

Mechanisms of Arsenic Accumulation and Biogeochemistry in Evaporation Ponds

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ABSTRACT

Selenium (Se) is known to be affected by several sink mechanisms in evaporation basins and does not accumulate in concentration in the water column with evapoconcentration but may accumulate in the underlying thin organic detrital matter and mineral sediments. The selenium ecotoxicity hazards to waterbirds in evaporation basins are minimized by these sink mechanisms and by establishment of compensation and alternative habitats when Se risk is high. In contrast, our preliminary data indicates that arsenic (As) in impounded water column in evaporation basins is subject to accumulation during evapoconcentration and may become a future possible environmental concern but not currently fully understood. The goal of this study is to acquire essential data to more fully understand the biogeochemical processes and conditions affecting arsenic accumulation in evaporation ponds. This research project has three specific objectives: 1. Determine primary productivity and biological factors affecting arsenic transformations in evaporation ponds. 2. Determine the potential for arsenic accumulation in pond waters and sediments as controlled by redox chemistry and precipitation/dissolution processes. 3. Predict the fate of arsenic by examining its speciation and partitioning, and compare with selenium from an ongoing study in the same evaporation basin. The study site is the 726 ha South Evaporation Basin facility in Tulare Lake Drainage District (TLDD) that contains 10 cells and is operated in series when subsurface drainage water production is high. In this first year, we examined water and sediment arsenic concentration and speciation within the cells and water samples following the flow path between cells. Pond water chemistry was also characterized. Results indicate that water arsenic concentration increased linearly with increases in EC and almost linearly with increases in concentrations of Cl. Reduced arsenic species as arsenite [As(III)] and organic arsenic also increased with increases in salinity. Water samples with elevated ECs (e.g., towards the end of flow path in the terminal cells) had high dissolved organic matter, depletion of dissolved oxygen, NO₃ and Fe(III), leading to a more reducing environment with elevated sulfide concentrations. These reducing conditions may have lead to reduction of arsenate to arsenite and organic species as the major mechanisms controlling the fate of drainage water arsenic disposed into in the evaporation basin.

INTRODUCTION

Although the hazards of selenium (Se) ecotoxicity to waterbirds in evaporation basins are a major concern, they are minimized by several sink mechanisms reducing selenium (Se) concentration in the evapoconcentrating water columns and by installation of compensation and alternative habitats when risk is high (Tanji et al., 2003). In contrast, our data indicate that the behavior and fate of arsenic (As) in impounded drainage water is different from Se but are not currently fully understood. Arsenic may be subject to accumulation when EC of waters increases from evaporation as in Owens dry lake (Ryu et al., 2002). We are investigating whether arsenic will accumulate to very high levels in evaporation pond facilities that are heavily relied for disposal of irrigation drainage in the Tulare Basin area of the San Joaquin Valley.

According to the National Recommended Freshwater Water Quality Criteria, the Criteria Maximum Concentration (CMC) for arsenic is 340 µg/L and the Criterion Continuous Concentration (CCC) for arsenic is 150 µg/L (USEPA, 1999). These recommended criteria were derived from data on As(III), but is applied to total arsenic assuming that As(III) and As(V) are equally toxic to aquatic life. Currently, there is no evidence of arsenic toxicity to waterbirds in the San Joaquin Valley. There is a need to investigate the mechanisms or processes governing arsenic biogeochemistry in evaporation ponds because arsenic tends to accumulate to elevated concentrations. Such basic knowledge would be essential to help establish whether or not arsenic is likely to be a future constituent of concern in evaporation basins.

The goal of this proposed study is to acquire essential data to more fully understand the processes and mechanisms of arsenic accumulation and biogeochemistry in evaporation basins. We hypothesize that arsenic accumulation in evaporation pond waters are affected by microbial transformations that affect arsenic speciation and evapoconcentration that affects precipitation and dissolution of arsenic minerals. Three specific objectives to be pursued are:

1. Determine primary productivity and biological factors affecting arsenic transformations in evaporation ponds.
2. Determine the potential for arsenic accumulation in pond waters and sediments as controlled by redox chemistry and precipitation/dissolution processes.
3. Predict the fate of arsenic by examining its speciation and partitioning, and compare with selenium from an ongoing study.

STUDY METHODS

STUDY SITE AND SAMPLING

The field study site is TLDD's South Evaporation Basin (Fig. 1), which consists of ten cells operated in series and covers a total surface area of 726 ha. The drainage water flows basically following the order of cell numbers. But when drainage water is limiting (e.g., late summer and winter), flow of drainage water is directed from Cell 1 to Cell 7 through Cell 6, and Cells 3 to 5 are kept dry. To avoid terminal Cell 10 from drying up, fresh drainage water has been occasionally introduced into Cell 10 to sustain *Artemia* (brine shrimp) production. Harvesting activity for brine shrimp were more active in Cells 9 and 10, and occasionally in Cell 8 but none in Cell 1 and others.

Before this project was funded, we sampled water along the flow path between cells and within Cells 1, 8, 9 and 10 in 2003, and also obtained intact core sediment samples. Two sampling locations were selected in each cell following prevailing wind directions in this area from northwest (NW) to southeast (SE) or southwest (SW). For each location, sediment cores (~25 cm depth) were also taken. The sampling locations are indicated in Figure 1. This report covers analytical data completed up to date. Since the initiation of this funded project in 2004, comprehensive sampling within Cells 1 and 9 have been carried out three times as well as water sampling along the flow path monthly. Sampling locations for the comprehensive sampling are shown in Figure 2. Water samples were taken from the top (near water surface) and the bottom (near sediment) in the water column. Sediments samples were taken at selective locations as indicated.

