

Arsenic in Groundwater, Soil, and Surface Water in Rice-growing Areas of the Sacramento Valley

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This technical memorandum (TM) summarizes existing water quality information and current knowledge of arsenic occurrence in the rice-growing areas of California's Sacramento River Watershed. Arsenic is of interest to the rice research community due to a scientific effort by the U.S. Food and Drug Administration (FDA) to assess human health risk of arsenic in rice and rice-based foods.

In September 2013, the FDA issued an official statement reflecting the results of inorganic arsenic testing of more than 1,000 rice and rice product samples (FDA 2013a). The FDA concluded that "the amount of detectable arsenic is too low in the rice and rice product samples to cause any immediate or short-term adverse health effects" (FDA 2013a). The FDA's official recommendation for consumers is to diversify grains in both infant and adult diets. The FDA published raw results of its analysis (FDA 2013b), which include samples of rice contributed to the FDA by the California rice industry. The FDA is currently completing a risk assessment to determine the potential for long-term health effects from rice consumption and whether risks vary among different population segments.

The evaluation of arsenic uptake by rice plants is complex because factors including naturally occurring background soil conditions, irrigation source water, and water management (which is closely related to pest management) influence the rice system. This TM is intended to support future efforts by rice researchers to assess rice plant uptake of arsenic by providing regional-level information on background source water quality and concentrations of arsenic in shallow groundwater.

The following discussion is organized under the following topics:

- **Background:** provides an overview of rice-growing lands; explains arsenic's chemistry, transport, and sources; describes the rice-farming practices employed by farmers in this region; and provides current relevant regulatory information regarding arsenic.
- **Arsenic in surface water:** describes sampling data collected by various agencies that shows arsenic concentrations in rivers and other drainages in the Sacramento Valley.
- **Arsenic in groundwater:** describes arsenic concentrations in shallow groundwater underlying rice fields as indicated by data recently analyzed for the California Rice Commission's (CRC's) *Rice-specific Groundwater Assessment Report (GAR)*.
- **Arsenic in soil:** describes the limited information currently available for the area being studied.
- **Conclusions and recommendations:** summarizes the current understanding, presence, and probable behavior of arsenic relative to rice-growing practices in the Sacramento Valley. Further, it identifies

recommended priorities for research areas that focus on the efficacy of irrigation and other rice farming practices on rice plant uptake of arsenic.

This review focuses on Sacramento Valley rice-growing areas that are part of the CRC and located generally north of the city of Sacramento. Rice is grown in areas naturally suited to rice agriculture and wetland habitat due to underlying soil characteristics that promote ponding of water.

Background

Rice is grown in the finer-grained (primarily clay) soils in the central portion (about 5 percent) of the Sacramento Valley (USGS 2009). Figure 1 shows farmlands identified as rice lands by the California Department of Water Resources (DWR) land use surveys and includes the boundaries of the DWR groundwater basins. California primarily produces medium-grained rice, with smaller acreages of wild rice, jasmine, and other specialty varieties.

The amount of land annually farmed in rice is influenced by factors such as market conditions, weather, and drought water bank agreements. The CRC reports annual acreage using the U.S. Department of Agriculture's (USDA) published values; total planted acreage in 2009 was 545,300 acres (USDA 2011). DWR land use surveys identify rice farmlands, including lands that are actively farmed in rice or are fallow but identifiable as rice lands. The total acreage of rice identified by DWR is approximately 590,000 acres, which represents an upper bound of lands typically considered suitable for rice farming.

Rice is primarily grown in eight Sacramento Valley counties (Butte, Colusa, Glenn, Placer, Sacramento, Sutter, Yolo, and Yuba) and is sometimes grown (on less than 1,000 acres) in Tehama County. Rice is also farmed in counties outside the Sacramento Valley; however, these acreages are generally small, and rice is a minor crop in these areas. Rice lands overlie 11 Sacramento Valley Groundwater Basin subbasins: Red Bluff, Corning, West Butte, East Butte, Sutter, North Yuba, South Yuba, North American, South American, Yolo, and Colusa.

Understanding how arsenic species occur in the rice field environment requires background knowledge of arsenic chemistry (species, fate, and transport), potential sources of arsenic in the environment, and rice-farming practices. A rice-specific understanding of arsenic uptake can inform field-level trials designed to assess management practices intended to reduce uptake.

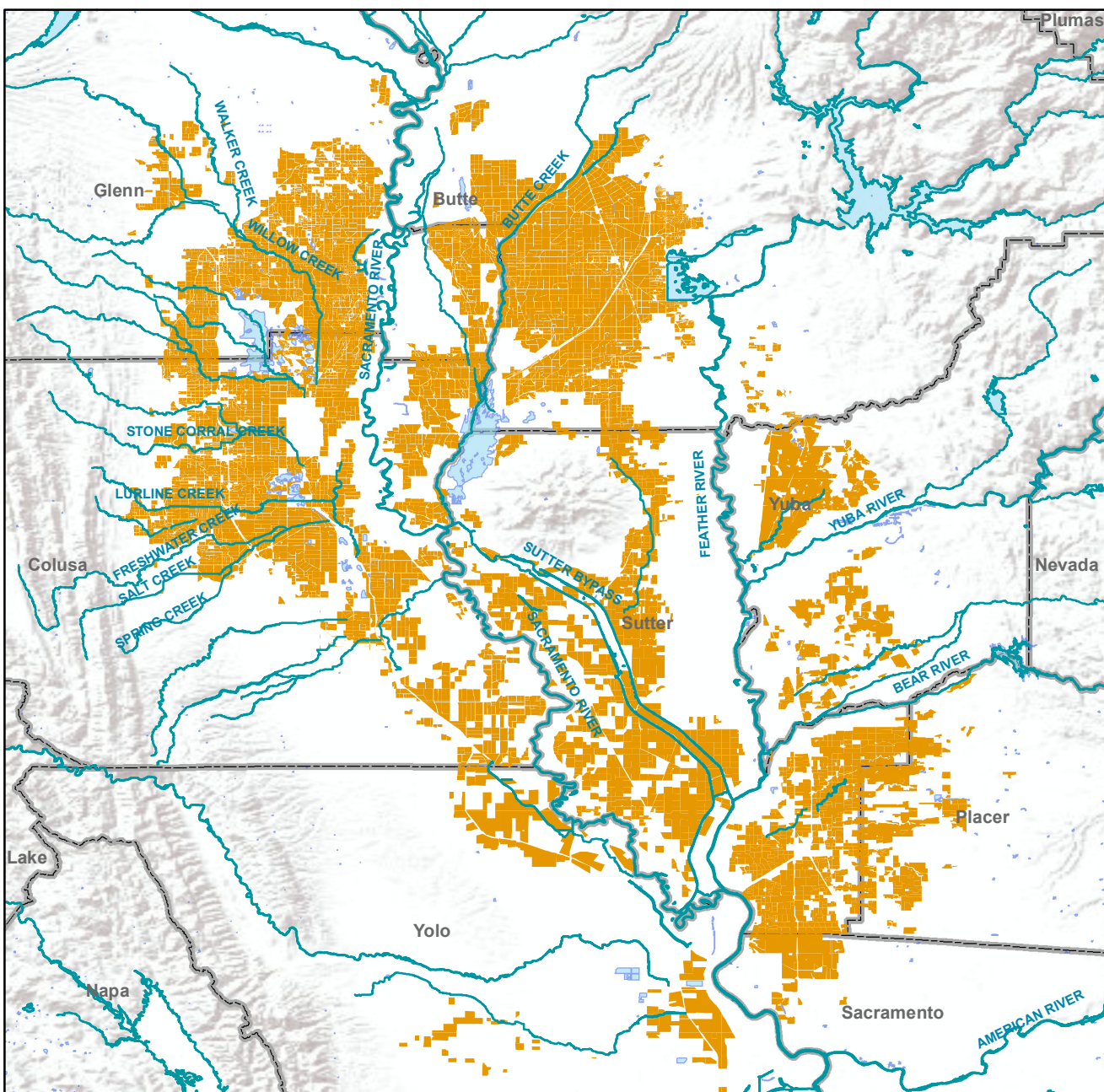
Arsenic Chemistry

Chemical Species

Arsenic in surface water or groundwater occurs in both organic and inorganic forms. Inorganic arsenic is considered the primary form of arsenic that poses a human health risk (Meharg and Zhao 2012) and occurs as both inorganic arsenate and inorganic arsenite:





- Inorganic *arsenate* is a weak acid present as H_2AsO_4^- and HAsO_4^{2-} over a normal pH range (5 to 9); the ambient pH determines which of these forms is dominant.
- Inorganic *arsenite* is also a weak acid, but in the neutral pH region is dominated by its neutral form H_3AsO_3^0 .

The difference between the arsenic in both of these inorganic species is the oxidation state of the arsenic atom, with arsenate as +5 or As(V) and arsenite as +3 or As(III). Ambient redox conditions dictate the dominant direction of the oxidation/reduction reaction (from arsenate to arsenite, or vice-versa); in oxidizing (typically aerobic) conditions, arsenite conversion to arsenate dominates, and in reducing (typically anaerobic and anoxic, such as those found in flooded rice fields) conditions, inorganic arsenite will dominate. Arsenite is more soluble than arsenate under environmental conditions having near neutral pH and ion concentrations typical of fresh water (Meharg and Zhao 2012). If the water contains sulfur at moderate concentrations, and redox conditions are strongly reducing, then As (III) will precipitate as arsenic sulfide instead of forming the arsenite ion.



Data Sources: Basemap (ESRI 2013); County, Stream/River (California 2008), Water Body (USGS 1999); Rice Land Use (DWR 2010). Datum is NAD 83.

