



Factors controlling tungsten concentrations in ground water, Carson Desert, Nevada

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Received 13 May 2004; accepted 2 September 2004

Editorial handling by W.B. Lyons

Abstract

An investigation of a childhood leukemia cluster by US Centers for Disease Control and Prevention revealed that residents of the Carson Desert, Nevada, are exposed to high levels of W and this prompted an investigation of W in aquifers used as drinking water sources. Tungsten concentrations in 100 ground water samples from all aquifers used as drinking water sources in the area ranged from 0.27 to 742 $\mu\text{g/l}$. Ground water in which W concentrations exceed 50 $\mu\text{g/l}$ principally occurs SE of Fallon in a geothermal area. The principal sources of W in ground water are natural and include erosion of W-bearing mineral deposits in the Carson River watershed upstream of Fallon, and, possibly, upwelling geothermal waters. Ground water in the Fallon area is strongly reducing and reductive dissolution of Fe and Mn oxyhydroxides may be releasing W; however, direct evidence that the metal oxides contain W is not available.

Although W and Cl concentrations in the Carson River, a lake, and water from many wells, appear to be controlled by evaporative concentration, evaporation alone cannot explain the elevated W concentrations found in water from some of the wells. Concentrations of W exceeding 50 $\mu\text{g/l}$ are exclusively associated with Na–HCO₃ and Na–Cl water types and pH > 8.0; in these waters, geochemical modeling indicates that W exhibits <10% adsorption. Tungsten concentrations are strongly and positively correlated with As, B, F, and P, indicating either common sources or common processes controlling their concentrations. Geochemical modeling indicates W concentrations are consistent with pH-controlled adsorption of W.

The geochemical model PHREEQC was used to calculate IAP values, which were compared with published K_{sp} values for primary W minerals. FeWO₄, MnWO₄, Na₂WO₄, and MgWO₄ were undersaturated and CaWO₄ and SrWO₄ were approaching saturation. These conclusions are tentative because of uncertainty in the thermodynamic data.

The similar behavior of As and W observed in this study suggests ground water in areas where elevated As concentrations are present also may contain elevated W concentrations, particularly if there is a mineral or geothermal source of W and reducing conditions develop in the aquifer.

Published by Elsevier Ltd.

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1. Introduction

Between 1997 and 2002, 15 cases of acute lymphocytic leukemia (ALL) and one case of acute myelocytic leukemia were diagnosed in children and teenagers who live, or have lived, in an area centered on the town of Fallon, Churchill County, Nevada (Fig. 1). As part of a State and Federal investigation of the cancer cluster, the US Geological Survey (USGS) sampled 100 wells in the Fallon area during Summer and Fall of 2001. The purpose of the USGS investigation was to support the Centers for Disease Control and Prevention (CDC) investigation of the cancer cluster by characterizing the chemical quality of ground water used as drinking water and by determining whether families of children with leukemia are exposed to the same concentrations of contaminants in their drinking water as the rest of the community (Seiler, 2004).

In March and April 2002, the CDC collected samples of, urine, blood and buccal cells for chemical and genetic analysis. A total of 205 residents from 69 families provided samples, including 13 children with leukemia and an additional 40 members of their families and 152 residents from the Fallon area who were used as controls. The results of the chemical analysis for urine showed that the community is exposed to much higher levels of W than the national population. About 68% of the study participants from the Fallon area had urine levels of W greater than the 95th percentile for a United States reference population (<http://www.cdc.gov/nceh/clusters/Fallon/study.htm> accessed August 4, 2003).

The occurrence of elevated W concentrations in urine was of immediate interest to the residents of Fallon and to State and Federal health officials because there are numerous W mines and prospects in western Nevada (Fig. 1) and there is an active W mill in the Fallon area that produces tungsten-carbide tools. Since little is known about the health effects of W, there was concern that W was related to the leukemia cluster even though the CDC data showed the median W concentration for families of a child with leukemia were the same as the W concentration in comparison families. Because limited data were available to assess long-term health effects of exposure to W, it was nominated in 2002 by the CDC National Center for Environmental Health for toxicological and carcinogenesis studies as a result of the findings in Fallon.

Tungsten is rarely analyzed in ground water and had not been analyzed in Fallon-area ground-water samples collected by the USGS during 2001. Following the CDC discovery in 2002, archived ground-water samples from 2001 were analyzed for W to determine the range of W concentrations in Fallon ground water and identify possible sources. Additional samples of tap water from the kitchens of Fallon residents who participated in the CDC study were collected and ana-

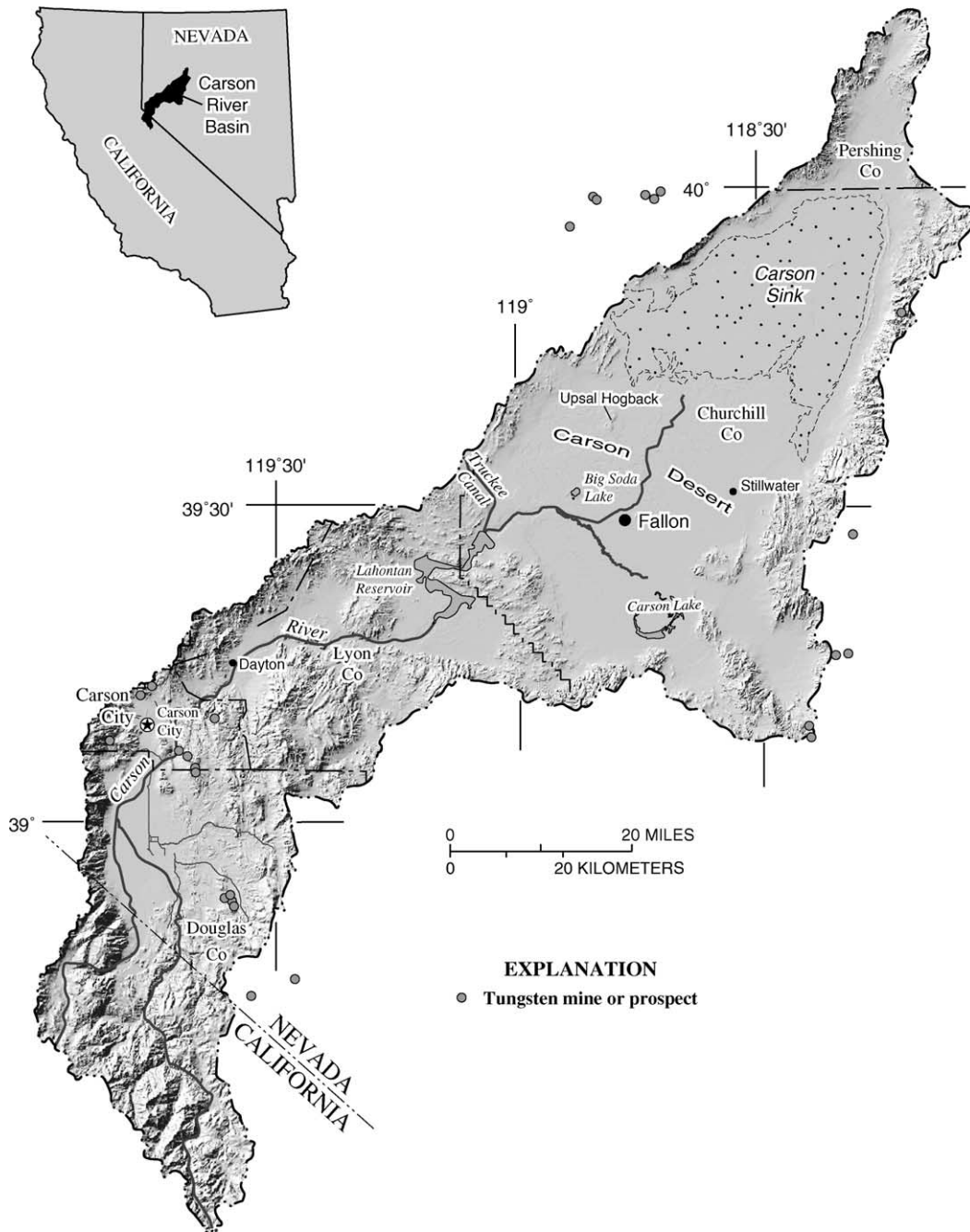
lyzed in 2002 by the USGS to further support the CDC investigation.

Several hydrological and geochemical studies of the Carson Desert (Olmsted et al., 1984; Morgan, 1982; Glancy, 1986; Lico and Seiler, 1994; Doyle et al., 1995; Maurer et al., 1996; Maurer and Welch, 2001; Welch and Lico, 1998; Seiler, 2004) provide a framework for identifying processes that lead to elevated W concentrations in the Carson Desert. The purposes of this paper are (1) to describe the occurrence and distribution of W in Carson Desert ground water; (2) to identify the possible source(s) of the W; and (3) to identify the processes leading to elevated W concentrations in Fallon area ground water. Because W is seldom measured, the results should be useful in identifying other areas where W concentrations may be elevated in drinking-water supplies because of similar geochemical and hydrological conditions.

2. Tungsten chemistry, mineralogy, and occurrence

Tungsten is a Group VIB transition element and, as such, has similar properties to Mo and Cr. Tungsten exists in several oxidation states (0, 2+, 3+, 4+, 5+, and 6+), with the 6+ state being the most stable in water (Baes and Mesmer, 1976). Tungstate (WO_4^{2-}) is the dominant aqueous species and occurs monomerically for the range of pH (6.9–9.3) and W concentration (0.27–742 $\mu\text{g/l}$) applicable to this study (Baes and Mesmer, 1976). Polymerization of WO_4^{2-} takes place with decreasing pH and increasing W concentrations forming polytungstate species. Ions such as NH_4^+ shift the pH at which polycondensation occurs, and polytungstate species in ammoniacal solution are stable at pH values where normally only monotungstate ions exist (Lassner and Schubert, 1999). Other ions, such as F^- , substitute for OH^- ions bound to the central W ion, which suppresses the ability to condense. Tungsten can also form aqueous heteropolytungstates with a number of elements, in which oxides of As, B, Mn, P, Si and V, are combined with a large number of WO_3 groups (Rieck, 1967).

