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Distribution of Major Anions and Trace Elements in the Unsaturated Zone at Franklin Lake Playa, California, USA

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ABSTRACT

The composition of surficial salts formed near dry and drying saline lakes are partly the product of processes active in the unsaturated zone between the ground surface and the water table. These processes were investigated by determining the abundance of water-extractable solutes in sediment from the ground surface to the water table (~2.8 m) beneath Franklin Lake playa, California. Accumulation of solutes in the sediment is attributed to evaporation of aqueous solutions transported upward from the water table through the capillary fringe to an evaporation front that is currently 20-30 cm below the ground surface. Salts in the sediment from 0 to 20 cm depth are depleted in chloride and enriched in carbonate relative to deeper samples. Chloride depletion is most likely a product of selective dissolution by vertical recharge. The entire unsaturated zone contains greater amounts of carbonate than expected for evaporation of ground water and is best explained by preferential dissolution of more soluble salts in recharging precipitation but may also reflect the assimilation of CO_2 as carbonate minerals precipitate. Variations in the concentrations of arsenic, molybdenum, tungsten, and uranium in the water-soluble fraction of the sediment are complex and suggest unique geochemical controls on the abundance of each element. The distribution of these trace element abundances indicates that arsenic is the element most likely to accumulate in near-surface salts.

INTRODUCTION

Surficial sediments exposed on the margins of saline lakes and other arid and semi-arid settings accumulate salts through evaporation of shallow ground water (Salama et al. 1999; Reynolds et al. 2007; Elmore et al. 2008). These salts limit agriculture, are implicated as a major contribution to dust emissions, and are an important component of salinization of surface water in endorheic basins (Salama et al. 1999; Reynolds et al. 2007; Abuduwaili et al. 2008; Elmore et al. 2008). In addition to the detrimental effects of salinization, salts formed on some evaporative surfaces accumulate bioavailable toxic trace elements that can be dispersed in atmospheric dusts (Reheis 1997). Although much is understood of the processes of salt accumulation, knowledge about controls on the major and trace element contents of the salts is incomplete. More complete descriptions of processes that affect the metal contents of salt crusts are necessary for understanding the implications to arid and semi-arid landscapes and their inhabitants.

Several studies have examined the processes responsible for salinization of soil as a result of transport of water and dissolved salts through the capillary fringe to an evaporative surface (Qayyum & Kemper 1962; Hassan & Ghaibeh 1977; Shimojima et al. 1996; Rose et al. 2005; Gowing et al. 2006). White, efflorescent salts coating sediment surfaces in arid and semi-arid settings are a visible reminder of these processes. Evaporative concentration also occurs in the subsurface at the depth of transition from liquid water to vapor-dominated transport–the zone of evaporation or evaporation front (Rose et al. 2005).

Although the physical aspect of salt accumulation has been described, relatively few investigations have explored chemical processes that might affect the distribution and accumulation of major salt components. One study in Spain showed that the relative abundances of chloride, sulfate, and carbonate species vary with depth in saline soil profiles, with chloride content generally increasing near the ground surface (Vizcayno et al. 1995). Szabolcs & Lesztak (1969) experimentally evaluated the distribution of sodium salts of chloride, sulfate, and carbonate and found that sodium chloride and sodium sulfate accumulated near the evaporation front whereas sodium carbonate inhibited the rise of water in the capillary fringe through changes in mechanical properties of the substrate.

Goldstein et al. (2007) reported that the chemical composition of soluble salts extracted from surface sediment in the center of Franklin Lake playa, California, could not be explained by simple evaporation of ground water found 2 to 3 m below the ground surface. This result contrasts with findings elsewhere in the drainage basin, where surface salts are compositionally similar to water in the immediately underlying saturated sediment.

A possible cause of the inconsistency is the separation of dissolved species by processes within the unsaturated zone underlying Franklin Lake playa. This paper describes the varied concentration of soluble major anions and selected trace elements within the unsaturated sediment beneath Franklin Lake playa and speculates on processes responsible for their accumulation at varying depths.

THE SETTING

Franklin Lake playa is located in Inyo County, California, approximately 60 km west of Las Vegas, Nevada. The playa covers an area of about 14 km^2 within the Mojave Desert and is at 600 m elevation (Czarnecki 1997). Temperatures range from -5 to 45ºC, annual precipitation is typically 8 to 10 cm yr^{-1}, and pan evaporation is estimated to be 250 cm yr^{-1} (Winograd & Thordarson 1975). Czarnecki (1997) determined that the playa has an average annual evaporation rate of 0.16 cm day^{-1} through loss of water vapor from the unsaturated zone. The surface of Franklin Lake playa is covered with a soft puffy crust near the center, with salt pans and hard crusts on the margins. Fluvial channels of the Amargosa River and Carson Slough cover the western area of the playa, and every few years they carry surface water in response to heavy rain events. Nonetheless, surface water has not been observed on the soft puffy surface during the span of recent investigations (Czarnecki 1997; Reynolds et al., this volume). The Franklin Lake playa has characteristics of a bypass playa (Motts 1970) by which ground water recharges sediment beneath the playa but also flows through sediment beneath the Amargosa River and continues to the south.