VICINITY MAP

- LEGEND**
-  County
 -  Stream/River
 -  Water Body
 -  Rice Land Use

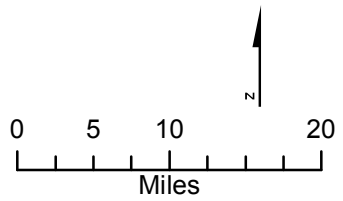


FIGURE 1
Rice Land Use in the Sacramento Valley
 Arsenic in Groundwater, Soil, and Surface Water
 in Rice-Growing Areas of California

The most common organic forms of arsenic are dimethylarsenic acid (DMA) and monomethylarsenic acid (MMA). Both of these compounds can be absorbed by plant tissues, along with inorganic arsenic, and both also have toxic properties. DMA and MMA are bioavailable when ingested through food, but less so than inorganic arsenic. Toxicity effects (including carcinogenicity) of DMA and other organic arsenic compounds are suspected but not yet well understood (Meharg and Zhao 2012).

Environmental Fate and Transport

The pathway from soil and groundwater to rice plant to rice grain is complex. Generally, the prolonged flooded, anoxic conditions typical of California fields contribute to localized mobility of arsenic, potentially making it bioavailable at various stages of plant growth. Figure 2 illustrates the general arsenic chemical cycle in the rice paddy environment. The degree of mobilization of arsenic into the rice plant is determined by soil redox conditions, pH, type and properties of iron hydroxides in the soil, and the availability of phosphate and dissolved organic matter (DOM) (Meharg and Zhao 2012). These processes are further described below.

Soil redox conditions and soil geochemistry play a major role in determining how much of the arsenic present in the environment is made available to and absorbed by plants. Reducing conditions in flooded, anoxic soil (typical of rice fields) are the primary influence on arsenic mobility and bioavailability (Meharg and Zhao 2012). Because arsenite has a greater tendency for dissolution than does arsenate, the mobility of arsenic increases as oxygen is depleted, reducing conditions are established, and it is reduced from arsenate to arsenite (HHS 2007, Meharg and Zhao 2012). Under reducing conditions, iron and other metal hydroxides dissolve and release arsenate and arsenite, as well as other compounds such as phosphate (an essential plant nutrient), from the surfaces of soil particles. Arsenic is more mobile at high pH, because the negative ion is repelled from the increasingly negative charge at mineral surfaces at higher pH. In summary, inorganic arsenic becomes more available to plant roots when (1) arsenate is reduced to arsenite, which is more soluble and more likely to remain in solution; and (2) solid-phase iron hydroxides are reduced and dissolved, releasing both arsenate and arsenite (see Figure 2).

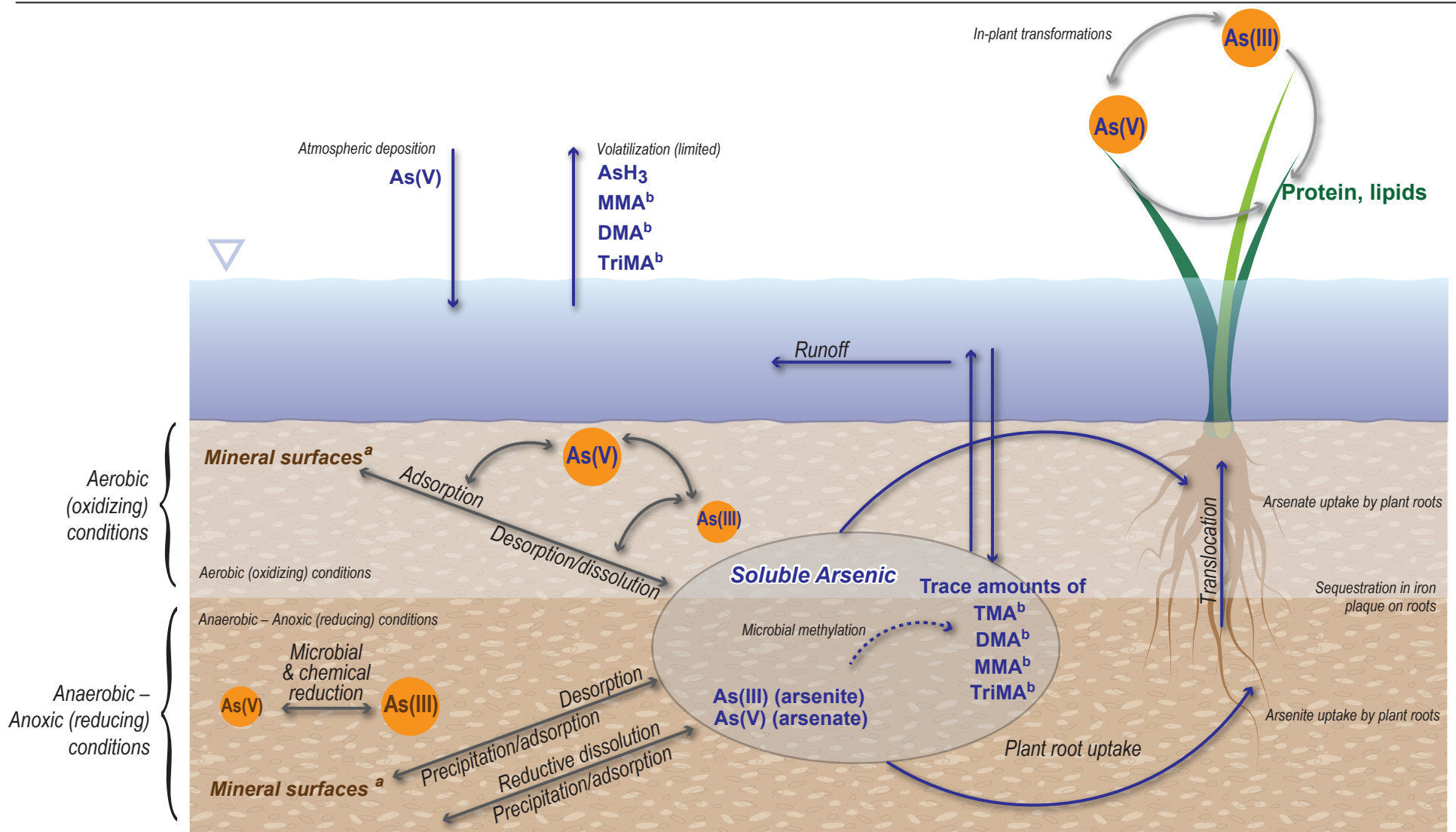
Arsenate is a chemical analog of phosphate, which means that plant roots do not distinguish one from the other when absorbing soil water chemicals (Meharg and Zhao 2012). However, the rate of phosphate uptake can exceed the rate of arsenate uptake. Root uptake of organic arsenic species DMA and MMA is dependent on soil water pH; uptake has been observed to decrease with increasing pH from 4.5 to 6.5 (Meharg and Zhao 2012).

Plants (both roots and shoots) can reduce arsenate to arsenite, which directs arsenic away from being metabolized and allows the plant to combine arsenic with organic compounds (proteins and lipids), which effectively detoxifies arsenic in the plant. However, regardless of whether arsenate or arsenite are dominant, ratios of shoot-to-root arsenic concentrations have been observed to be low, indicating limited mobility of arsenic species from roots to plant shoots (Meharg and Zhao 2012).

Potential Sources of Arsenic

Global research has shown that arsenic in rice field water can be attributed to several different sources, including natural sources and anthropogenic sources. Rice farming techniques and sources of arsenic vary globally.

The following potential sources have been identified in the literature: past or current use of agricultural pesticides and fertilizers containing (or contaminated with) fertilizers, irrigation of rice paddies with soils and groundwater containing naturally-elevated levels of arsenic, atmospheric deposition from industrial pollution and mining, and structures with wood preservatives such as wooden poles and utility poles (HHS 2007).



NOT TO SCALE

^a Arsenic adsorbed to or complexed with soil minerals, particularly iron hydroxides, as well as aluminum hydroxides, clay particles, and organic matter, or co-precipitated with iron hydroxides or sulfides.

^b Tetramethylarsonium (TMA), trimethylarsenic oxide (TriMA), dimethylarsinic acid (DMA) and monomethylarsinic acid (MMA) are organic arsenic compounds formed by microbial methylation of inorganic arsenic.

Note: the chemical species and processes shown are typical at neutral or near-neutral pH.
Sources: Ferguson and Gavis 1972; Meharg and Zhao 2012

FIGURE 2
**Arsenic Transformations in Flooded Soils-
Rice Specific Arsenic Cycle**

In other regions of the U.S., it has been hypothesized that historical arsenic-based herbicides are the primary contributor of arsenic to the rice environment. Unlike these other regions, based on information from California rice experts, Sacramento Valley rice lands were not previously farmed in crops that were historically treated with arsenic-based herbicides, such as cotton. Rice has been grown in California on reclaimed wetland soils for approximately the past 100 years. No arsenic-based herbicides are registered for use on rice in California, and no studies or reports were identified that show historical registrations of such materials on California rice. Regulatory information regarding arsenic in fertilizers in California is provided under the Regulations section of this TM.

Within the Sacramento Valley, it is hypothesized that the predominant source of arsenic is naturally occurring. This hypothesis is supported by a comparison of levels of arsenic in shallow groundwater as compared to deep groundwater, which is presented in the Arsenic in Groundwater section of this report.

Over 200 minerals contain arsenic (Meharg and Zhao 2012). In soils, the most common minerals that contain arsenic are iron oxyhydroxides (e.g. ferrihydrite, goethite) and, under reducing conditions, sulfides such as pyrite. When soils rich in arsenic are weathered by water and wind, elevated levels of arsenic in soils, groundwater, and surface water occur (Meharg and Zhao 2012). In particular, arsenic has been found to be naturally elevated in areas of active or past volcanic or hydrothermal activity. The USGS found that arsenic concentrations in groundwater in the Willamette Basin in Oregon were associated with the aquifer's natural geology, and distribution patterns were not consistent with anthropogenic (industrial and past agricultural) sources (USGS 1999). As of the time this TM was prepared, no similar study has been performed to definitively determine the source of naturally occurring arsenic in the Sacramento Valley.