Tungsten is not found as native metal in nature, rather it is chemically combined in 14 known minerals (Lemmon, 1966). Most W deposits are spatially associated with granitoid plutons where W is derived from fluids equilibrated with the granitic magma and subsequently deposited in the pluton and/or silicate and/or carbonate country rock (Wood and Samson, 2000). Of the two principal groups of W minerals, the scheelite group is a solid solution, with scheelite (CaWO_4) and powellite (CaMoO_4) being the end members. These end members commonly occur as primary minerals; however, mixtures commonly occur as secondary minerals (Hurlbut and Klein, 1977). Scheelite is



Base from U.S. Geological Survey digital data, 1:100,000
 Universal Transverse Mercator projection
 Zone 11

Fig. 1. Location of Carson River Basin, California and Nevada, and W mines and prospects in Nevada.

found in granite pegmatites, contact metamorphic deposits, and high temperature hydrothermal veins in granites; common mineral associations are fluorite, apatite, molybdenite, and wolframite (Hurlbut and Klein, 1977).

The wolframite group is a solid solution with ferberite (FeWO_4) and heubnerite (MnWO_4) as its end members. The name wolframite is applied to intermediate compounds that contain less than 80% of either end member (Stager and Tingley, 1988). Wolframite is com-

paratively rare and usually is found in pegmatites and high temperature quartz veins in granites; pyrite and arsenopyrite commonly are associated with wolframite (Hurlbut and Klein, 1977).

Between 1900 and 1957, Nevada produced about 30% of the total domestic output of W (Lemmon, 1966). Although scheelite is the most commonly found W mineral in Nevada, heubnerite also is an important W source in the State (Stager and Tingley, 1988). Tungsten-rich hot springs deposits also have been mined near Golconda, about 306 km NE of Fallon. Tungsten minerals were not observed in the W-rich deposits of psilomelane and limonite by Kerr (1940), who proposed that W was adsorbed in colloidal suspensions of Fe and Mn while they were in a gel state in the spring water.

A recent review of the biology of W (Kletzin and Adams, 1996) summarized the distribution of W in natural environments. They concluded that W is present in concentrations of >50 nM (~ 9 $\mu\text{g/l}$) in 4 types of natural waters: ground waters directly associated with W containing ore deposits; in alkaline, nitrogenous fissure-vein thermal waters of crystalline rocks; in alkaline waters of lakes in arid areas; and in hot-spring waters and hydrothermal vents. The greatest reported values for a natural water, >0.27 mM (~ 49 mg/l), are from Searles Lake, California, a briny lake draining an area of scheelite deposits.

Although ground water is rarely analyzed for W, elevated W concentrations in Nevada ground water have been reported previously. Grimes et al. (1995) reported concentrations ranging from 1 to 260 $\mu\text{g/l}$ in ground water around disseminated Au deposits along the Getchell Trend, Humboldt County, Nevada. Benson and Spencer (1983) reported that W concentrations in 9 well-water samples from the Walker River basin, California and Nevada, ranged between 8 and 128 $\mu\text{g/l}$ and in 10 spring-water samples ranged between 2.6 and 332 $\mu\text{g/l}$. The 3 highest W concentrations (>60 $\mu\text{g/l}$) were in geothermal springs whose temperature exceeded 38 °C.

3. Study area

3.1. Geographic and geohydrologic setting

The town of Fallon is in the southern end of the Carson Desert, a hydrologically closed basin at the terminus of the Carson River (Fig. 1). The Carson Desert lies in the rainshadow of the Sierra Nevada and annually receives about 12.7 cm of precipitation (Maurer et al., 1996). Annual potential evaporation rates are more than 10 times this amount. Average temperatures range from about -8 to 32 °C.

The principal land use in the Fallon area is agricultural, however, the area is rapidly urbanizing and agri-

cultural land is being converted to residential areas. Carson River water and imported water from the Truckee River via the Truckee Canal are the sources of water used for agriculture. Water for irrigation is stored about 30 km west of Fallon in Lahontan Reservoir (Fig. 1). Fields typically are flood irrigated, water being delivered to the fields through an extensive network of mostly unlined canals. Drain water discharges to surface drains and is ultimately delivered to wildlife areas near Carson Lake and Stillwater (Fig. 1).

The Carson Desert occupies a valley in the Basin and Range physiographic province. Maurer et al. (1986) summarized available information on the geologic history of the Carson Desert and its influence on groundwater movement. During the Quaternary period, the ancestral Carson, Truckee, and Walker Rivers carried water and sediment from the eastern slopes of the Sierra Nevada into ancient Lake Lahontan. At its maximum stand, the ancient lake covered 21,500 km² and was about 150 m deep in the Fallon area. Depositional environments in the basin during the Quaternary period were controlled by large changes in the level of Lake Lahontan, from deep-lake intervals to intervals of complete desiccation.

Glancy (1986) defined 3 basin-fill aquifers (shallow, intermediate, and deep) and a basalt aquifer in the Carson Desert (Fig. 2). Unconsolidated Quaternary sediments from ancient Lake Lahontan and unconsolidated and semi-consolidated Tertiary sediments form the basin-fill aquifers. The shallow aquifer extends from the water table (generally less than 3 m) to a depth of 15 m. Infiltration of surface water from the Carson River and numerous unlined canals and ditches that crisscross the area is the principal source of recharge to the shallow aquifer. The construction of the Newlands Project in the early 1900s supplied irrigation water to the Fallon area and resulted in water levels in the shallow aquifer rising up to 5 m in large areas NE of Fallon and from 7.5 to 12 m near Big Soda Lake (Maurer et al., 1996). Under present-day conditions water levels are within 2–3 m of land surface in irrigated areas.

The boundary between the shallow and intermediate basin-fill aquifers is indistinct and poorly correlated with geologic units. The intermediate aquifer is confined, with water levels in wells rising to within 3–12 m of land surface (Maurer and Welch, 2001). The vertical hydraulic gradient between the shallow and intermediate aquifers is downward west of Fallon and upward in the rest of the basin. Infiltration of Carson River water through the shallow aquifer provides the bulk of recharge to the intermediate aquifer (Maurer et al., 1996), with minor amounts of recharge from the basalt aquifer, upwelling geothermal water, and infiltration of precipitation in mountains surrounding the Carson Desert.

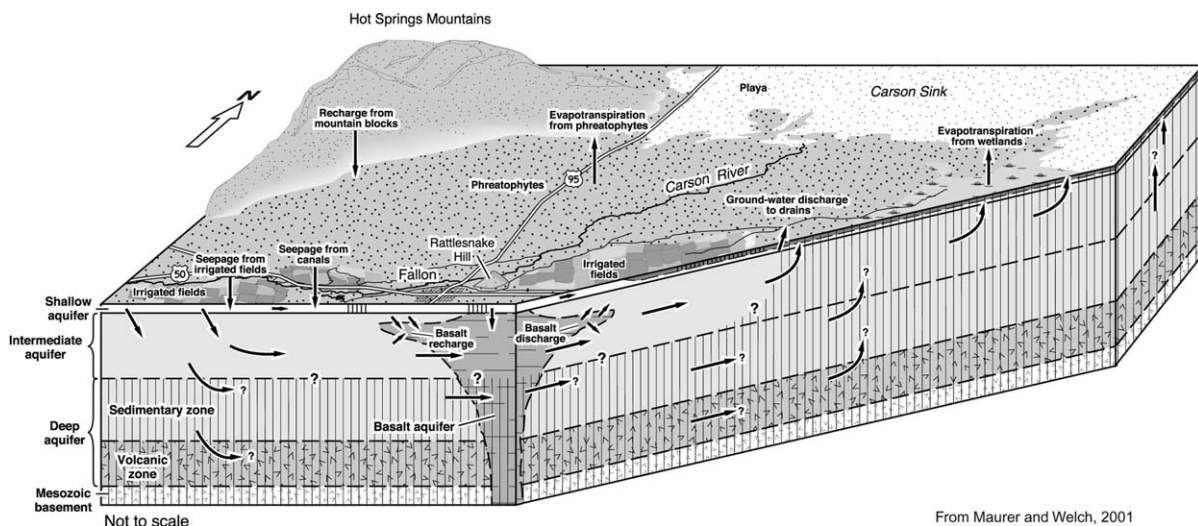


Fig. 2. Conceptual model of ground water flow in basin fill and basalt aquifers in Carson Desert, Nevada. Boundaries between aquifers are dashed where uncertain; arrows depicting ground-water flow are queried where uncertain.

The boundary between the intermediate and deep aquifers is about 150–300 m below land surface. The boundary, which is poorly known because few wells penetrate the deep aquifer, is based on the salinity of the water and may correspond to the boundary between Quaternary and Tertiary age sediments (Maurer et al., 1996).

The basalt aquifer is an asymmetrical, mushroom-shaped body, mostly buried by Lake Lahontan sediments. It is composed of consolidated rock of widely ranging permeability, ranging from dense, fractured lava flows to basalt rubble and cinders in zones between the flows (Maurer et al., 1996). The basalt aquifer was formed when volcanic activity during the Quaternary period resulted in a volcanic cone that has eroded, and is now exposed at Rattlesnake Hill (Fig. 2). Recharge to the basalt aquifer is from surrounding basin-fill aquifers; however, the actual flow paths for recharge are largely unknown.