Water samples were stored in ice coolers in the field and during transfer to the lab at UC Davis. Field measurements were done on site for water temperature, EC, dissolved oxygen and treatments for chlorophyll-a and sulfide measurements. In the laboratory, water samples were filtered through 0.45 μm and analyzed for pH, major cations, major anions, and total As concentration and As speciation. Arsenic speciation was determined for arsenate [As(V)], arsenite [As(III)], and organic-As as monomethylarsonic acid [MMAA, $\text{CH}_3\text{AsO}(\text{OH})_2$] and dimethylarsinic acid [DMAA, $(\text{CH}_3)_2\text{AsOOH}$]. MMAA and DMAA are the dominant organic species of arsenic in aquatic systems and others are minor (Andreae, 1977; Cullen and Reimer, 1989). The samples were stored in a refrigerator (3 $^\circ\text{C}$) until completion of analyses. For arsenic speciation that was done at later times, a portion of the samples was frozen until ready for analysis.

Sediment cores were taken using 5-cm diameter acrylic tubes. The cores were sealed immediately in the field with a plastic cap, duct-taped, and stored on ice. After transferring to the lab, the core samples were frozen until ready for processing and analysis. Organic detrital materials (DM) were separated from the mineral sediment cores by scraping off the top materials containing visible brownish DM. The mineral cores were then sectioned into 0-5, 5-10, 10-15, 15-20, and below 20 cm segments. The samples were freeze-dried, ground, sieved and mixed thoroughly before digestion for total As analysis.

CHEMICAL ANALYSIS

Water characterization and redox chemistry

After measuring pH and EC, water samples were passed through a 0.45 μm pore-size membrane filter. The filtrate were analyzed for major cations (Na, Mg, K, Ca) and anions (Cl, SO_4 , Br, NO_3 , PO_4) by atomic absorption spectrophotometry (AAS) and ion chromatography (IC), respectively. Alkalinity was determined by titration to an end-point of pH 4.5 using an autotitrator and corrected for ions that consume protons. Boron was analyzed using azomethine-H method (John et al., 1975; Bingham, 1982). Dissolved organic carbon was determined on the filtrate (0.45 μm) using a Shimadzu carbon/nitrogen analyzer. Chlorophyll-a samples were collected by filtering an aliquot of sample through a pre-ashed Gelman A/E glass fiber filter (0.45 μm). The filters were placed in a vial, immediately frozen, and stored in darkness until analyzed. Chlorophyll-a was extracted in 90% reagent-grade ethanol and determined by a fluorometric method (APHA, Standard Methods, 1992). As an indication of redox conditions in pond waters, dissolved oxygen (DO) was measured when sampling in field using a YSI model 54A oxygen meter with DO probe. Fe(II) and total Fe were determined by the ferrozine method. Sulfide concentration was determined by ion selective electrode (model 9416; Orion Research Inc., Beverly, MA).

Total As and As speciation for As(V), As(III), MMAA, and DMAA

Total As concentration in water samples was determined using Cutter's procedure (Cutter, 1982) modified by Yoshimoto (1992). This method uses a combination of heat, acid (HCl and HNO_3), and oxidizer (persulfate) to oxidize all As species to As(V), which was then reduced to As(III) by KI following the procedures in Glaubig and Goldberg (1988). Arsenic was quantified by hydride generation atomic absorption spectrophotometry (HGAAS) technique. Total As for sediment samples were determined using acid digestion (Zasoski and Burau, 1977) and quantified by HGAAS.

Prior to setting up the apparatus for organic As speciation, As(III) species and total As in water samples were determined previously using the method by Glaubig and Goldberg (1988). In this case, the difference between the total and As(III) was the sum of As(V) plus org-As. Arsenic speciation in selected water samples was further performed using a modified hydride generation with cold trapping and atomic absorption spectrophotometry (HGCT-AAS) technique from Andreae (1977), Crecelius et al. (1986) and Masscheleyn et al. (1991). This method is time-

consuming but can accurately identify all arsenic species. The detailed procedure is described in Gao and Burau (1997). The followings are a brief description of the method. When As(V), As(III), MMAA and DMAA in solution react with nascent hydrogen from the decomposition of NaBH_4 , volatile arsine (AsH_3), monomethyl arsine (MMA, AsH_2CH_3), and dimethyl arsine (DMA, $\text{AsH}(\text{CH}_3)_2$) are produced respectively from corresponding arsenic compounds [As(V and III), MMAA, and DMAA]. These volatile compounds are trapped in a column immersed in liquid nitrogen. When the liquid nitrogen is removed and as the column is warmed up by heating, these arsines are released serially as their boiling points (-55, 2, and 35°C for arsine, MMA, and DMA, respectively) are reached. The released arsines are then introduced into a heated quartz cell by an inert carrier gas. The absorbance by arsenic atoms measured by AAS is used for quantification of arsenic species. Because As(V) and As(III) form the same volatile compound (AsH_3), As(III) was analyzed by forming arsine at pH 6 when other forms of arsenic could not react in formation of arsines. As(V) was obtained from the difference between total inorganic As (V + III) and As(III).

RESULTS AND DISCUSSION

GENERAL WATER CHEMISTRY

General pond water chemical characteristics and constituents in pond waters are shown in Table 1. EC of water samples ranged from 19 to 116 dS/m. pH was in the range of 8.2 to 8.9, reflecting carbonate dominated buffer system. Major anions were Cl and SO_4 . Nutrients level (N and P) were very low. The dominant cations were Na followed by Mg. Ca concentrations were much lower than Mg, especially when EC was high. The increase of EC in pond water was mainly due to evapoconcentration. Chloride is considered the most conservative element in water. A relationship between EC and Cl was obtained for pond waters in this basin was: $\text{Cl (mmol/L)} = 9.06 * \text{EC (dS/m)} - 95.8$. When EC exceeds 120 dS/m, this linear relationship does not hold anymore due to precipitation of minerals and relatively high proportional increase of Cl in solution. The ratio of $[\text{Cl}]_{\text{pond water}} / [\text{Cl}]_{\text{inlet}}$ is defined as Evapoconcentration Factor or ECF (Tanji, 1990). The values of ECF obtained for Cells 1, 8, and 9 were 2, 22, and 48, with standard deviations of 0.1, 0.6 and 2.0, respectively. This indicates that as water flows from Cell 1 to the terminal cells, such as Cells 9 and 10, water can be significantly concentrated. As the waters evapoconcentrate, the solubility product constants (Ksp) of minerals can be exceeded and certain minerals (calcite, gypsum, etc.) precipitate out from the water column and along the shoreline. Chloride minerals such as halite (NaCl) have very high Ksp and will precipitate only in hypersaline waters. Thus, evapoconcentration based solely on increases in EC may not be an appropriate evapoconcentration index.

