behavior in groundwater.

There are methods for determining the redox conditions within an aquifer. Groundwater monitoring wells can be measured for oxidation reduction potential (ORP), which is a commonly used metric for redox condition. Interpreting ORP as a standalone measurement can be challenging because the measurement depends on a reference measurement that can vary depending on the ORP method used. However, ORP is useful as a relative indicator of changes in redox condition. Sharp changes in ORP can signal that redox conditions within an aquifer are changing, and therefore shifts in groundwater quality could also be occurring.

Dissolved oxygen (DO) is also often used as a proxy for redox conditions within an aquifer. Generally, when oxygen is abundant, substances are more likely to be present in their more oxidized form. When oxygen is absent or very low, contaminants are more likely to be present in their more reduced form. For simplicity, we will use the terms *oxygen-abundant* (DO > 2 mg/L) and *oxygen-limited* (DO < 2 mg/L) to describe the redox conditions of an aquifer.

For example, the impacts of DO on redox condition can be visually observed with iron. In groundwater with no exposure to oxygen, iron is well-dissolved and mobile in groundwater. With exposure to DO, iron oxidizes and forms rusty solid particles (or iron oxide minerals) that separate out of water and/or coat other mineral surfaces (Figure 4). These rust particles range in color from yellow to red, with orange predominating, and can be seen in soils and sediment which have been exposed to oxygen.

Knowing the DO concentration of water is a strong indicator of whether iron will be dissolved in water or present as an iron oxide solid. More generally, knowledge of oxygen concentrations can serve as a useful proxy for redox condition and understanding of which geogenic contaminants may exist in groundwater. Measurement of DO is typically easier and more cost-effective than analyzing trace metal concentrations. Therefore, it can be measured more frequently than other *analytes* (the substances being measured) in a monitoring program. Based on which redox-sensitive analytes are measured, the redox processes occurring can be more thoroughly characterized using existing United States Geological Survey (USGS) resources for characterizing redox chemistry.⁶



Figure 4: Oxygen-limited (anoxic) groundwater rich in dissolved iron seeping into a stream, oxidizing due to exposure to the atmosphere where oxygen is abundant. This causes oxidation of the dissolved iron to occur, converting it into solid iron oxides (rust particles). (Photo credit J. Walton <http://windowoutdoors.com/WindowOutdoors/Iron%20in%20Springs%20and%20Seeps.html>)

3.2.3 pH

pH is one of the most important groundwater quality parameters and often strongly correlates with the presence of different contaminants. Low pH values are acidic and higher pH values are basic. Typical groundwater pH values fluctuate near neutral (pH of 7). Groundwater pH depends on the composition of the groundwater (i.e., which substances are present) and the chemical reactions occurring within the aquifer. For example, aquifers with high carbonate concentrations tend to have a higher pH and a high buffering capacity (meaning pH does not easily change). pH affects the substances dissolved in groundwater because certain chemical reactions are more likely to occur at higher or lower pH values.

Similarly, a solid mineral surface can be positively or negatively charged depending on the pH, and this in turn affects the ability of contaminants to adsorb to those surfaces and be removed from the groundwater (Figure 5). pH can also make certain minerals in sediment particles or within the rock structure more or less likely to dissolve in groundwater. In general, negatively charged ions (such as arsenic) are more mobile at high pH (> 8.5), while positively charged ions (such as iron and manganese) are mobilized at low pH.

3.2.4 Solubility and groundwater age

Solubility in the context of groundwater geochemistry refers to the maximum concentration at which a

substance can be found dissolved within groundwater. Solubility can refer to solids (e.g., minerals), liquids (e.g., solvents, pesticides), and gases (e.g., oxygen, carbon dioxide) and their ability to dissolve in water. Some of these substances are more likely to dissolve (i.e., more soluble) compared to others. For example, table salt (sodium chloride) is highly soluble and dissolves when mixed with water, releasing both sodium and chloride ions into the surrounding water.

The materials that adsorb or contain contaminants have varying degrees of solubility. In the presence of water, highly soluble materials will not retain their solid form in water and will dissolve, releasing contaminants embedded within the sediment particle/rock matrix to groundwater. Insoluble contaminants will stay in the sediment particle/rock matrix and will not contaminate groundwater unless conditions promoting their dissolution evolve. For example, under certain geochemical conditions arsenic will reside in a sulfidic (sulfide-containing) mineral called arsenian pyrite. This mineral has limited solubility but can dissolve under certain low pH and/or oxygen-abundant conditions, causing arsenic to be released into groundwater.

The rate (how quickly) a substance dissolves also determines how likely it is to be found in groundwater. Near natural recharge sources, such as streams, groundwater may contain relatively small amounts of total dissolved solids (TDS) which is a measure of the amount of dissolved *species*. This is because the water is not in equilibrium with the soils and sediments (i.e.,

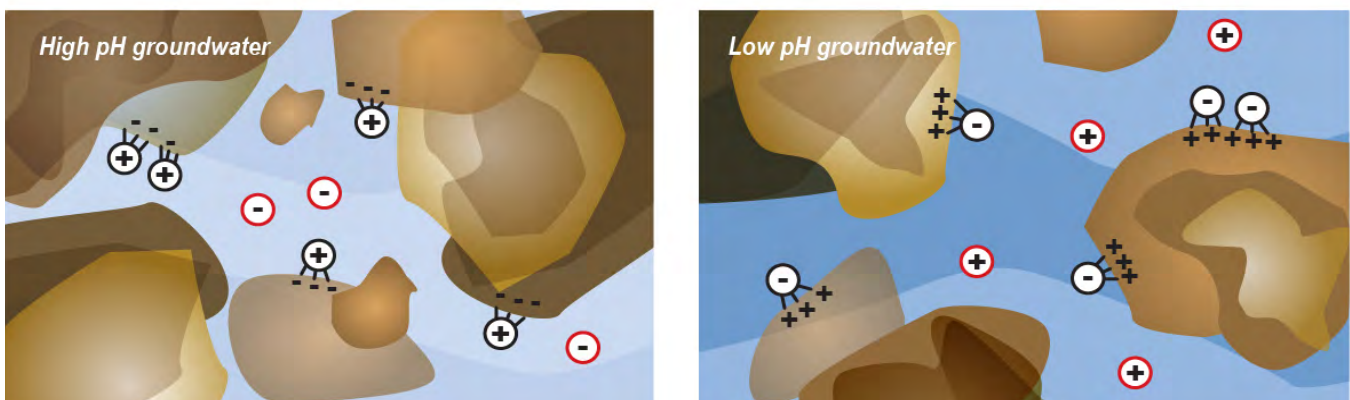


Figure 5: Schematic showing pH effects on charged particles. Mineral surface charge changes with the pH of the surrounding groundwater, causing changes in the type of contaminant likely to occur in groundwater.

the minerals in soils and sediments have not had time to dissolve because freshwater is recharging faster than the minerals are dissolving). The mineral surfaces of the sediment particles gradually dissolve over time.

These rates are an important concept relating groundwater chemistry to groundwater age. Older groundwater is typically more enriched in TDS (including naturally occurring contaminants) compared to younger groundwater. However, younger groundwater will often respond quicker to management actions owing to shorter recharge times. More information relating groundwater age to groundwater vulnerability is available through the USGS.⁷

3.3 Hydrological impacts on geochemistry

The hydrology and geochemistry of a groundwater system are closely intertwined. As water flows in the subsurface, it carries contaminants as well as other dissolved (or aqueous) substances which can react with each other. Additionally, many of the chemical reactions occurring in groundwater occur at different timescales; some are very fast while others are extremely slow. Generally, groundwater moves slowly, allowing enough time for reactions to occur between aquifer solids and groundwater. However, in heavily pumped or managed systems, groundwater movement can be accelerated and the aqueous substances in the groundwater may have less time to react with aquifer solids.

A significant rise or fall in the depth of the water table in response to pumping or recharge will also change the interaction between groundwater and the overlying unsaturated (vadose) zone, potentially affecting contaminant partitioning between the solid and mobile, dissolved phase. Depending on which chemical reactions are possible in a given aquifer, this can either have a positive, negative, or minimal impact on groundwater quality. In summary, the physical movement of groundwater can induce different types of geochemical responses.

4. Protecting groundwater quality

4.1 Managing for both groundwater quantity and quality

To the extent possible, management actions should be planned in a holistic way that incorporates both water quantity and quality considerations. Special caution should be taken if a new management action is planned in an area containing drinking water wells with no current groundwater quality problems. In these locations, there is a risk of causing groundwater contamination by changing the geochemical and hydrological conditions within the aquifer that may lead to the release of geogenic contaminants.

By the same token, if a project is being considered in an aquifer with existing contamination, it is important that the problem not be worsened by management actions. It is possible to design a proposed management action in ways that may provide groundwater quality improvements. For example, if a proposed managed aquifer recharge project does not create adverse shifts in water quality (i.e., no shifts in redox or pH which release contaminants), it has the potential to reduce existing contaminant concentrations.

Understanding the geochemical and hydrological conditions in these cases will be critical to anticipating whether contaminated water can potentially be diluted or will spread contamination to previously uncontaminated areas of the aquifer. Table 1 lists common water management actions and how they might impact groundwater quality. As mentioned previously, these projects can also offer water quality improvements. However, here we focus on the protection of groundwater supplies and prevention of unintentional, new contamination resulting from management actions. Additionally, while we provide general guidance, much of the considerations will depend on site-specific characteristics and local contaminants of concern.

TABLE 1

Common water management actions and potential impacts

Management action	Common examples	Potential water quality impacts
Managed aquifer recharge (MAR)	Infiltration ponds	If the infiltrating water is of a different chemistry than the native groundwater, geochemical changes can occur during infiltration (e.g., change in pH, redox chemistry). Infiltration processes gradually introduce recharge water which can allow enough time for the aquifer sediments to buffer changes in water chemistry. Infiltration can alter the shallow groundwater levels and/or cause a fluctuating water table. Resulting changes in the water table and the wetting and dewatering of shallow sediments can induce changes in redox chemistry.
	Injection wells	Potential impacts are similar to those of infiltration ponds (i.e., differences in recharge water chemistry and native groundwater chemistry can cause adverse interactions). However, during direct injection, these changes are likely to be more abrupt compared to infiltration processes as injection wells can also alter the flow regime and can cause faster transport between different zones of the aquifer.
	Agricultural managed aquifer recharge (Ag-MAR)	Ag-MAR involves the use of irrigation water for recharge on agricultural lands during fall, winter, and/or spring. Because the water has continuously been introduced to the aquifer through previous irrigation, it is unlikely to create new, abrupt changes to geochemical conditions. Since volumes of recharge water are similar to past recharge volumes, hydrological conditions would not be expected to deviate strongly from historic conditions. These areas can still mobilize contaminants, but new and significant water quality problems are less likely to occur compared to other types of recharge.
	Flood-managed aquifer recharge (Flood-MAR)	Flood-MAR involves the use of flood water from rainfall or snow melt for recharge on agricultural and working lands (e.g., refuges, floodplains). Here, the recharge water may be of differing chemistry than the native groundwater or previously applied irrigation water which may cause geochemical changes releasing geogenic or other existing contaminants. Additionally, hydrological changes may also occur and contribute to the transport of contaminants and/or changes in the underlying water table. The Department of Water Resources is working to identify research needs, including water quality, for Flood-MAR projects (see Section 4.4).
Changing timing, magnitude, and/or spatial distribution of pumping	Water trading	Trading programs can change the volume and use of groundwater supplies in ways that may affect return flows, magnitude and timing of pumping, and contaminant loading. Some examples include (1) increasing pumping in an area with deteriorated water quality and subsequently causing the migration of contaminants or (2) increased water use by a user with higher contaminant loading, resulting in higher contaminant concentration in return flows.
	New pumping	New pumping can increase vertical and lateral movement of water, resulting in transport of contaminants or reactants that may induce contaminant mobilization. Pumping in new regions of an aquifer can also cause fluctuating water tables which can alter geochemical conditions.
	Retiring wells	While inactive wells are no longer causing movement of groundwater via pumping, they can still serve as conduits for groundwater. Shallow groundwater, often of poorer quality, can migrate downward and degrade deeper water supplies (Gailey, 2017).

When planning and selecting locations for a new management action, careful consideration should be given to the proximity of the management action to production wells and the ultimate end use of water produced from those wells. As a first principle, it is best to exercise caution to avoid actions that are likely to cause significant geochemical and/or hydrological changes in the vicinity of clean drinking water supplies.

If a management action in the vicinity of clean drinking water supplies is required, appropriate stakeholder engagement is necessary to ensure that the whole suite of community and stakeholder considerations is acknowledged in shaping the proposed project. To aid in this process, Community Water Center (CWC) has developed guidance focused on protecting drinking water under SGMA.^{8,9} Projects in these areas can take the three steps outlined below to help protect groundwater quality.

Step 1. Characterize existing groundwater quality issues where new management actions are planned.

Any existing groundwater quality issues should be identified when first planning management actions in order to avoid exacerbating or spreading existing contamination. Precautions should also be taken to avoid causing new contamination. Any available groundwater quality data should be analyzed to understand which contaminants are currently present and what trends exist for those contaminants, both spatially and temporally (i.e., Do concentrations vary seasonally? Is it a constant problem? Are concentrations increasing over time or is it getting worse?).

A summary of publicly available datasets is included in a report by Stanford University's Program on Water in the West, titled "A Guide to Water Quality Requirements under the Sustainable Groundwater Management Act" (Moran and Belin, 2019). All water quality data collected by water agencies is also publicly available via formal public records request if it is not otherwise accessible via a state or local database.

Additionally, if groundwater age data is available, it can help estimate how quickly groundwater quality will respond to new management actions. Younger groundwater tends to be more responsive to new management actions than older groundwater supplies.

Step 2. Anticipate how aquifer geochemistry and hydrology might change as a result of the planned management action.

Anticipating changes to aquifer geochemistry and hydrology requires a knowledge and understanding of the existing geochemical and hydrological conditions. Of key concern are indicators of redox condition (both DO and ORP), pH, and water composition (concentrations of substances including salts, carbonates, sulfates, phosphate). A change in redox condition is the most likely to trigger the release of geogenic contaminants, followed by a change in pH and then ionic composition (the type and concentration of different ions in the water). If the management action involves introducing a new water source into the aquifer (e.g., MAR with surface water in a region where previous recharge has been primarily from irrigation reliant on groundwater), characterizing the chemistry of this new water source will help determine if any adverse shifts may occur.