The stable-isotope composition of water and ^3H concentrations suggest that near the center of the Carson Desert, under the current hydrologic regime, recharge of water from the Carson River is restricted to the upper 15 m of the aquifer system (Maurer and Welch, 2001). The stable-isotope composition of waters from the intermediate and basalt aquifers are similar, but much more depleted than current Carson River water and most water in the shallow aquifer. Recharge to the intermediate and basalt aquifers may have occurred during periods prior to construction of Lahontan Reservoir when the climate was wetter and colder (Maurer and Welch, 2001; Lico and Seiler, 1994).

Municipal wells tapping the basalt aquifer supply drinking water to about one-half of the people who re-

side in the Fallon area. These wells are all more than 120 m deep, except for one well at the base of Rattlesnake Hill. Domestic wells in rural areas surrounding the town of Fallon tap the shallow and intermediate basin-fill aquifers. The deep aquifer is unused as a water source because of its high salinity.

3.2. Ground-water chemistry

Water entering the Carson Desert from the Truckee and Carson Rivers is a dilute Na-Ca-HCO_3 water, which, as it flows through the basin-fill aquifers, evolves to a more concentrated Na-HCO_3 water and ultimately to a saline Na-Cl type in discharge areas (Lico and Seiler, 1994). Water with dissolved-solid concentrations greater than 10,000 mg/l is found in the shallow aquifer in non-irrigated discharge areas such as the Stillwater, Carson Lake, and Soda Lakes/Upsal Hogback areas.

The composition of water in the shallow aquifer is highly variable because flow is determined by locations of unlined ditches and canals, amount and timing of irrigation, depth to water, and physical characteristics of sediments (Lico and Seiler, 1994). Typically, water in the shallow aquifer is moderately hard (>70 mg/l as CaCO_3) with a median pH of 7.4 (Seiler, 2004). The composition of water in the intermediate aquifer is of two types: a saline Na-Cl water associated with the Soda Lakes/Upsal Hogback area and the other a dilute Na-HCO_3 water in the central Fallon area (Lico and Seiler, 1994). Water in the basalt aquifer is a Na-Ca-HCO_3 type. Water from the intermediate and basalt aquifers is soft (<25 mg/l as CaCO_3) with median pHs of 8.3 and 9.3 (Seiler, 2004).

Major elements in ground water in the Carson Desert are primarily the result of chemical reactions with minerals derived from rocks in upland areas. Sediments in Carson Desert aquifers are derived from intrusive and extrusive igneous, sedimentary, metavolcanic, and meta-sedimentary rocks in adjacent mountains and the headwaters of the Carson River in the Sierra Nevada (Lico and Seiler, 1994). In recharge areas, Na and HCO_3 concentrations increase through the dissolution of albite, whereas Ca, Na, Cl, and SO_4 concentrations increase through the dissolution of small amounts of calcite, halite, and gypsum (Lico and Seiler, 1994). As water flows through the aquifer system, Na concentrations increase and Ca concentrations decrease because of evapoconcentration, calcite precipitation, and exchange of Ca for Na on clay minerals. Processes involving halite dissolution and calcite precipitation in discharge areas likely drive the final evolution from a Na– HCO_3 to Na–Cl water type.

Ground water in the aquifer system typically contains dissolved- O_2 (DO) concentrations <0.5 mg/l and commonly has an odor of H_2S (Seiler, 2004). Nitrate concentrations typically are less than 1 mg/l in all of the aquifers, with the highest concentrations being in the shallow aquifer (Lico and Seiler, 1994). Concentrations of SO_4 range from <1 to 810 mg/l and the presence of H_2S indicates that loss of SO_4 from ground water is the result of microbial reduction. Water in all aquifers is undersaturated with respect to gypsum; thus precipitation of gypsum does not account for decreases in SO_4 concentrations (Lico and Seiler, 1994).

Unusually high concentrations of As and U are widespread in shallow ground water in the Carson Desert (Welch and Lico, 1998; Seiler, 2004) and are of particular concern because they commonly, sometimes greatly, exceed drinking-water standards. Concentrations of As in filtered samples from drinking-water wells in the Carson Desert ranged from <1 to 2200 $\mu\text{g/l}$ with a median concentration of 65 $\mu\text{g/l}$ (Seiler, 2004). Concentrations of U in filtered samples from the same wells ranged from <0.02 to 340 $\mu\text{g/l}$ with a median concentration of 1.7 $\mu\text{g/l}$. Most of the high As and U concentrations can be attributed to evaporative concentration in the Carson River water that recharges the aquifer (Welch and Lico, 1998), however, dissolution reactions involving metal oxides and sedimentary organic matter also contribute As and U.

4. Methods

One-hundred samples of Fallon area ground water were collected from 99 domestic and public-supply wells and 1 industrial well during June–September 2001, following the USGS National Water Quality Assessment (NAWQA) protocol described in Koterba et al. (1995).

Before sample collection, wells were purged of at least 3 casing volumes of water and field measurements had stabilized in a flow-through chamber that measured temperature, pH, DO, and specific conductance, although DO was not measured when a strong odor of H_2S was present. During sample collection, the water had contact only with materials in the well and pump system, Teflon[®] tubing, and stainless steel connections. Filtered samples for major ions, most trace elements, N and P species, and dissolved organic C (DOC) were collected after passing through a disposable 0.45 μm inline capsule filter. Arsenic species were separated in the field using solid-phase extraction (SPE) cartridges; As(V) was retained on the cartridge and the eluate containing As(III) was preserved with EDTA. Filtered water for alkalinity, expressed as HCO_3 and CO_3 , was analyzed in the field by titration of filtered sample. Samples for filtered trace elements, including W, were acidified in the field to pH <2 using 7.7 N Ultrex HNO_3 . Samples for DOC and As, N, and P species were kept chilled between collection and analysis. Between wells, the Teflon[®] tubing and all materials used for sample collection were decontaminated by washing and scrubbing with a low-phosphate dilute detergent and thoroughly rinsed with deionized water at least 3 times. Cleaned sampling equipment was inspected and then stored in new plastic bags until used.

Samples were analyzed at the USGS National Water Quality Laboratory (NWQL) for major ions, trace elements, and nutrients following methods described in Fishman and Friedman (1989), Fishman (1993), Garbarino and Taylor (1994), and Jones and Garbarino (1999). Samples for determining As speciation were analyzed using the method of Bednar et al. (2003). Unfiltered samples were digested using HNO_3 and HCl and filtered prior to analysis using a procedure described in Hoffman et al. (1996).

The concentration of W was determined using inductively coupled plasma-mass spectrometry. A pneumatic cross-flow nebulizer with an Ar flow rate of 0.8 ml/min was used to introduce samples into a 1300 watt Ar plasma. Two W isotopes, nominally mass-to-charge ratios of 182 and 183, were measured to corroborate analytical results. These isotopes were selected because they have no direct isobaric interferences and interference corrections for polyatomic ions (Eu oxides) are minimal. Data was acquired in triplicate for both isotopes using a dwell time of 10 ms and a total integration time of 1000 ms. The Re internal standard, corrected for isobaric interference from Os, was added automatically to the segmented-flow sample stream through a tee followed by a 10-turn mixing coil and debubbler. Both W isotopes were calibrated using multi-point linear regression ($r^2 \geq 0.999$) based on a series of W standards ranging in concentration from 0 to 1000 $\mu\text{g/l}$. The method detection limit

(MDL) was 0.09 µg/l. Laboratory blanks, continuing calibration verification standards (CCV), spike recovery samples, and duplicates were analyzed with every batch of samples for quality control. All laboratory blank W concentrations were less than the MDL. The average spike recovery for 30 samples selected at random and spiked with 50–100 µg/l W was 99 ± 5%. There is no known source for certified aqueous standard reference materials, however the solution used to prepare the calibration standards was traceable to National Institute of Standards and Technology. All CCV results were within ±5% at 100 µg/l W. The median relative percent difference for replicates was 1.7% for sample W concentrations ranging from 0.1 to 85 µg/l.

To verify that decontamination of sampling equipment was adequate, field blanks were collected at 10% of the ground-water sampling sites and analyzed for the same target analytes as the environmental samples. In the 10 equipment blanks collected, W concentrations were nondetects (<0.09 µg/l) in 8 samples, and were 0.28 and 0.65 µg/l in the other two samples. Concurrent replicate samples were collected at 12% of the ground-water sampling sites. The % difference between replicate and environmental samples was <4% in 11 of the 12 samples (W concentrations ranging between 0.93 and 673 µg/l), and was 7.8% in the twelfth sample (W concentration 1.83 µg/l).

Filtered, acidified samples of ground water were held for a year after sample collection before being analyzed for W. Archived sample material held at NWQL was analyzed for W following reports by CDC in Aug. 2002 that W concentrations were elevated in the urine of Fallon residents. During 2002, unfiltered samples were collected by USGS from kitchen taps of 76 Carson Desert residents. The tapwater samples were collected after running the water for 2 min until cool and acidified in the field and immediately analyzed at NWQL for trace elements, including W. The data were primarily used by CDC to compare exposure of case and control

families to W and other trace elements, but it was also used for this study to assess whether the long holding time had affected W concentrations in the archived ground-water samples. The tapwater samples included samples from 4 houses where wells were sampled in 2001 and from 27 houses and apartments using public water supplies.

Geochemical modeling was done using PHREEQC (Parkhurst and Appelo, 1999). Equilibrium constants for W derived from the published literature (Table 1) and those for As speciation and mineral solubility products (Nordstrom and Archer, 2003) were added to the PHREEQC database.