According to a recent comprehensive USGS study (USGS 2012), geology has a significant influence on arsenic concentrations in basin-fill aquifers, such as the Sacramento Valley aquifer. Volcanic rocks and crystalline rocks are important sources of arsenic. Geologic materials are the major sources of arsenic in the western United States. Reducing conditions in the subsurface can dissolve iron or manganese oxides, subsequently releasing arsenic (along with iron or manganese) into the groundwater. Therefore, reducing environments are often associated with higher arsenic concentrations in aquifer systems. In contrast, arsenic concentrations tend to be low where dissolved-oxygen concentrations or nitrate concentrations are high and indicative of oxic conditions (USGS 2012). The study further indicates that agricultural and urban lands are not generally direct sources of arsenic to groundwater.

A review of groundwater well samples collected over the past 15 years in and around rice fields provides an insight into the quality of groundwater underlying rice fields and the potential for areas of naturally occurring elevated arsenic in groundwater. A few constituents known to be present in natural geologic aquifer formations of the Sacramento Valley, including arsenic, iron, manganese, and sulfate, were found to be above their respective drinking water maximum contaminant level (MCL) in localized areas (CRC 2013). Arsenic detected in shallow groundwater and surface waters at the foot of the Sutter Buttes is likely the result of volcanic sources.

Some naturally occurring constituents might be periodically mobilized through human practices, such as rice farming, as well as through natural seasonal drying and wetting cycles; however, in cases where soils were flooded under native hydrologic regimes (such as the wetland conditions present before land reclamation), historical flooded conditions would have had similar effects on these constituents so that they would have been similarly mobilized (and thus leached and depleted) under pre-development conditions. Due to this type of natural history and the slow vertical seepage through clay rice soils, rice lands are not plausible as significant sources of any of these naturally occurring elements, especially when compared to voluminous reduced aquifer materials (CRC 2013).

Rice Farming

Rice farming in California has been refined over the past century. Rice varieties, irrigation management, fertilization, and pest control provide a well understood and carefully managed system. Rice farming techniques have been developed to withstand the unique growing environment of the Sacramento Valley,

primarily the arid conditions that persist throughout the growing season that require managed, prolonged irrigation. Further, California's relatively small number of pesticides registered for use on rice combined with stringent pesticide-related water quality restrictions presents unique weed management challenges that place irrigation management pressures on Sacramento Valley rice farming. Thus, irrigation and pest management are closely related and managed together in this region.

Irrigation Management

Most California rice is produced by direct seeding into standing water; limited acreage is drill-seeded (planted with ground equipment). A continuous flooded condition is maintained after stand establishment (approximately April through September) until draining for harvest. After harvest, about one-third to one-half of the fields is again flooded in the winter (from October through February). This land management regime results in flooded conditions during 5 to 10 months of the year, making rice fields prime and highly valued habitat for migratory waterfowl. Non-winter-flooded fields may also remain relatively moist, particularly in areas where the soils are poorly drained.

Maintenance of the flooded field serves as an important weed control mechanism. Drained fields provide the opportunity for the establishment of non-wetland weeds, which, if uncontrolled, can outcompete rice plants for nutrients and sunlight. For these reason, fields remain flooded during the stand establishment phase of plant growth. Herbicides are used to provide additional weed control, and must be held on the flooded fields for an extended period, to allow the breakdown of the products and protection of surface water quality. The water holds are established and required by regulation, and are enacted through label restrictions and associated pesticide use permits. During pesticide-related water holds, there is extremely limited ability to release water, and fields remain flooded. The source of irrigation water to rice fields is mostly from surface water, with only a few areas that use groundwater and some that use both surface water and groundwater depending on type of water year (in dry years, farmers that receive less surface water rely on groundwater pumping to irrigate their fields). The rice-growing areas that use groundwater for irrigation are located in southeast Sutter County, south Yuba County, and south Butte County. Areas that use both surface water and groundwater are East Sutter and Placer counties, south Yuba County, portions of Butte County, and a few small areas in Colusa County (DWR 2010).

Applied Materials

Like most other farmland, rice acreage is fertilized annually. Fertilizer suppliers are a primary source of information regarding the rates of fertilizer application. Fertilizer may be applied to rice before planting (anhydrous and aqua ammonia, granular starter, zinc) and/or later in the season to correct deficiencies in an actively growing crop (topdressing). The most commonly needed nutrients for rice production in California are nitrogen, phosphorus, and zinc (UC-ANR 2010). Potassium, sulfur, and iron are less commonly deficient in California rice soils (UC-ANR 2010). Nitrogen fertilizer is typically applied annually, and phosphorus is applied nearly as often. Zinc is applied on approximately 50 percent of fields annually, although the trend has been decreasing in recent years (UC-ANR 2010).

Current use of arsenic in agriculture is expected to be minimal to none. Arsenic is not a component of conventional fertilizers for rice (although there can be trace contamination of arsenic in some fertilizers). Some researchers have identified arsenic-contaminated chicken manure pellets as a potential source of arsenic in processed rice; however, chicken manure is not used on conventional rice in California. Organic rice production may use chicken manure. Nutrients are supplied to organic rice culture through three methods: (1) rotation method with legumes; (2) Organic Materials Review Institute–certified chicken manure pellets (of which some is feather meal); and (3) a 3-year cycle of first year no fertilizer, second year with fertilizer, and third year without rice (fallow). Organic rice in the Sacramento Valley production does not exceed 25,000 acres. The evaluation of arsenic present in chicken manure is not the focus of this TM.

Regulations

Several federal and California agencies have authority over the regulation of arsenic in the environment and food: U. S. Environmental Protection Agency (USEPA), the FDA, and California EPA's Office of Environmental Health Hazard Assessment (OEHHA), Regional Water Quality Control Boards (RWQCB), and California Department of Public Health (CDPH). In addition, the California Department of Food and Agriculture (CDFA) regulates fertilizer products.

The USEPA established a 50 micrograms per liter ($\mu\text{g/L}$) MCL for arsenic in drinking water in 1975. In 2001, in response to research indicating that greater protection from the effects of chronic arsenic exposure was needed, the USEPA lowered that MCL to 10 $\mu\text{g/L}$ (USEPA 2013), which was effective January 2006. As of November 2008, California drinking water regulations match the federal MCL of 10 $\mu\text{g/L}$ for arsenic (CDPH 2008). The public health goal (PHG) is 0.004 $\mu\text{g/L}$ in drinking water, based on studies linking arsenic to lung and bladder cancers (CDPH 2008). PHGs are established by Cal/EPA's OEHHA. They are concentrations of drinking water contaminants that pose no significant health risk if consumed for a lifetime, based on current risk assessment principles, practices, and methods.

Fertilizer products sold in California are regulated by the CDFA. Non-nutritive elements, such as arsenic, are regulated under the California Code of Regulations Title 3, Division 4, Chapter 1, Subchapter 1 §2300 to §2323. This regulation establishes maximum trace concentrations of arsenic in fertilizers.

Arsenic in Surface Water

A review of surface water sampling data collected by various agencies enables an understanding of arsenic concentrations in rivers and other drainages in the Sacramento Valley. The following databases were queried:

- California Environmental Data Exchange Network (CEDEN) under the Irrigated Lands Regulatory Program (Central Valley RWQCB 2013)
- California DWR Water Data Library (DWR 2013)
- USGS National Ambient Water Quality Assessment (NAWQA) Surface Water: Cycle I (1994-2004) report (USGS 2013).

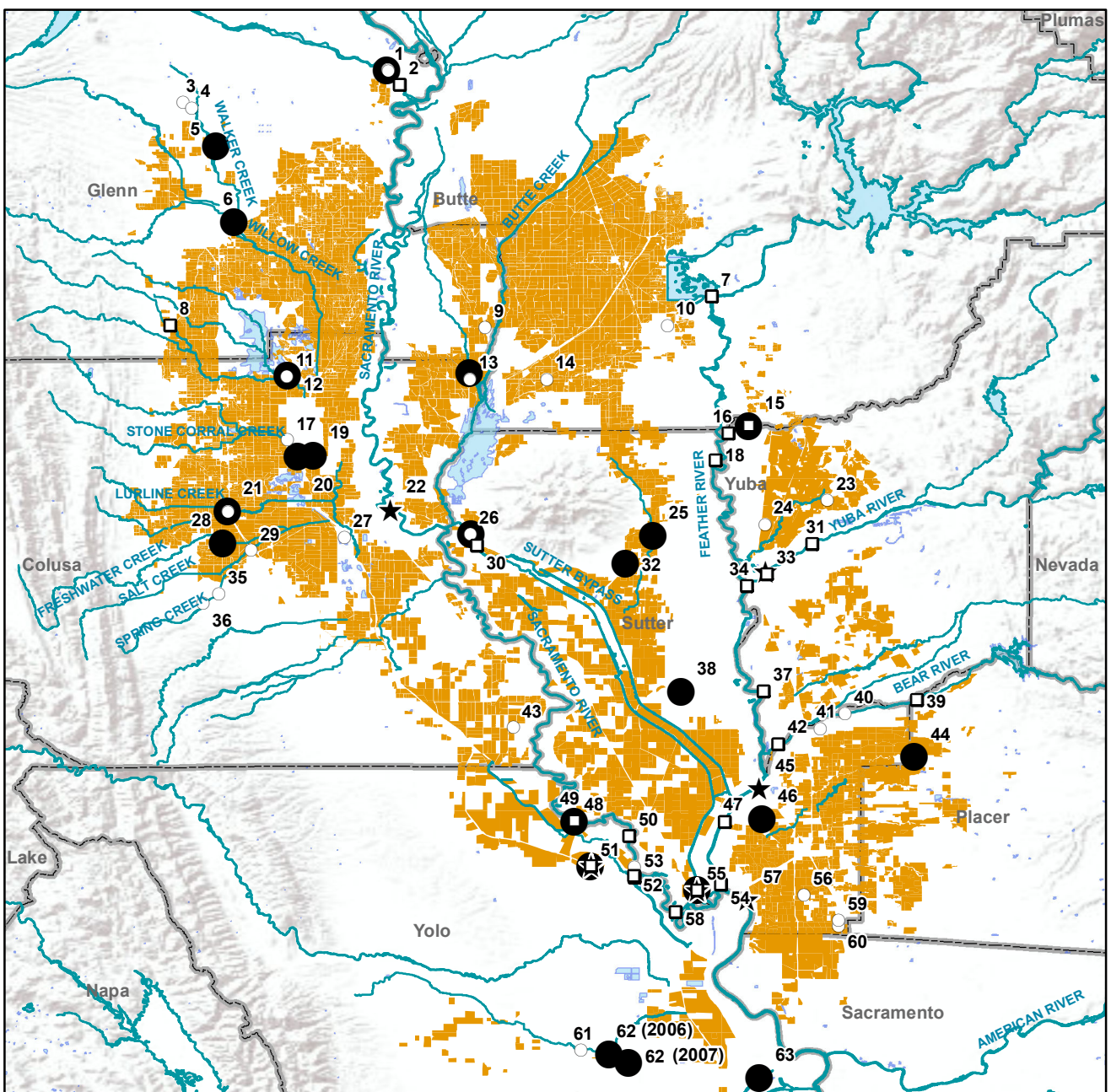
These agencies sampled for dissolved arsenic and/or total arsenic in surface waters at 63 sites near rice land use areas in the Sacramento Valley. CEDEN data covered various sites between 2005 and 2011. The DWR Water Data Library provided sample data as early as 1957 and as recent as 2012. The USGS NAWQA study sampled from 1996 to 1998. Among these three databases, total of 1,478 samples were collected to test for arsenic; Attachment 1 lists the number of samples collected at each site, some of which were sampled by multiple agencies. Figure 3 shows the location of surface water sampling sites with arsenic data in rice-growing areas of the Sacramento Valley; the site ID numbers correspond to those in the first column of the table in Attachment 1.