METHODS

Sample Collection

Sediment samples were collected in April 2007 from an area of the playa characterized by relatively soft puffy crusts that lack visible accumulations of salt (Figure 1). Vegetation is absent on this part of the playa, with the closest plants found only in shallow channels 300 m east of the sample site. A soil pit was excavated to a depth of 95 cm, and a hand auger was used to collect samples from the base of the soil pit to 281 cm. The near-surface pit samples were collected at 0 to 1 cm, 1 to 5 cm, and 5 to 10 cm. The remaining samples from the soil pit were collected at 10 cm intervals. The augered samples were collected in depth intervals that varied from 6 to 16 cm thick (Table 1). Immediately upon excavation of a depth interval, approximately 20 g of the sample was placed into a pre-weighed scintillation vial that was then sealed with a lid and electrical tape. A corresponding bulk sample was placed in a plastic bag for grain-size, mineralogic, and water-extraction analyses.

Ground-water composition was determined in 2006 on samples drawn from two shallow wells (GS-15 and GS-18; Figure 1). Well GS-15 is 300 m north of the sediment sample site, and GS-18 is 700 m to the south. The wells were installed in 1982 by Czarnecki (1997) to depths of 7 and 8 m, respectively. Water depths below ground surface at the time of sampling were 2.6 m for GS-15 and 3.2 m at GS-18; these water levels are similar to values reported in 1983–1984 (Czarnecki 1990). Wells were pumped dry, and then within 5 hours were sampled using a peristaltic pump. Water was filtered to < 0.2 μm with a polyethersulfone syringe filter, and the resulting filtrate was collected in HDPE bottles. Cation sample bottles were cleaned in the laboratory with nitric acid and deionized water; anion sample bottles were soaked in deionized water prior to field work. All bottles were rinsed with sample water prior to filling. Cation and trace element samples were acidified with high-purity nitric acid to pH < 2. Anion samples were stored with ice or refrigerated until analyzed.

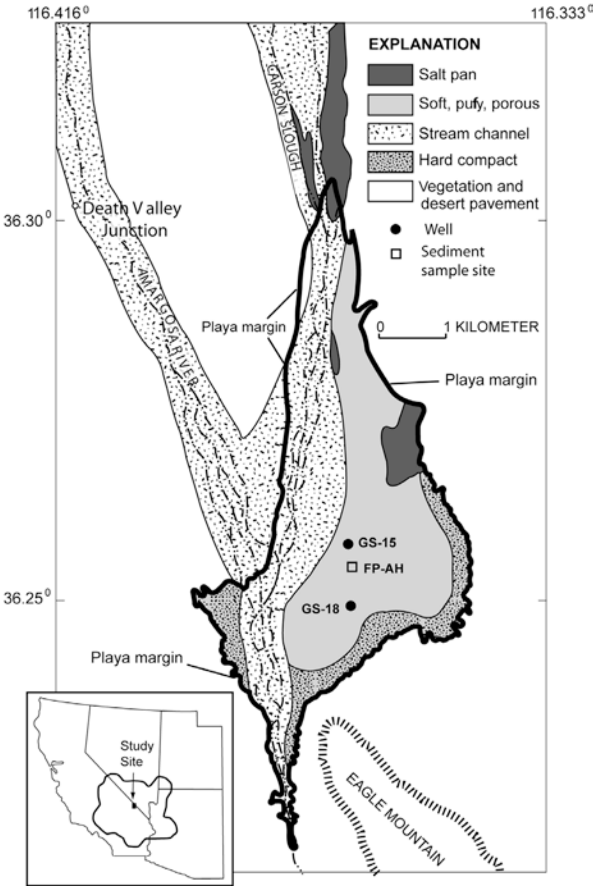

Figure 1–Map of the distribution of surficial materials and locations of well and sediment sample sites within the Franklin Lake playa. Index map depicts the western United States with an outline of the Mojave Desert.

Table 1–Chemical composition of water-extract solutions prepared by reacting 1 gram of dried sediment from Franklin Lake playa with 30 ml of de-ionized water for one hour. (Alkalinity is expressed as $CaCO_3$; Na, sodium; As, arsenic; Mo, molybdenum; W, tungsten; U, uranium; ---d, duplicate).

Depth (cm)	Alkalinity mg l^{-1}	Chloride mg l^{-1}	Sulfate mg l^{-1}	Na mg l^{-1}	As mg l^{-1}	Mo mg l^{-1}	W mg l^{-1}	U mg l^{-1}
0-1	317	1.6	159	252	38	<2	0.6	<0.1
0-1d	357	14.2	171	238	46	<2	1.7	<0.1
0-5	693	3.8	312	506	46	<2	1.1	0.3
5-10	633	0.5	364	494	65	<2	1.8	0.4
10-20	977	162	631	880	260	30	8.4	9.8
20-30	1000	468	607	1050	850	140	14.0	100
20-30d	1047	510	655	1040	890	142	15.4	104
30-40	617	524	426	693	790	134	11.3	57
40-50	510	450	333	636	730	127	9.6	37
50-60	467	420	297	665	700	129	9.4	28
50-60d	470	409	289	669	700	127	9.4	28
60-70	427	402	292	607	750	141	10.2	26
70-80	390	426	311	610	740	144	8.7	24
80-90	347	314	246	497	630	116	7.2	19
90-95	353	372	290	527	690	125	9.1	20
95-101	308	283	236	466	660	121	6.7	13.3
101-124	353	263	229	485	660	121	7.8	15.5
124-137	373	230	200	463	460	112	4.9	12.6
124-137d	360	233	203	432	430	107	4.5	11.4
137-145	232	151	131	316	240	70	5.9	7.5
145-159	161	116	91	213	140	46	6.9	4.2
159-163	139	87	70	168	100	36	9.5	3.1
163-169	150	108	83	173	119	41	13.9	3.4
169-177	151	121	87	218	119	49	15.3	4.1
169-177d	150	128	93	216	125	50	16.1	4.0
177-184	140	89	61	107	68	29	14.2	2.6
184-193	168	181	113	157	152	66	7.7	6.7
184-193d	170	170	109	155	146	65	7.6	6.5
193-203	177	211	134	175	176	79	4.5	7.9
203-217	179	217	139	180	169	80	8.9	8.4
217-228	115	88	58	93	81	33	14.5	3.3
217-228d	104	100	63	92	114	43	24.1	4.6
228-237	125	108	71	107	95	36	7.3	3.7
237-248	129	114	78	113	103	44	11.6	3.8
248-258	136	164	105	136	111	57	11.4	4.4
258-266	201	170	126	177	141	67	7.9	8.0
266-281	149	211	130	161	132	80	7.2	7.2