The correlations between Cl and other constituents are plotted in Figure 3. As Cl concentration increased, Na and B as well as Mg increased linearly indicating no significant precipitates associated with these ions. Sulfate increased linearly only up to a certain level (~500 mM/L). There were no apparent correlations of alkalinity and Ca concentration increase as Cl concentration increased. This is most likely due to the formation of calcite (CaCO_3), which has the lowest solubility and thus readily precipitates out from evapoconcentrating waters. Using a brine chemistry model for hypersaline waters, Smith (1989) predicted that Mg and SO_4 as well as Na can accumulate to relatively high levels in brines before their precipitates form. The typical sequence of minerals to precipitate out in San Joaquin Valley evaporation basins as evapoconcentration continues (Smith et al., 1995) is CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{Ca}(\text{SO}_4)_2$, Na_2SO_4 , $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and NaCl . Generally speaking, hypersaline waters would have solute abundances in a typical order of $\text{Na} > \text{Mg} > \text{Ca}$ and $\text{Cl} > \text{SO}_4 > \text{HCO}_3$, which we have observed for the pond waters.

To examine increases in arsenic concentration from evapoconcentration, changes in arsenic concentration in pond waters as a function of EC and Cl are plotted in Figure 4. Arsenic increased dramatically in a linear relationship with increases in EC and up to a certain level of Cl concentration (~500 mmol/L). When Cl concentration continues to rise, the increase in As concentration reduced indicating some removal of As from the water column. This indicates that arsenic behaves initially as a conservative element in pond waters but not at elevated salinities. Precipitation from evapoconcentration or other mechanisms in removal of As during evapoconcentration from pond waters appears to be occurring in this pond facility. This phenomenon begs further in-depth examination because it is important in understanding how high As concentration may accumulate in the pond water columns. A similar phenomenon was observed in brine shallow groundwaters in Owens dry lake (Ryu et al., 2002) where dissolved arsenic concentrations ranged from 0.1 to 96 mg/L and showed a general increase from the shoreline to the center of the lakebed as evapoconcentration factor increased. Arsenic concentrations were found to be strongly correlated to EC and δD suggesting that evapoconcentration was an important process regulating total As concentrations to very high levels. The pond water conditions in TLDD Southern Evaporation Basin may be different from Owens dry lake groundwater but a similar trend was observed.

ARSENIC SPECIATION

Reduced As (III) species and total As were initially determined for samples taken in Year 2003 using the method by Glaubig and Goldberg (1988) (Figure 5). Total As concentrations dramatically increased along the flow path (ascending cell number). As(V) was dominant in drainage water and As(III) was less than 1% of the total As in the

inlet drainage water. Along the flow path between cells, As(III) was a minor species until the water reached Cell 8. Within the cells, Cells 8 and 9 contained similar As(III) concentrations. Cell 10 contained a much lower As(III) concentration or percentage as compared to Cells 8 and 9 and this is probably due to the dilution factor from introduction of fresh drainage water. The difference between As(III) and the total is the sum of oxidized As(V) and org-As. As the concentration of reduced As(III) increases, it is expected that oxidized As(V) would decrease.

Additional arsenic speciation, including both inorganic [As(V), As(III)] and organic [MMAA, DMAA], were performed for pond water samples taken in the Year 2004. The speciation results are shown in Table 2. Reported are water samples collected from top (near surface) and bottom (near sediment) of the water column as well as along the flow path: from main inlet channel to terminal ends of Cells 1, 8, 9 and 10. The main inlet channel (fresh drainage water from agricultural fields) was dominated by the oxidized form of As(V) (95%) with 5% As(III) and non-detectable organic As. Cell 1 showed almost similar percentage of As speciation with non-detectable org-As. Cell 8 showed lower (87%) As(V) and higher As(III) (11%) and org-As (MMAA+DMAA, 2%) compared to the inlet channel and Cell 1. The percentage of As(V) continuously decreased in Cell 9 to 75-84% corresponding to increases in As(III), 8-16%. Organic -As increased to 3-11% in Cell 9 for all the samples monitored. Cell 10 showed much lower total As concentration due to the dilution factor from addition of fresh drainage from the inlet channel but the highest reduced As (III) (34%) and org-As (14%) was observed.

Distribution of As(V) and As(III) was primarily regulated by reducing condition, because the pH is relatively constant for all sample sites. The proportion of As(III) increased through water paths as reducing processes occurred. Increases in organic arsenic indicate microbially-mediated activity that results in methylation. Organic arsenic is often in trace amount unless microbial activity is very high such as in a wetland environment (Andreae, 1977; Cullen and Reimer, 1989). An earlier report indicated even higher organic As species (31-50% DMAA and 11-17% MMAA of total soluble arsenic) in an agricultural evaporation pond (Tanji and Dahlgren, 1993). Methylation process also can lead to volatilization by forming volatile organic As compounds as monomethyl arsine (MMAA), dimethyl arsine (DMAA) and trimethyl arsine (TMAA). We have not been able to measure this transformation that causes loss of As from the water. Apparently, arsenic volatilization is not significant enough to suppress As concentration in water columns. Further, it should be noted that although arsenic reduction occurred in pond waters, oxidized As(V) was still predominant in all pond waters (>50%). It is believed that this partial reduction controlled by pond conditions is critical in understanding the fate of As entering the pond facility.