The principal means by which a shift in redox can occur is either the influx of water with differing oxygen levels or influx of an organic carbon compound that stimulates biological (e.g., bacterial) activity and the subsequent consumption of oxygen. For example, if a MAR project introduces high concentrations of organic carbon (e.g., recycled wastewater) into an oxygen-abundant aquifer, oxygen may be consumed and reducing conditions may evolve within the now oxygen-limited aquifer. Similarly, if a recharge project introduces water with high DO concentrations into a previously oxygen-limited aquifer, a shift in redox will occur.

pH-related release of certain contaminants can occur when infiltrating or injecting recharge water with a differing pH than the native groundwater. A shift in pumping regime can also cause the mixing of groundwaters with various chemistry if water from various regions within the aquifer is being transported to new locations. Therefore, it is important to obtain information on baseline geochemical conditions (including pH, DO, ORP) and, if available, any previously collected soil and/or sediment analyses or samples (e.g., soil cores and drill cuttings). These samples can be used for laboratory analysis to determine their composition and likelihood of contaminant release.

Step 3. Potential management strategies can be identified to minimize adverse changes in geochemical conditions.

Limiting changes in geochemical and hydrological baseline conditions will help limit potential adverse impacts. For instance, if recharging water, is it possible for the recharge water to have a more similar geochemical composition to the native groundwater? This could be achieved by pretreating recharge water or using an alternate source of water for recharge. If matching source water chemistry is not possible, see Table 2 to determine which contaminants to prioritize in a robust monitoring program.

Soil and aquifer sediment samples (e.g., soil cores and drill cuttings) also provide valuable information about the aquifer solids and the chemical state of contaminants residing within those solids, but are more expensive than water sampling. If there is potential for significant geochemical shifts, sediment samples should be obtained to measure the abundance of various natural contaminants in the region where the management action is taking place and what chemical form these contaminants are in.

In some areas, it may be possible to retrieve old samples from previous well drilling or core activity as a more cost-effective way of obtaining samples. While older samples may not retain the same chemical properties as those found *in situ*, they can provide valuable information about the total contaminant concentrations. It is possible that soils or sediments can contain high concentrations of certain contaminants either naturally or as a result of historic anthropogenic inputs that accumulate. Soil and sediment heterogeneity pose a complex challenge to sampling as concentrations can vary greatly within small spatial areas. Priority sampling locations should be in the region closest to the proposed management actions where the most significant shifts in geochemical and/or hydrological conditions are likely to occur. For a MAR project that includes use of recycled water, the construction of required monitoring wells presents an opportunity to collect aquifer solids samples.

For the installation of new water supply wells and associated well screening, it should be taken into account that wells can affect the transport and mixing of water from different zones within an aquifer (Gailey, 2018). For example, if contamination exists in a shallow portion of the aquifer, high rates of deep pumping can draw shallow groundwater down over time. Additionally,

production wells with large screened intervals can serve as a preferential pathway connecting and transporting groundwater from different depths and potentially of varying quality. Generally, clay layers are likely to have more elevated concentrations of geogenic contaminants. While wells are typically not screened in clay layers because of their poor hydraulic conductivity, caution should be taken to avoid these layers for groundwater quality considerations as well.

4.2 Managing for co-occurring contaminants

It is likely that there will be multiple contaminants to consider and monitor, including geogenic and emerging contaminants as well as nitrates and salts. As an oxidant, nitrates create problems for geogenic contaminants that are released under oxidizing conditions, which include uranium and selenium. The co-occurrence of contaminants can be exacerbated in projects that mobilize nitrate into systems with limited prior exposure to oxygen or other oxidants.

The migration of dissolved salts into groundwater supplies can also have adverse impacts for other contaminants. One concerning example of this is the migration of high calcium and carbonate waters into groundwater prone to uranium release. Calcium and carbonate can react with uranium to form a complex that prevents uranium from adsorbing to solids and releases it into groundwater (see Section 5.5).

Table 2 describes the geochemical conditions that can cause the release of each contaminant. Rather than considering each contaminant as an individual management concern, contaminants can be conceptually grouped by the geochemical conditions that cause their release. Then, management actions can be taken to avoid specific geochemical conditions and the group of contaminants associated with those conditions. In general, trying to maintain native aquifer geochemical conditions will minimize the likelihood of releasing new contaminants.

TCP and PFASs are not included in Table 2 as they are not geochemically released like geogenic contaminants. Sections 5.8 and 5.9 provide specific information related to the management of TCP and PFAS contaminated aquifers, respectively.

TABLE 2

Groundwater conditions that can result in an increase or decrease in the mobility of each contaminant

Contaminant	Contaminant Mobility Due to Aquifer Conditions				Aquifer conditions to avoid
	Oxygen-abundant	Oxygen-limited	High pH	Low pH	
Iron (Fe)	↓	↑	↓	↑	Oxygen-limited, low pH
Manganese (Mn)	↓	↑	↓	↑	Oxygen-limited, low pH
Arsenic (As)	↓	↑	↑	↓	Oxygen-limited, high pH, high phosphate, compaction of clay layers from overpumping
Chromium (Cr)	↑	↓	↑	↓	Oxygen-abundant, high pH, fluctuating water table
Uranium (U)	↑	↓	↑	↓	Oxygen-abundant, high pH, high bicarbonate, high nitrate
Vanadium (V)	↑	↓	↑	↓	Oxygen-abundant, high pH
Selenium (Se)	↑	↓	↑	↓	Oxygen-abundant, high pH

4.3 Developing a monitoring program

A monitoring program will be critical for new management projects where an initial assessment determined that existing geochemical and hydrological conditions may be perturbed. A survey of existing wells appropriate for monitoring and resources available for drilling additional monitoring wells will help determine how best to deploy new monitoring efforts.

Detailed design of a water quality monitoring program is beyond the scope of this report, but the following are some suggestions to inform early thinking and conceptualization of a rigorous monitoring program. Design of an appropriate water quality monitoring program should be conducted by a qualified professional in an adaptive process with thorough stakeholder engagement. More detailed resources and guidance on monitoring networks and programs are available through the California Department of Water Resources (DWR).^{10, 11}

Monitoring wells should provide adequate spatial and temporal coverage to identify groundwater quality

problems in a timely manner. Spatial requirements will depend on the scale of the project and regulatory requirements. Understanding the flow and transport conditions in the aquifer will be critical for determining the spatial extent of monitoring. Accordingly, groundwater flow (level) monitoring should be used to help design appropriate groundwater quality monitoring programs, since groundwater gradients determine the direction and speed of groundwater flow.

Coupled with and informed by the groundwater level monitoring, groundwater flow models with particle tracking and/or mass transport capabilities or planned empirical tracer tests can help determine how fast and in which directions groundwater is moving further informing the appropriate design of water quality monitoring programs. This is important because there are often delayed effects; problems can arise as water moves downgradient. Monitoring wells should be placed in locations between the new project and production wells/users in such a way that provides sufficient response time should a migrating groundwater problem be observed. If groundwater quality issues are first observed in drinking water wells or in monitoring wells placed too close to the supply well to provide an adequate response time, it will be too late to address the issue before contaminated water reaches users.

Additionally, monitoring wells should span the impacted depths of the aquifer. Multi-screened wells and/or nested wells provide depth resolved data and should be used where appropriate.

Temporal coverage should allow enough frequency of monitoring to capture seasonal and short-term trends in groundwater quality. Seasonal variation in geochemical and hydrological conditions occurs naturally, and similarly, management projects often have seasonal variation (e.g., recharging in specific seasons). Looking at historical seasonal trends of groundwater quality data can provide some insights into the timescales of seasonal trends in a given location. It should be noted that seasonal timescales may vary year to year and with future variations in dry and wet conditions.

Lastly, measuring contaminants at trace concentrations is often expensive and requires laboratory instrumentation. If it is not feasible to directly measure trace contaminants on a regular basis, then close attention should be paid to the measurement of other common water quality parameters that control contaminant concentrations. Most critically, monitoring programs should include regular measurement of pH, dissolved oxygen, and ORP as proxies for the geochemical conditions in the aquifer. These parameters can be measured *in situ* at relatively low cost. Should shifts in pH, DO, and/or ORP be observed in monitoring data, there is a higher likelihood that contaminant mobilization is occurring, and samples should be taken immediately to assess whether contaminants are present. Table 2 summarizes which contaminants are most likely to occur under various geochemical conditions.

4.4 Careful implementation of managed aquifer recharge

Managed aquifer recharge is an increasingly applied method of artificially recharging groundwater aquifers. Of the possible management actions discussed in this document, MAR projects are the most likely to alter the native or preexisting geochemical and hydrological conditions within an aquifer. Accordingly, in addition to the above general guidelines, we highlight some specific recommendations for MAR. There are various types of MAR projects and each can have differing impacts on the geochemistry and hydrology of a site as summarized in Table 1.

First, the extent to which MAR will cause new changes to geochemical and hydrological conditions depends

on historic recharge and land use in the area. For example, in the case of Ag-MAR, the volume and chemistry of the recharge water is the same (or very similar) to historic irrigation. Therefore, geochemical and hydrological conditions are not likely to deviate substantially from preexisting conditions, which may be less concerning for the release of geogenic contaminants as compared to other types of recharge. For Ag-MAR, knowing the historical nutrient and pesticide application is important for determining the likelihood of anthropogenic contaminants like TCP and nutrient release to groundwater. By contrast, MAR via injection wells can cause a direct, abrupt change in water chemistry. For example, if an injection well is drilled in a deep, confined aquifer with limited prior exposure to oxygen and oxic water is used for recharge, a sudden shift in redox chemistry can occur and cause the release of geogenic contaminants.

In general, sandy soils are less likely to contain, and subsequently release, geogenic contaminants. Agricultural areas will have additional water quality considerations related to legacy pesticides, nitrate, and salts. Recharge projects can be designed to help dilute pesticides, nitrate, and salt. However, in addition to mobilizing these substances, introducing nitrate and salts into the underlying groundwater can impact geogenic contaminants in the area. For example, nitrate can transform uranium into a more mobile form (see Section 5.5).

Calcium and carbonate can be introduced into underlying groundwater supplies and can also react with uranium to increase its mobility in groundwater. In general, prioritizing areas with sandy soils that have high infiltration rates and low calcium and carbonate contents is beneficial to avoiding issues related to uranium release. Additionally, continued use of the same infiltration site will deplete calcium and carbonate concentrations, decreasing the threat of contaminant mobilization over time compared to developing new recharge sites.

Water quality impacts of MAR remain a subject of ongoing research. Information and expertise specific to managed aquifer recharge on agricultural lands using flood water from rainfall or snowmelt (Flood-MAR) is currently being developed by DWR.¹² Current research at the University of California Santa Cruz includes the use of permeable reactive barriers made of woodchips for changing redox chemistry to remove nitrates during MAR via infiltration at a site in Pajaro Valley, CA (Beganskas et al., 2018).

4.5 Developing a contingency plan for groundwater contamination

After all necessary precautions have been taken to avoid creating new contamination or exacerbating existing issues, a plan should be developed if a groundwater contamination event occurs. This is particularly important if groundwater supplies are used for drinking water. The plan should account for how to (1) increase or augment monitoring, (2) assess the potential for end user well contamination, (3) notify users of water supplies, and if necessary, (4) provide alternate, safe water supplies, (5) discontinue use of affected water supplies as needed, (6) address the contamination by remediation or permanently discontinuing use, and (7) develop targeted future monitoring once the problem has been addressed to ensure it does not occur again. Having a plan for how to address these points will lead to improved response times and protection of water users.

5. Contaminant summary overview

Each contaminant behaves uniquely in the environment and is affected differently by various management actions. In this section, we provide a brief summary of each contaminant and its mobility in the environment. We include the public health considerations and regulatory limits. Some contaminants are regulated using a primary maximum contaminant level (MCL) while others have a secondary MCL. In California, the State’s primary and secondary MCLs are enforceable. MCLs are determined based on the technical and economic feasibility of water treatment for each contaminant in addition to their toxicity to human health.

Notification Levels exist for certain contaminants that do not have MCLs and represent the concentration at which certain public notification requirements and recommendations apply depending on the contaminant. Notification Levels may turn into MCLs as toxicological and public health knowledge of a contaminant increases.

Finally, California’s Office of Environmental Health Hazard Assessment (OEHHA) has public health goals (PHGs) for certain contaminants that are non-enforceable goals based only on toxicity and health hazards. These are summarized for each contaminant in Table 3. Detailed information on regulatory requirements surrounding groundwater quality is provided in a report

recently published by Stanford University’s Program on Water in the West titled “A Guide to Water Quality Requirements under the Sustainable Groundwater Management Act” (Moran and Belin, 2019).

TABLE 3
Regulatory limits and public health goals for California

Contaminant	Level of regulation	Limit	Public Health Goal (OEHHA)
Arsenic	Primary MCL	10 µg/L	0.004 µg/L
Chromium	Primary MCL	50 µg/L (total)	0.02 µg/L (hexavalent)
Uranium	Primary MCL	20 pCi/L	0.43 pCi/L
Vanadium	Notification level	50 µg/L	-
Manganese	Secondary MCL	50 µg/L	-
Iron	Secondary MCL	300 µg/L	-
Selenium	Primary MCL	50 µg/L	30 µg/L
1,2,3 TCP	Primary MCL	0.005 µg/L	0.0007 µg/L
PFASs	Notification level	0.013 µg/L for PFOA	-
		0.014 µg/L for PFOS	-

Each contaminant summary in this section shows maps of groundwater concentrations over the last year (January 2018 – January 2019) of available data from the Groundwater Ambient Monitoring and Assessment (GAMA) Program (SWRCB, 2018a). Groundwater concentrations are listed as mass of contaminant in micrograms per liter of water. These data are obtained from multiple sources including the GAMA Domestic Well Project, the USGS, Lawrence Livermore National Lab (LLNL), and public water system well data collected by the State Water Resources Control Board’s (SWRCB’s) Division of Drinking Water (DDW). For PFASs which are more data-limited, we include all available measurement for public supply wells on the GAMA website, which spans a measurement period from August 2016 – May 2019.