Surface water samples are typically only analyzed for total and/or dissolved arsenic; no speciation of inorganic and organic arsenic is reported. For simplicity, the data reported in Attachment 1 and related figures do not differentiate between dissolved and total arsenic. Attachment 1 lists the maximum and most recent arsenic concentrations found in surface water samples throughout the Sacramento Valley.

In all of the sites with multiple samples, the most recent arsenic concentrations are lower than the maximum historical concentration, and none of the measurements within the last 30 years exceed 6.5 $\mu\text{g/L}$ (Attachment 1; see also Figure 4). Figure 4 shows the historical arsenic measurements for those sites with multiple years of data; numbers in the legend correspond to the numbers in the first column of Attachment 1.

Figures 5 and 6 show the historical maximum and most recent arsenic concentrations reported for the surface water sampling locations, respectively.

Note that the historical results showing maximum arsenic at 10 µg/L were originally reported in mg/L and used a laboratory method that is no longer used for arsenic (Standard Method 3500-As).



Data Sources: Basemap (ESRI 2013); County, Stream/River (California 2008), Water Body (USGS 1999); Rice Land Use (DWR 2010); Sampling Sites (USGS 2011; CE DEN 2013; DWR 2013). Datum is NAD 83.

VICINITY MAP

LEGEND

- County
- Stream/River
- Water Body
- Rice Land Use
- Surface Water Sampling Site - Data Source
Label = Site ID (Table 1)
- USGS NAWQA
- DWR Water Library
- CE DEN-"Ag Waiver" Project
- CE DEN-SVWQA Monitoring

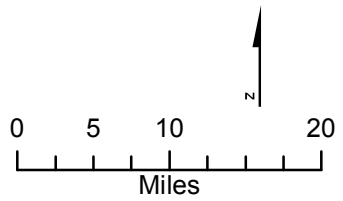
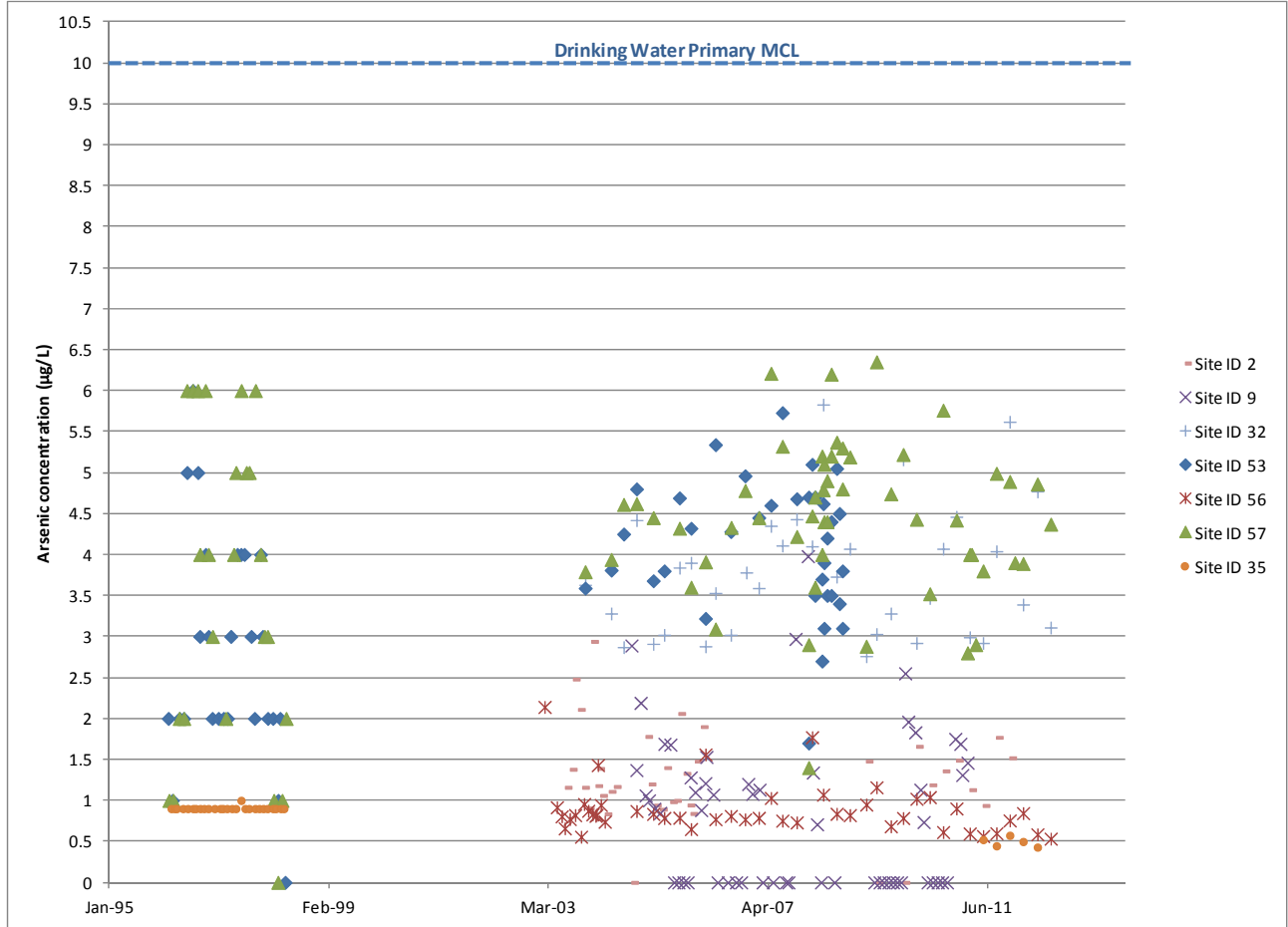
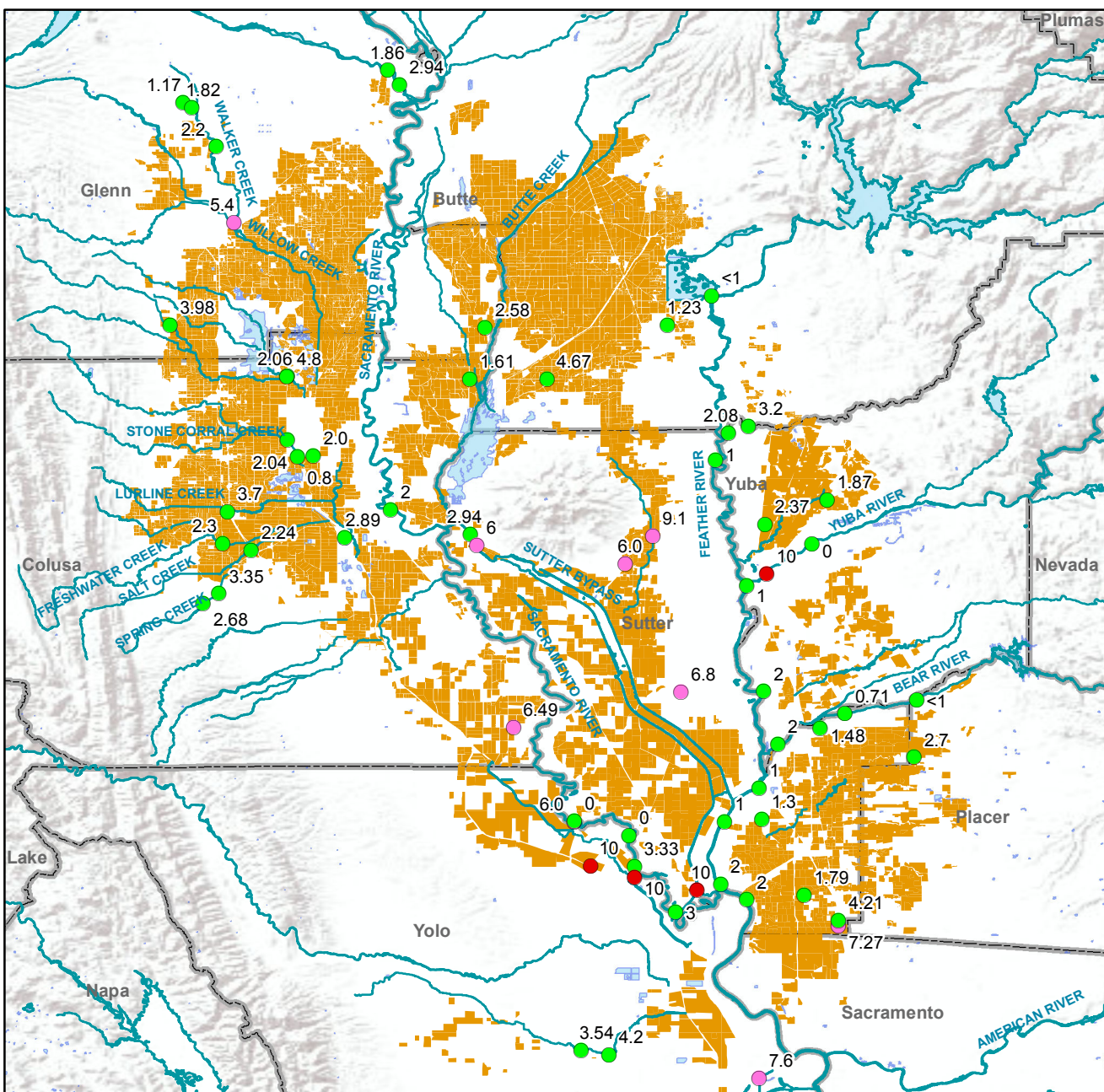