Some of parameters that represent microbial activity and redox conditions of the water were measured (Figure 6 and Table 3). Organic matter is the primary energy source driving microbial activity and occurs as both solid and dissolved organic matter. Figure 6 shows total dissolved organic carbon (DOC) in the pond waters. The concentrations of DOC were surprisingly high with increase in EC values. There may be two reasons that cause increases in DOC with increases in EC: First, transport of DOC with soluble salts and concentration as the evapoconcentration process takes place, i.e., recalcitrant organic carbon fraction leads to accumulation of organic carbon in waters with lower consumption of DOC by microbes. Second, addition of chicken manure to enhance production of brine-shrimp in Cells 9 and 10 can be a source of organic carbon in the water. Both factors may be involved since neither one singly could fully explain the increases in DOC.

While EC and solute concentrations showed a strong evapoconcentration pattern from the inlet to the terminal end of the pond facility, reducing conditions also developed due to growth, death and decay of phytoplankton and increased hydrologic residence time (Table 3). In the decomposition of phytoplankton and other organic debris bacteria successively consume O_2 , NO_3^- , Fe(III) and SO_4^{2-} as electron acceptors. The depletion of dissolved oxygen (DO) concentrations occurred as drainage water reached the terminal end of the pond facility. The lowest average dissolved DO (2.1 mg/L) was found at the bottom layer of Cell 9. These values indicate that anaerobic respiration occurred at the bottom layer of Cell 9. The depletion of nitrate concentrations was also observed in water flows from Cells 1 to 9. In addition, dissolved Fe(III) decreased in water flows from Cells 1 to 9. The depletion of electron acceptors such as O_2 , NO_3^- , and Fe(III) allow for the development of sulfate reduction resulting in elevated sulfide concentrations in the bottom layer of Cell 9 (up to 69 mg/L). The sulfide concentrations were much higher than other previous cells within the water flow paths where the sulfide concentrations were often under detection limit. Although reducing condition showed a general trend in the drainage flow path, we found significant spatial variance in reducing condition at different locations within the cells. The results indicated that reducing processes may have occurred in rather isolated spots in a cell.

ARSENIC IN SEDIMENTS

Total As concentrations in the sediment profiles varied greatly with depth, as well as spatially among locations in a cell (Figure 7.). Arsenic concentration was the lowest in Cell 1 near the inlet location and reached a high value of about 80 mg/kg in the surface sediment of Cell 9. The distribution of arsenic with depth is somewhat uneven. The SW location of Cell 1 (S1-SW), a stagnant area, accumulated very high arsenic concentrations. This indicates that As tends to accumulate in the sediments. However, this trend is not reflected in all cells and may be due to bank erosion from wind-driven wave action that causes deposition of soils (bank materials) on near shore areas where sediment core samples were taken. Arsenic concentration profiles in the sediments at S8-NW, S10-NW and S10-SE appear to

show buried surface sediments. It is certain, however, that the sediment serves as a sink for arsenic in the pond facility.

SUMMARY AND CONCLUSIONS

This study demonstrates that arsenic distribution and speciation in the evaporation ponds were strongly affected by evaporation and redox chemistry. Arsenic concentration increases linearly with increasing evapoconcentration factor or EC due to evapoconcentration in the studied pond facility operated in-series. The reducing condition due to the decay of organic debris affected arsenic speciation. Although arsenic toxicity to wildlife has not been reported, high accumulation of arsenic in some ponds may become a potential environmental concern of the future.

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Table 1. Important parameters and constituents in pond waters of South Evaporation basin, TLDD.

	EC	pH	HCO ₃ ⁻	Cl	SO ₄	NO ₃ -N	NH ₄ -N	PO ₄	Na	Ca	Mg	K	B	Br-
	dS/m		meq/L	mM/L	mM/L	mM/L	mM/L	mM/L	mM/L	mM/L	mM/L	mM/L	mM/L	mM/L
	Average													
S1-NW	18.8	8.9	7.9	94.8	71.5	0.04	0.02	0.00	210.7	1.5	14.6	0.7	1.1	3.3
S1-SW	19.1	8.9	8.1	92.0	72.1	0.01	0.06	0.00	217.5	1.4	14.5	0.6	1.2	2.2
S8-NW	113.3	8.8	56.3	1060.2	552.2	0.02	0.01	0.02	1951.1	2.1	130.9	7.9	11.6	9.0
S8-SE	115.8	8.7	57.4	1054.9	349.0	0.00	0.02	0.02	1514.0	2.0	127.5	6.7	11.4	9.1
S9-NW	113.7	8.2	84.0	2343.2	621.5	0.02	0.02	0.02	3141.5	4.5	330.0	24.4	26.7	0.1
S9-SE	116.4	8.6	83.0	2371.3	535.3	0.03	0.02	0.02	2950.2	4.6	314.5	23.9	27.5	0.0
Cell10 NW	81.5	8.8	N/A	474.6	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Cell10 SE	81.4	8.8	N/A	483.8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Standard deviation													
S1-NW	0.1	0.1	0.6	2.5	0.8	0.03	0.03	0.00	14.2	0.0	1.0	0.1	0.3	0.6
S1-SW	0.2	0.0	0.3	4.4	3.3	0.01	0.01	0.00	1.9	0.1	2.1	0.1	0.2	0.0
S8-NW	0.3	0.0	2.2	41.2	86.4	0.02	0.01	0.00	64.0	0.1	6.6	0.5	0.7	3.7
S8-SE	1.8	0.0	2.7	28.1	47.1	0.00	0.02	0.00	82.9	0.2	11.2	1.4	0.3	4.1
S9-NW	1.5	0.0	4.0	74.3	78.8	0.00	0.00	0.00	190.9	0.2	5.3	1.8	0.3	0.1
S9-SE	4.6	0.0	4.4	130.2	57.1	0.00	0.00	0.00	291.9	0.1	23.0	1.2	2.1	0.0

Table 2. Arsenic speciation for inlet and pond water samples collected from March through November, 2004 (n=4).