It should be noted that these data are collected at various times of year and different aquifer depths. Variation in temporal trends and depth often occurs and cannot be inferred from these maps. Additionally, these data include contamination from both anthropogenic and natural sources. We present these data to provide an overview of the magnitude of concentrations generally observed in California as well as the spatial extent of each contaminant’s impact on groundwater quality.

Similarly, we show soil concentrations for each map from the USGS mineralogical database (Smith et al., 2014). Soil concentrations are listed as mass of contaminant in milligrams per kilogram of bulk soil, with the exception of iron which is listed at percent iron by weight of the bulk soil owing to iron's high abundance in soils. The soil concentrations are shown for the C horizon, which is approximately 2.6-3.3 feet deep within the soils examined, and consists primarily of unconsolidated, weathered parent material (i.e., rock or deposited sediments).

Soil C horizons are much shallower than groundwater aquifers and wells. These soil concentration maps do not provide depth information about geogenic contaminants. Ultimately, contaminant concentrations within the aquifer waters will depend on several factors including the chemical conditions of the aquifer and historic anthropogenic inputs. We show the soil C horizon maps to offer a general summary of the abundance of these contaminants as well as their relationship with underlying geologic formations.

5.1 Contaminant Summaries

Within this section, we begin with summaries of iron and manganese. Iron has limited toxicity and is of concern only at very high concentrations. Furthermore, iron and manganese solids are highly reactive in groundwater systems and are presented first because they (1) have major impacts on the overall chemistry of an aquifer, often regulating the concentration of contaminants through adsorption processes, and (2) are excellent indicators of the redox condition of an aquifer. Next, we provide summaries for arsenic, chromium, uranium,

vanadium, and selenium. Finally, we discuss TCP as an emerging contaminant of critical concern.

5.2 Iron

5.2.1 Background

Iron is an essential nutrient for human health at low concentrations and has a secondary MCL of 300 µg/L. Compared to other contaminants discussed in this document, it is much less toxic and is generally associated with taste and odor issues in drinking water. Iron is highly reactive and is involved in many important chemical reactions that affect the concentrations of other toxic contaminants including arsenic, chromium, and uranium. It is important to understand iron geochemistry, as it plays a critical role in controlling overall groundwater quality.

5.2.2 Iron in the environment

In most natural systems, iron exists as either “ferrous iron” or “ferric iron.” In oxygen-limited environments, ferrous iron exists and is dissolved in groundwater. By contrast, under oxygen-abundant conditions, ferric iron exists and readily forms iron oxide solids of limited solubility. There are various types of iron oxides, which collectively are commonly known as “rust.” Iron oxides have colors ranging from yellow to red, with orange solids predominating, and they are a critical component of aquifer solids that control the overall groundwater quality by interacting with numerous contaminants as discussed below. From an operational standpoint, iron oxide solids can also cause clogging and biofouling issues in wells. Biofouling occurs when bacteria that consume iron are active near the well and create a slimy film of

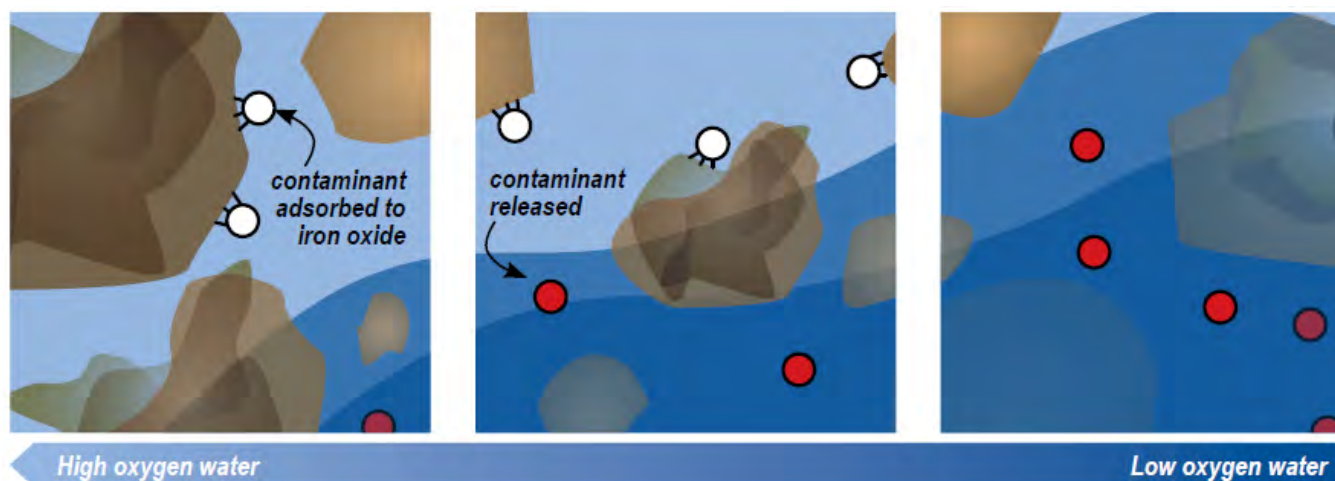


Figure 6: Iron oxides dissolving as DO concentrations become limited and subsequent release of contaminants adsorbed to the iron oxides.

bacterial residue. Both clogging and biofouling reduce water flow in a well and can cause staining.

5.2.3 Iron oxides as contaminant sinks

Dissolved contaminants including arsenic, chromium, and uranium have a strong ability to adsorb or “stick to” iron oxide solids. This adsorption process removes contaminants from groundwater and immobilizes them on iron oxide solids. Subsequently, the concentration of groundwater contaminants often depends on the stability of these iron oxide solids. For example, if oxygen becomes limited within an aquifer, the redox conditions will shift and iron oxides will no longer be stable. Once

the iron oxides dissolve, they will release any adsorbed contaminants, causing an increase in iron and previously adsorbed contaminant concentrations into groundwater (Figure 6). Each contaminant has a varying ability to adsorb on iron oxides and some contaminants adsorb more strongly than others. Additionally, the extent of contaminant adsorption on iron oxides is usually pH dependent -- and may also change with the composition of the surrounding water.

5.2.4 Iron in California

Iron is widely distributed across rock types and associated soils and sediments. It is the second most

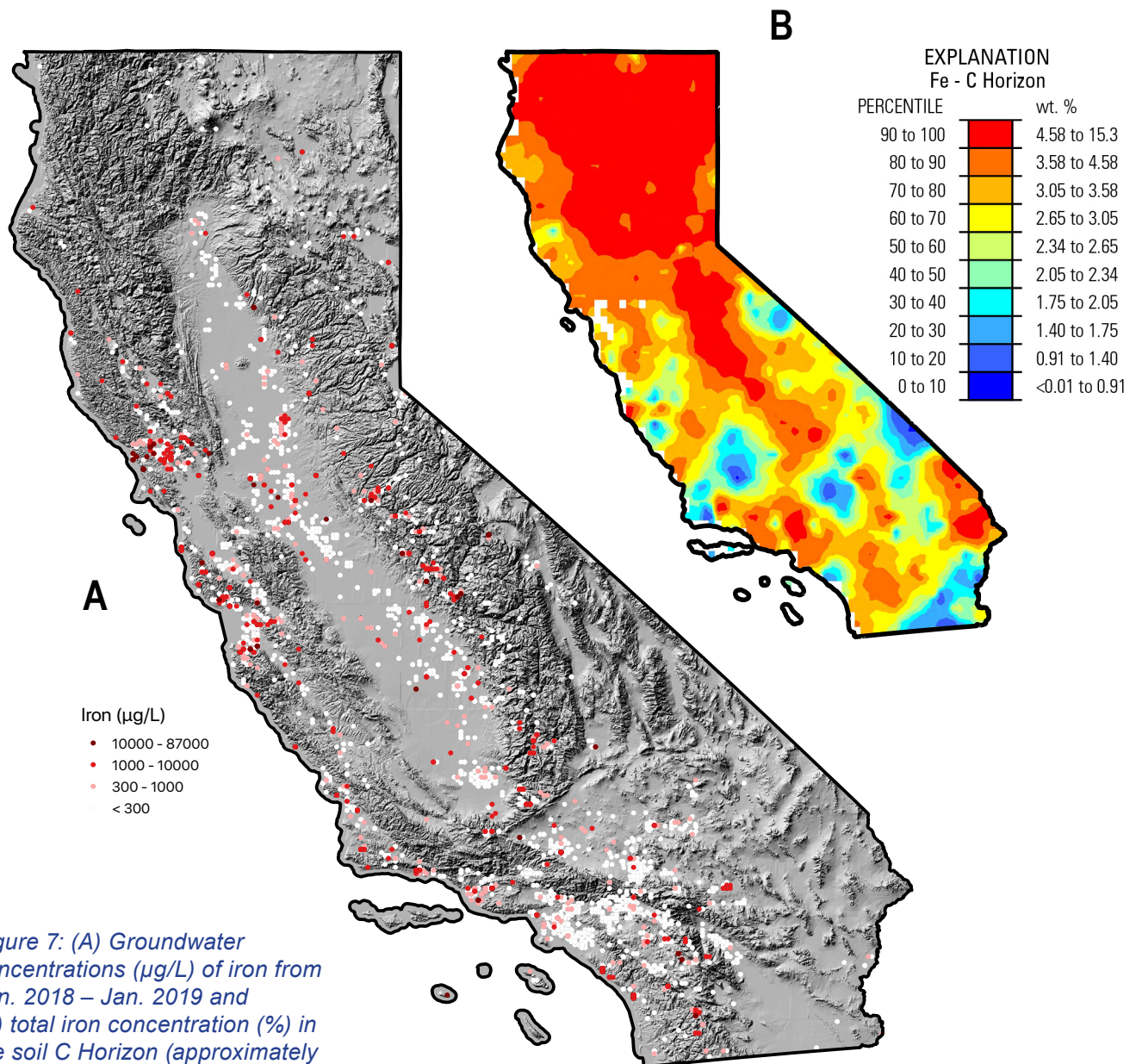


Figure 7: (A) Groundwater concentrations (µg/L) of iron from Jan. 2018 – Jan. 2019 and (B) total iron concentration (%) in the soil C Horizon (approximately 2.6-3.3 ft depth interval). The secondary MCL for iron is 300 µg/L.

abundant metal element in the Earth's crust and can be found at much higher concentrations than other geogenic metals throughout soils (Figure 7). Subsequently, iron in groundwater can occur at any location with geochemical conditions conducive to iron release. Generally, oxygen-limited groundwaters have higher iron concentrations in groundwater.

5.2.5 Management considerations for iron

If an aquifer has abundant oxygen, iron will generally reside as an iron oxide solid, and thus dissolved concentrations of iron are low. The largest threat to the stability of iron oxides is a shift in the oxygen content of an aquifer; if oxygen becomes limiting, iron oxides will dissolve. Should iron oxides dissolve, iron concentrations will increase in the groundwater, which can cause operational problems including clogging and biofouling in production wells. Conversely, if water with high concentrations of DO is introduced into an aquifer with perennially low DO, significant quantities of iron oxides could be produced through the oxidation of existing iron. This could decrease the concentration of other contaminants in the water by providing mineral surfaces with iron oxides to adsorb them.

5.3 Manganese

5.3.1 Background

Manganese is geochemically similar to iron in many ways. At low concentrations, manganese is an essential nutrient for human health. However, at high concentrations manganese causes neurological disorders, particularly in children, who are more susceptible to manganese exposure. Manganese has a secondary MCL of 50 µg/L, and a notification level of 500 µg/L. Like iron, manganese causes operational problems in wells, including clogging and staining. In drinking water, it is often associated with odor and a metallic taste. Manganese also forms oxide minerals which can adsorb and subsequently immobilize groundwater contaminants on aquifer solids, much like iron oxides.

5.3.2 Manganese in the environment

Manganese is the third most abundant metal element in Earth's crust. Under oxygen-limited conditions, manganese can dissolve in groundwater. At pH values greater than 7, manganese increasingly adsorbs to mineral surfaces within aquifer solids and groundwater concentrations will decrease. It forms solid manganese carbonates above pH 7.5, further removing it from groundwater. Under oxygen-abundant conditions, manganese forms manganese oxide solids which limit its groundwater concentrations.

5.3.3 Manganese interactions with other contaminants

Similar to iron oxides, manganese oxides play a critical role in determining the overall groundwater quality of an aquifer. Several toxic contaminants including arsenic, uranium, and selenium adsorb strongly to manganese oxides, limiting their concentrations in groundwater. However, in most oxygen-abundant groundwater systems, iron oxides will be more prevalent than manganese oxides owing to the higher abundance of iron. Therefore, iron oxides generally exert a greater control than manganese oxides on contaminant retention. Additionally, manganese oxides can have a large impact on groundwater quality through their ability to oxidize contaminants. After DO, manganese oxides are among the most reactive oxidants found in the environment and are capable of reacting with other contaminants. Manganese oxides have the most notable effect on chromium; they have the ability to transform chromium from its benign form (trivalent chromium) into a highly toxic and mobile form (hexavalent chromium), as discussed in Section 5.4.

5.3.4 Manganese in California

Similar to iron, manganese is widely distributed and abundant in rocks and associated soils and sediments (Figure 8). Manganese concentrations can be observed in groundwater in any aquifer under oxygen-limiting conditions. Historically, approximately 30 percent of drinking water supplies which monitor for manganese have observed manganese above the detection limit (SWRCB, 2019).

5.3.5 Management considerations for manganese

To promote the stability of manganese oxides and avoid manganese concentrations in groundwater, oxygen-limited conditions should be avoided. In oxygenated

groundwater, manganese (like iron) will usually persist as manganese oxides. Similar to management considerations for iron, a depletion of oxygen will dissolve manganese oxides, increasing dissolved manganese concentrations and releasing adsorbed contaminants.

