Water Quality and Trace Element Evapoconcentration in Evaporation Ponds for Agricultural Waste Water Disposal

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Evaporation ponds in California's San Joaquin Valley are an interim disposal solution for saline drainage waste water from irrigated agriculture. A water quality monitoring program was initiated to gauge the environmental fate of potential inorganic toxicants (As, B, Mo, and Se) upon evapoconcentration. Chemical composition is dominated by Na, Cl, and SO₄, with electrical conductivities ranging from 8 to 34 dS/m in inflow and from 48 to 178 dS/m in pond waters. Trace element levels are largely determined by (1) geomorphic landscape position, (2) degree of evapoconcentration, and (3) chemical reactivity in the water column-sediment system. Cl-based evapoconcentration factors were calculated to evaluate trace element chemical reactivity. B was readily conserved, whereas As, Mo, and Se underwent loss from the water column. As, B, and Se approached or exceeded hazardous waste criteria. Continued operation within environmental standards requires careful management.

Keywords: Agricultural waste water; evapoconcentration; evaporation pond; water quality

INTRODUCTION

Irrigation of agricultural lands on the west side of the San Joaquin Valley of California has led to the production of a vast quantity of highly saline drainage waste waters (Kelley and Nye, 1984). Irrigation waters imported to the San Joaquin Valley contain low levels of dissolved mineral salts, but mineral salt additions from the chemical weathering of alluvium from marine sedimentary parent material in the Coast Ranges produce saline drainage waters (Biggar et al., 1984) which also contain appreciable concentrations of arsenic (As), boron (B), molybdenum (Mo), and selenium (Se). An unfavorable salt balance in this region exists because salt inputs from imported water and chemical weathering greatly exceed salt outputs by about 3 million tons per year (San Joaquin Valley Drainage Program, 1990).

Agricultural evaporation ponds are one means for disposing drainage waste waters (Hedlund et al., 1990; Lee, 1990). Technologically, they are similar to solar ponds used for the harnessing of solar energy and salt harvesting ponds in the commercial production of common table salt. The engineering application of evaporation ponds to environmental problems could see widespread use in remediation efforts when precipitation is intercepted and becomes runoff to holding ponds before being able to seep into contaminated soils. Twentyeight evaporation ponds were installed between 1972 and 1985 in regions with limited opportunities for surface discharge of drainage water. Five ponds are now inactive or being closed. These ponds occupy about 2800 ha that vary in surface area from 4 to 730 ha (Chilcott et al., 1990) and annually receive about 39.6 million cubic meters of drainage water. The majority of the ponds are located in the environs of the Tulare Lake Basin, a hydrologically closed basin, where opportunities do not exist to discharge saline drainage waters out of the basin. A California Regional Water Quality Control Board survey showed a wide range of dissolved solids and targeted Se, Mo, As, and B for future trace element monitoring (Westcot et al., 1988).

Between 1978 and mid-1986, agricultural drainage water in a portion of the Westlands Water District was collected by subsurface drains and discharged into the San Luis Drain, which terminated at Kesterson Reservoir (Tanji et al., 1986). The impounded waters were subsequently managed as habitat for migratory and resident waterfowl. However, evaporation of this surface water body led to elevated levels of soluble Se (Presser and Barnes, 1985), which then resulted in Se bioaccumulation and toxicosis in waterfowl (Ohlendorf et al., 1986). Selenium also was immobilized in the sediments of Kesterson Reservoir (Long et al., 1990; Benson et al., 1991), which limited the contamination of regional ground water (White et al., 1991). The adverse ramifications of Se poisoning in waterfowl eventually caused the closure of Kesterson Reservoir and created a shift toward greater reliance on regional and on-farm agricultural evaporation ponds for the disposal of salt-laden drainage waters (Letey et al., 1986).

Due to the environmental impact that Se had at Kesterson Reservoir, evaporation ponds have been closely monitored with respect to chemical, biological, and hydrological changes, with special focus on the evapoconcentration of solutes to hazardous levels (Tanji et al., 1985, 1992; University of California, Committee of Consultants on San Joaquin River Water Quality Objectives, 1988).