Time	Description	Total As ($\mu\text{g/L}$)	% As(III)	%MMAA	%CA	%As(V)
				Averages (Stdev)		
Mar., 2004	Cell 1-top	116.0 (7.6)	5.5 (0.6)	0.0 (0.0)	0.0 (0.0)	94.5(0.6)
	Cell 1-bottom	125.5 (6.9)	5.1 (0.3)	0.0 (0.0)	0.0 (0.0)	94.9 (0.3)
	Cell 9-top	526.0 (48.2)	16.5 (1.9)	0.7 (0.2)	2.3 (0.6)	80.5 (2.5)
	Cell 9-bottom	1444.7 (489.9)	15.7 (1.8)	1.9 (1.1)	7.3 (5.8)	75.1 (8.6)
Nov., 2004	Cell 1-top	142.3 (7.2)	4.6 (0.4)	0.0 (0.0)	0.0 (0.0)	95.4 (0.4)
	Cell 1-bottom	141.5 (9.2)	5.1 (0.8)	0.0 (0.0)	0.0 (0.0)	94.9 (0.8)
	Cell 9-top	737.9 (78.7)	8.3 (1.0)	3.8 (3.0)	7.9 (2.0)	80.0 (4.2)
	Cell 9-bottom	768.4 (101.2)	8.3 (1.9)	2.1 (0.3)	4.9 (0.7)	84.7 (1.8)
Mar. & Nov., 2004	Central Inlet	119.0 (10.3)	4.9 (2.7)	0.0 (0.0)	0.0 (0.0)	95.1 (2.7)
	End of Cell 1	124.1 (13.3)	7.0 (2.8)	0.0 (0.0)	0.0 (0.0)	93.0 (2.8)
	End of Cell 8	1219.6 (747.8)	11.4 (7.1)	0.6 (0.4)	1.2 (0.6)	86.8 (7.8)
	End of Cell 9	681.9 (252.0)	16.3 (7.3)	2.0 (0.8)	4.1 (1.0)	77.6 (6.9)
	End of Cell 10	535.2 (400.7)	33.9 (25.3)	6.1 (4.3)	8.3 (3.5)	51.6 (31.6)

Table 3. Redox species measurements in pond waters (n=15).

Time	Description	DO (mg/L)	NO ₃ -N (mg/L)	Fe (total) (mg/L)	Fe(II) (mg/L)	SO ₄ (mg/L)	Sulfide (mg/L)
Mar-04	Cell 1-top	14.6 (0.9)	7.0 (1.2)	0.46 (0.55)	0.06 (0.08)	4545 (224)	<0.01
	Cell 1-bottom	11.8 (0.8)	7.5 (1.2)	0.45 (0.46)	0.13 (0.13)	4619 (132)	<0.01
	Cell 9-top	4.4 (1.0)	2.4 (0.3)	0.46 (0.60)	0.22 (0.30)	28003 (5001)	0.10 (0.17)
	Cell 9-bottom	2.1 (1.4)	3.2 (0.7)	0.40 (0.56)	0.29 (0.51)	32699 (7927)	18.37 (37.57)

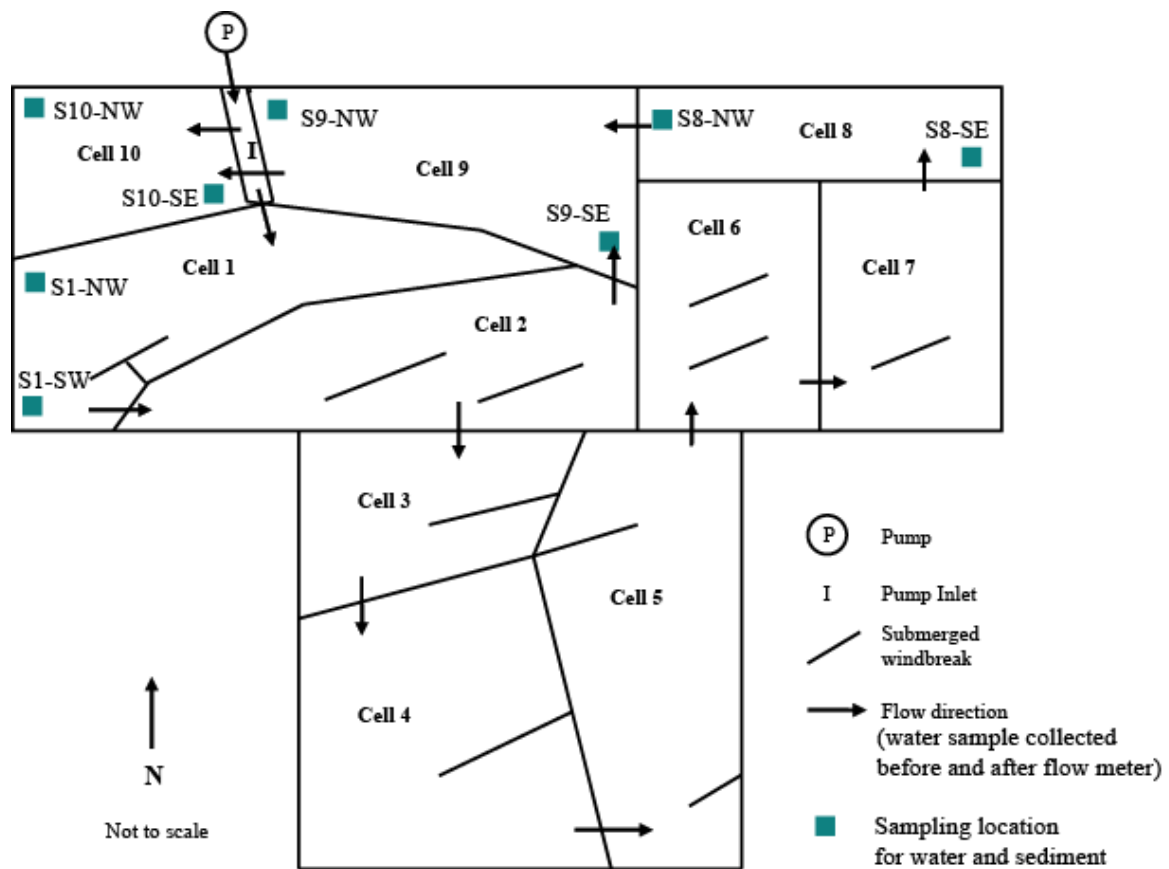


Figure 1. Sampling locations in the 726 ha South Evaporation Basin in Tulare Lake Drainage District (TLDD)