ANALYSES

Water content, particle size, mineralogy, and the chemical composition of water extracts were determined on the sediment samples. Gravimetric water content was determined by difference between the weight of sediment samples in the scintillation vials on arrival to the laboratory and after drying for 1 week at 50ºC and 110ºC. After drying at 110ºC the samples were placed in a chamber at 100% humidity at 22ºC ± 2 until the weekly weight gain was less than 0.2% (approximately 6 weeks). Particle size was determined on weighed air-dried splits of the bulk samples that were treated to remove organic matter (30% H_2O_2) and carbonate minerals (15% HCl). Samples were sieved to obtain the > 2 mm and < 2 mm size fractions. The > 2 mm size fraction was weighed and reported as gravel. The

< 2 mm size fraction was suspended in water amended with sodium hexametaphosphate and analyzed with a Malvern particle-size laser diffraction analyzer. Bulk mineralogy for all samples was determined by X-ray diffraction (XRD) on the ground < 2 μm fraction. Clay mineralogy was determined by XRD of oriented mounts of the < 2 μm fraction.

Water-soluble constituents of the sediment were determined by shaking 1 gram of dried, homogenized sediment with 30 ml of 18 mega-Ohm water for 1 hour. The samples were then filtered using a 0.2 μm filter and subsequently centrifuged to remove particles larger than 50 nm. Specific conductance and pH were measured on the resulting solution with calibrated meters. The solutions were analyzed in USGS laboratories to determine cation, anion and trace metal concentrations according to the procedures for ion chromatography (IC), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) described in Taggert (2002). Total alkalinity as $CaCO_3$ was determined by titration of a 10 ml aliquot of the solution with 0.16, or 1.6 N sulfuric acid. Replicate extractions of separate sample aliquots were reproducible generally within 10 relative percent for all analytical methods (Table 1), indicating that the 1 gram sample was representative.

Water samples were analyzed at the time of collection and later at USGS laboratories. Specific conductance, temperature, and pH were determined in the field using calibrated meters; total alkalinity as $CaCO_3$ also was determined in the field by titration of a 50 ml unfiltered aliquot with 1.6 N sulfuric acid. Cation, anion, and trace metal concentrations were determined by the same procedures used for analysis of water-extract solutions.

Geochemical Modeling

The saturation states of salt minerals in the water extracts and groundwater samples were evaluated with geochemical modeling. PHREEQC v. 2.14.2 (Parkhurst & Appelo 1999) calculated the saturation states using the Pitzer thermodynamic database.

RESULTS

Sediment Characteristics

Sediment at the sample site consists of 137 cm of reddish silt overlying a unit composed mostly of sand and gravel (Figure 2). The upper 20 cm of reddish silt has low field moisture content, is hard, and exhibits a blocky structure. Below this depth, the silty sediment is visibly moist and has a loose, granular texture. Below 137 cm, the pale gray sand and gravel mixture has greater apparent water content and a very loose structure. The contact of the two units is gradational as indicated by the change in median grain size (Figure 2).

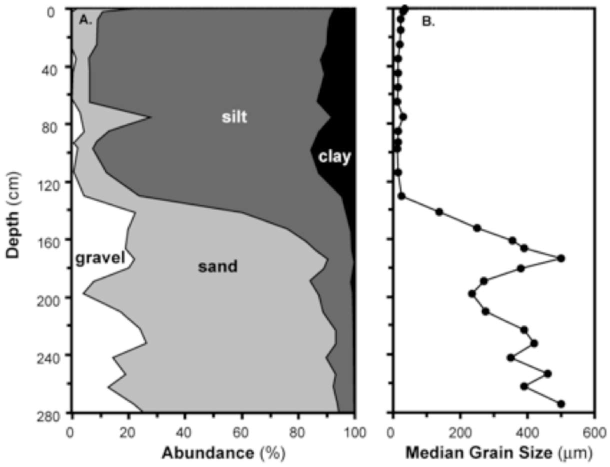

Figure 2–A) Abundance of gravel, sand, silt, and clay, and B) median grain size of Franklin Lake playa sediment samples collected from the ground surface to a depth of 281 cm. Samples were collected continuously in intervals of varied thickness (Table 1). Values are plotted at the mid-points of sampled intervals.

The sediment consists mainly of quartz and calcite. Other minerals common to most samples include plagioclase, analcime, and halite. Muscovite, dolomite, and barite were identified in only a few of the samples. The < 2 μm fraction of the sediment is composed of smectite (aluminum- and magnesium-rich varieties), illite, illite-smectite, and traces of kaolinite. The mineralogy is consistent with detritus eroded from rock and sediment units in the drainage basin (Winograd & Thordarson 1975; Khoury et al. 1982) except for halite, which formed by evaporation at the sample site and as a result of drying in the laboratory.