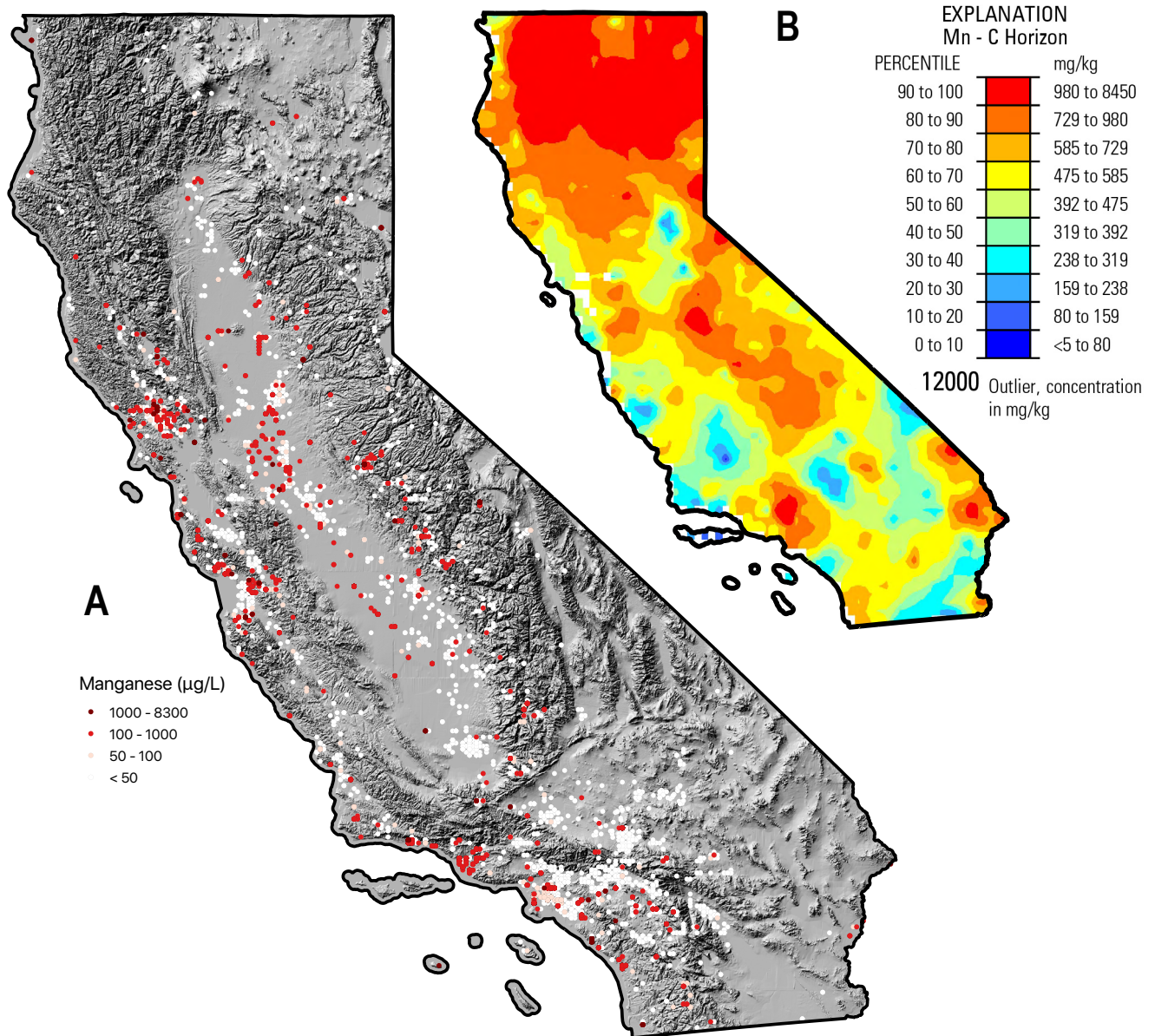


Figure 8: (A) Groundwater concentrations ($\mu\text{g/L}$) of manganese from Jan. 2018 – Jan. 2019 and (B) total manganese concentration (mg/kg) in the soil C Horizon (approximately 2.6-3.3 ft depth interval). The secondary MCL for manganese is $50 \mu\text{g/L}$.

5.4 Arsenic

5.4.1 Background

Arsenic is one of the most toxic and ubiquitous geogenic contaminants. While arsenic can be incorporated into food supplies (e.g., rice crops) through contaminated soil and irrigation water, it poses the greatest threat to public health in drinking water supplies. Chronic exposure to arsenic-contaminated drinking water is known to cause cancers of the lungs, skin, bladder, and kidneys. The primary MCL for arsenic in drinking water is 10 $\mu\text{g/L}$ and the PHG is set at 0.004 $\mu\text{g/L}$. While anthropogenic sources of arsenic, including mining and pesticide application, have historically led to point source contamination of groundwater, both natural and anthropogenic mobilization of arsenic has led to wide-scale contamination of groundwater aquifers.

5.4.2 Arsenic in the environment

Under most environmental conditions, arsenic can be found in one of two forms. Under oxygen-limited conditions, arsenic exists as arsenite in the +3 oxidation state (AsIII). Arsenite is generally considered more soluble in groundwater and more toxic than the oxidized form, arsenate, which occurs in the +5 oxidation state (AsV). This is because arsenate binds strongly to minerals found in soils and sediments under oxygen-abundant conditions including iron oxides. Under oxygen-limited conditions, these oxidized host minerals are not stable, and arsenic is more likely to exist as arsenite.

There are three primary biogeochemical triggers that mobilize arsenic from soils and sediments into

groundwater. First, the most common trigger is a change in redox condition from an oxygen-abundant environment to oxygen-limited conditions. This can transform arsenate to the more soluble arsenite and/or dissolve the iron oxides hosting the adsorbed arsenate which releases it to groundwater. Shifts in redox condition can result in concentrated releases of arsenic. A second trigger of arsenic release is an increase in pH to values greater than 8.5. At these elevated pH values, iron oxides are less effective sorbents for arsenic due to changes in surface charge characteristics and lead to the release of arsenic to groundwater. Third, competitive ions can cause the mobilization of arsenic. Competitive ions are ions that closely resemble arsenic in structure and chemistry and will therefore compete for the same surface sites to bind onto minerals (Figure 9). Competitive ions like phosphate can replace arsenate on the surface of an iron oxide mineral and cause its release into groundwater.

5.4.3 Arsenic in California

In addition to the geochemical triggers of arsenic release described above, arsenic is increasingly being linked to historic pumping. Several regions within California have existing problems with geogenic arsenic, particularly the Central Valley, where arsenic release has been exacerbated by historic pumping. In the Central Valley, arsenic is deposited by granitic materials from the Sierra Nevada. Additionally, recent work has attributed arsenic release to land subsidence due to overpumping in the Tulare Basin in the San Joaquin Valley (Smith et al., 2018). Arsenic can reside in the porewater of clay layers (where oxygen-limited conditions persist). As aquifer pressures decrease and these layers compact during subsidence (Figure 2), arsenic is released and mobilized

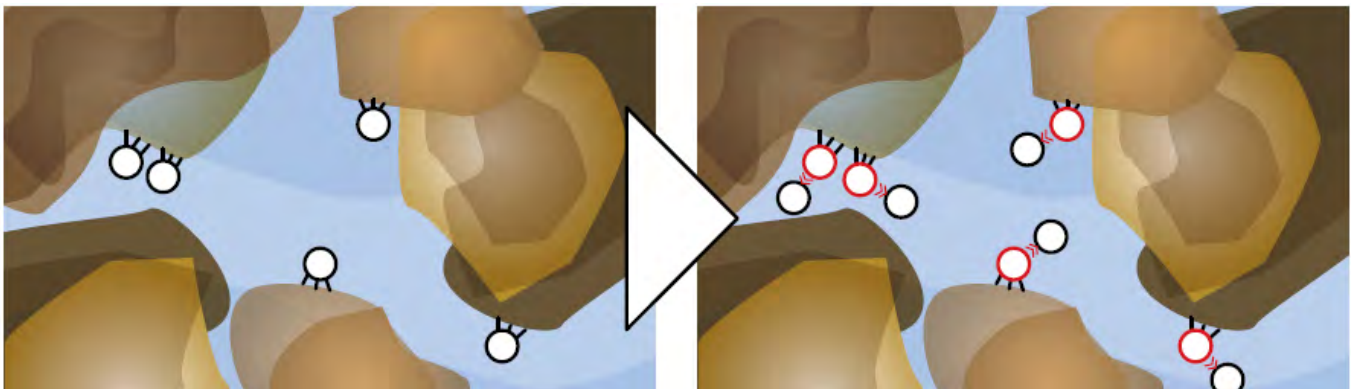


Figure 9: Competitive ion displacement. Ions with similar properties displace each other and limit adsorption to aquifer particles.

into productive aquifer units where it can reach pumping wells. This has been analogized to the release of dirty water when a sponge is squeezed. Once overpumping stops, arsenic concentrations can gradually decrease, declining to background levels as the aquifer is flushed.

5.4.4 Management considerations for arsenic

Conditions to avoid due to arsenic concerns are primarily oxygen-limited conditions and high pH (> 8.5). Inputs

of competitive ions including phosphate, sulfate, and carbonate are a secondary concern. In other words, arsenic is generally not expected to be a problem in well-aerated, oxygen-abundant environments with pH values below 8.5. With respect to arsenic release from overpumping, managing for land subsidence will concurrently limit the arsenic release associated with compaction of clay layers and allow impacted aquifers to recover to background concentrations.

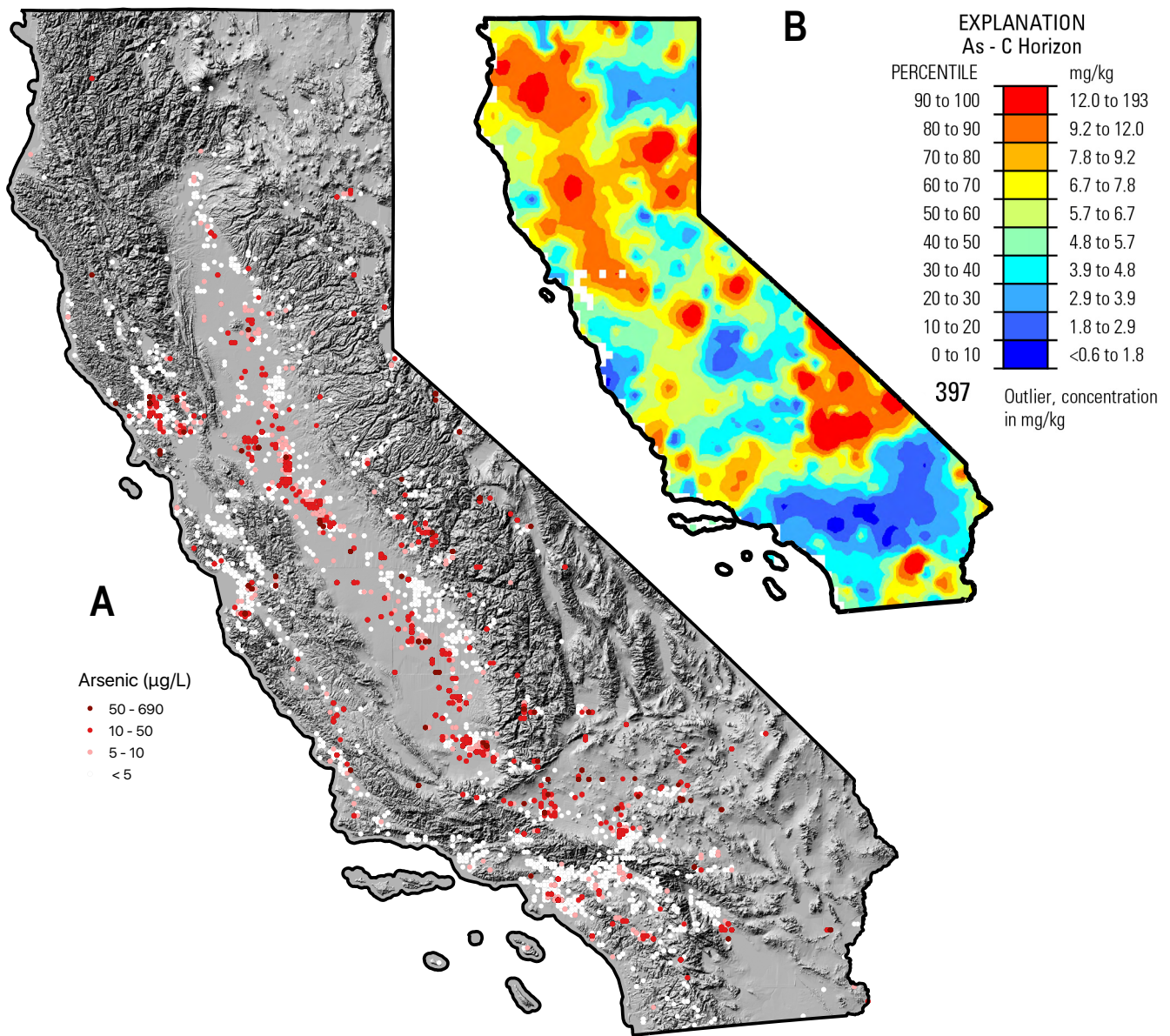


Figure 10: (A) Groundwater concentrations (µg/L) of arsenic from Jan. 2018 – Jan. 2019 and (B) total arsenic concentration (mg/kg) in the soil C Horizon (approximately 2.6-3.3 ft depth interval). The primary MCL for arsenic is 10 µg/L.

5.5 Chromium

5.5.1 Background

Chromium is a naturally occurring metal that is widely used in industrial processes (e.g., electroplating, automobile and steel manufacturing, leather tanning, pigmentation, wood treatment). It persists in two forms within natural environments: trivalent chromium (Cr³⁺) and hexavalent chromium (Cr⁶⁺). Hexavalent chromium is toxic, mutagenic, and carcinogenic, while trivalent chromium is non-hazardous and considered an essential micronutrient in human nutrition. Hexavalent chromium is known to damage the lungs, GI tract, liver, and kidneys and is a known carcinogen that causes cancer by inhalation and possibly by ingestion. The federal MCL for total chromium in drinking water is 100 µg/L. California currently enforces a limit of 50 µg/L. In 2014, California's Department of Public Health set a separate MCL for hexavalent chromium (not total chromium) at 10 µg/L, but this MCL was repealed in 2017 due to the analytical limitations of many water districts (SWRCB, 2018b). The PHG for hexavalent chromium is 0.02 µg/L, stressing the severe toxicity of the chemical to human health. The conversion of hexavalent chromium to trivalent chromium by human stomach acid has been documented, but this was not incorporated in the development of the PHG.