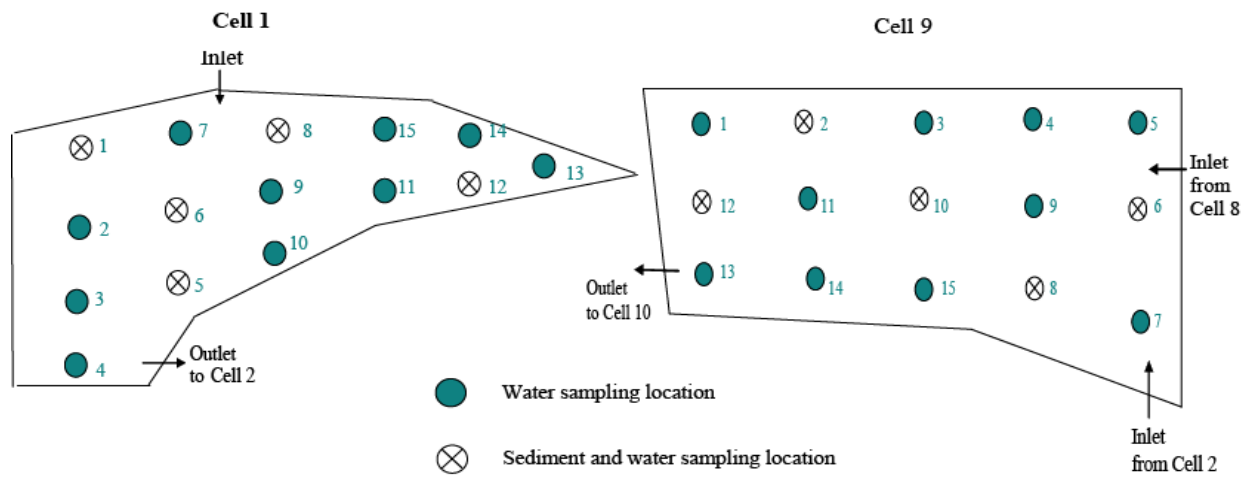


Figure 2. Sampling locations within Cells 1 and 9 for water and sediment samples.

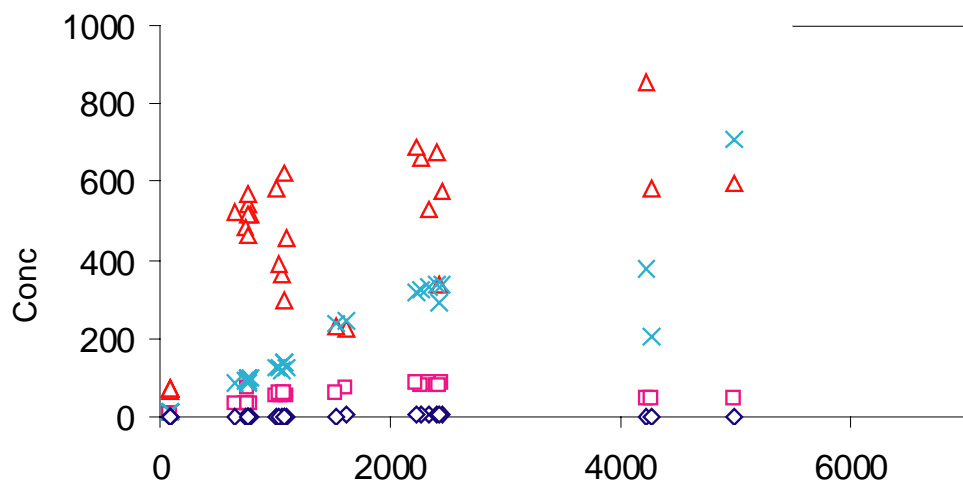


Figure 3. Correlation between chemical constituents with conservative Cl concentration.

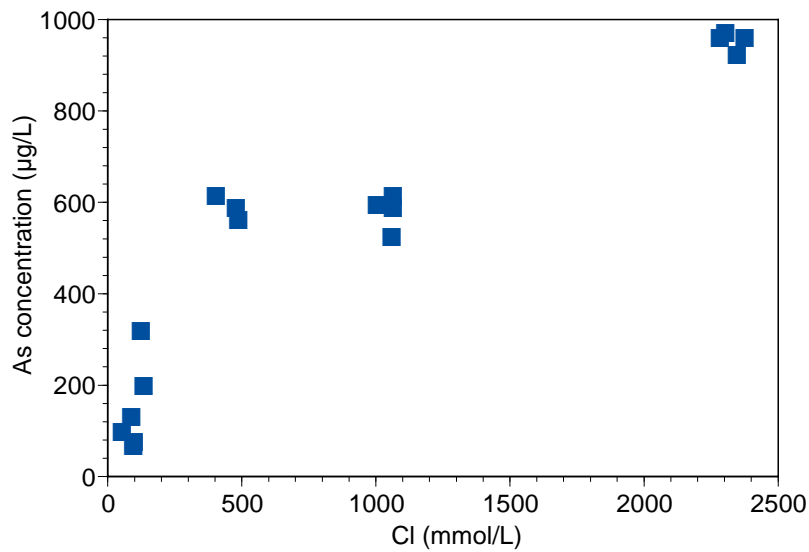
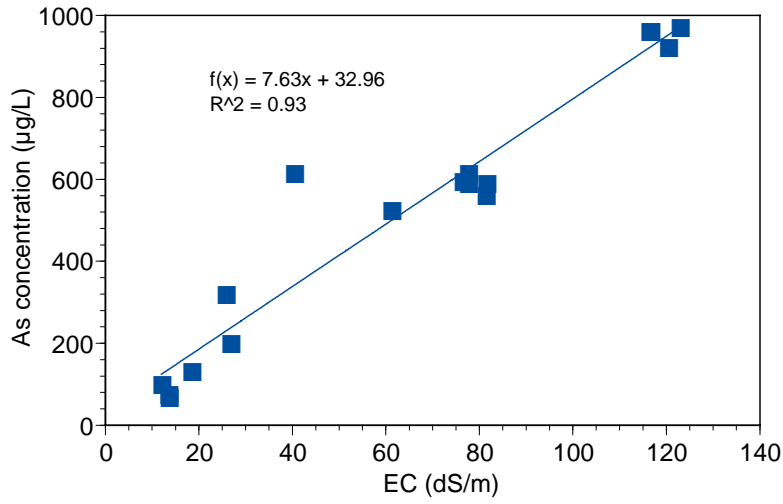