The water content of the sediment based on weight loss upon heating to 110ºC ranged from 4 to 20 weight percent (Figure 3a). This water likely includes 'free' water, water adsorbed to mineral surfaces, water within the interlayers of expansive clays, and water of crystallization in some hydrated salts. The amount of water lost varied with depth as a function of particle size and position relative to the ground surface and the water table. The lowest water content was measured in the near-surface samples, with similarly low concentrations reported for the coarse-grained sediment between 120 and 180 cm and 220 to 250 cm depth. The high water content between 10 and 120 cm is consistent with the greater matric potential of fine particles in this depth range. The increased water content in the 180 to 210 cm interval is attributed to the proximity of the saturated zone and the smaller median grain size of this interval relative to adjacent sediment. The high water content of the deepest sample is attributed to underlying water-saturated sediment. Figure 3b presents the amount of water adsorbed by the dried sample relative to the gravimetric water content. The ratio indicates that sediment shallower than 20 cm was undersaturated with respect to water vapor at the time of sample collection. Sediment from 20 to 50 cm depth has a ratio that is slightly greater than one. Deeper sediment is characterized by increasing ratios with increasing depth, which is interpreted to indicate the presence of greater amounts of *in situ* liquid water as the saturated zone is approached.

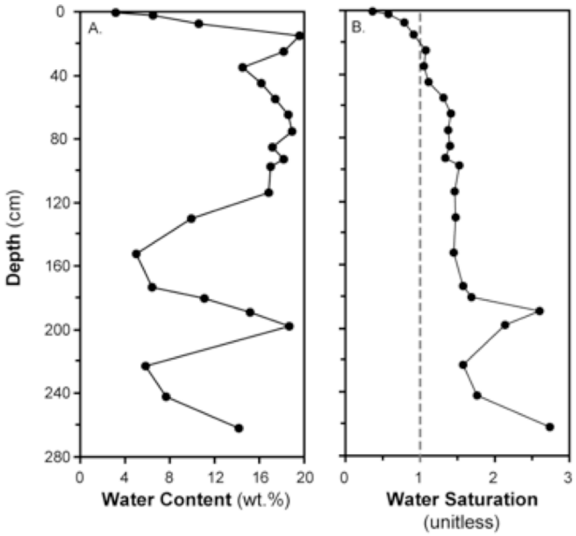

Figure 3–A) Gravimetric water content of Franklin Lake playa sediment samples as determined by weight loss after drying at 110ºC. B) The water saturation of the sediment samples as determined by the ratio of the gravimetric water content (110ºC) divided by the weight gain of the dried sediment exposed to 100% humidity for 6 weeks. Water content was not determined for all samples analyzed for water-soluble extracts. Samples were collected continuously in intervals of varied thickness. Values are plotted at the mid-points of sampled intervals.

Ground Water Composition

Select compositional parameters measured on water samples from wells GS-15 and GS-18 are presented in Table 2. The ground water is characterized by elevated pH (> 9.4), specific conductance (> 90 mS cm^{-1}), and total alkalinity (> 9000 mg l^{-1} as $CaCO_3$). Sodium is the dominant cation, with major amounts of chloride, sulfate, and carbonate species present. Calculations with PHREEQC determined that > 95% of the alkalinity was attributable to carbonate species. Arsenic (As), molybdenum (Mo), tungsten (W), and uranium (U) are commonly considered as trace constituents in ground water but are present in high concentrations beneath Franklin Lake playa. If the ground water was evaporated, the resulting anhydrous residue would be expected to contain from 160 to 200 ppm As, 120 to 190 ppm Mo, 3 to 4 ppm W, and 40 to 55 ppm U. The relatively high content of dissolved nitrate and absence of dissolved iron and manganese (Table 2) are interpreted to indicate that the water has a high oxidation potential. Evaluation of the saturation state of minerals in this water with PHREEQC determined that all sodium salts are undersaturated. Comparison of our water analyses with data of McKinley et al. (1991) found that major ion concentrations have increased by approximately 50% since 1983.

Table 2–Chemical composition of ground water sampled from wells in the Franklin Lake playa near the sediment sample site.

Parameter	**GS-15**	**GS-18**
Specific Conductance (mS cm^{-1})	90.30	99.50
pH	9.49	9.65
Sodium (mg l^{-1})	28000	37000
Potassium (mg l^{-1})	1170.00	1080.00
Calcium (mg l^{-1})	<1.00	<1.00
Magnesium (mg l^{-1})	<1.00	<1.00
Fluoride (mg l^{-1})	26.00	6.00
Chloride (mg l^{-1})	26000	28500
Nitrate (mg l^{-1})	500	1100.00
Sulfate (mg l^{-1})	16800	23500
Alkalinity as $CaCO_3$ (mg l^{-1})	9360.00	15510
Iron (mg l^{-1})	<0.01	<0.01
Manganese (mg l^{-1})	<0.01	<0.01
Arsenic (mg l^{-1})	15.50	15.80
Boron (mg l^{-1})	84.00	157.00
Molybdenum (mg l^{-1})	14.60	12.10
Uranium (mg l^{-1})	4.30	4.00
Tungsten (mg l^{-1})	0.33	0.30
Total Dissolved Solids (mg l^{-1})	**78200**	**100800**

Water Extraction

Concentrations of selected dissolved species in the extract solutions are presented in Table 1. The water-soluble weight fractions of the dried samples based on summing the dissolved species range from 0.009 to 0.10 (Figure 4). Specific conductance of the extract solutions varied from 700 to 4300 µS cm^{-1} and correlated with total salt extracted (r = 0.98). Soluble content increases from the ground surface to the 20-30 cm-depth interval and then decreases to approximately 160 cm; below this depth the water-soluble fraction varies in a narrow range. The change in the slope corresponds approximately to the change in grain size (Figures 2, 4). The extract solutions had pH values ranging from 10.5 to 9.5.