Competitive adsorption of H⁺, Ca²⁺, Mn²⁺, Mg²⁺, Sr²⁺, AsO₃⁻³, AsO₄⁻³, F⁻, PO₄⁻³, SO₄²⁻, and WO₄²⁻ was simulated using the generalized two-layer model of Dzombak and Morel (1990). Equilibrium constants for adsorption of all species except W were derived from experimental adsorption on ferrihydrite (Dzombak and Morel, 1990). Equilibrium constants for adsorption of W were derived from linear free-energy relationships (LFER's) (Dzombak and Morel, 1990). Gustafsson (2003) quantified W adsorption on ferrihydrite; however, these equilibrium constants predicted unreasonably high W adsorption in this study (greater than 99% at pH 10). This was most likely a result of much greater ratios of W to adsorption sites (Gustafsson, 2003) than were defined for this study. The Dzombak and Morel (1990) equilibrium constants for W provide an internally consistent database among all adsorbed species that were considered.

The simulations used a single adsorption site having a concentration of 0.03 moles/l, a surface area of 600 m²/g, and a solid concentration of 8 g/l. These values were calculated according to the method of Dzombak and Morel (1990) and are based on the average amount of Fe extracted by hydroxyl-amine hydrochloride from 20 sediment samples collected from the southern Carson Desert (Welch and Lico, 1998).

Table 1
Tungsten reactions added to PHREEQC database

Reaction	Log <i>k</i>	References
WO ₄ ²⁻ + H ⁺ = HWO ₄ ⁻	3.67	Naumov et al. (1974)
HWO ₄ ⁻ + H ⁺ = H ₂ WO ₄ ⁰	2.20	Naumov et al. (1974)
CaWO ₄ = Ca ²⁺ + WO ₄ ²⁻	-9.47 ^a	Naumov et al. (1974), Robie et al. (1978)
MgWO ₄ = Mg ²⁺ + WO ₄ ²⁻	-6.30	Naumov et al. (1974)
SrWO ₄ = Sr ²⁺ + WO ₄ ²⁻	-10.6	Naumov et al. (1974)
Na ₂ WO ₄ = 2Na ⁺ + WO ₄ ²⁻	3.9	Naumov et al. (1974)
FeWO ₄ = Fe ²⁺ + WO ₄ ²⁻	-12.1	Polya (1990)
MnWO ₄ = Mn ²⁺ + WO ₄ ²⁻	-7.92	Naumov et al. (1974)
SiteOH + WO ₄ ²⁻ + H ⁺ = SiteWO ₄ ⁻ + H ₂ O	9.2	Dzombak and Morel (1990)
SiteOH + WO ₄ ²⁻ = SiteOHWO ₄ ²⁻	2.1	Dzombak and Morel (1990)

^a Calculated using free energy values for Ca²⁺ and WO₄²⁻ from Naumov et al. (1974) and for CaWO₄ from Robie et al. (1978) for internal consistency with other values from Naumov et al. (1974).

5. Results and discussion

5.1. Tungsten occurrence and distribution

Tungsten concentrations in filtered ground-water samples from the Fallon area ranged from 0.27 to 742 $\mu\text{g/l}$, with a median concentration of 13.4 $\mu\text{g/l}$. Comparison of results for the same sites from archived 2001 ground-water samples and 2002 tapwater samples indicate the extended holding time for the ground-water samples did not substantially affect W concentrations (Fig. 3).

Wells yielding water with W concentrations exceeding 50 $\mu\text{g/l}$ are mainly SE of Fallon in an area centered on Naval Air Station (NAS) Fallon (Fig. 4). Most of these wells are finished in the intermediate aquifer. Wells from the intermediate aquifer sampled in this study produced water that was alkaline (median pH 8.1), anaerobic (median DO <0.2 mg/l), and commonly was SO_4 reducing. Tungsten concentrations exceeding 50 $\mu\text{g/l}$ also are found in water from 3 wells in the shallow and intermediate aquifers E–SE of Big Soda Lake and 3 wells in the intermediate aquifer N–NE of Rattlesnake Hill.

The median W concentrations in water from the basalt and intermediate aquifers do not significantly differ, but are significantly greater than the median W concentration in the shallow aquifer (Fig. 5). The range of values observed in waters from the basalt aquifer is much smaller than in waters from the shallow and intermediate aquifers. Of the 27 samples with W concentrations exceeding 50 $\mu\text{g/l}$, 23 were from the intermediate aquifer. Concentrations of W exceeding 50 $\mu\text{g/l}$ are exclusively associated with Na– HCO_3 and Na–Cl water types (Fig. 6). The correlations between W and selected constituents are listed in Table 2.

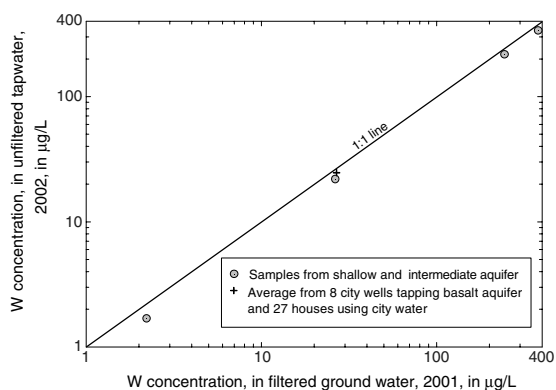


Fig. 3. Comparison of W concentrations in tapwater samples and archived ground-water samples indicating extended holding time did not substantially affect W concentrations.

5.2. Sources of tungsten in Carson Desert ground water

5.2.1. Anthropogenic sources

For more than 20 ka, W ore was smelted in an open-air kiln about 15 km north of Fallon during the manufacture of tungsten-carbide tool bits and other products. Wastewater was flushed onto the desert floor without treatment until 1990; however, wastewater from the W mill is an unlikely source of W to ground water in the Fallon area because it is located hydrologically down-gradient of Fallon. Uncontrolled atmospheric emissions from the mill before controls were installed in 1994 were a potential source of W to land surface where it could infiltrate to the water table. The prevailing winds are from the south which places Fallon upwind of the mill during most of the year.

There is a significant correlation between orthophosphate and W (Table 2) and phosphate fertilizers applied to fields in Fallon could be a source of W. Concentrations of W tend to be low in non-phosphate fertilizers (Senesi et al., 1988), but can range from 1.2 to 7.8 mg/kg in commercial phosphate fertilizers (Charter et al., 1995).

Stable isotopic data of the ground water show modern anthropogenic sources of W are unlikely in ground water from the intermediate and basalt aquifers. The majority of ground-water samples with W concentrations exceeding 50 $\mu\text{g/l}$ are associated with δD values of -110‰ to -115‰ (Fig. 7), whereas δD values in Carson River samples, where evaporation takes place, are less negative. The change in stable isotope composition at a depth of 15 m indicates recharge of water under the current hydrologic regime is restricted to the upper 15 m of the aquifer in most areas, with present-day water in the intermediate aquifer probably originating from flow of the Carson River before construction of Lahontan Reservoir in 1915 (Maurer and Welch, 2001). Thus, modern anthropogenic sources are unlikely to have contributed W to water tapped by most wells sampled during this investigation.

5.2.2. Natural sources

Most of the W mines in the mountains surrounding the Carson Desert are outside the Carson River watershed (Fig. 1). Water passing over and through W-rich deposits in the headwaters of the Carson River has eroded and dissolved W-containing minerals, resulting in the transport of W by the river into the Carson Desert. In 1992, during a drought period, W concentrations in filtered samples collected from nine sites along the East Fork, West Fork, and main stem of the Carson River above Lahontan Reservoir ranged from 1.5 to 22.6 $\mu\text{g/l}$ (Johannesson et al., 2000). During a more normal climatic period in the spring of 2003, W concentrations in 7 filtered samples collected during this study from 3 sites along the East Fork of the Car-