5.5.2 Chromium in the environment

Hexavalent chromium is much more mobile in groundwater than trivalent chromium because it does not bind extensively to minerals within soils and sediments. By contrast, trivalent chromium binds strongly to organic matter and mineral surfaces and may exist as solid minerals (e.g., chromite, aluminosilicate clays, hydroxides). Trivalent chromium is generally stable in oxygen-limited environments. The primary natural pathway for trivalent chromium transformation to hexavalent chromium occurs by reaction with manganese oxides. Although both trivalent chromium and manganese oxides reside in solids of limited solubility, they can react when in close proximity, leading to the generation of toxic hexavalent chromium. Oxygen can also generate hexavalent chromium, but this reaction is only significant at pH values greater than 9. For example, within high-pH, oxygen-abundant aquifers with very slow recharge rates or long residence times — such as in parts of the Mojave Desert, California — indigenous hexavalent chromium generation is appreciable (Izbicki

et al., 2008). Once oxidized, hexavalent chromium does not adsorb to aquifer solids extensively and is easily replaced on surfaces by competitive ions such as sulfate and phosphate. Hexavalent chromium is more likely to remain in groundwater and pose a water quality threat.

5.5.3 Hexavalent chromium in California

Industrial activities that use chromium are important point sources of hexavalent chromium contamination in California, particularly in the San Francisco Bay and Los Angeles areas. In addition, geogenic chromium can be unintentionally oxidized by oxidants (e.g., permanganate, persulfate, hydrogen peroxide) injected during *in situ* chemical oxidation, a clean-up process for organic solvent pollution. Hexavalent chromium contamination in groundwater has historically been linked to industrial practices; however, widespread natural occurrences of hexavalent chromium concentrations approaching or exceeding the MCL also occur in groundwater wells unaffected by upstream industrial sources (Hausladen et al., 2018). These high hexavalent chromium levels in oxygen-abundant, alkaline groundwater are associated with the natural oxidation of geogenic chromium and typically affect larger geographic areas and more people than industrial sources.

In California, mafic and ultramafic rocks extend throughout the Coast Range, Klamath Mountains, northern Sierra Foothills, and San Gabriel Mountains. Soils derived from mafic/ultramafic parent material contain high amounts of geogenic chromium-bearing minerals. This leads to soil chromium concentrations exceeding the global average. Recent work proposed that distance from ultramafic outcrops is a primary control on hexavalent chromium concentrations in groundwater in some areas of California, like the western Sacramento Valley (Hausladen et al., 2018, Manning et al., 2015). The western Sacramento Valley receives extensive chromium-rich sediment deposition from the Coast Range Mountains. Here, hexavalent chromium concentrations reach up to 46 µg/L, and 11% of the measured public supply wells have hexavalent chromium levels that exceed 10 µg/L (Izbicki et al., 2015). Groundwater with mafic/ultramafic contributions also tends to be alkaline, which supports hexavalent chromium mobility. It is important to highlight that the high correlation with mafic/ultramafic outcrop proximity does not hold across all of California due in part to sediment transport processes. In these locations, hexavalent chromium contamination in groundwater may also be strongly influenced by human activities, such as agriculture.

5.5.4 Management considerations for hexavalent chromium

Multiple studies have examined geochemical signatures of groundwater in California and posited links between high hexavalent chromium concentrations and human activities, including agriculture (Izbicki et al., 2015, 2008, Hausladen et al., 2018, Manning et al., 2015, Mills et al., 2011). For example, hexavalent chromium is commonly correlated with nitrate concentrations in public-supply

wells across the Central Valley. It is presumed that water management practices, like irrigation regimes, influence the geochemical processes driving hexavalent chromium contamination; however, we currently lack direct scientific evidence to confirm and explain how agricultural practices contribute to hexavalent chromium concentrations. Below is a summary of considerations about hexavalent chromium for water management based on laboratory experiments and spatial analyses of groundwater chemistry.

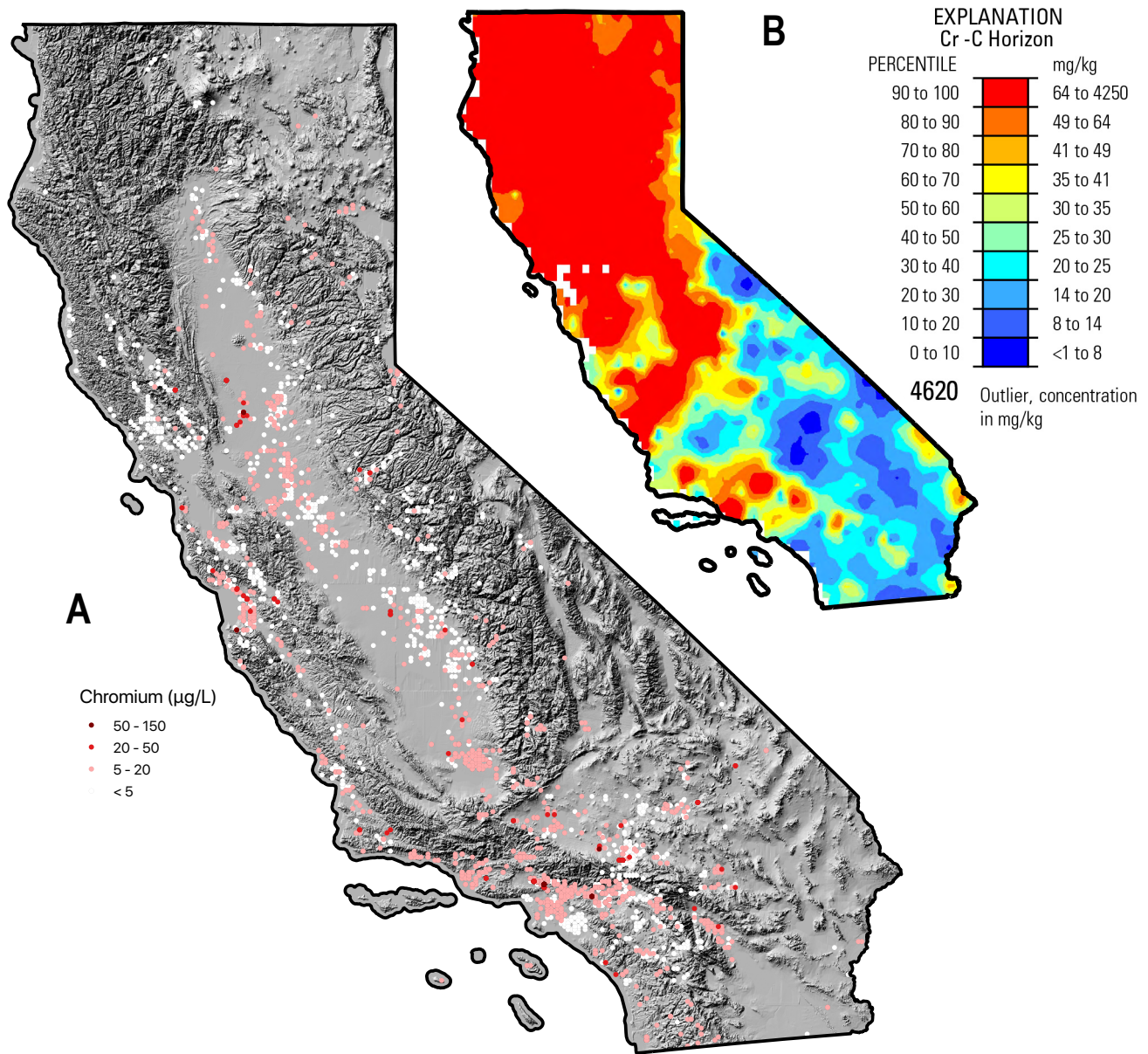


Figure 11: (A) Groundwater concentrations ($\mu\text{g/L}$) of chromium from Jan. 2018 – Jan. 2019 and (B) total Cr concentration (mg/kg) in the soil C Horizon (approximately 2.6-3.3 ft depth interval). The primary MCL for chromium is $50 \mu\text{g/L}$.

In environments containing mafic/ultramafic-derived sediments, biogeochemical conditions to avoid for hexavalent chromium in groundwater are oxygen-abundant, alkaline (pH > 7.5) conditions. Hexavalent chromium is not considered a concern in oxygen-limited aquifers where dissolved iron is present. The use of ammonium fertilizers can introduce acidity to soil and multiple studies suggest that nitrification enhances trivalent chromium release, which leads to greater oxidation by manganese oxides (Mills et al., 2011, 2012). The downward migration of hexavalent chromium generated in the unsaturated zone to shallow aquifers can be accelerated by irrigation recharge.

Although the process remains poorly understood, hexavalent chromium concentrations have been shown to correlate with heavily pumped agricultural areas. One hypothesis is that irrigation schemes which cause the regular wetting and drying of soils leads to manganese oxides dissolving and reforming in new locations at the water table, which in turn leads to the formation of hexavalent chromium. This suggests that irrigation schemes can be modified to decrease or inhibit hexavalent chromium contamination in aquifers. When the water table fluctuates frequently, such as on a weekly basis from turning pumps on and off, soil redox conditions oscillate and activate manganese cycling. Dissolved manganese migrates in the soil during oxygen-limited, saturated conditions, and reforms manganese oxides near chromium-bearing minerals during unsaturated conditions, inducing greater hexavalent chromium production. It is suspected that by changing the pumping schedule to allow for gradual declines in the water table and more stable redox conditions in the subsurface soil and sediments, manganese cycling can be disrupted or stopped, which minimizes hexavalent

chromium generation. If an irrigated area does not currently have problems with hexavalent chromium in groundwater and a management action may lead to new irrigation practices which cause intermittent wetting and drying, it should be noted that this can potentially cause the release of hexavalent chromium particularly in areas near ultramafic outcrops.

5.6 Uranium

5.6.2 Background

Uranium is a metal that naturally occurs in rocks. Igneous rocks, like the Sierra Nevada granites, typically contain more uranium than other types of rocks. The MCL for uranium in California is 20 picocuries per liter (pCi/L), which is roughly equivalent to the federal drinking water limit of 30 µg/L. While uranium is radioactive, radioactivity is not a health concern near the MCL. However, the chemical toxicity of uranium in drinking water above the MCL can lead to kidney damage.

5.6.2 Uranium in the environment

Uranium exists in the environment in two different forms: the more reduced form, uranium(IV) and the more oxidized form, uranium(VI). Uranium in groundwater is almost always uranium(VI). Uranium(IV) typically occurs in oxygen-limited environments and forms a solid that precipitate out of water and are sparingly soluble. Dissolved uranium also adsorbs to aquifer solids and organic matter. Uranium(IV) can be transformed to uranium(VI) by reacting with oxygen and nitrate within groundwater. Shallow groundwater tends to contain

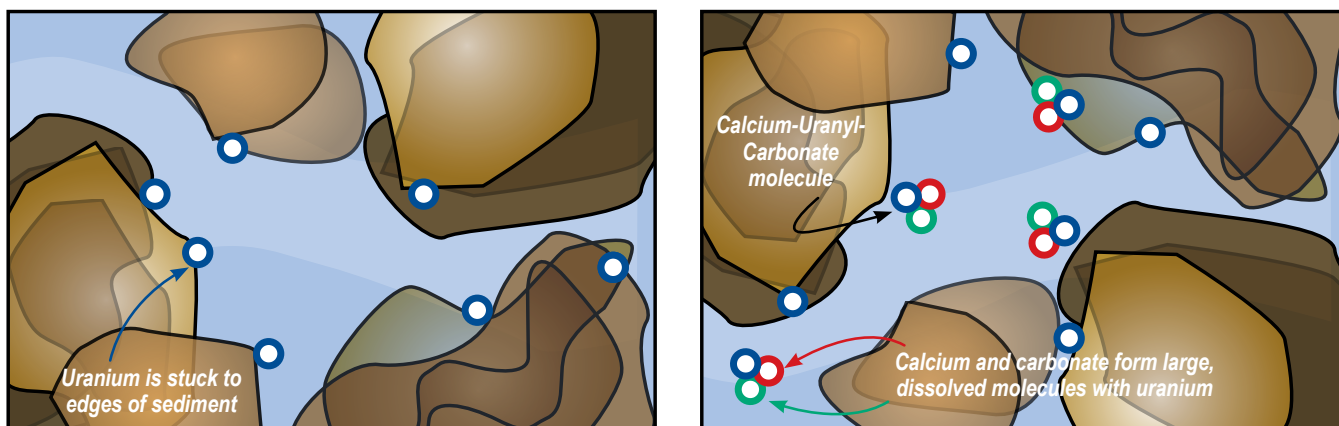


Figure 12: Schematic of calcium-uranyl-carbonate molecule keeping uranium concentrations in groundwater and preventing adsorption.

more DO, leading to uranium(VI). Deeper aquifers often have lower DO, and resulting oxygen-limited conditions promote uranium(IV) solids and subsequently lower uranium concentrations in groundwater. This is one reason why shallower wells tend to pump water with higher uranium concentrations whereas deeper wells have lower concentrations. Additionally, nitrate, when present, also tends to be higher in shallower aquifers, making uranium(VI) a concern in agricultural areas with legacy nitrate contamination.

Although uranium(VI) does not form solids regularly, it does adsorb on aquifer solids, which can limit its dissolved concentrations and mobility. However,

uranium(VI) also forms molecules with calcium and carbonate that limit its ability to stick to aquifer solids, thus leading to higher groundwater concentrations of uranium. Groundwater with high levels of calcium and carbonate lead to calcium-uranyl-carbonate complexes (Figure 12) that do not easily adsorb to sediments. Studies have identified a link between increasing uranium concentrations in the Central Valley and increasing bicarbonate concentrations in groundwater due to the effects of increased plant productivity and irrigation return flow (Jurgens et al, 2009). Increased pCO₂ in the root zone results in increased bicarbonate in shallow groundwater; high bicarbonate concentrations lead to higher uranium concentrations.