Variations in the soluble components of the sediment were assessed by normalizing the element abundance data to the relative amount of salt extracted. The concentration of a dissolved constituent in the extract solution (Table 1) was normalized to the amount of water used, the dried sediment weight, and the total mass of salt extracted. The result of this calculation estimated the concentration of the selected constituent in an evaporated residue of anhydrous salt.

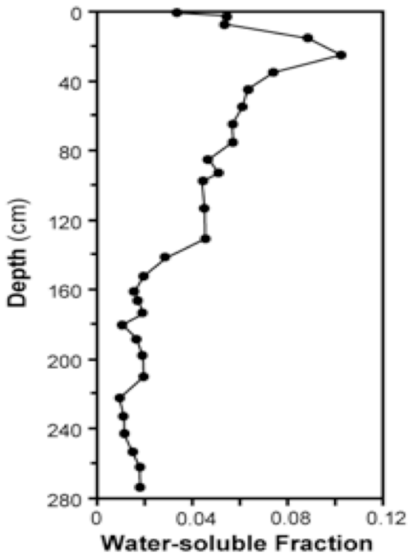

Figure 4–Mass fraction of water-soluble substances extracted from the Franklin Lake playa sediment samples by reaction with distilled water for 1 hour. Mass was calculated as the sum of dissolved major ions. Samples were collected continuously in intervals of varied thickness. Values are plotted at the mid-points of sampled intervals.

The water-extract solutions contained large amounts of sodium, chloride, sulfate, and carbonate species (Table 1). Their abundance on a bulk-sediment basis varied with depth in parallel to the total water-soluble fraction of the sediment (Figure 4; Table 1). In addition, the relative abundances of chloride, sulfate, and total carbonate (as estimated from alkalinity) vary with depth. These abundances are plotted as normalized, equivalent values to facilitate direct comparison (Figure 5). Nitrate was not considered in this evaluation because its fraction of the total anions is relatively low (0.02 to 0.05). Samples shallower than 20 cm are notable for the high abundance of carbonate and low content of chloride relative to the deeper samples. This relation is somewhat reversed from 30 to 100 cm, where chloride exceeds carbonate. Between 100 and 190 cm chloride and carbonate contents are subequal. Below 190 cm, carbonate and chloride vary inversely. The relative abundance of sulfate is greatest in the upper 20 cm; below 20 cm sulfate decreases gradually to the bottom of the sampled interval. The relative abundance of chloride, sulfate, and carbonate in the water extracts deviate from the amounts expected based on groundwater composition. The average equivalent proportion of chloride, sulfate, and carbonate in ground water sampled from GS-15 and GS-18 are 0.54, 0.29, and 0.17, respectively (Figure 5). Similar proportions of anions were obtained for water samples collected in 1983 (McKinley et al. 1991).

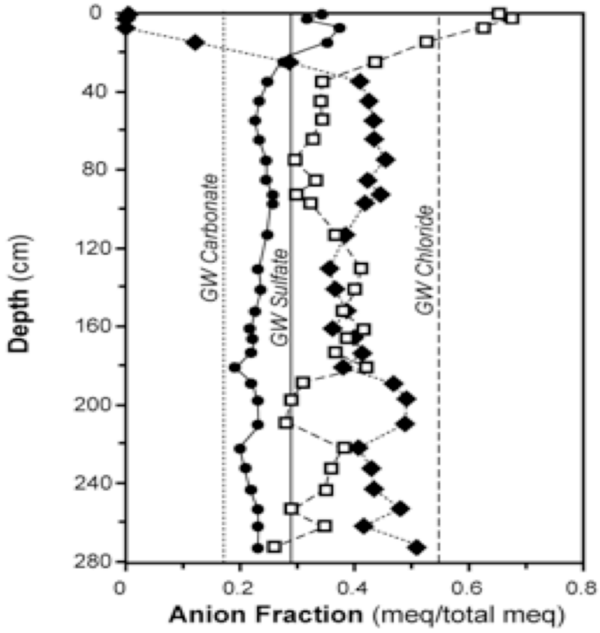

Figure 5–The relative abundance of water-soluble carbonate, sulfate and chloride extracted from the Franklin Lake playa sediment. Values were calculated by dividing the equivalents of each ion by the sum of anion equivalents. (♦ - chloride; ● - sulfate; □ - carbonate; vertical lines indicate proportions of anions in ground water (GW; Table 1)). Samples were collected continuously in intervals of varied thickness. Values are plotted at the mid-points of sampled intervals.

The amounts of anions and sodium extracted (Table 1) were combined with the gravimetric water content (Figure 3) to evaluate the saturation state of soluble salts in the sediment. These calculations were performed using PHREEQC and assuming that all water lost by heating is available as liquid water. Calculations with PHREEQC determined that samples from 0 to 40 cm depth are variably oversaturated with phases such as trona ($Na_3H(CO_3)_2{\bullet}2H_2O$), burkeite ($Na_6CO_3(SO_4)_2$), mirabilite ($Na_2SO_4{\bullet}10H_2O$), glaserite ($NaK_3(SO_4)_2$), nahcolite ($NaHCO_3$), halite (NaCl), and natron ($Na_2CO_3{\bullet}10H_2O$). Oversaturation predicts that some solid salts are components of the sediment as sampled. Samples between 40 and 177 cm are at saturation or slightly undersaturated with phases such as trona, mirabilite, and nahcolite. Two samples in this interval, 124 to 137 cm and 159 to 163 cm, were oversaturated with trona and burkeite. Below 177 cm, water contained in the sediment was undersaturated with all salts, indicating that the extracted ions were dissolved in residual water in the lowest 1 m of sediment.