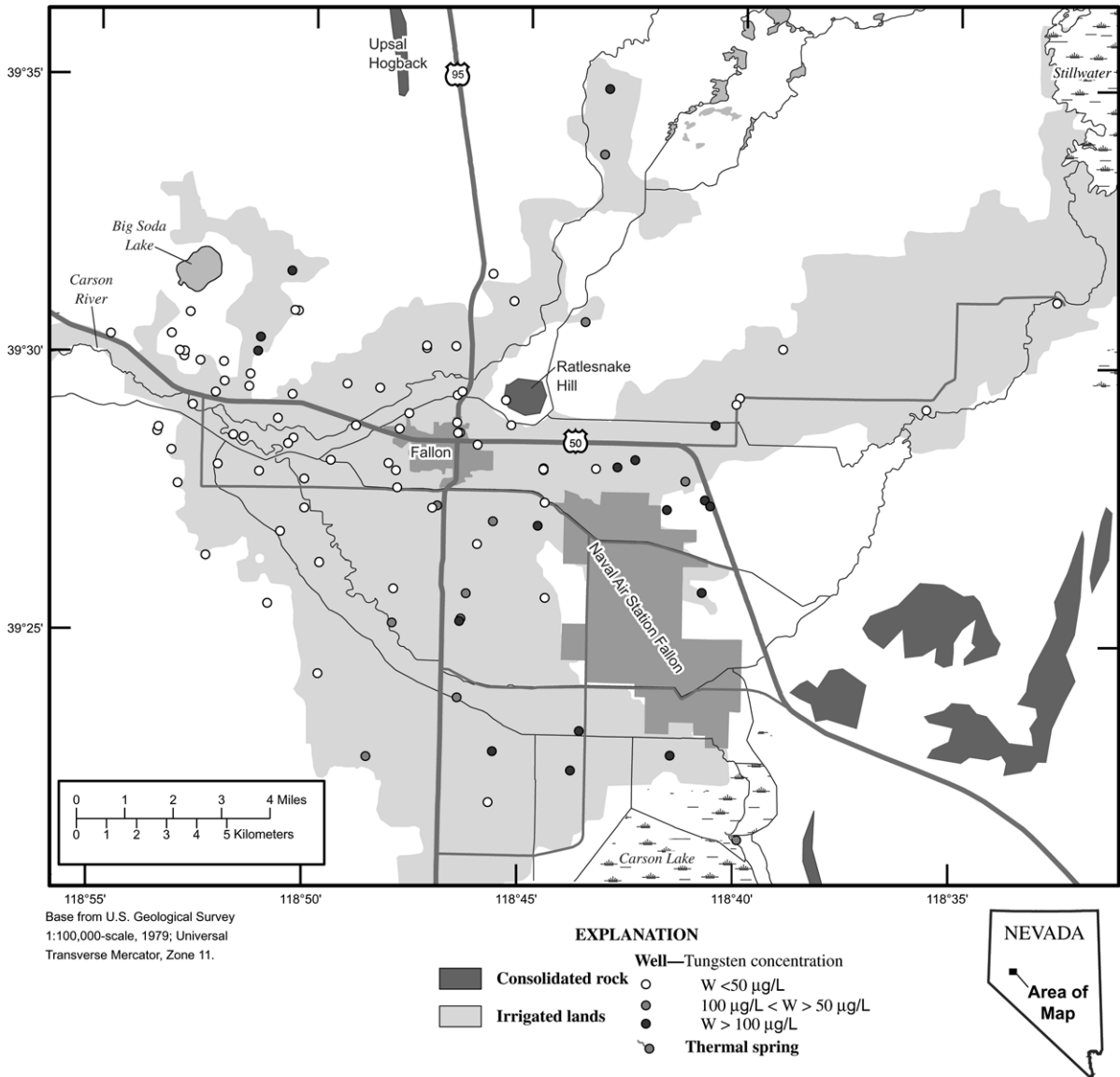


Fig. 4. Location of sampling sites, town of Fallon, and W concentrations in wells.

son River and the main stem above and below Lahontan Reservoir ranged from 0.1 to 4.6 µg/l. The W concentration in Lahontan Reservoir during the 1992 drought was 31 µg/l (Johannesson et al., 2000), which is greater than the W concentration in 70% of the wells sampled in 2001. Four W mines in the Truckee River watershed are upstream of the diversion of water into the Truckee Canal (Stager and Tingley, 1988). These deposits could have become W sources to the Carson Desert following completion of the Truckee Canal in 1905. In 1992, W concentrations in the Truckee River upstream of the diversion ranged from 0.32 to 2.2 µg/l (Johannesson et al., 2000). These data indicate

the importance of the Carson River, and to a lesser extent the Truckee River, as sources of W and suggest the possibility that evaporative concentration in Lahontan Reservoir, particularly during drought periods, may be an important control on W concentrations in Carson Desert aquifers.

Upwelling water in geothermal areas beneath the Carson Desert may be a source of W, as W concentrations ranging from 1 to more than 1000 mg/l are readily attainable in geothermal fluids (Wood and Samson, 2000). About 4.9×10^6 m³/a of geothermal water flows upward from depths greater than 2400 m where it mixes with non-thermal water in shallow, intermediate, and

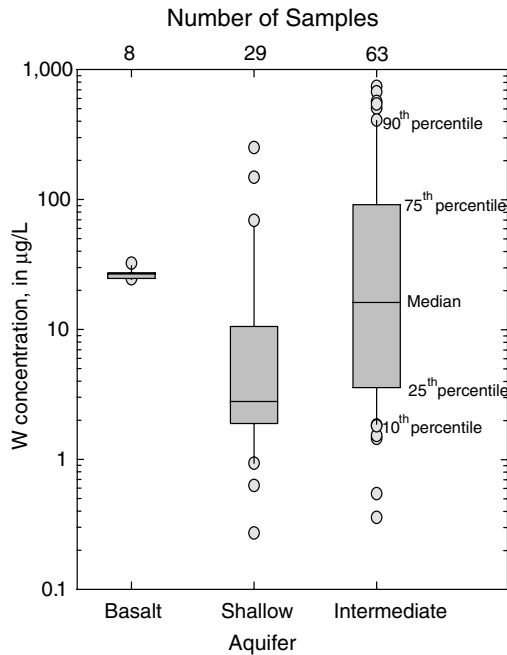


Fig. 5. Statistical summary of W concentrations in basalt and shallow and intermediate basin-fill aquifers.

deep aquifers in the Carson Desert (Maurer et al., 1996). The Carson Desert contains geothermal areas near Stillwater (Fig. 1) and between Big Soda Lake and Upsal Hogback that have been developed to produce geothermal electricity. A third geothermal area exists near NAS Fallon and is being evaluated by the Navy for its potential to produce electricity (Katzenstein and Bjornstad, 1987). Wells near NAS Fallon have encountered hot water, and hot springs discharge at the NE end of Carson Lake (Figs. 1 and 4)

A third natural source for W is its release to solution via reductive dissolution of Fe and Mn oxyhydroxides through oxidation of organic C. This mechanism is proposed by Smedley and Kinniburgh (2002) as one of the principal causes of high As concentrations in ground water. There is a significant correlation between W and As (Table 2), suggesting they have similar sources or processes controlling their concentrations. Tungsten is readily precipitated by hydrous Fe oxides with pH > 3.5–4.0 (Kraynov, 1971) and As has a high affinity for freshly formed amorphous Fe oxyhydroxides (Smedley and Kinniburgh, 2002). Unfortunately, direct evidence that Fe and Mn oxyhydroxides in Carson Desert sediments contain high W concentrations is not available.

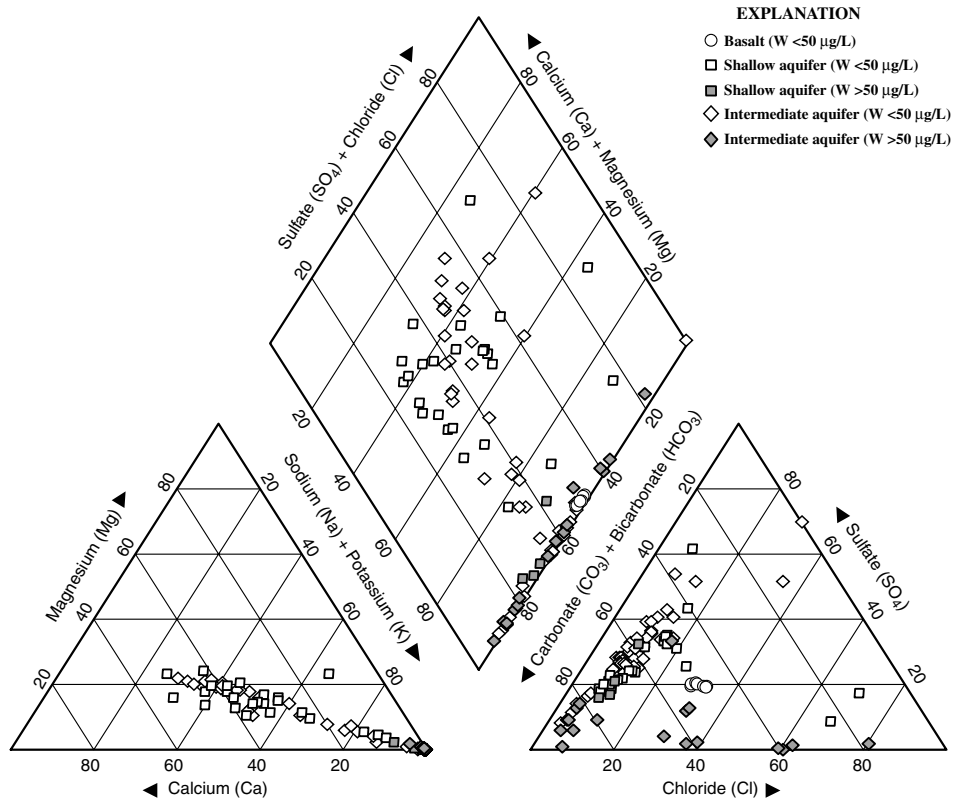


Fig. 6. Relationship between chemical characteristics of Carson Desert ground water and W concentrations.

Table 2
Correlation coefficients for W and physical and chemical parameters

Variable	W	pH	DO ^a	Temp	Ca	Mg	Na
Correlation coefficient	1.00	0.35	-0.06	0.07	-0.31	-0.14	0.54
	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 99	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100
Variable	K	Alk ^b	Cl	SO ₄	F	Si	TDS ^c
Correlation coefficient	0.07	0.73	0.25	-0.07	0.78	-0.17	0.41
	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100
Variable	As	B	Fe	Li	Mn	Mo	P ^d
Correlation coefficient	0.63	0.71	0.00	-0.09	-0.20	0.11	0.85
	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 98
Variable	Sr	V	U	NH ₃	DOC ^e		
Correlation coefficient	-0.22	0.19	0.05	0.66	0.38		
	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 100	<i>n</i> = 99		

Chemical concentrations are for filtered samples. Correlations in italics are significant at $p < 0.05$.

^a Dissolved O₂. Oxygen was measured in 88 samples. In 11 samples where O₂ was not measured because of strong H₂S odor, O₂ concentrations were assigned a value of 0.05 mg/l.

^b Field alkalinity as CaCO₃.

^c Residue on evaporation at 180 °C.

^d Orthophosphate.

^e Dissolved organic C.

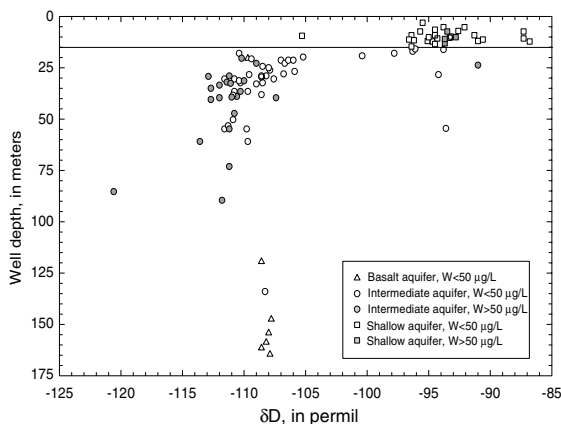


Fig. 7. Relationship between well depth, δD , and W concentration in Carson Desert ground water. Line at 15 m indicates bottom of shallow aquifer.