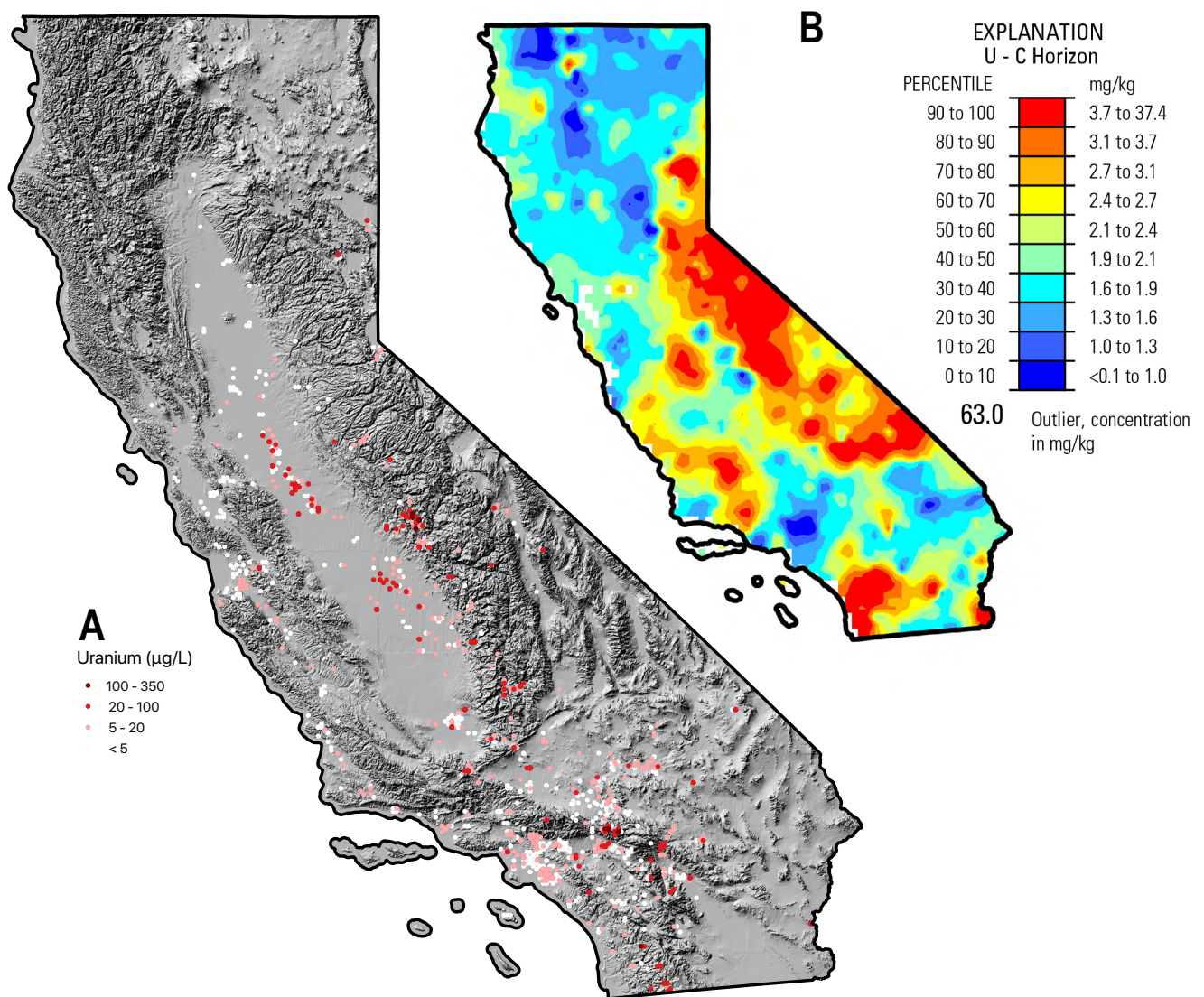


Figure 13: (A) Groundwater concentrations (pCi/L) of uranium from Jan. 2018 – Jan. 2019 and (B) total uranium concentration (mg/kg) in the soil C Horizon (approximately 2.6-3.3 ft depth interval). The primary MCL for uranium is 20 pCi/L.

5.6.3 Uranium in California

In California, wells with high uranium concentrations often occur near the Sierra Nevada (Figure 13). This is because the groundwater picks up uranium from the granitic rocks in the Sierra Nevada or from sediments in valleys that are derived from granitic materials in the Sierra Nevada (like the Eastern San Joaquin Valley). Uranium concentrations in these regions are higher in shallow wells as opposed to deeper wells. Increased pumping can transport uranium from shallow to deeper parts of the aquifer. In parts of the Eastern San Joaquin Valley, uranium levels in some wells have increased significantly over the past 30 years.

5.6.4 Management considerations for uranium

Conditions to avoid to prevent uranium contamination include increasing concentrations of DO or nitrate in an aquifer with limited prior concentrations. The transport of calcium and carbonate to the groundwater below is an additional concern. For example, during managed aquifer recharge via infiltration, when recharge water flows through shallow, calcareous (calcium carbonate containing)-alkaline soils, it can dissolve calcium and carbonate. This also can occur by when waters have elevated carbon dioxide concentrations, which leads to increased carbonates in the water. The calcium- and carbonate-rich water can then react with uranium adsorbed to sediment, promoting release (desorption) of uranium from the sediments into the groundwater. By infiltrating through sandy areas or by removing shallow, calcareous layer of soil in an infiltration basin, calcium and carbonate can be prevented from entering the groundwater. This is particularly relevant for field flooding in the Eastern San Joaquin Valley with legacy agricultural contamination.

5.7 Vanadium

5.7.1 Background

Vanadium is becoming more recognized as a geogenic groundwater contaminant. There is no formal MCL for vanadium, but a Notification Level of 50 µg/L exists. Daily exposure through food is assumed not to have negative impacts, but experiments on rats and mice have shown elevated developmental problems correlated with increasing exposure to vanadium. Concern over potential health effects has led the US Environmental Protection Agency (EPA) to list vanadium on its Contaminant

Candidate List 4, which lists contaminants that are not currently regulated at the federal level but may become so in the future.

5.7.2 Vanadium in the environment

Vanadium has three forms most commonly found in the environment: vanadium(III), vanadium(IV), and vanadium(V). Vanadium is considered immobile under oxygen-limited conditions because the reduced form, vanadium(III), forms a solid of limited solubility and will thus be separate from groundwater. The geochemistry of vanadium(IV) and vanadium(V) is more complex owing to their ability to adsorb on various mineral surfaces. Vanadium(IV) is only appreciably present and mobile in groundwater at very low pH, which is generally not relevant to most natural systems. Vanadium(V) tends to partition into groundwater and is thus mobile; it is found under oxygenated conditions. If vanadium is observed in groundwater, it most likely exists as vanadium(V). While vanadium(V) can adsorb to aquifer solids including iron oxides, adsorption is limited at pH values greater than 9.

5.7.3 Vanadium in California

Vanadium is generally more abundant in mafic rocks, and shales have been shown to have extremely high concentrations reaching 16,000 mg/kg in some parts of the world (Nriagu, 1998). In California, vanadium concentrations above 25 µg/L are associated with oxygen-abundant and alkaline (pH > 8) groundwater that interacts with vanadium-bearing source rock. This interaction can take place two ways. First, the water can be located with the source rock. Second, the water can be on the borders of areas with vanadium-bearing source rock. This is evident in the eastern San Joaquin Valley near the western Mojave, Temecula Valley, and in the Tule River Basin of the Sierra Nevada. However, the presence of source rock does not necessarily mean that there will be groundwater vanadium concentrations above 25 µg/L. For instance, the Cascades, Modoc Plateau, and Sonoma Volcanics of the Northern Coast Ranges have vanadium-bearing source rocks but low vanadium concentrations in the groundwater. This is attributed to their oxygen-limited and low pH conditions. However, areas such as the Owens Valley have been shown to have volcanic source rock and oxygen-abundant, alkaline groundwater, but also have low vanadium concentrations. Other areas, such as parts of the North Coast Range and the Owens Valley, also have vanadium-bearing source rocks but do not have groundwater vanadium concentrations above 25 µg/L. This indicates the need to establish and pay close attention to the hydrologic flow paths of the

regions, as well as establishing the redox conditions of the groundwater in areas of concern (Wright and Belitz, 2010).

5.7.4 Management considerations for vanadium

General conditions which cause vanadium release to groundwater are oxygen-rich and alkaline (pH > 8) waters. This is also true for uranium and chromium, and

vanadium has similar management considerations to both uranium and chromium. If an aquifer has previously limited exposure to oxygen, any management practice that introduces oxygen can cause vanadium mobilization to groundwater. Additionally, uranium and vanadium concentrations are often correlated in groundwater. If an aquifer is experiencing issues with uranium, it is recommended to also monitor for vanadium as there is a possibility these contaminants will co-occur.

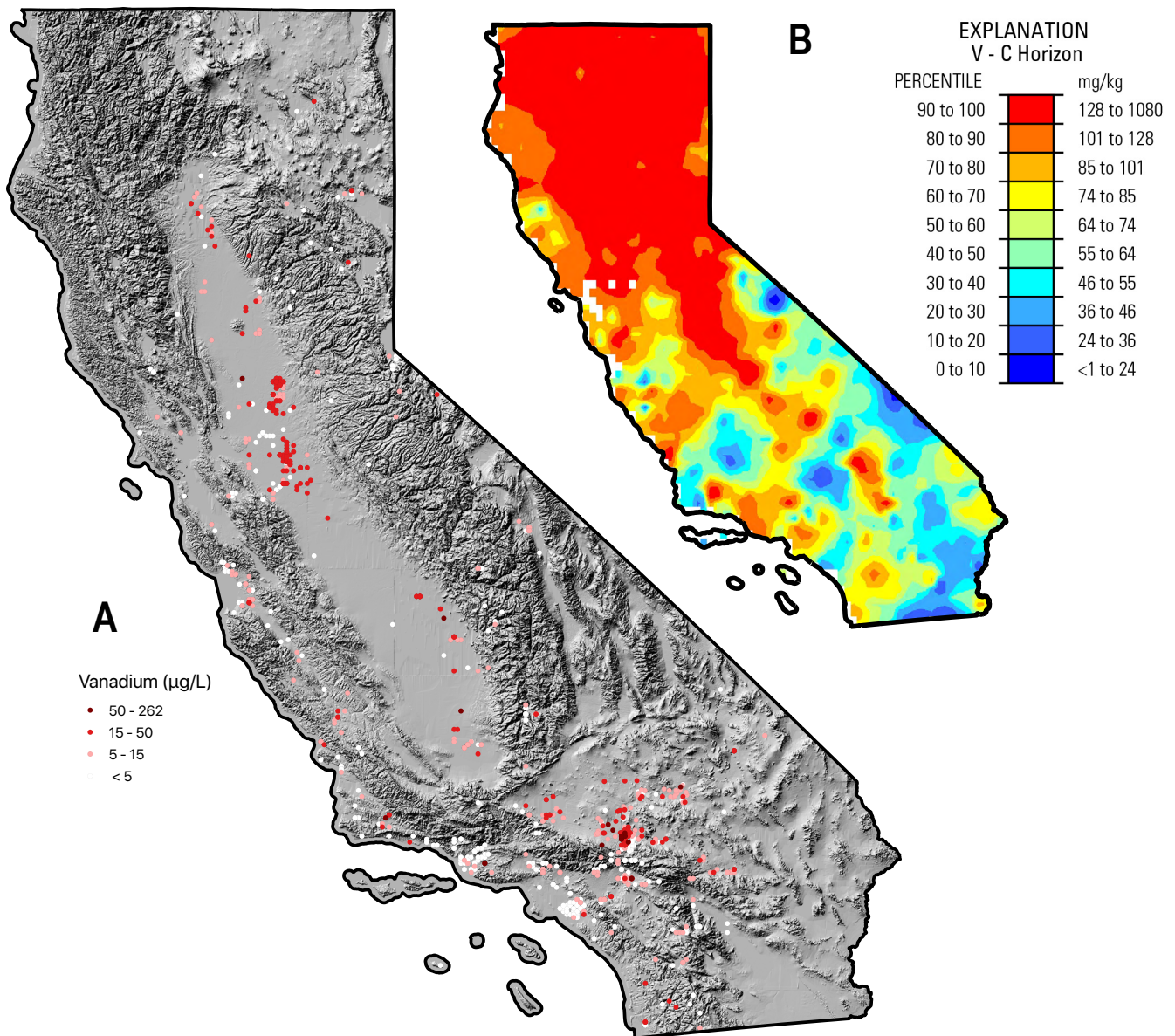


Figure 14: (A) Groundwater concentrations (µg/L) of vanadium from Jan. 2018 – Jan. 2019 and (B) total vanadium concentration (mg/kg) in the soil C Horizon (approximately 2.6-3.3 ft depth interval). The notification level for vanadium is 50 µg/L.

5.8 Selenium

5.8.1 Background

Selenium is an essential nutrient at low, trace concentrations. However, excessive selenium concentrations are toxic to human and ecosystem health. The current MCL is 50 $\mu\text{g/L}$ and long-term exposure of selenium at concentrations above the MCL has been shown to cause damage to kidneys, livers, and nervous and circulatory systems in humans. Historically, selenium has been more dangerous for fish and waterfowl, for whom it is known to cause congenital disorders and death

through ingestion of high doses which bioaccumulate in food sources. Anthropogenic sources of selenium include mining metal ores and coal burning.