FIGURE 3
Arsenic Sampling Sites in Surface Waters of the Sacramento Valley
 Arsenic in Groundwater, Soil, and Surface Water in Rice-Growing Areas of California

FIGURE 4
Arsenic Concentration Trends in Sacramento Valley Surface Water Samples
Arsenic in Groundwater, Soil, and Surface Water in Rice-growing Areas of the Sacramento Valley





Data Sources: Basemap (ESRI 2013); County, Stream/River (California 2008), Water Body (USGS 1999); Rice Land Use (DWR 2010); Sampling Sites (USGS 2011; CEDEN 2013; DWR 2013). Datum is NAD 83.

VICINITY MAP

LEGEND

- | | | | |
|--|---------------|--|--------------------------------|
| | County | | Surface Water Sampling Site |
| | Stream/River | | Maximum Arsenic Measured, ug/L |
| | Water Body | | <5 |
| | Rice Land Use | | 5 - 9.9 |
| | | | 10+ |

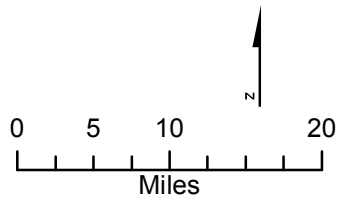
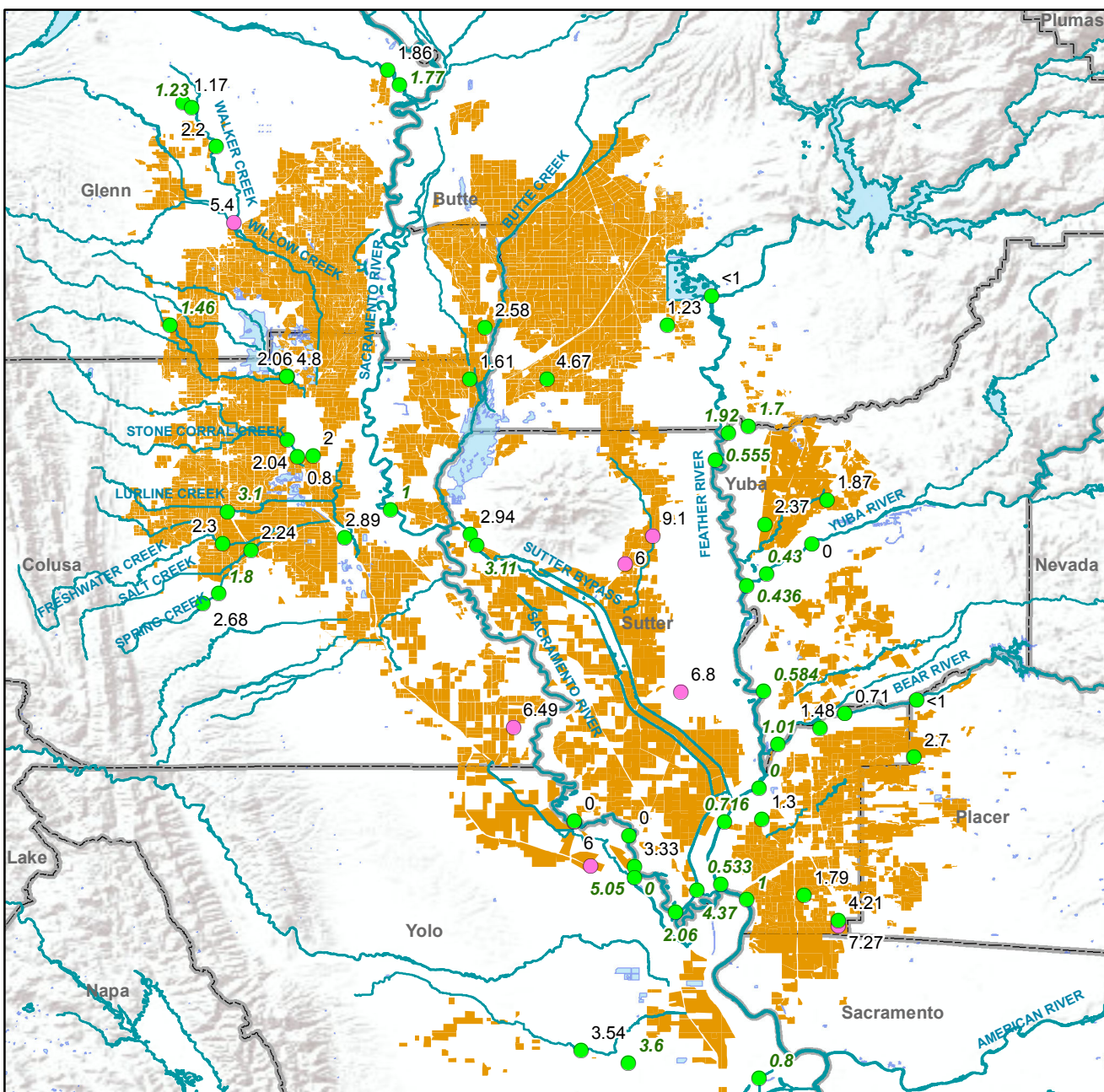


FIGURE 5
Historical Maximum Arsenic Concentrations
 Arsenic in Groundwater, Soil, and Surface Water
 in Rice-Growing Areas of California



Data Sources: Basemap (ESRI 2013); County, Stream/River (California 2008), Water Body (USGS 1999); Rice Land Use (DWR 2010); Sampling Sites (USGS 2011; CEDEN 2013; DWR 2013). Datum is NAD 83.

VICINITY MAP

LEGEND

- County
- Stream/River
- Water Body
- Rice Land Use
- Surface Water Sampling Site
- Most Recent Arsenic Measured, ug/L
- <5
- 5 - 9.9

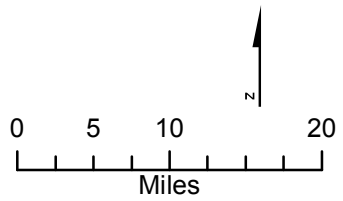


FIGURE 6
Most Recent Arsenic Concentrations
 Arsenic in Groundwater, Soil, and Surface Water
 in Rice-Growing Areas of California

Arsenic in Groundwater

As stated previously, arsenic is a naturally occurring element present in some areas in Sacramento Valley geology, and a detailed analysis of constituents (including arsenic) in groundwater underlying rice fields was performed for the development of the *Rice-specific Groundwater Assessment Report (GAR)* (CRC 2013). Figure 7 shows the mapped maximum observed arsenic results for sampling data from three USGS datasets as presented in the GAR (see Table 1). Figure 8 shows all of the arsenic results from the shallow USGS monitoring wells that were installed specifically to monitor groundwater quality underlying rice fields for the period 1997 through 2010. Figure 9 shows the arsenic trends in the five wells that were sampled at greatest frequency (USGS 2001; CRC 2013). Groundwater quality samples are typically only analyzed for total and/or dissolved arsenic; no speciation of inorganic and organic nitrogen is conducted.