5.3. Factors affecting W concentration in ground water

The data indicate that the source of W in Carson Desert ground water is natural. Four main processes regarding natural sources of W and factors affecting concentrations of W in Carson Desert ground water are tested with the available data. The processes are: (i) evaporative concentration of W in river water, (ii) mixing with water from W-rich geothermal sources, (iii) dissolution/precipitation of primary W minerals in sediments, and (iv) adsorption of W to Fe and Mn oxyhydroxides and release through reductive dissolution of W-rich Fe and Mn oxyhydroxides.

5.3.1. Evaporative concentration of W in river water

Evaporation of Carson River water should cause proportional increases in Cl and W concentrations, assuming that both constituents behave conservatively during this process and that there are no other sources of the constituents. A positive trend for Cl and filtered W concentrations in Carson River water is present (Fig. 8). A sample of water with a W concentration of almost 3 mg/l from Big Soda Lake (Johannesson et al., 1992) follows the trend expected for evaporation of Carson River water (Fig. 8). Stage in Big Soda Lake is maintained by seepage losses from large canals carrying Carson River water (Rush, 1972). The canals pass 500 m or more from Big Soda Lake, which indicates the W/Cl ratio of Carson River water can be maintained following substantial evaporation and migration through the subsurface.

Many of the ground-water samples plot near samples of Carson River water (Fig. 8). Concentrations of W and Cl fall in, or near, the empirically-defined band for evaporation of Carson River water for nearly two-thirds of the Carson Desert ground-water samples. The W and Cl concentrations for water from several wells in the shallow aquifer plot below and to the right of the evaporation band shown in Fig. 8, indicating other processes such as dissolution of halite or adsorption of W may be occurring. Most of the samples with W concentrations exceeding 50 µg/l plot above and to the left of the trend for evaporative concentration (Fig. 8), indicating other processes may be occurring. Processes which can account for samples plotting above the evaporation band include release of W from sediments or

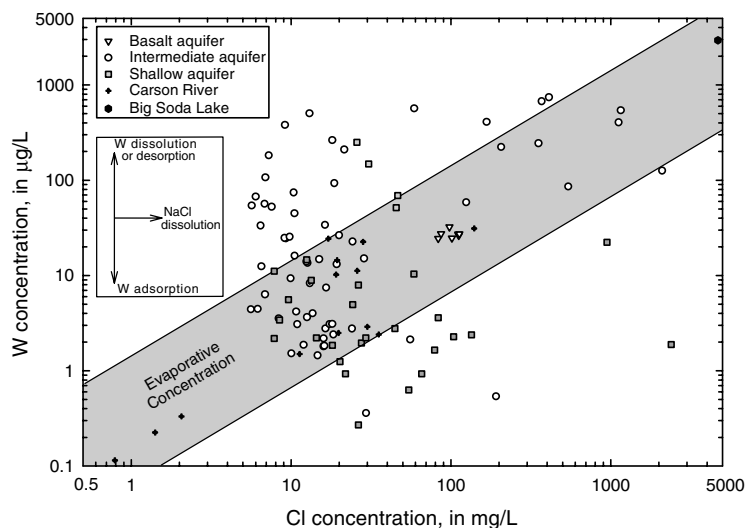


Fig. 8. Relationship between W and Cl concentrations in Carson River and Carson Desert ground water.

minerals, or alternatively, mixing with hydrothermal water containing elevated W concentrations relative to Cl. Loss of Cl through halite precipitation also could account for samples plotting above and to the left of the band, however, this is unlikely because water in all of the samples is undersaturated with respect to halite.

5.3.2. Mixing with tungsten-rich geothermal water

The spatial association of wells with elevated W concentrations with geothermal areas near Soda Lake/Up-sal Hogback and NAS Fallon (Fig. 4) suggests geothermal water is influencing W concentrations in at least some of the wells. There is positive correlation between W and As, B, F and Na (Table 2; Fig. 9), all of which are associated with geothermal water (White et al., 1971; Nordstrom and Jenne, 1977; Smedley and Kinniburgh, 2002). A sample of water collected from a hot spring about 5 km SE of NAS Fallon (Fig. 4) indicates that geothermal water in the study area contains elevated concentrations of W, As, B, F and Na (Table 3).

Wells with elevated W concentrations tend to have high B concentrations and Na/K ratios (Fig. 10). Water in volcanic areas and water in many thermal springs contain considerable concentrations of B (Hem, 1985). The Na/K ionic ratios for water samples with elevated W concentration are similar to samples from geothermal wells and springs in the Carson Lake and Stillwater areas. Several factors may affect the Na/K ratio in the Carson Desert. In non-thermal waters, the increase in the Na/K probably is the result of ion-exchange reactions on clay minerals which preferentially remove K over Na. In geothermal systems, the Na/K ratio is a function of temperature at depth because of tempera-

ture-dependent ion exchange of Na and K between coexisting alkali feldspars (Fournier and Truesdell, 1973).

Although geothermal water provides a source of W to Carson Desert ground water beyond the Carson River, measured concentrations of W, and also As, F, and P, in geothermal water are not high enough that simple mixing between thermal and non-thermal waters would explain the concentrations measured in ground water. Additionally, mixing does not provide an explanation for the observed correlations between W and other ions in the ground-water samples collected during this study (Table 2).

5.3.3. Dissolution/precipitation of primary tungsten minerals

Primary W-minerals carried into the Carson Desert in suspended sediment and deposited in Carson Desert sediments in the past could be weathering under present-day conditions, which could increase concentrations of W in ground water. Alternatively, precipitation of W minerals could lower ground-water concentrations. To test these possibilities, ion-activity products (IAP) for CaWO_4 , FeWO_4 , MnWO_4 , SrWO_4 , Na_2WO_4 , and MgWO_4 were calculated for the well-water temperature using PHREEQC (Table 1). IAP values for FeWO_4 , MnWO_4 , Na_2WO_4 , and MgWO_4 were considerably less than their Ksp values for 25 °C, indicating the water samples are undersaturated with respect to these minerals. Thus, these mineral phases in contact with the ambient ground water could be dissolving. IAP values indicate that CaWO_4 and SrWO_4 are slightly less than the Ksp, indicating they are approaching saturation. Significant uncertainty exists in Ksp values for

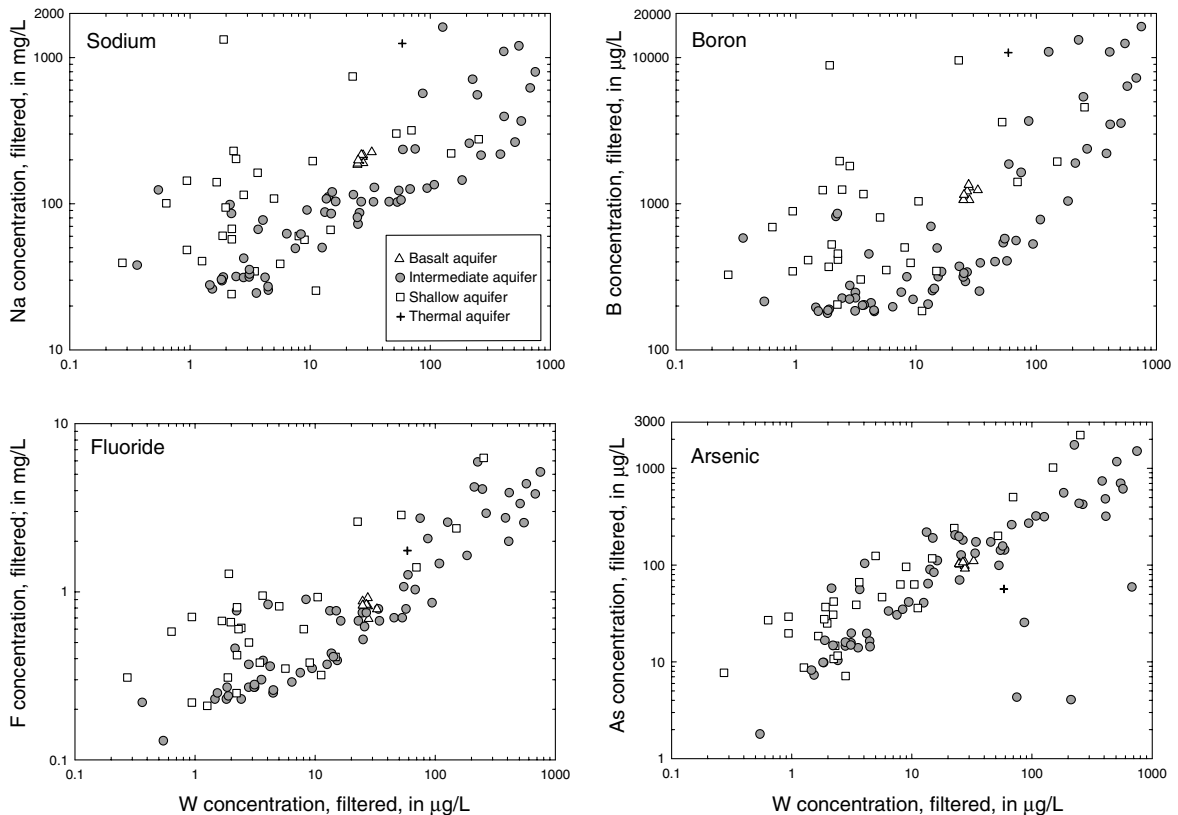


Fig. 9. Relationship between concentrations of W and selected geothermal indicators.