Figure 4. Relationship between EC or Cl and total concentrations of arsenic in the evaporation pond waters.

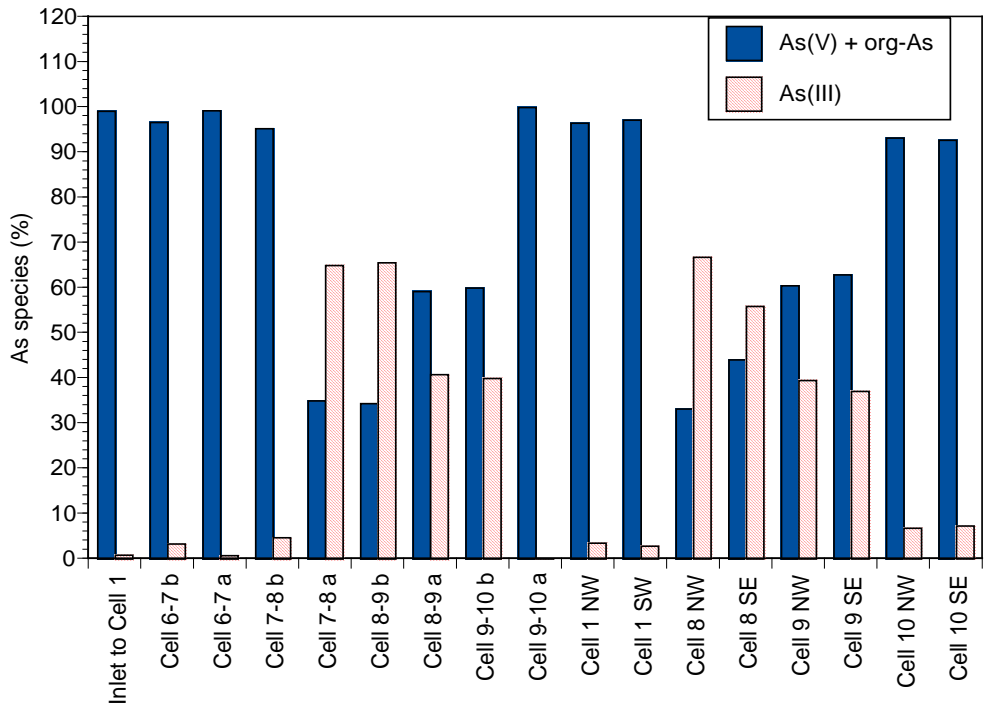
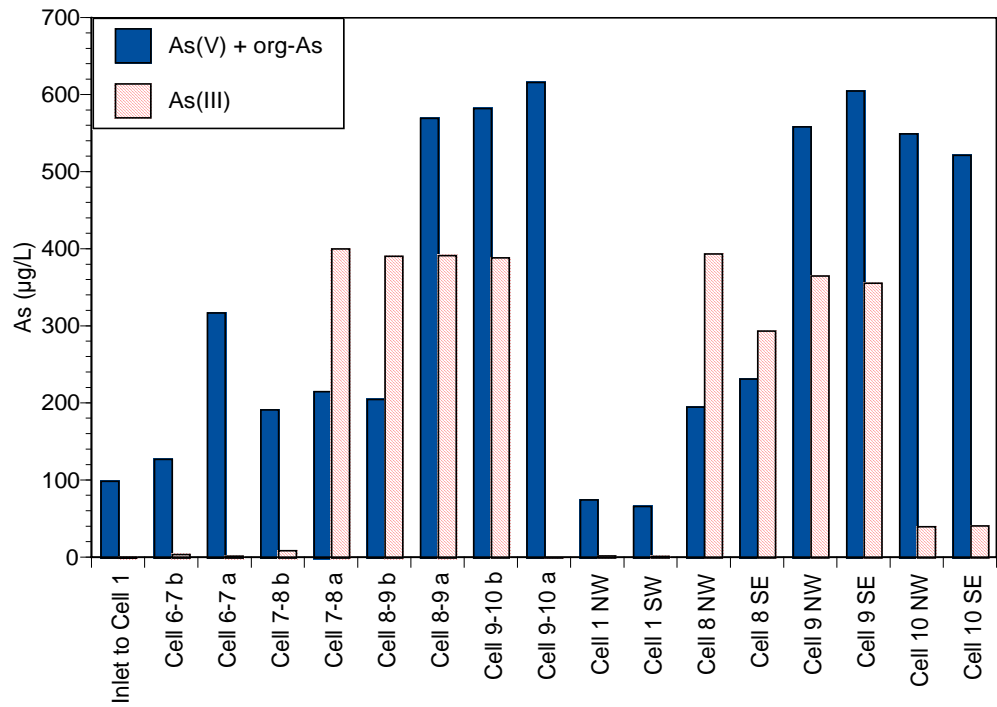


Figure 5. Total arsenic and As(III) speciation data. The symbols “b” and “a” indicate water samples taken before and after flowing to next cell, respectively. The left columns are samples taken along water flow path. The right columns are samples taken within cells.