TABLE 1

Summary of Water Quality Datasets Used in the Rice-Specific GAR

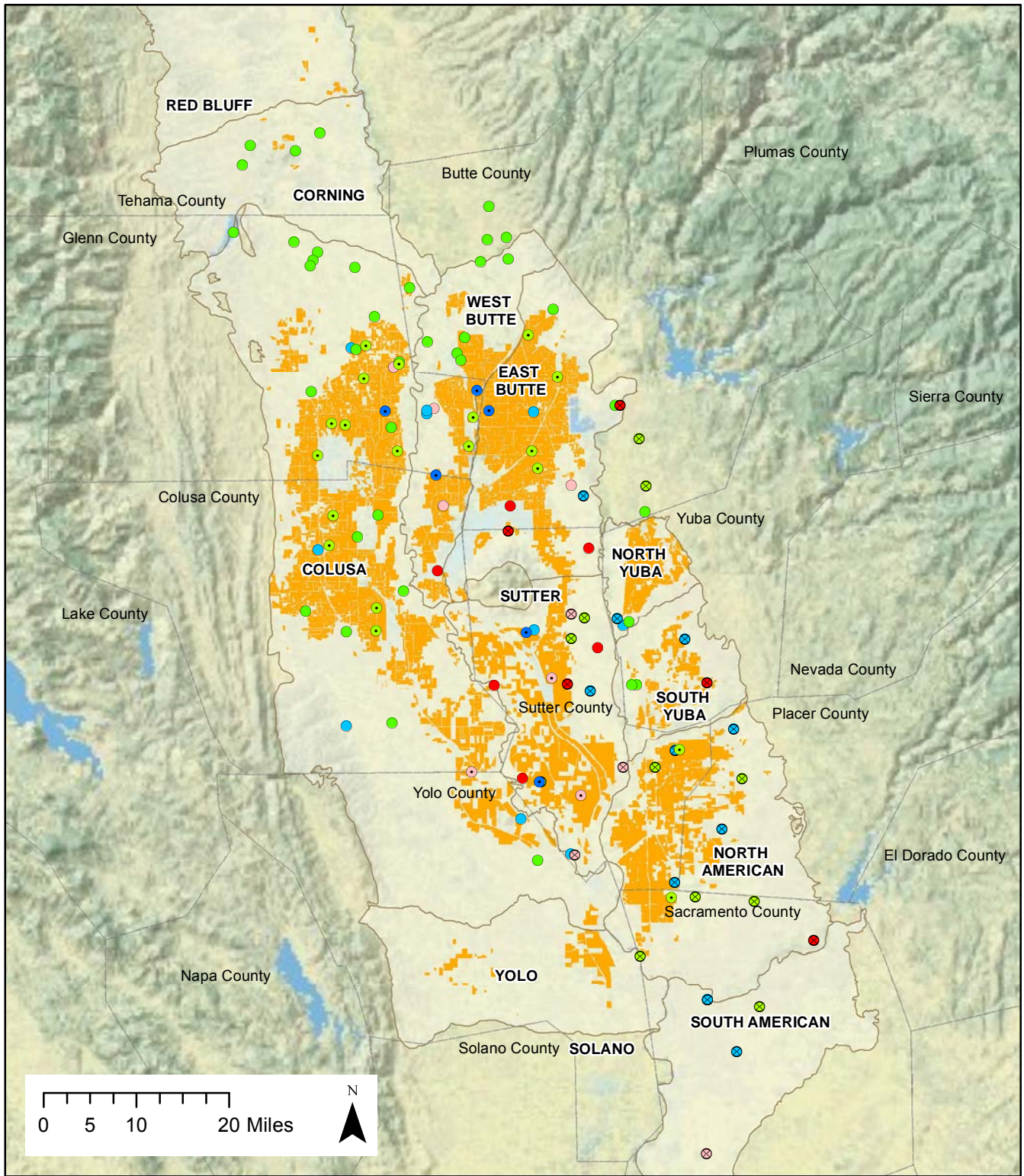
Arsenic in Groundwater, Soil, and Surface Water in Rice-growing Areas of the Sacramento Valley

Dataset	Subsurface Zone	Summary
USGS Rice Wells	Shallow groundwater (30 to 50 feet deep) located near rice fields	The USGS Rice Well network provides a sufficient spatial and temporal dataset on which to base conclusions about the influence of rice farming on groundwater quality. The USGS Rice Wells provide a substantial network of shallow wells considered to be representative of lands on which rice is farmed (rice lands). This well network was constructed in 1997 by USGS, who continues to monitor it. The network initially included 28 wells distributed throughout the Sacramento Valley rice lands. This dataset provides the best water quality data for shallow groundwater quality potentially affected by rice farming.
Shallow Domestic Wells	Shallow groundwater used for domestic supply (average top perforation is 112 feet and average bottom perforation is 149 feet below land surface) in eastern portion of the Study Area	The Shallow Domestic Wells provide additional shallow groundwater quality data to complement data from the USGS Rice Wells. Shallow Domestic Wells are not all located near rice fields and may have mixed land uses around them, but nevertheless can provide an understanding of groundwater quality upgradient and downgradient of rice lands (all sampled in 1996, and a subset in 2008).
USGS GAMA Middle Sacramento Valley Study Unit	Deep public groundwater supply wells (average top perforation is 197 feet and average bottom perforation is 340 feet below land surface)	The USGS GAMA Wells include deeper water supply wells and represent groundwater quality near rice fields and under the influence of prolonged rice farming on land in the region (sampled in 2006).

Source: CRC 2013

The following summarizes the arsenic results from the USGS Rice Wells:

- In 25 of 28 USGS Rice Wells, maximum observed arsenic concentrations were less than 10 µg/L.
- The maximum arsenic detection of 15 µg/L occurred at Well 2 in 1997. A subsequent 2006 measurement at Well 2 showed a concentration of 4.9 µg/L. Well 2 is located in the Sutter groundwater basin, south of the Sutter Buttes. Wells 4 and 6 had maximum concentrations of 11 and 10.4 µg/L, respectively.
- An analysis of the results of the five wells that have been sampled six times shows relatively stable concentrations in each well, with some fluctuations in the 2 to 3 µg/L range.



Data Sources: Groundwater Basins, Rice Crop (California DWR 2010); Basemap, County (ESRI 2011), USGS (2001a, 2001b, 2008). Datum is NAD83. Reproduced from Rice-Specific GAR (CRC 2013)

Legend

USGS Rice Wells

- < 5 µg/L As
- 5 µg/L - 10 µg/L As
- 10 µg/L - 15 µg/L As (Max 15.25 µg/L)

Shallow Domestic Wells

- ⊗ < 5 µg/L As
- ⊗ 5 - 10 µg/L As
- ⊗ 10 - 15 µg/L As
- > 15 µg/L As (Max 46 µg/L)

GAMA Wells

- < 5 µg/L As
- 5 - 10 µg/L As
- 10 - 15 µg/L As
- > 15 µg/L As (Max 80.6 µg/L)

- County Boundary
- Groundwater Basins
- Rice Lands (DWR)

FIGURE 7
Maximum Observed
Arsenic Concentrations in Groundwater

FIGURE 8

Concentrations of Arsenic in USGS Rice Wells

Arsenic in Groundwater, Soil, and Surface Water in Rice-growing Areas of the Sacramento Valley