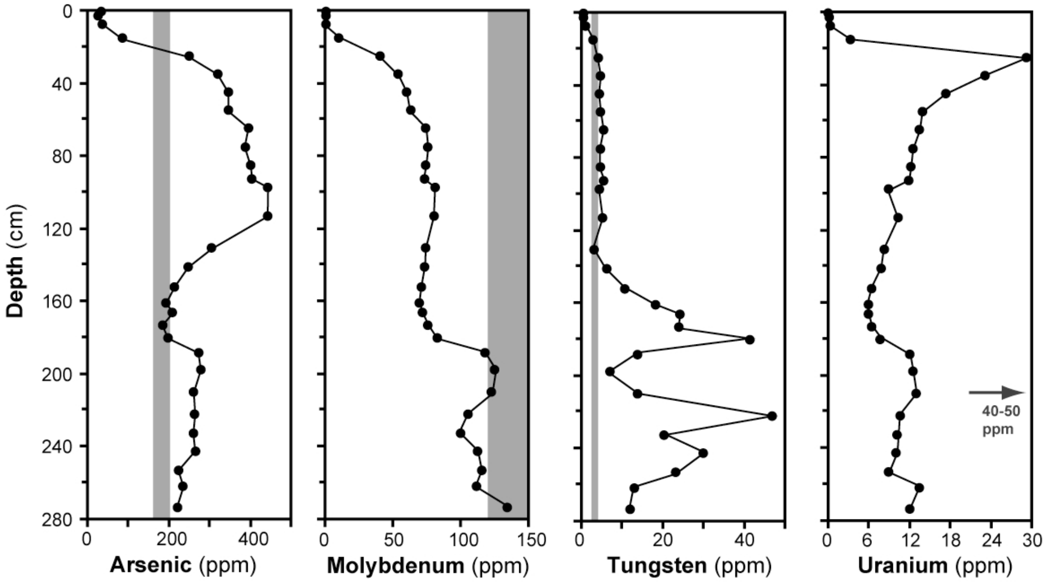

Figure 6–Concentration of water-soluble arsenic, molybdenum, tungsten, and uranium extracted from the Franklin Lake playa sediment expressed as amount in the water-soluble fraction of each sample. Vertical gray bars indicate concentrations expected by evaporation of ground water compositions (Table 1) except for uranium, which is indicated by a numeric range. Samples were collected continuously in intervals of varied thickness. Values are plotted at the mid-points of sampled intervals.

The concentrations of As, Mo, W, and U in the water soluble fraction vary with depth (Table 2; Figure 6). All four elements have relatively low abundances in the shallowest samples, with variations below 20 cm that are unique to each element. Arsenic content increases systematically from the ground surface to a maximum near 110 cm. From 120 to 190 cm, the As concentration decreases through the interval characterized by increasing grain size (Figure 2). Arsenic contents in samples below 190 cm are relatively constant. The upper 180 cm of the Mo profile is similar to that of As, although the concentration decrease between 120 and 190 cm is more subtle. Below 190 cm Mo content increases to approach values expected for evaporated ground water. Tungsten has a concentration profile similar to As and Mo in the upper 130 cm of sediment. Beginning at 140 cm depth, the W concentration is substantially greater than that measured in the shallow sediment, and two maxima of 40 to 50 ppm W are apparent. Uranium concentrations are below detection in the shallowest samples and reach an abrupt maximum of 29 ppm in the 20 to 30 cm sampled interval. Below this depth, uranium content declines systematically to 6 ppm at 160 cm, and then varies between 9 and 14 ppm through the 160 to 280 cm interval.

Chemical analyses detected high contents of silica (186 mg l^{-1}) and iron (12 mg l^{-1}) in a few of the water extract solutions. The concentrations of SiO_2 and Fe are attributed to colloids smaller than 50 nm. Suspended particles were expected given the high pH and Na content of the extract solutions and clay content of the sediment. Colloids can interfere with resolving dissolved elements from those bound to colloids. Nevertheless, the soluble elements considered in this analysis have sufficiently high concentrations in the extract solutions and chemical characteristics such that colloids are unlikely to account for a significant portion of the measured amounts.

DISCUSSION

The gross distribution of soluble components in the unsaturated zone beneath Franklin Lake playa is generally similar to results of previous studies that examined salt accumulation in evaporative environments where the evaporation front is below the ground surface (Hassan & Ghaibeh 1977; Gowing et al. 2006). These studies demonstrated that the depth of salt deposition is dependent on the position of the water table, grain size of the substrate, ground-water salinity, and evaporation rate. Maximum salt content of the Franklin Lake playa sediment at 20 to 30 cm depth is attributed to the transport of salt upward through the capillary fringe to the evaporation front (Figure 3). The depth of the evaporation front at 20 cm is consistent with the position expected in silty loam overlying a water table at a depth of approximately 2.5 m (Gowing et al. 2006). Salt in the 0 to 20 cm deep samples may reflect accumulation as a previous, higher water table receded, possible diffusion upward subsequent to rainfall or flood events, or accumulation from limited amounts of liquid water that continue to move upward. The latter explanation is consistent with the observed increase in salt contents above an evaporation front during column experiments (Hassan & Ghaibeh 1977).