CaWO_4 , however, because of the tendency for W to form colloids and the protonation of the tungstate ion (Wood and Samson, 2000). Given the uncertainty in the available thermodynamic data, any conclusions concerning precipitation or dissolution of W minerals are tentative at best. For example, IAP's for CaWO_4 calculated from PHREEQC are plotted in Fig. 11 and are compared to the K_{sp} values of different investigators. Compared to the log K_{sp} values used by Pina et al. (2000) and calculated based on thermodynamic data from Robie et al. (1978) and Naumov et al. (1974), all samples are undersaturated with respect to CaWO_4 (Fig. 11). However, most samples with elevated W concentrations are oversaturated compared to log K_{sp} values from other investigators. Further uncertainty is introduced because formation of ammonia, phosphate and fluoride complexes with tungstate was neglected in calculating the IAP for CaWO_4 because of a lack of thermodynamic data. Given the uncertainty in K_{sp} values and lack of thermodynamic data for complex formation, it is difficult to ascertain the importance of SrWO_4 and CaWO_4 as controls on W concentrations in the study area.

5.3.4. Tungsten adsorption to release from Fe and Mn oxyhydroxides

During the Pleistocene, W from the Carson River and upwelling geothermal water could have adsorbed onto freshly formed Fe and Mn oxyhydroxides and been buried in Lake Lahontan sediments. Welch and Lico (1998) describe prehistoric formation of Fe and Mn oxyhydroxides during surface-water transport on grains in the presence of dissolved O_2 , followed by deposition with organic matter in the sediments of Pleistocene Lake Lahontan. Release of some fraction of the W that long ago combined with or adsorbed onto Fe and Mn oxyhydroxides could be promoted by the development of strongly reducing environments that characterize present-day conditions. Thus, control of W concentrations may involve redox-driven dissolution of metal oxyhydroxides, which releases bound W and other elements to solution. Alternatively, adsorption or desorption reactions may occur without dissolution of the metal oxyhydroxides. Whatever the source of W, once in solution W concentrations can be affected by adsorption processes. Under present-day conditions, the strong relation between pH and W concentrations (Fig. 12)

Table 3
Chemical analysis of water collected September 2003 from Carson Lake hot spring

Date	Temperature (°C)	pH	Specific conductance (µS/cm)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg/l as CaCO ₃)	SO ₄ (mg/l)
September 3, 2003	>45	7.38	7390	72	3.8	1250	34	158	54.7
Cl (mg/l)	F (mg/l)	Br (mg/l)	Si (mg/l)	As (µg/l)	B (µg/l)	Fe (µg/l)	Mn (µg/l)	P (mg/l)	W (µg/l)
2090	1.76	4.39	128	56.7	10,800	55	142	<0.02	58.5

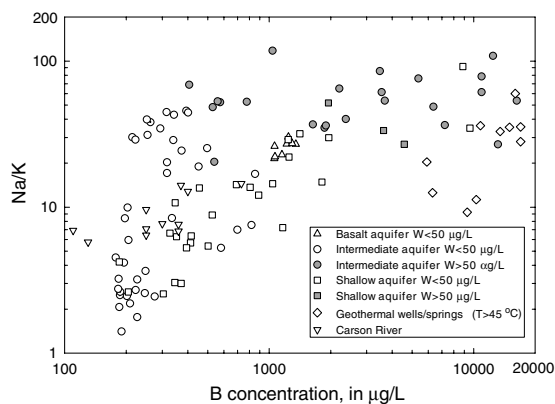


Fig. 10. Relationship between Na/K ratio (mass/mass) and B and W concentrations in Carson Desert ground water.

indicates that adsorption-related processes play a significant role in controlling W concentrations.

All samples with W concentrations greater than 50 µg/l have pH values greater than 8. Geochemical modeling, using average extractable Fe from area sediments with ferrihydrite as the adsorbent {properties from Dzombak and Morel (1990)} indicates less than 10% W adsorption for these samples (Fig. 13). These samples also plot above the evaporation trend in Fig. 8, indicating a source of W in addition to evaporation. Whatever the source of W (mineral dissolution, upwelling geothermal water, etc.), the high pH of these ground-water samples results in less relative adsorption and greater aqueous concentrations of W. Several ground-water samples from the intermediate aquifer and all of the samples from the basalt aquifer also have pH greater than 8, but contain less than 50 µg/l of W (Fig. 12). These samples apparently are associated with areas lacking any significant source of W. In ground-water samples with pH values less than 8, W concentrations are less than 50 µg/l. These include almost all of the sampled wells in the shallow aquifer, and several of the wells in the intermediate aquifer. Five of these wells are in the high W area near NAS Fallon (Fig. 4). Thus, it appears that W adsorption at lower pH controls W concentrations near NAS Fallon and elsewhere in the study area.

The significant and positive correlation between concentrations of W and As, F, and orthophosphate (Table 2; Figs. 9 and 12) indicates that they have similar sources or that similar processes are controlling their concentrations. Tungsten, As(V), F, and P are anions in water and have similar adsorption properties characterized by decreasing adsorption with increasing pH. All of these anions compete with each other for adsorption sites. Additionally, high concentrations of HCO₃, H₄SiO₄ and possibly organic C compete with As for adsorption sites (Smedley and Kinniburgh, 2002) and probably have similar effects on W.

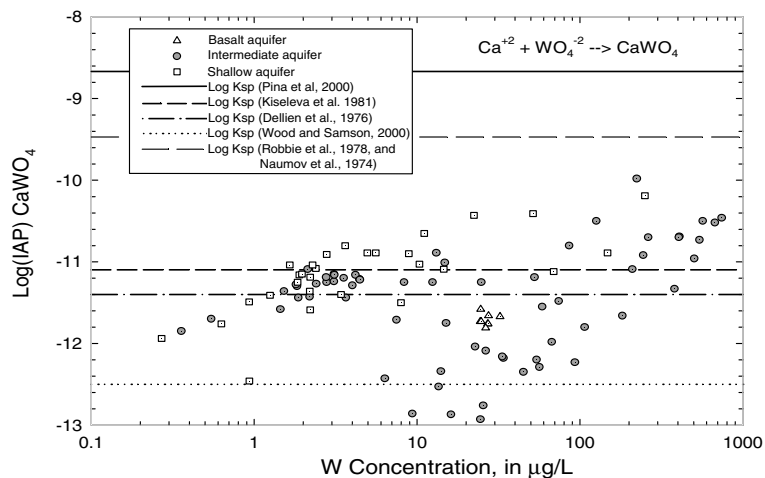


Fig. 11. Relationship between W concentrations and IAP for CaWO_4 in Carson Desert ground water. Ksp values are for 25 °C and IAP values are based on measured water temperature.

Welch and Lico (1998) suggested the source of some As in Carson Desert ground water was As-rich metal oxides under conditions that thermodynamically favored reductive dissolution of the metal oxides. Assuming that the metal oxides also contain W and that the ground water is sufficiently reducing that the metal oxides will dissolve, then W could also be released to the ground water. Elevated DOC and NH_3 concentrations are associated with elevated W concentrations in water from wells in the intermediate aquifer (Fig. 12). This association is consistent with oxidation of organic matter consuming O_2 and releasing reduced N while creating redox conditions that favor dissolution of metal oxides and release of W. DO concentrations are predominantly <1 mg/l in Carson Desert ground water and are less than 0.3 mg/l in most samples containing W concentrations >50 µg/l (Fig. 12). Redox conditions in the aquifers as indicated by the As(V)/As(III) couple are not correlated with W concentrations (Fig. 12); however, the As redox couple generally is not in equilibrium in ground water (Welch et al., 2000).

If reductive dissolution of Fe and Mn oxyhydroxides is releasing W, high W concentrations might be expected to correlate with high Fe and Mn concentrations. There is, however, no positive association between W and either Fe or Mn (Table 2; Fig. 12). Water in all samples is extremely undersaturated with respect to FeCO_3 , so this could not act as a control on Fe concentrations. The strong odor of H_2S in many of the wells suggests solubility of Fe sulfides may act as a control instead. Manganese is unlikely to accumulate in most samples with elevated W concentrations because the water is saturated with respect to MnCO_3 for those samples (Fig. 14).

Although the evidence for reductive dissolution of Fe and Mn hydroxides releasing W to ground water is not conclusive, W concentrations in ground water are broadly consistent with adsorption as a control. In general, simulations indicate that there is an increase in the % W adsorbed with decreasing pH (Fig. 13). The % W adsorbed in the absence of any competing solutes (0.005 M NaCl) also was simulated. The presence of other adsorbing solutes in ground water from the study area decreases W adsorption compared to the solution containing only 0.005 M NaCl (Fig. 13).

5.4. Comparison with other systems

Because of its toxicity, numerous studies (e.g. Welch et al., 2000; Smedley and Kinniburgh, 2002) have identified ground-water environments with As concentrations that may be harmful to human health. The similarity in behavior of As and W observed in this study indicates that settings where As problems in ground water have been identified also may have elevated W concentrations, particularly if there is a geothermal or mineral source of W and reducing conditions develop in the ground water. Support for this conclusion is provided by Grimes et al. (1995) who reported anomalously high concentrations of As and W in ground water associated with disseminated Au deposits in Nevada. The Au deposits were formed through intrusions of hydrothermal fluids into Paleozoic carbonate and siltstone host rocks. The highest As and W concentrations in ground water near the deposits occurred where Eh measurements and distribution of As species indicated reducing conditions (Grimes et al., 1995).