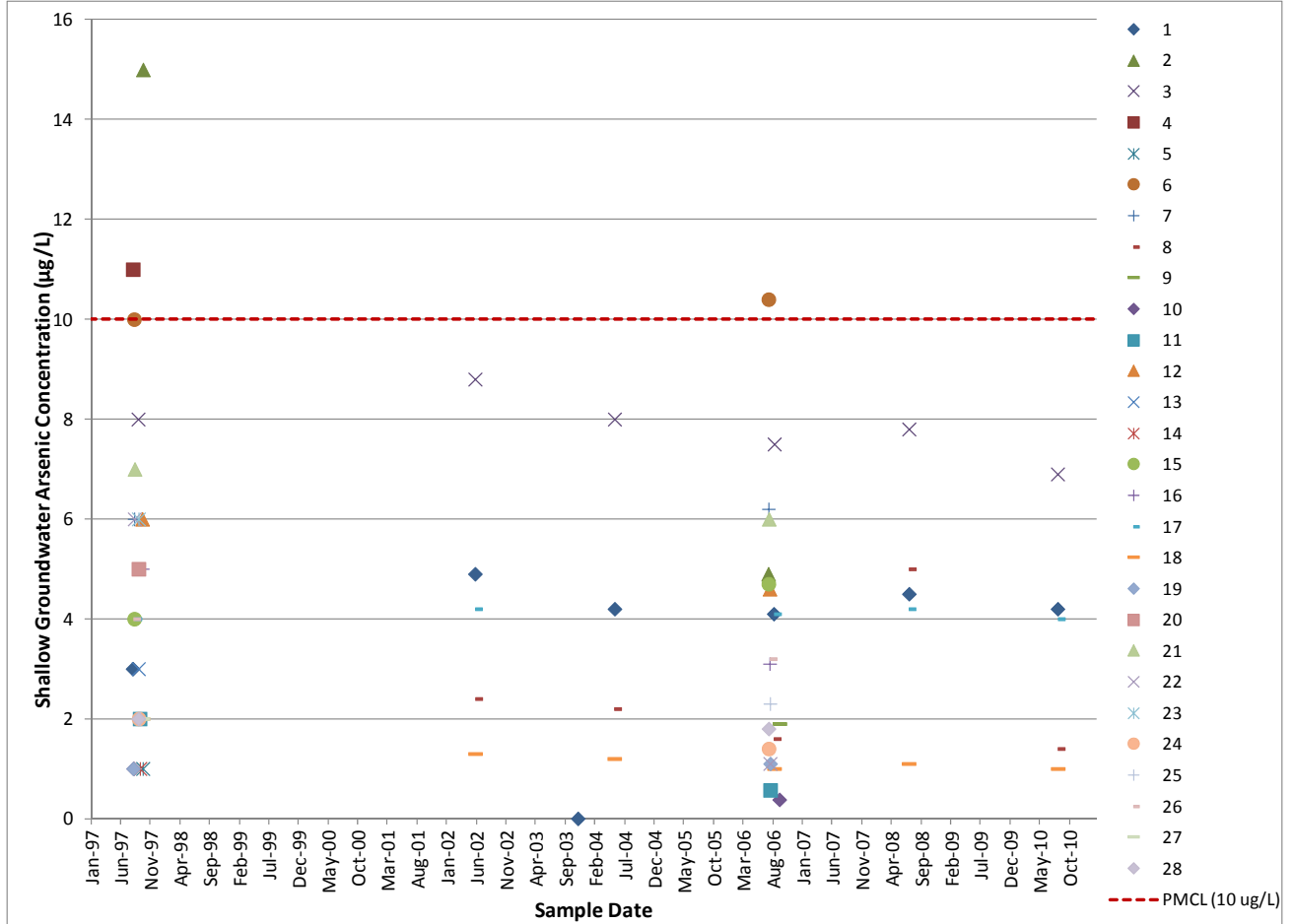


FIGURE 9

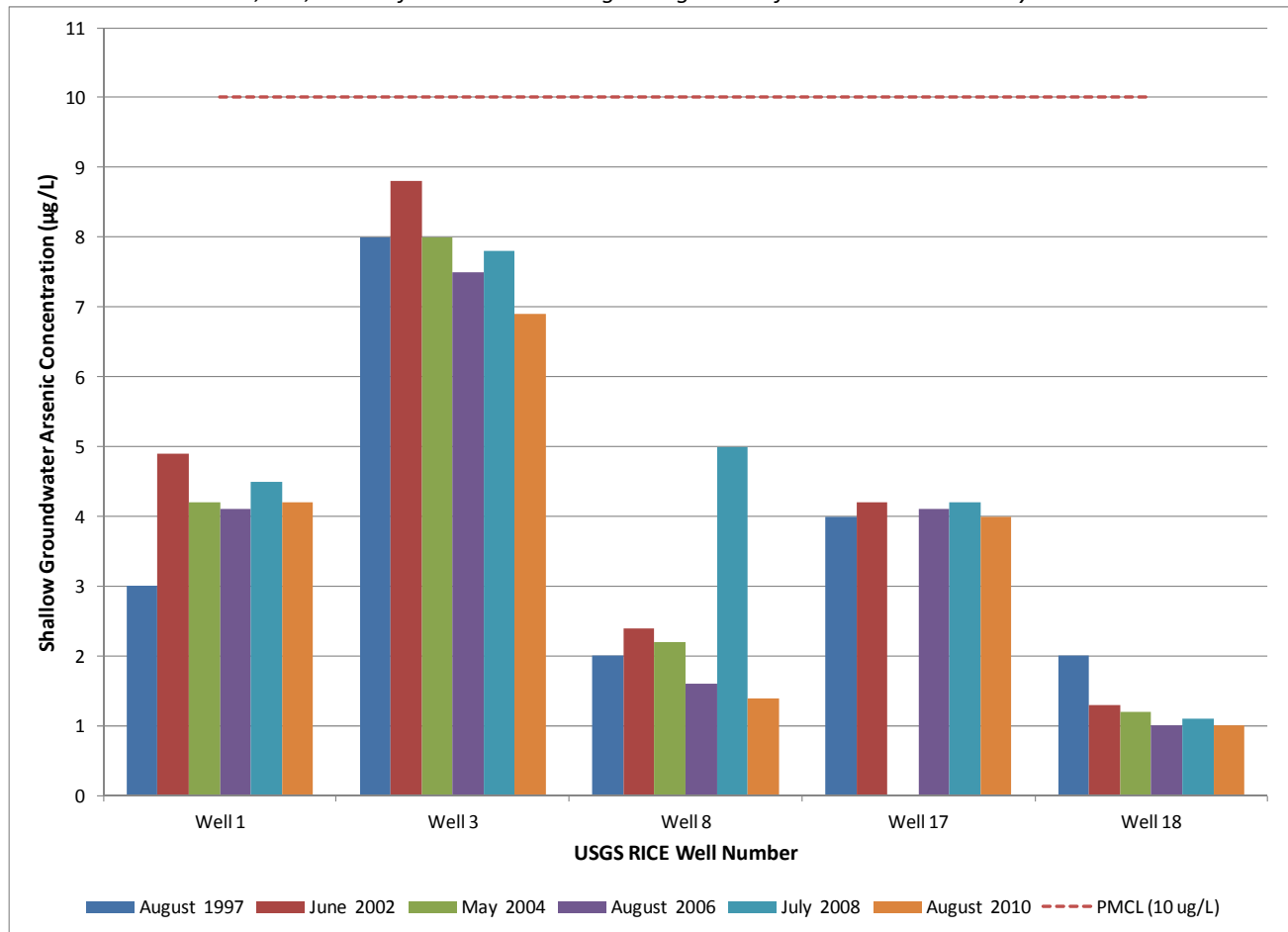
Arsenic Concentration Trends in USGS Rice Wells*Arsenic in Groundwater, Soil, and Surface Water in Rice-growing Areas of the Sacramento Valley*

Figure 7 shows that the portion of the valley north of the Sutter Buttes has generally lower groundwater arsenic concentration than the region south of the Sutter Buttes. The area with the highest detection of arsenic above the MCL is located around the Sutter Buttes and in the Sutter Basin; specifically, locations around the Sutter Buttes and in the Sutter Basin demonstrate elevated levels of arsenic in shallow groundwater in the vicinity of rice fields. In addition, none of the wells in this area are shallow USGS Rice Wells. The wells that show high concentrations of arsenic are mostly the deeper USGS GAMA wells. The elevated levels of arsenic in shallow groundwater are co-located with significantly higher levels in the deeper USGS GAMA wells, suggesting that arsenic is naturally occurring (Sutter Buttes is an extinct volcano).

These recent observations, analyses, and results suggest that arsenic is naturally occurring and that rice agriculture is not adding to the background arsenic content in areas that are low in arsenic.

Arsenic in Soil

Arsenic and other trace elements can contaminate agricultural fertilizers and potentially accumulate in cropland soils (Chang et al. 2004). The mean concentration for arsenic in the western U.S. (west of 96th meridian) is 5.5 milligrams per kilogram (mg/kg), with a range of <0.1 to 97 mg/kg (Shacklette and Boerngen 1984). Worldwide, in uncontaminated soils, the average concentration is estimated range from a low of 4.4 mg/kg for podzolic soils to 9.3 mg/kg for histosols (Kabata-Pendias, 2001). Higher concentrations tend to be associated with alluvial soils (Kabata-Pendias, 2001). The most active soil constituents in fixing arsenic are

hydrated Fe and Al oxides, but subsequent release can readily follow with reducing conditions (Kabata-Pendias, 2001).

CDFA has conducted a limited study evaluating soil concentrations of arsenic in California agricultural soils. This study included two Sacramento Valley sites (Colusa and Glenn counties); however, the precise locations are not available. No studies evaluating background levels of arsenic in soils of Sacramento Valley rice areas were identified.

Conclusions

Arsenic occurs naturally in soils and groundwater of the Sacramento Valley, with higher concentrations in areas with volcanic or hydrothermal geologic influence. The most common sources of arsenic in soils are iron oxyhydroxide minerals in oxidizing environments and from sulfide minerals in reducing environments.

Surface irrigation water is not indicated to be a primary source of arsenic to rice fields, as demonstrated by the low arsenic concentrations at surface water sampling sites. Surface water samples included sites of both irrigation and drainage water. Available data do not support significant current sources of applied anthropogenic arsenic in Sacramento Valley rice fields. Flooding of rice fields creates a chemically reducing environment that can partially dissolve the iron oxyhydroxide source minerals and release arsenic to the root zone; however, the amount of leaching to groundwater through the clay-bottomed rice fields is likely very slow, indicating a limited potential source to deeper groundwater. Further, data do not suggest that rice farming is a source of arsenic to shallow groundwater.

Recommendations

The primary focus of arsenic-related rice research is the potential for inorganic arsenic to be mobilized in soils, taken up by plant roots, and translocated through plant shoots into the rice grain. Because the analysis of inorganic arsenic in rice plants is costly and time-consuming, it is important to prioritize research investments. If it is determined that additional information is needed to characterize arsenic uptake into the rice grain, or to assess practices that may influence arsenic uptake, the prioritization of research areas should be focused on the efficacy of irrigation/pest management practices on minimizing rice grain uptake. In order to assess the feasibility of such field-level trials, the associated impacts of these practices on yield, pest pressures, and plant health would need to be assessed at the production scale. The following concepts are presented for consideration:

- **Soil Sampling:** As there are no identified arsenic soil samples in rice-growing areas of the Sacramento Valley, this information would help provide an understanding of background conditions. It is recommended that soil samples be collected near the existing USGS Rice Wells, in areas of both high and typical shallow groundwater arsenic concentrations.
- **Soil and pore water arsenic evaluations:** Currently, there is no Sacramento Valley specific literature on the partitioning of arsenic from soil and pore water into the rice plant. Such a study would inform an understanding of arsenic's bioavailability to the rice plant under varying Sacramento Valley arsenic soil concentrations, and at different stages of plant growth and irrigation management.
- **Regional analysis:** Areas of the Sacramento Valley south of the Sutter Buttes demonstrate relatively higher levels of arsenic in shallow groundwater compared to other areas where rice is grown. Some of these high-arsenic areas may also rely on groundwater for supplemental irrigation water. These areas could be prioritized for future field-level research investigations, and may provide a basis for assessment of peak irrigation supply conditions. The arsenic maps inform areas of typical Sacramento Valley arsenic levels, in which the majority of rice is grown. Field trials could be performed in both peak and typical arsenic concentration areas.

- **Phosphate related studies:** Because the rice plant uptakes phosphate and arsenic analogously, variation of phosphate management practices could be evaluated as a method for reducing arsenic uptake. The net effect of phosphorus additions on arsenic uptake is not clear, in that some studies suggest reduced uptake from the competition between arsenic and phosphorous, but others emphasize the impact of P on desorption of fixed or complexed arsenic, increasing the solubility and therefore availability of arsenic (Kabata-Pendias, 2001). Further, the impact of increasing phosphorus on yield and profitability would need to be considered.
- **Trace arsenic in fertilizers:** Trace concentrations of arsenic can be present in phosphate-based fertilizers. It is recommended that an analysis be performed to evaluate the loading of arsenic from trace fertilizer contamination. This evaluation would take into consideration the applied rates and trace levels of arsenic in fertilizer brands preferred by growers in the Sacramento Valley.
- **Field flooding duration:** One area of evaluation already under study is reduced duration of flooded conditions on rice fields. This concept is based on the premise that reducing the frequency and duration of flooded conditions in rice soils helps decrease the bioavailability of arsenic to rice. Variable water levels (i.e., cycles of wetting and drying) have been identified as a potential strategy for greatly increasing the redox potential of soils and therefore the availability of arsenic to rice (Xie and Hung 1998 as cited in Kabata-Pendias 2001). Field level trials are underway in California; however, the impacts of this modified irrigation on pest management and yield and the feasibility of these measures in production scale implementation should be co-evaluated.