The relative abundance of water-soluble anions in the upper 30 cm of sediment changes rapidly with increasing depth (Figure 5). The processes responsible for the increase of chloride and decrease of sulfate and carbonate are uncertain. Ground water in the past may have been compositionally distinct, with lower chloride and greater carbonate contents than modern ground water. The anion composition of this upper sediment may also be modified by atmospheric input, although this seems unlikely given the mass of salt in the underlying ground water. The normalized anion equivalent fractions of recent precipitation in Death Valley, 50 km to the northwest, is 0.34 nitrate, 0.09 chloride, 0.17 sulfate, and 0.4 carbonate (NADP 2008). In contrast, the surface sediment at Franklin Lake playa contains less than 0.05 nitrate, and chloride (Figure 5) is depleted relative to these precipitation values. Loss of nitrate is plausible due to denitrification and other processes (Walvoord et al. 2003), but chloride is expected to be conservative. The low relative chloride content in the unsaturated zone requires either selective removal of chloride or preferential enrichment of sulfate and carbonate. Similar depletion of chloride relative to ground water is recognized in efflorescent salts formed from alkaline water in Spain (Vizcayno et al. 1995). Selective dissolution (Shimojima et al. 1996) of chloride salts may favor elution from the surface sediment during infrequent vertical recharge events or from water condensed when the ground surface is colder than the subsurface (Fritton et al. 1967; Nassar & Horton 1989). Consistent with selective elution of chloride salts, the solubility of sodium chloride is markedly greater than that of sodium sulfate and sodium carbonate phases. Chloride may also be lost by preferential transport in dust emissions from the playa surface, although our observations suggest that chloride-rich salt crusts are hard and resistant to wind erosion. No mechanism for enhanced transport of carbonate and sulfate relative to chloride through the capillary fringe has been recognized, though the inverse behavior has been observed (Szabolcs & Lesztak 1969; Shimojima et al. 1996).

Considering the long history of Franklin Lake playa, the amount of salt in the unsaturated zone is remarkably small, which may further support the downward transport of some salts. Applying the 0.16 cm day^{-1} evaporation rate of Czarnecki (1997) to ground water in GS-18 would result in deposition of 5.8 g of salt cm^{-2} yr^{-1} if the water mass were evaporated to dryness. Considering a 2.8 m column of sediment with an estimated bulk density of 1.8 g cm^{-3}, the measured mass of the soluble fraction of the sediment could be acquired in less than 3 years. Two explanations are offered to account for the apparent lack of salt. Vertical recharge events may remove soluble phases from the unsaturated zone and transfer them to ground water. Vertical recharge through the sediment is likely considering that water does not pond on the puffy surface following heavy rain events, despite the anticipated deflocculation of expansive clays in the sodium-rich and high pH environment (Szabolcs & Lesztak 1969). An alternative explanation is that soluble constituents accumulate more slowly than the vapor transfer indicated by Czarnecki (1997). This would require the upward vertical movement of water without the transfer and storage of dissolved salts. Either hypothesis might account for the 50% increase in total dissolved solids of the ground water in the 20 years between our analyses and those presented in McKinley et al. (1991).

Relative anion abundances vary within a narrow range in samples below 30 cm. Sulfate declines slightly with increasing depth, whereas the fractions of chloride and carbonate vary inversely. The increased chloride content between 30 and 100 cm is consistent with downward movement of chloride from the upper 20 cm with vertical recharge that was insufficient to reach the water table. Of greater interest is the contrast in relative abundance of anions in the soluble fraction and the underlying ground water. Chloride is lower than expected, whereas sulfate is slightly lower and carbonate is much greater. The compositional contrast could reflect stratification such that ground water at the water table near 2.6 to 3.2 m below ground surface would be different from that intersected by the approximately 7 m deep screened intervals of the sampled wells (Czarnecki 1997). Preferential elution of chloride and lesser amounts of sulfate due to greater solubility may also account for the apparent deficiency of those ions. The concentration profile in Figure 5 could reflect the superposition of sulfate and chloride that accumulated on residual sodium carbonate subsequent to a recent recharge event. Based on weather records presented by Reynolds et al. (this volume), 7.37 cm of rain fell in the area two months prior to collection of the sediment samples.

A third, more speculative explanation for the relative contrasting anion content between the unsaturated zone and subjacent ground water is assimilation of carbon dioxide from pore gases in the unsaturated zones. PHREEQC was used to simulate geochemical reactions as ground water from GS-15 and GS-18 evaporates during rise through the capillary fringe. Simulations reacted ground water with calcite and a pore gas having a partial pressure of CO_2 from atmospheric to 0.01 atmosphere (pCO_2 = -3.5 to -2). This range of pCO_2 is consistent with measured values in the unsaturated zone elsewhere along the Amargosa River

(Walvoord et al. 2005). Evaporation was simulated to proceed to a loss of 95% of contained water, and mirabilite, burkeite, halite, nahcolite and trona were permitted to precipitate. In an environment where CO_2 content is equal air, there is a net loss of CO_2 from the resulting salts and residual brines into the gas phase (Figure 7). This result is consistent with the general similarity of the anion composition of salts formed at the ground surface directly overlying water-saturated sediment with the composition of associated ground water. In contrast, at a pCO_2 of -2, the amount of CO_2 in the salts and residual brines increased by 47%. The amount of added CO_2 is insufficient to account for the carbonate excess. Greater amounts of CO_2 may be provided by higher pCO_2 or reactions not considered in this evaluation.