5.8.2 Selenium in the environment

Under most environmental conditions, selenium can be found as either the oxidized selenate or the reduced selenite. Under oxygen-abundant conditions, selenium exists as selenate and is more likely to be found in groundwater owing to selenate's limited ability to adsorb to aquifer solids. Selenate is also the more toxic form of selenium. By contrast, under oxygen-limited

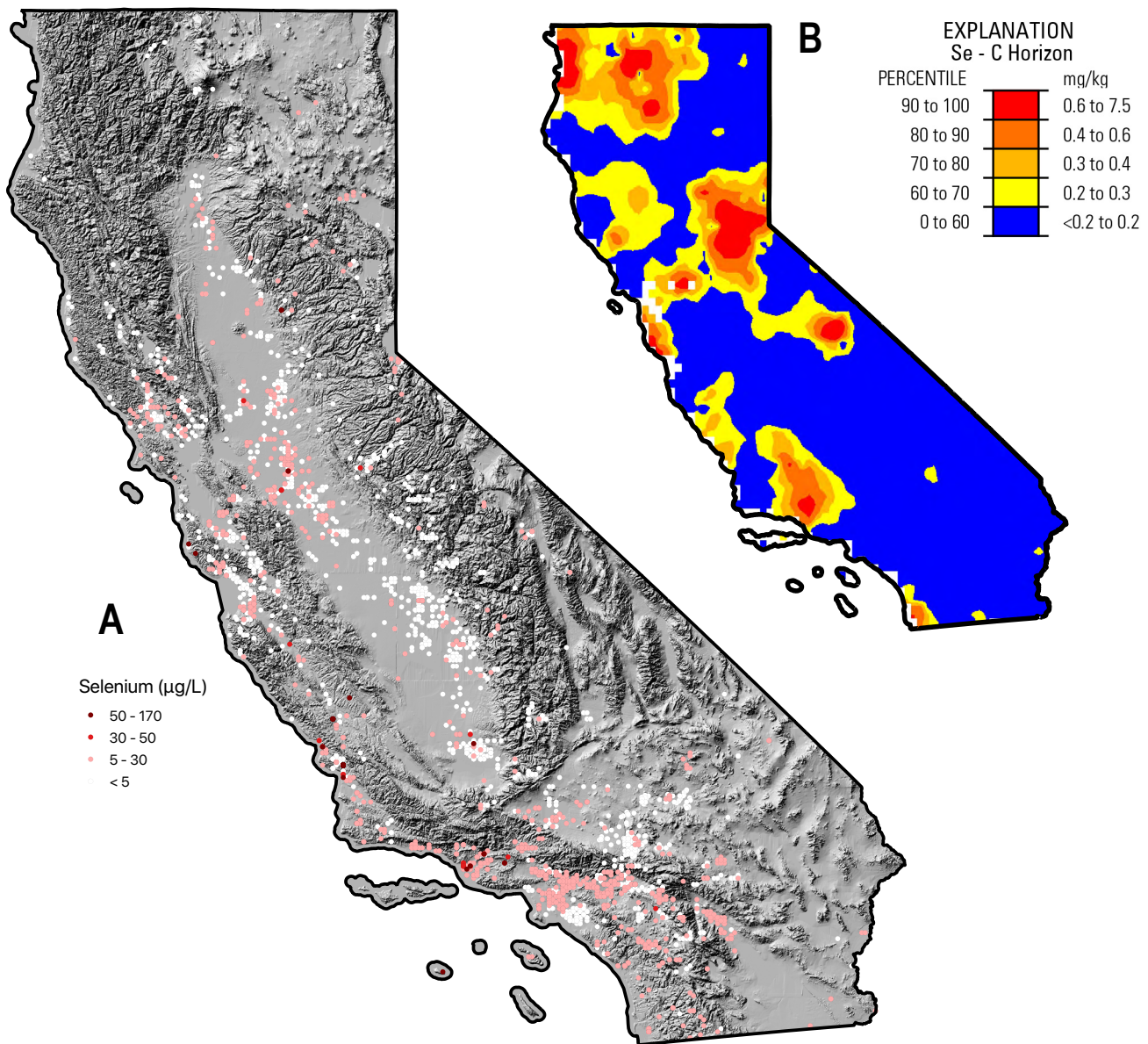


Figure 15: (A) Groundwater concentrations ($\mu\text{g/L}$) of selenium from Jan. 2018 – Jan. 2019 and (B) total selenium concentration (mg/kg) in the soil C Horizon (approximately 2.6-3.3 ft depth interval). The primary MCL for selenium is 50 $\mu\text{g/L}$.

conditions, selenium exists as selenite and will adsorb strongly to aquifer particles, limiting its concentration in groundwater. High selenium concentrations are typically found under oxygen-abundant conditions. Additionally, at high pH values, both selenate and selenite do not adsorb strongly to aquifer solids and concentrations will increase in groundwater. Similar to arsenic, selenium can be mobilized through the presence of competitive ions (e.g., phosphate). While groundwater selenium concentrations are typically low (Plant et al. 2003) and not problematic for human health, contaminated groundwater that may reach surface water bodies, particularly surface water bodies subject to high evaporation, can have adverse impacts on fish and waterfowl.

5.8.3 Selenium in California

Generally, groundwater selenium concentrations are low and soil concentrations tend to correlate with the source bedrock of the California Coast Ranges (Figure 15). Selenium is concentrated in shallow groundwaters in semi-arid regions under irrigation (Deverel et al., 1994). Irrigation water can mobilize geogenic selenium and high evaporation rates can subsequently concentrate salt and selenium concentrations on the surface. Historically, this phenomenon has been observed in the San Joaquin Valley. In the 1980's in the San Joaquin Valley, this led to one of the most documented cases of selenium toxicity in animals. Near the Kesterson reservoir, agricultural drainage tiles were installed to mitigate soil salinization problems. The agricultural drainage water that flowed into the reservoir had high selenium concentrations (250 – 650 µg/L) which were further concentrated due to evaporation losses in the reservoir. This caused significant health effects on fish and wildlife, leading to the death of at least 1,000 birds (Plant et al., 2003).

5.8.4 Management considerations for selenium

Conditions to avoid for selenium release to groundwater include oxygen-abundant and high pH environments. Of secondary concern is a high influx of phosphate concentrations. Introducing nitrate (e.g., infiltration from nitrate-contaminated areas) can also transform selenium to its more mobile form and cause an increase in groundwater concentrations. Additionally, the pumping of groundwater for irrigation can concentrate selenium in addition to concentrating salts. Selenium mobilization could be an issue during changes to irrigation methods, agricultural drainage, or on-farm recharge.

5.9 TCP

5.9.1 Background

1,2,3-Trichloropropane (TCP) has recently been identified as a widespread, emerging contaminant in California. Unlike the geogenic contaminants described above, TCP does not have natural sources. This clear, colorless liquid was present in certain agricultural products applied in California throughout the 20th century, leading to widespread nonpoint contamination. In addition, TCP was historically used as an industrial solvent and cleaning agent, and therefore has many urban point sources. Because TCP does not easily break down, groundwater contamination from these historic practices remains an issue today.

TCP is of concern for human health because of its cancer-causing properties. Research by the National Toxicology Program (NTP) found that TCP causes tumors in multiple sites in both rats and mice at low doses (Irwin, Haseman, & Eustis, 1995). Based on these and other findings, TCP is considered a known human carcinogen by the State of California. California established an MCL for TCP in drinking water (0.005 µg/L) in December 2017, recognizing TCP's health risks and widespread distribution (Figure 16).

5.9.2 TCP in the environment

TCP is not known to have the same geochemical controls as redox-sensitive and ionic contaminants. Nonetheless, TCP is detected at much higher frequencies within oxic groundwater, suggesting it could be impacted by redox conditions; however, this mechanism is currently not well documented (Burow, 2019). Transport of TCP in groundwater is therefore controlled primarily by the physical properties of TCP, the mode of source application, and the characteristics of the affected aquifer, rather than geochemical or redox conditions.

TCP is a short hydrocarbon molecule with a chlorine atom bonded to each carbon. TCP is dense, slightly water soluble, and moderately volatile (prone to evaporation). While less volatile than industrial counterparts like trichloroethylene (TCE), TCP tends to evaporate from surface water. However, TCP does not adsorb easily to soil, and TCP that does not volatilize will migrate into groundwater.

Because it is denser (heavier) than water, TCP is classified as a dense non-aqueous phase liquid (DNAPL). Like all DNAPLs, TCP that enters an aquifer will sink downward, and eventually dissolve into groundwater.

TCP that originates from a diffuse, nonpoint source will tend to dissolve relatively quickly into groundwater. However, when a large amount of TCP enters the aquifer at a single location (generally from a point source), the pure, “free product” TCP can remain in the application source zone for decades – or centuries. This free product may be trapped in large pore spaces as “residual” free product or “pooled” above low-permeability sediments, often with highly irregular distribution within the source zone. Because TCP free product dissolves very slowly over time, groundwater passing through source zones may become enriched in TCP even after application has ceased.

Once dissolved into groundwater, TCP will be transported with groundwater flow. TCP is chemically stable and resistant to degradation. A typical molecule of TCP has a half-life of 44-74 years (i.e., it takes 44-74 years to degrade to half the initial concentration in water) (Ellington, 1986). Therefore, TCP plumes persist until they are diluted by diffusion or mixing.

5.9.3 TCP in California

TCP was detected above the MCL in 8% of domestic wells and 5% of public-supply wells recently sampled in California (Burow 2019). These detections are concentrated in the San Joaquin Valley, with some affected wells in the Los Angeles basin and Salinas Valley (Figure 16). In the San Joaquin Valley, 16-18% of domestic and public supply wells have TCP concentrations above the MCL.

Unlike geogenic contaminants, the distribution of TCP is largely determined by the location of historic source applications. In agricultural regions, TCP in groundwater likely originates from the use of TCP-containing soil fumigants marketed as D-D and, later, Telone, Telone II, and Vidden D. These fumigants were composed primarily of 1,3-dichloropropene (1,3,-DCP) and 1,2-dichloropropene (1,2-DCP) but contained up to 7% TCP by weight (Cheremisinoff & Rosenfeld, 2011). TCP-containing fumigants were widely applied beginning in the 1940s to many of California’s croplands, including citrus fruits, pineapples, soy beans, cotton, tomatoes, sugar beets, grapes, potatoes, and various row crops, until they were discontinued in 1984 (CH2M Hill, 2005).

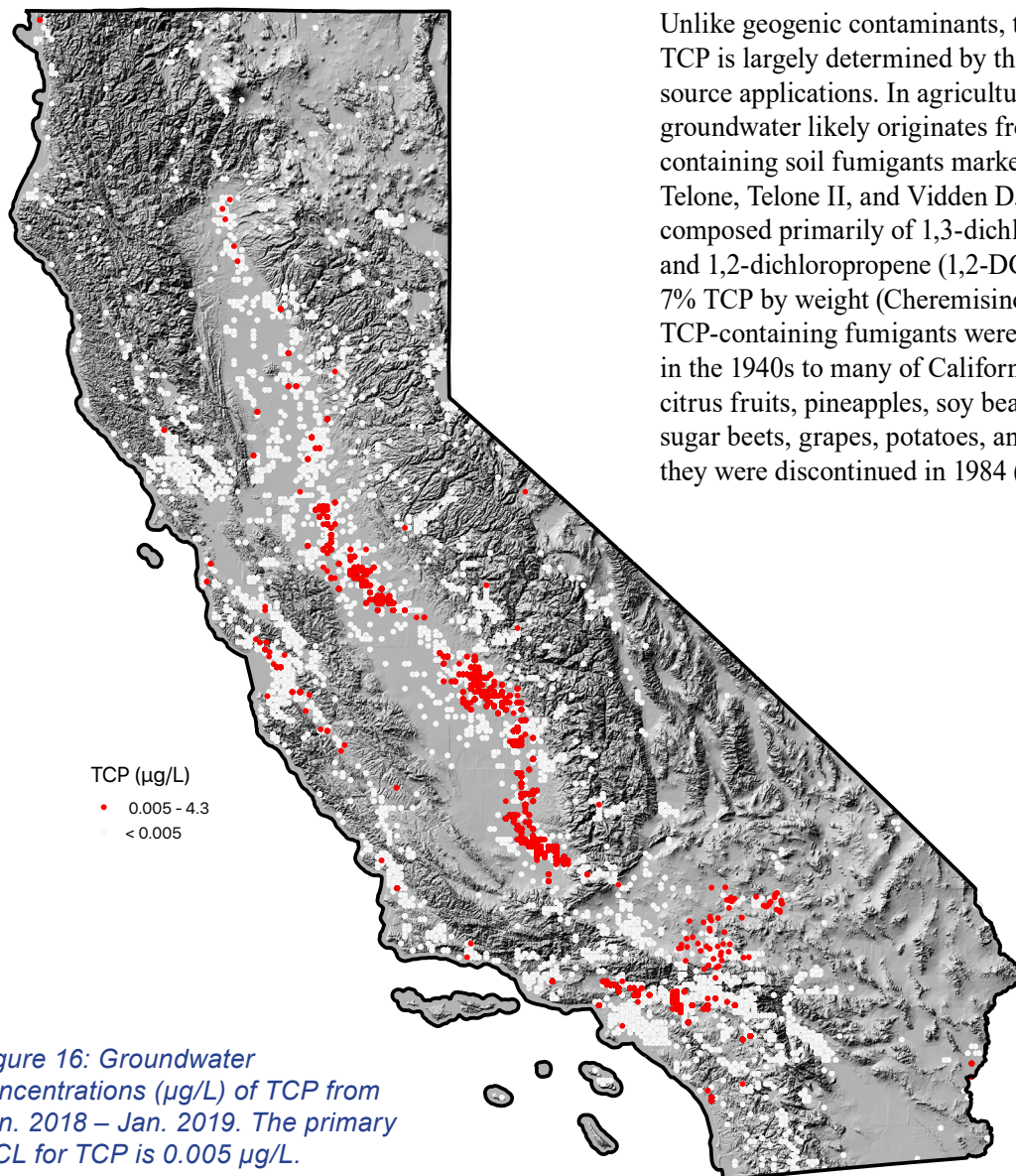


Figure 16: Groundwater concentrations ($\mu\text{g/L}$) of TCP from Jan. 2018 – Jan. 2019. The primary MCL for TCP is $0.005 \mu\text{g/L}$.

TCP also has many point sources. These include facilities where TCP-containing fumigants were stored or where TCP was used as a solvent or cleaning agent. Suspected point sources of TCP in California include agricultural chemical supply sites, aviation facilities, chemical processing and manufacturing plants, and waste disposal sites (CH2MHill 2005, Burow 2019).

A recent evaluation of TCP in California groundwater identified several factors that are associated with TCP occurrence and concentrations: oxygen-abundant conditions; young, shallow groundwater; orchard/vineyard land use in the early 1990s; and high recharge rates (Burow 2019). Overall, TCP was found to be most prevalent and at highest concentrations near alluvial fans in the central and southern San Joaquin Valley, where orchards and vineyards are common and coarse-grained sediments and irrigation lead to high recharge. TCP was prevalent at similar rates in wells of all depths, though TCP concentrations were slightly higher in shallower wells. The authors also found that TCP co-occurs with 1,2-dibromo-3-chloropropane (DBCP, another soil fumigant) and 1,2-DCP (a TCP breakdown product and primary component of TCP-containing fumigants).

5.9.4 Management considerations for TCP

Active groundwater remediation is not a focus of this document. Best practices for TCP *in situ* remediation are still under study and will depend on the specific conditions of each plume. In general, *in situ* remediation of TCP can be achieved by injection of a strong oxidant and catalyst or by reductive dechlorination with zero-valent iron. However, California considers pump-and-treat with Granular Activated Carbon (GAC) as the Best Available Technology for affected water systems (SWRCB, 2018c).