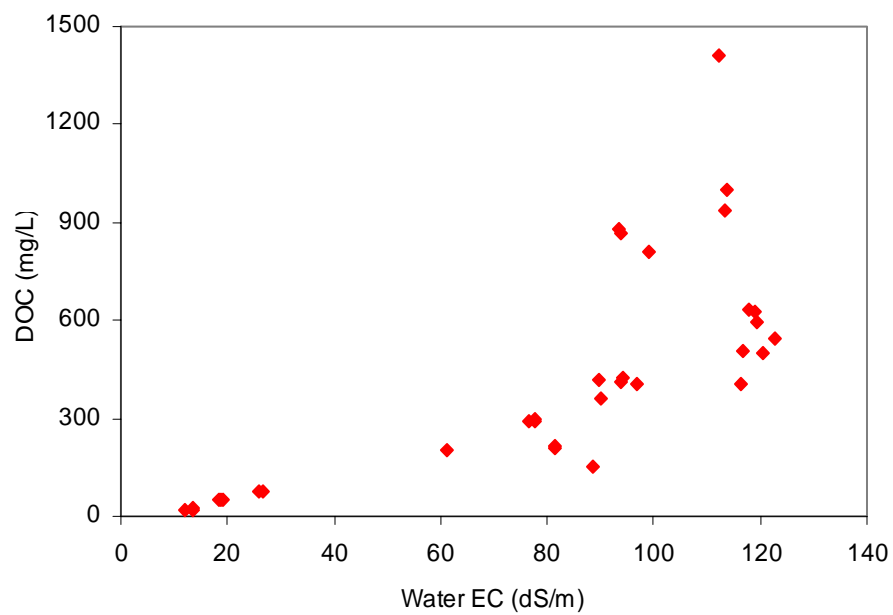


Figure 6. Relationship between total dissolved organic carbon (DOC) and water EC.

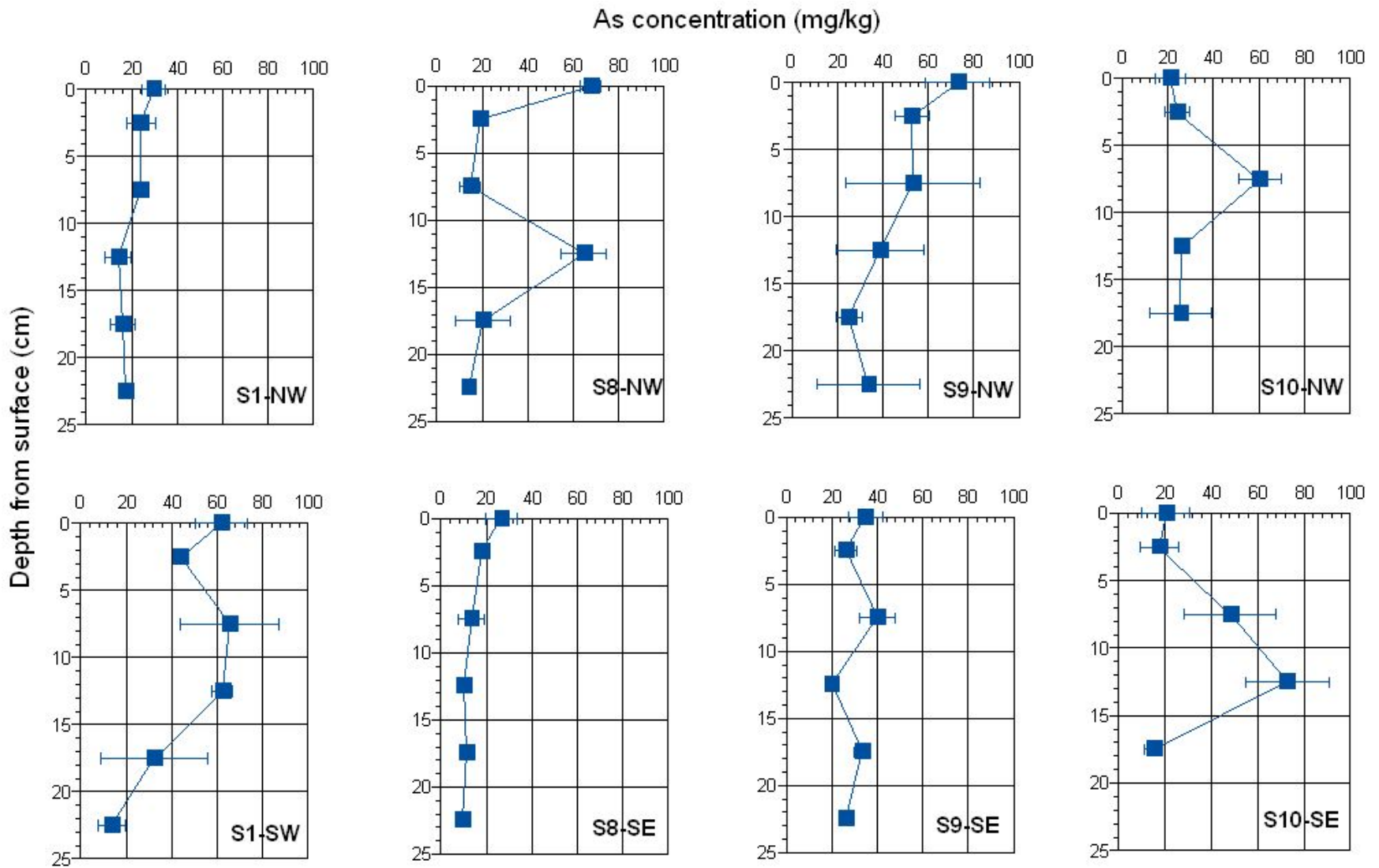


Figure 7. Arsenic concentration profile in pond sediments sampled in 2003.