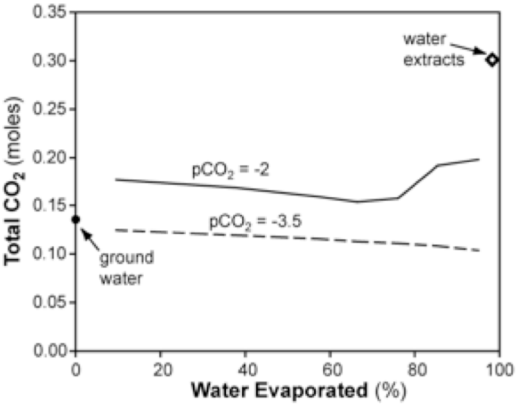

Figure 7–Total moles of carbon dioxide contained in residual water and precipitated salts relative to the amount of water lost during evaporation of one liter of ground water. Results were calculated using PHREEQC assuming partial pressures of carbon dioxide of 10^{-2} and $10^{-3.5}$ and allowing mirabilite, burkeite, halite, nahcolite and trona to precipitate. Although the pCO_2 of -2 increases the total carbonate species, the amount of increase is inadequate to explain the typical water-extractable carbonate content of the sediment.

The amount and composition of salt stored in the unsaturated zone has implications for the evolution of groundwater composition and surface water, if present. Preferential retention of sulfate and carbonate salts relative to chloride in the upper portion of the unsaturated zone could account for the enrichment of chloride in ground water beneath the playa. During an evaluation of the water composition beneath the Franklin Lake playa, Root (2000) simulated the mixing and evaporation of probable recharge waters in the basin and found that the concentration of chloride exceeded the amount accounted for by simple evaporation. An unrecognized chloride-rich recharge component was proposed to account for the discrepancy (Root 2000). Alternatively, selective elution of chloride from the unsaturated zone into the ground water during recharge events also could account for the apparent enrichment.

The concentration profiles for As, Mo, W, and U in the soluble fraction of the sediments (Figure 6) supports differentiation based on chemical characteristics of each element. Unfortunately, available thermodynamic data are insufficient for accurate simulation of adsorption, ion pairing, and solubility of these metals in high-pH, saline solutions. Nonetheless, general aspects of the concentration profiles are understandable from the chemical characteristics of the metal species. At the pH > 9 and oxidizing conditions of the ground water and unsaturated zone, As, Mo, and W are expected to occur dominantly as negatively charged arsenate ($HAsO_4^{2-}$), molybdate (MoO_4^{2-}), and tungstate (WO_4^{2-}) ions (Nordstrom & Archer 2003; Seiler et al. 2005). The parallel concentration profiles of these elements in the upper 120 cm of the sediment are consistent with their shared characteristic as divalent anions. The lower concentrations in the upper 30 cm may reflect depletion by dissolution and transport in vertical recharge, similar to chloride. Although the profiles are similar relative to the concentrations predicted from ground water (Table 1), As is enriched, Mo is depleted, and W is similar. Below 120 cm, where salt content is attributed to residual brine rather than solid salts, As, Mo, and W have different concentration profile characteristics. Arsenic decreases and Mo increases, as both approach concentrations expected for evaporated ground water. In contrast, W contents are substantially greater than predicted. A simplistic interpretation is that W and Mo favor the aqueous phase, whereas As is accumulated in precipitated salts below the depth of maximum salt accumulation. The As-containing salts must have relatively low solubility to avoid flushing in the recharge water that eluted chloride and possibly Mo. All three element profiles show decreasing concentration upward as the evaporation front is approached. The differential behavior of the three elements may reflect differences in transport by upward-moving liquid water, solubility in vertical recharge, or possibly metal extraction from, or binding to, sediments by reaction with residual brines.

In contrast to the As, Mo, and W anions, U is expected to be present as the uranyl cation (UO_2^{2+}) in ground water and the unsaturated zone beneath Franklin Lake playa. Based on the composition of the salts and water, dissolved uranyl ion is predicted to be strongly complexed by two or three carbonate ions (Langmuir 1978). The accumulation of uranium at 20 cm below the ground surface coincident with the maxima of salt accumulation implies preferential transport to the evaporation front. Nonetheless, the concentration of uranium in the water-soluble extractions is markedly lower than the 40 to 50 ppm predicted for evaporation of ground water. This may indicate a strong preference for retention of uranyl ion in ground water rather than accumulation in forming salts during transport to the evaporation front, or preferential elution with downward recharge. The latter is unlikely to solely account for the lack of U because the abrupt enrichment of that element is not matched by any other soluble species.

The unsaturated zone beneath Franklin Lake playa contains significant amounts of salt and readily soluble As, Mo, W, and U. Climate change, disturbance of the subsurface, and anthropogenic modification of the water balance could cause redistribution of significant amounts of these constituents. Their distribution in arid and semi-arid basins is poorly documented, and the processes that affect their retention and accumulation are incompletely known. Nevertheless, wind erosion at these types of settings produces saline mineral-rich dust that may contain toxic metals (Reheis 1997). Agricultural development, water diversions, and evaluation of air quality therefore should include storage of salt and trace elements in the subsurface as part of any environmental assessment. Disturbances of these settings can potentially exacerbate wind erosion and dust emission, resulting in wider dispersion of the salts and trace elements.

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