Without active treatment, TCP plumes are likely to persist for many years. However, an awareness of aquifer characteristics, hydrology, and current/former land use can help water managers to avoid increasing TCP concentrations. Managers can avoid siting new wells in areas known to be associated with higher TCP concentrations, particularly shallow groundwater near orchards and vineyards in the central and southern San Joaquin Valley. Wells with elevated concentrations of DBCP and 1,2-DCP are also more likely to have elevated TCP.

Water managers should also be aware of historic point sources of TCP. As described above, residual or pooled TCP may be found near application zones in the pore

spaces of coarse sediments or in lenses above low-permeability sediments. If water pumped from these strata becomes enriched in TCP relative to up-gradient wells, free product may be present. Subsurface soil samples can also reveal whether free product remains in source zones.

Depending on hydrological conditions of the site, managed aquifer recharge can help to reduce TCP concentrations through dilution of existing contamination. However, recharge zones should also avoid historic point source TCP contamination, as free product in the subsurface may dissolve into percolating groundwater and reach previously unaffected water supplies. Monitoring groundwater conditions down-gradient of the recharge will also allow water managers to track changes in TCP concentrations following recharge.

5.10 PFASs

5.10.1 Background

Per- and polyfluoroalkyl substances (PFASs) are a large and diverse class of fluorinated organic compounds. Like TCP, PFASs are synthetic chemicals that have no natural sources. PFASs are used to make consumer products stain-, soil-, and water-repellent, and in aqueous film-forming foam (AFFF) to extinguish flammable liquid fires. The carbon-fluorine chemical bonds that give PFASs their useful properties also make many of these chemicals extremely persistent. Interest in PFASs has increased due to recent discoveries of their widespread environmental occurrence and potential impacts on human health and biota.

Perfluoroalkyl acids (PFAAs) are a subclass of PFASs that are the focus of much scientific and regulatory attention. Exposure to PFAAs such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) is associated with human health harm including immune suppression, liver damage, high cholesterol, cancer, thyroid disease, reduced fertility, low birth weight, and effects on children's cognitive and neurobehavioral development. In 2016, U.S. EPA issued a Lifetime Health Advisory Level of 70 ng/L for PFOA, PFOS, or the sum of both. Researchers know less about the prevalence and toxicity of other PFASs, but the science is evolving rapidly.

PFOA, PFOS, and other long-chain PFASs have been phased out in the U.S. due to concerns over their

persistent, bioaccumulative, and toxic properties. Over the past 15 years, industry has replaced long-chain PFASs with short-chain PFASs and perfluoroether carboxylic and sulfonic acids. One notable perfluoroether carboxylic acid called GenX is used as a PFOA replacement in fluoropolymer manufacturing. GenX contamination has recently been detected in several watersheds in the eastern U.S.

5.10.2 PFASs in the environment

PFOA, PFOS, and other PFAAs are highly persistent. They are not expected to degrade at appreciable rates under environmental conditions. PFAAs are strong acids that usually carry a negative charge, which contributes to their relatively high water solubility and low volatility. PFAA releases are often associated with dissolved phase

plumes. However, considerable PFAA mass can also be retained in source zones, especially in unsaturated soils. Partitioning to sediment and bioaccumulation are more pronounced for longer-chain PFAAs.

In contrast to PFAAs, polyfluorinated compounds contain a fluorinated carbon chain and at least one nonfluorinated carbon. The nonfluorinated carbons make polyfluorinated compounds more reactive than PFAAs, and some are susceptible to oxidation reactions. Polyfluorinated compounds that produce PFAAs are known as PFAA-precursors. Little is known about the fate, transport, or toxicity of many PFAA-precursors. Most are not included in standard analytical methods. PFAA-precursors are likely to serve as an ongoing source of PFAAs (e.g., PFOA) in the environment. Analytical techniques for measuring PFAA-precursors, such as the total oxidizable precursor (TOP) Assay, are increasingly available.

Important point sources of PFAS contamination include manufacturing facilities that make or use PFASs, locations where AFFF firefighting foam was used, landfills, and wastewater treatment plants.

5.10.3 PFASs in California

PFASs are not regulated under the Safe Drinking Water Act and public water systems are not required to perform routine monitoring of these chemicals. PFASs were detected in 133 drinking water samples from California through EPA's Third Unregulated Contaminant Monitoring Rule (UCMR3). The same study identified nine public water systems in the state with detections of PFOA and/or PFOS above EPA's 70 ng/L health advisory.

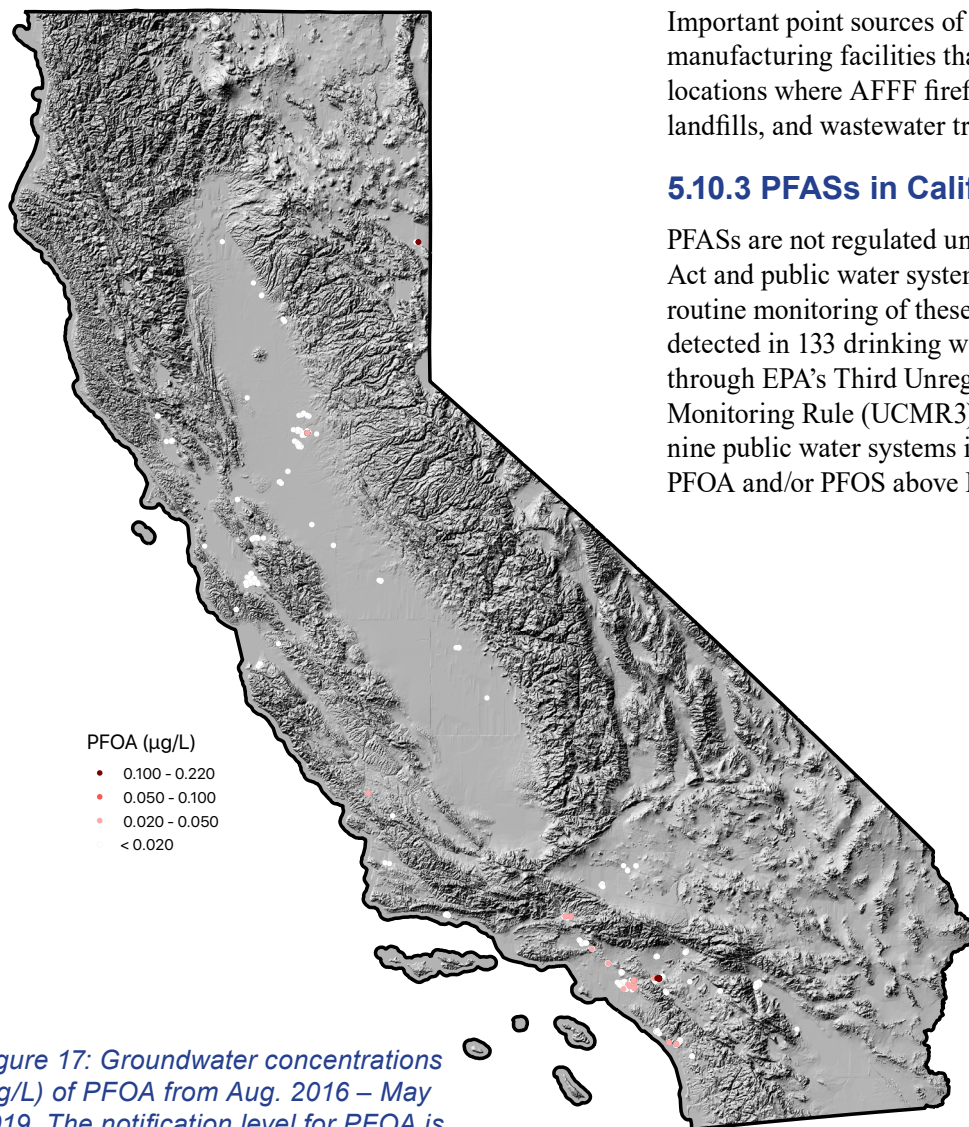


Figure 17: Groundwater concentrations ($\mu\text{g/L}$) of PFOA from Aug. 2016 – May 2019. The notification level for PFOA is $0.013 \mu\text{g/L}$.

Aside from the UCMR3 study, there is a lack of drinking water monitoring data for PFASs in California. The Department of Defense has identified high PFAS concentrations in groundwater at military sites where AFFF was used, but none of these sites are known to have impacted drinking water off-base in California. In 2019, the State Water Resources Control Board announced a plan to require PFAS monitoring at hundreds of suspected release sites around the state, including manufacturing facilities, airports, landfills, refineries, wastewater treatment plants, and urban wildfire areas. The results of this monitoring should increase our understanding of the extent and sources of PFASs in California groundwater. When the state of Michigan carried out a similar testing program in 2018, it identified dozens of previously unknown PFAS contamination sites.

California's Division of Drinking Water has established notification levels of 13 ng/L and 14 ng/L, respectively, for PFOS and PFOA, and a response level of 70 ng/L for each individual compound or the sum of both.

5.10.4 Management considerations for PFASs

Under aerobic conditions, PFAA-precursors can undergo biotic transformation reactions to form PFAAs. Thus, if PFAA-precursors are present, management actions that introduce oxygen to an aquifer may have the unintended effect of increasing PFAA concentrations. Examples of such actions include remedial activities designed to treat contaminants other than PFASs, such as biosparging or in-situ chemical oxidation.

Recycled water is a potential source of PFASs in receiving aquifers. Given the decreasing trend in PFAS regulatory values, water managers should consider monitoring for PFASs before implementing aquifer recharge with recycled water.

Glossary

Analytes: substances being measured

Anoxic: Condition with low concentrations of dissolved oxygen

Anthropogenic: Man-made

Aqueous: Dissolved in water

Calcareous: rich in calcium carbonate

Cation: positively charged substance

Competitive ion: an ion (or charged substance) that behaves similar to another ion. Because they behave similarly, they

Desorption: The process of a substance adsorbed to a particle surface being released into the surrounding water

Felsic: describes type of volcanic rock that is rich in minerals like feldspar and quartz

Geogenic: naturally occurring in rocks

Mafic: describes a type of volcanic rock that is rich in magnesium and iron

Mobility: ability of a substance to move or be transported with water

Nonpoint source: contamination resulting from a diffuse source

Oxidant: a substance which causes the oxidation of another substance

Oxidation: the process of losing electrons or increasing oxidation state

Oxidation reduction potential: a measure of redox conditions

Oxidation state: a measure of the number of electrons a substance has gained or lost relative to its native state

Oxyanion: negatively charged substance

pH: a measure of the acidity of water

Point source: contamination resulting from a single, specific source (e.g., a leaking waste container)

Redox: chemistry related to the gain or loss of electrons also called the reduction or oxidation of substances

Reductant: a substance which causes the reduction of another substance

Reduction: the process of gaining electrons or decreasing oxidation state

Sediment: sediments are materials consisting of rocks and minerals, and remains of plants and animals; they are moved to new locations and deposited by water, ice, or wind

Sedimentary: describes rocks formed by deposition of other rocks

Shale: a fine-grained, sedimentary rock that forms when silt and clay-size mineral particles compact

Soil: unlike sediments, soil weathers in place and requires time and a stable ground surface to develop. It is a mixture of organic material, rock and mineral particles

Solubility: ability to dissolve in water

Sorption: the process of a substance adsorbing to a particle surface

Specie: a chemical substance or entity such as an atom, ion, or molecule

Ultramafic: describes a type of volcanic rock with very low silica content

Unsaturated zone: zone of an aquifer above the water table

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Endnotes

- 1 SWRCB's Nitrate Project https://www.waterboards.ca.gov/water_issues/programs/nitrate_project/
- 2 CV-SALTS <https://www.cvsalinity.org/>
- 3 SWRCB's Irrigated Lands Regulatory Program (ILRP) https://www.waterboards.ca.gov/centralvalley/water_issues/irrigated_lands/
- 4 Sustainable Conservation's Nutrient Management Field Guide <https://suscon.org/pdfs/dairies/pdfs/NMFieldGuideFinal.pdf>
- 5 For certain contaminants, the SWRCB has contaminant-specific thresholds for which it is recommended to notify users. The response level refers to a concentration threshold greater than the notification level where the SWRCB recommends the water source be taken out of service. https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/NotificationLevels.html
- 6 USGS 'An Excel Workbook for Identifying Redox Processes in Ground Water' <https://pubs.usgs.gov/of/2009/1004/>
- 7 USGS Report "Factors affecting public-supply-well vulnerability to contamination: understanding observed water quality and anticipating future water quality" <https://pubs.usgs.gov/circ/1385/pdf/Cir1385.pdf>
- 8 Community Water Center and Stanford's "Groundwater Quality in the Sustainable Groundwater Management Act: Scientific Factsheet on Arsenic, Uranium, and Chromium" https://d3n8a8pro7vhm.cloudfront.net/communitywatercenter/pages/293/attachments/original/1560371896/CWC_FS_GrwndtrQual_06.03.19a.pdf?1560371896
- 9 Community Water Center's "Guide to Protecting Drinking Water Quality Under the Sustainable Groundwater Management Act" https://d3n8a8pro7vhm.cloudfront.net/communitywatercenter/pages/293/attachments/original/1559328858/Guide_to_Protecting_Drinking_Water_Quality_Under_the_Sustainable_Groundwater_Management_Act.pdf?1559328858
- 10 DWR's Best Management Practices 1 'Monitoring Protocols Standards and Sites' [\[Groundwater-Management/Best-Management-Practices-and-Guidance-Documents/Files/BMP-1-Monitoring-Protocols-Standards-and-Sites.pdf\]\(https://water.ca.gov/-/media/DWR-Website/Web-Pages/Programs/Groundwater-Management/Sustainable-Groundwater-Management/Best-Management-Practices-and-Guidance-Documents/Files/BMP-1-Monitoring-Protocols-Standards-and-Sites.pdf\)](https://water.ca.gov/-/media/DWR-Website/Web-Pages/Programs/Groundwater-Management/Sustainable-</div><div data-bbox=)

- 11 DWR's Best Management Practices 2 'Monitoring Networks and Identification of Data Gaps' <https://water.ca.gov/-/media/DWR-Website/Web-Pages/Programs/Groundwater-Management/Sustainable-Groundwater-Management/Best-Management-Practices-and-Guidance-Documents/Files/BMP-2-Monitoring-Networks-and-Identification-of-Data-Gaps.pdf>
- 12 DWR's Flood-MAR website <https://water.ca.gov/Programs/All-Programs/Flood-MAR>

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