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Attachment 1
Maximum Arsenic Concentrations in
Rice Area Surface Waters

TABLE 1

Maximum Arsenic Concentrations in Rice Area Surface Waters*Arsenic in Groundwater, Soil, and Surface Water in Rice-growing Areas of the Sacramento Valley*

Site ID	Location (Site Name)	Number of Measurements	Maximum As ($\mu\text{g/L}$)	Month, Year Maximum was Measured	Most Recent As ($\mu\text{g/L}$) ^a	Month, Year Most Recent was Measured	Data Source ^b
1	Stony Creek near Hwy 45	10	1.86	January 2006	1.86	January 2006	CEDEN-Ag Waiver
2	Stony Creek at the Nature Conservancy	38	2.94	January 2004	1.52	November 2011	DWR Water Library
3	Drain to Walker Cr at County Rd F	2	1.17	July 2005	1.17	July 2005	CEDEN-Ag Waiver
4	Unnamed Drain of Walker Creek on Co. Rd. 28	10	1.82	August 2004	1.23	July 2005	CEDEN-Ag Waiver
5	Walker Creek near 99W and CR33	7	2.2	December 2009	2.2	December 2009	CEDEN-SVWQC
6	Walker Creek at County Road 48	32	5.4	June 2008	5.4	June 2008	CEDEN-SVWQC
7	Thermalito Afterbay A Feather R	125	< 1	All 1998-2011	< 1	September 2011	DWR Water Library
8	Logan C at Tehama-Colusa Canal	57	3.98	January 2008	1.46	January 2011	DWR Water Library
9	Howard Slough at Afton Road	4	2.58	July 2007	2.58	July 2007	CEDEN-Ag Waiver
10	Hamilton Slough at Hwy 99	5	1.23	September 2004	1.23	September 2004	CEDEN-Ag Waiver
11	Hunters Creek at Four Mile Road	5	2.06	July 2007	2.06	July 2007	CEDEN-Ag Waiver
12	Logan Creek at 4 Mile-Excelsior Road	16	4.8	April 2007	4.8	April 2007	CEDEN-SVWQC
13	Butte Creek at Gridley Road	1	ND	March 2006	ND	March 2006	CEDEN-SVWQC
13	Butte Creek at Gridley Road	4	1.61	February 2006	1.61	February 2006	CEDEN-Ag Waiver
14	Main Drainage Canal at Colusa Highway	12	4.67	October 2007	4.67	October 2007	CEDEN-Ag Waiver
15	Lower Honcut Creek at Hwy 70	16	3.2	December 2009	1.4	December 2011	CEDEN-SVWQC; DWR Water Library
16	Honcut C A Pacific Ranch NR Palermo	14	2.08	August 2003	1.92	April 2004	DWR Water Library
17	Stone Corral Creek at Four Mile Road/Excelsior Road	12	2.04	October 2007	2.04	October 2007	CEDEN-Ag Waiver
18	Feather R A Archer AVE	14	0.987	February 2004	0.555	April 2004	DWR Water Library
19	Colusa Drain near Maxwell Road	2	2	March 2006	2	March 2006	CEDEN-SVWQC

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20	Stone Corral Creek near Maxwell Road	1	0.8	March 2006	0.8	March 2006	CEDEN-SVWQC
21	Lurline Creek at Hwy 99	32	3.7	April 2007	2.3	September 2008	CEDEN-SVWQC
22	Sacramento River at Colusa, CA	27	2	Various 1996, 1997	1	January–April 1998	NAWQA
23	Jack Slough	6	1.87	February 2006	1.87	February 2006	CEDEN-Ag Waiver
24	Simmerly Slough at Ellis Avenue	5	2.37	September 2004	2.37	September 2004	CEDEN-Ag Waiver
25	Lower Snake River at Nuestro Road	32	9.1	January 2008	9.1	January 2008	CEDEN-SVWQC
26	Butte Slough at Lower Pass Rd	4	2.94	February 2006	2.94	February 2006	CEDEN-Ag Waiver, SVWQC
27	Colusa Basin Drain #5 (CBD5)	4	2.89	January 2006	2.89	January 2006	CEDEN-Ag Waiver
28	Freshwater Creek at Gibson Road	32	2.3	August 2007, 2008	2.3	August 2008	CEDEN-SVWQC
29	Salt Creek at Old Hwy 99	12	2.24	June 2007	2.24	June 2007	CEDEN-Ag Waiver
30	Butte Slu Nr Meridian	41	5.83	May 2008	3.11	August 2012	DWR Water Library
31	Yuba R Nr Marysville	12	< 1	April, September, August 1977–2004	< 1	April, September, August 2004	DWR Water Library
32	Wadsworth Canal at South Butte Road (Weir #4)	2	6	March 2006	6	March 2006	CEDEN-SVWQC
33	Yuba River at Marysville	39	10	September 1966	0.43	May 2012	DWR Water Library; NAWQA
34	Yuba R A MO	10	1.03	May 2009	0.436	February 2011	DWR Water Library
35	Spring Creek at Walnut Drive	43	3.35	February 2005	1.8	October 2007	CEDEN-Ag Waiver
36	Spring Creek at E. Camp Rd.	4	2.68	June 2005	2.68	June 2005	CEDEN-Ag Waiver
37	Feather R Bl Star Bend	15	1.63	February 2004	0.584	April 2004	DWR Water Library
38	Gilsizer Slough at George Washington Road	16	6.8	May 2007	6.8	May 2007	CEDEN-SVWQC

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Site ID	Location (Site Name)	Number of Measurements	Maximum As (µg/L)	Month, Year Maximum was Measured	Most Recent As (µg/L) ^a	Month, Year Most Recent was Measured	Data Source ^b
39	Bear R Nr Wheatland	3	< 1	September, June, May 1965, 1967, 1971	< 1	May 1971	DWR Water Library
40	Bear River at Pleasant Grove Rd.	4	0.71	July 2005	0.71	July 2005	CEDEN-Ag Waiver
41	Yankee Slough at Swanson Road	6	1.48	July 2004	1.48	July 2004	CEDEN-Ag Waiver
42	Bear R NR MO	16	1.77	February 2012	1.01	August 2012	DWR Water Library
43	Unnamed Canal at Hwy 45	4	6.49	July 2004	6.49	July 2004	CEDEN-Ag Waiver
44	Coon Creek at Brewer Road	32	2.7	May 2008	2.7	May 2008	CEDEN-SVWQC
45	Feather River near Nicolaus, CA	27	1	April 1996	< 1	January–April 1998	NAWQA
46	Coon Creek at Striplin Road	2	1.3	February 2006	1.3	February 2006	CEDEN-SVWQC
47	Feather R Ab Verona	2	1	March 1989	0.716	August 2004	DWR Water Library
48	R-D 108 Dr to Sac R	3	< 1	July, May, August 1957, 1971, 1989	< 1	August 1989	DWR Water Library
49	Rough and Ready Pumping Plant at Road 108	2	6	March 2006	6	March 2006	CEDEN-SVWQC
50	R-D 787 Drainage to Sacramento R	2	< 1	May, August 1971, 1989	< 1	August 1989	DWR Water Library
51	Colusa Basin Drain near Knights Landing	90	10	June 1981	5.05	August 2008	DWR Water Library; CEDEN-SVWQC; NAWQA
52	Colusa Basin Drain above Knights Landing (CBD1)	5	3.33	February 2006	3.33	February 2006	CEDEN-Ag Waiver
53	Ag Drain on Colusa Basin Drain	7	10	October 1957	< 1	May 1971	DWR Water Library
54	Feather R NR Verona	47	2.14	February 2003	0.533	August 2012	DWR Water Library
55	Sacramento Slough (Sutter Bypass) near Knights Landing	97	10	September 1961	4.37	August 2012	
56	North Main Canal at Sankey Rd.	5	1.79	July 2005	1.79	July 2005	CEDEN-Ag Waiver
57	Sacramento River at Verona, CA	27	2	Various 1996, 1997	1	January–April 1998	NAWQA

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Site ID	Location (Site Name)	Number of Measurements	Maximum As ($\mu\text{g/L}$)	Month, Year Maximum was Measured	Most Recent As ($\mu\text{g/L}$) ^a	Month, Year Most Recent was Measured	Data Source ^b
58	Sacramento R Bl Knights Landing	28	2.85	May 2007	2.06	August 2008	DWR Water Library
59	Unnamed Ditch at SW corner of Levee and Riego Rd	4	4.21	August 2004	4.21	August 2004	CEDEN-Ag Waiver
60	N-S Ditch along Natomas Rd	5	7.27	June 2005	7.27	June 2005	CEDEN-Ag Waiver
61	Willow Slough at Road 99	5	3.54	July/August 2004	3.54	July/August 2004	CEDEN-Ag Waiver
62	Willow Slough Bypass at Pole Line	24	4.2	June 2007	3.6	August 2008	CEDEN-SVWQC
63	Tule Canal at North East corner of I-80	10	7.6	July 2005	0.8	March 2006	CEDEN-SVWQC

^a Bolded values indicate where the most recent maximum arsenic concentrations are different from historical maximum arsenic concentrations.

^b Online data sources: CEDEN: California Environmental Data Exchange Network; Ag Waiver: project under the Irrigated Lands Regulatory Program; SVWQC: Sacramento Valley Water Quality Coalition; NAWQA: National Ambient Water Quality Assessment study conducted by USGS; DWR Water Library: California Department of Water Resources water quality database.