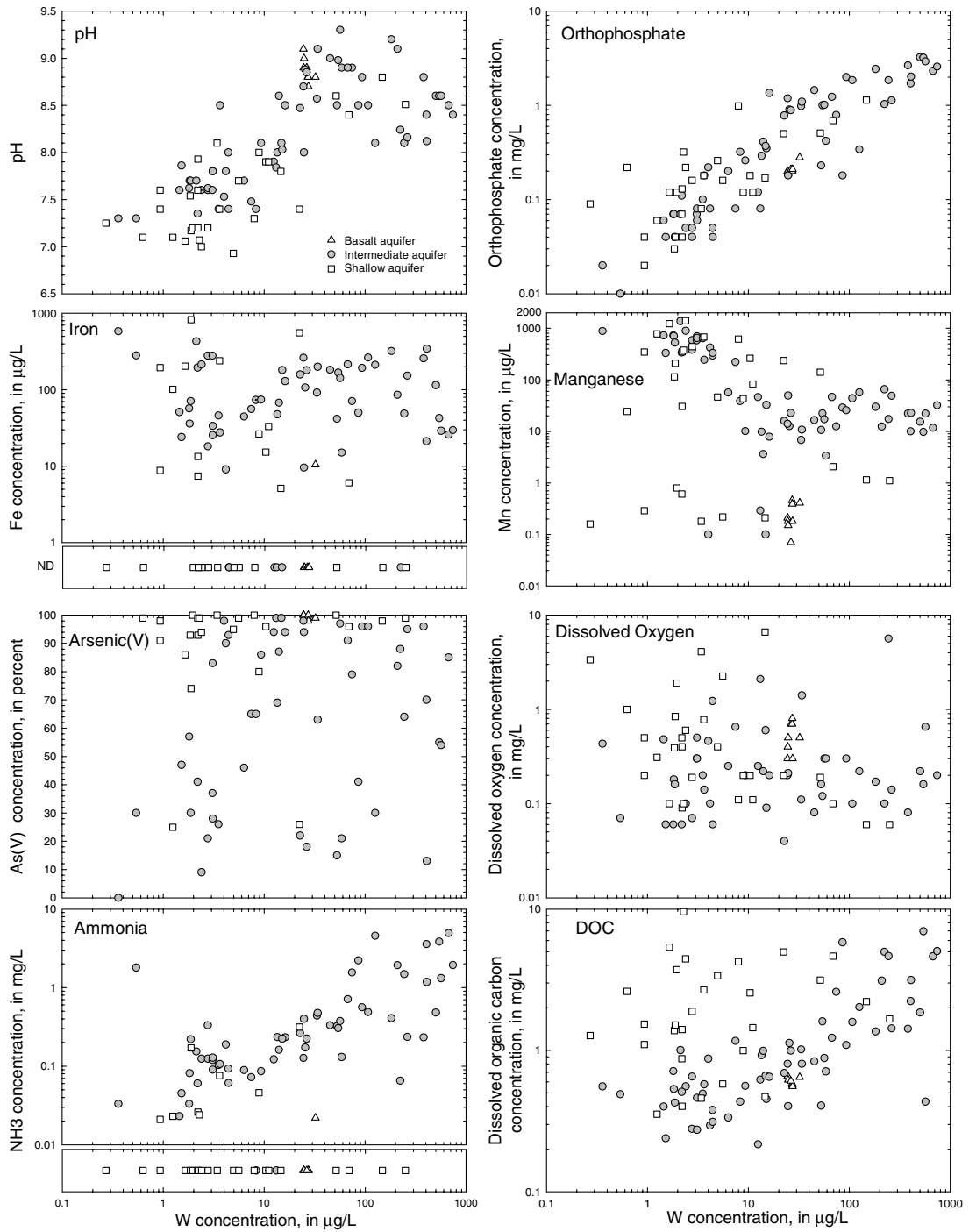


Fig. 12. Relationship between pH, and concentration of W and selected constituents.

Application of W-rich phosphate fertilizers to fields and atmospheric deposition of W from mills before emissions controls were employed could theoretically provide sources of soluble W capable of migrating to

the water table. Soluble P interacts strongly and rapidly with soils and sediments under oxic conditions (House, 2003), and it is likely W would behave similarly. Given the similarity in behavior observed between W and P

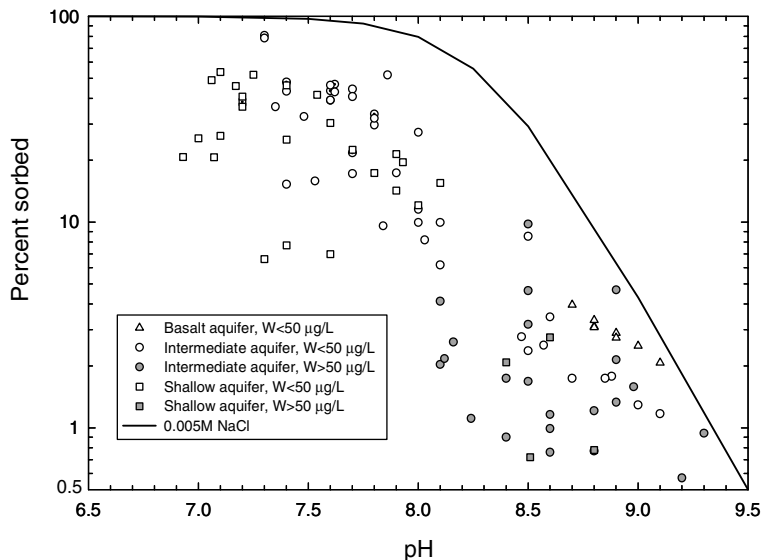


Fig. 13. Relationship between pH and % of W adsorbed predicted by adsorption modeling.

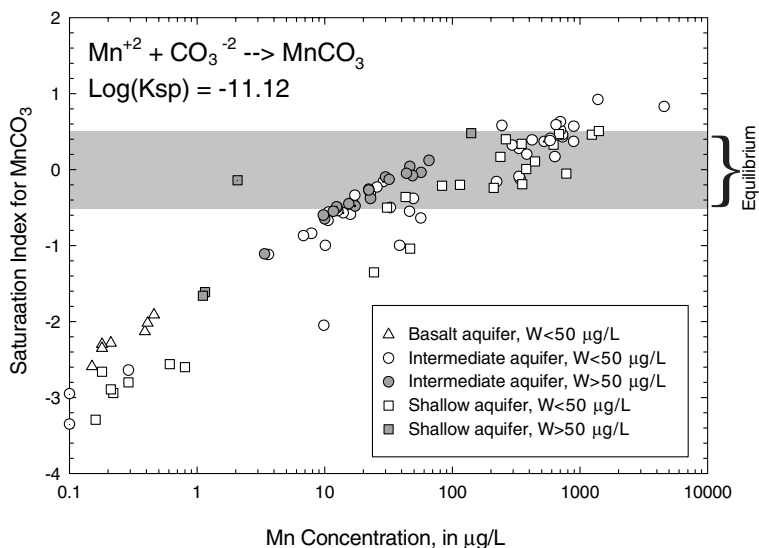


Fig. 14. Relationship between concentration of aqueous Mn and saturation index for MnCO₃.

in this study, it seems unlikely that these sources could result in serious ground-water contamination except in rare settings where ground water is P contaminated.

6. Summary

Tungsten is seldom measured in ground water so its concentrations in ground-water used to provide drinking water in the United States are poorly known. Concentrations in water from 3 aquifers used as sources of

drinking water in the Carson Desert ranged from 0.27 to 742 μg/l. The greatest W concentrations typically were found in the intermediate aquifer, a basin-fill sedimentary aquifer in which the water typically is alkaline, strongly reducing, and dominated by Na–HCO₃ or Na–Cl. Stable isotopes of water in the intermediate aquifer indicate it probably has not received recharge from the Carson River for almost 100 a, thus, modern anthropogenic sources of W likely are not the source of W in most wells. Natural sources of W include upwelling geothermal waters and erosion and transport of

W-bearing minerals in the Carson River watershed upstream from the Carson Desert. In the ancient past, W from these sources may have adsorbed to freshly formed Fe and Mn oxyhydroxides and been deposited along with organic matter in sediments of Pleistocene Lake Lahontan. These metal oxides could be a current source of W because low DO concentrations and sulfide odor in many of the wells indicate reducing environments conducive to release of W from the oxides. However, the metal oxides have not been analyzed for W.

The relationship between W and Cl indicates that evaporation of recharge water from the Carson River can explain W concentrations in many of the wells. However, evaporation alone cannot explain the high W concentrations (>50 µg/l) found in water from some wells. Geochemical modeling indicates ground water was undersaturated with respect to FeWO₄, MnWO₄, Na₂WO₄, and MgWO₄, and CaWO₄ and SrWO₄ were approaching saturation. These conclusions are tentative because of considerable uncertainty in the thermodynamic data for W.

The association of W with As, B and F suggests a geothermal source of W and most wells in the Fallon area with W concentrations greater than 50 µg/l are associated with known geothermal areas. Simple mixing of thermal and non-thermal water, however, may not provide an explanation for observed W concentrations because water from a geothermal spring in the study area only contained 58.5 µg/l of W.

Tungsten concentrations are significantly and positively correlated to pH, and are consistent with pH-controlled adsorption of W. All samples with W concentrations greater than 50 µg/l have pH values greater than 8.0 and geochemical modeling indicates that W in these samples exhibits less than 10% adsorption. Further evidence for pH controlled adsorption of W is the strong correlation between W and As, F, and orthophosphate. These anions are also characterized by decreasing adsorption with increasing pH.

The similar behavior of As and W observed in this study indicates that other areas with elevated As concentrations in ground water also may have elevated W concentrations, particularly if there is a mineral or geothermal source of W and reducing conditions develop in the aquifer.

Acknowledgement

The work on which this paper is based was funded in part by the USGS National Water Quality Assessment Program. The senior author thanks the well owners who gave permission to sample their wells and the residents of the Carson Desert for their overwhelming support of the ground-water investigation. The assistance of George Lubert, CDC, who provided information on the results of

CDC investigations concerning W concentrations in urine in the Fallon and the National population, is appreciated. We thank Julia Barringer, Karen Johannesson, James Tindall, and an anonymous reviewer for their valuable comments on earlier versions of this manuscript.

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