Evapoconcentration is the term used to describe the process by which the ratio of solute to water solvent is increased by the removal of the solvent and retention of the solute. The change in the ratio is called the evapoconcentration factor (ECF). An ideal reference solute would remain in solution due to nonreactive or conservative behavior during the course of evapoconcentration. Cl is an especially viable choice in this study because of the relatively high solubility of chloride

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Figure 1. Location map of evaporation ponds in this study.

evaporites such as halite (NaCl). The reference solute is hence used as a gauge of the ECF (Tanji, 1989).

This paper reports on a 3 year water quality monitoring project at three selected evaporation ponds. A summary of water quality data is presented and is followed by an assessment of the influence of evapoconcentration on the fate of trace constituents of toxicity concern including As, B, Mo, and Se using the ECF concept. The evapoconcentration of trace elements in a multicell evapoconcentration pond at particular times showed that As, Se, and Mo were dissipated by such a design, while B easily transferred across the series of increasingly saline pond cells (Ong and Tanji, 1993). The formulation in this paper examines evapoconcentration as a time process and is applicable independent of the number of cells.

MATERIALS AND METHODS

Study Area Descriptions. The evaporation ponds are located in central California (Figure 1) along the western side of the San Joaquin Valley. Each of the ponds lies in a region with distinguishable geomorphic characteristics: the alluvial fan (AF) region, the basin rim (BR) region, or the lakebed (LB) region (Westcot et al., 1988; Bradford et al., 1989). Since the evaporation pond waters are derived from subsurface drainage waters of nearby locations, the pond water composition should be characteristic of the region. The AF region was reported to have elevated concentrations of B, Mo, and Se, the BR region was high in B, and the LB region was found to have high As, B, and Mo concentrations. However, this study shows that the trace element characterizations do not strictly adhere.

FIEL C

Pond I, located in the BR region and put into operation in 1985, is a unicell type design divided into three connected sections by windbreak berms (Figure 2a). Water from the field collection system is pumped to the northwest corner inlet by a sump. A perimeter drain outside the pond intercepts lateral subsurface flow from the pond and adjacent farmland. The intercepted water is returned at the southwest inlet via another sump. The pondbed material had a sandy clay loam texture, but under continuous ponding, pond seepage rates declined as conducting pores were plugged with clays and detrital matter (Grismer and McCullough-Sanden, 1988), preventing significant chemical contamination of underlying ground water. During the study period, all three sections of this pond contained about 0.6 m of water.

Pond II, located in the AF region and established in 1984, is an in-series (multicell) type pond comprising a consecutive sequence of five cells interconnected by gravity flow transfer pipes (Figure 2b). A sixth cell acts as an overflow cell and occasionally receives water from cell 1. Field drainage and intercepted lateral flow is pumped from the same sump to the inlet in cell 1. During the study period, cells 1-3 and 5 consistently contained approximately 0.9 m of water, but cell 4 was drained dry in late 1987 to conduct remediation studies involving Se volatilization. The pondbed material consisted of clay.

Pond III, located in the LB region and built in 1985, is also an in-series type pond, comprising only two cells (Figure 2c). Field drainage is brought to the inlet at the south side of cell 1 via a sump. One gravity flow transfer pipe is located at the north end of the berm dividing the cells. There is no perimeter interceptor drain system at this pond. During the study period, both cells contained water, but the water depth in cell 2 varied from 0.9 m to near dryness. The pondbed material had a loam texture.

Sampling and Analysis. Pond water samples were collected quarterly in the months of August, November, February, and May beginning August 1986 and ending May 1989 inclusively, for a total of 12 collections corresponding to consecutive seasons. During this study, salinity levels had not risen to the point that evaporite minerals, especially those having Cl as the anion component (e.g., NaCl), would form. Therefore, Cl is assumed to have been conserved in the pond waters. Water samples were collected from near-shore locations in each section (pond I) or cell (ponds II and III) in 1 L polypropylene bottles. At each sampling location, one sample was used for on-site measurements of electrical conductivity (EC), pH, and Eh. Another sample was transported to the nearby U. C. West Side Field Station at Five Points, CA, for filtration and sample preservation.

The samples were filtered initially through Whatman No. 2 filter paper and finally through 0.45 μ m membrane filters (Gelman). Half of the filtered sample was acidified with nitric



Figure 2. Schematic layout and operational design of ponds I-III.

acid to ~pH 2, while the other half was untreated and kept in cold storage (~3 °C). The acidified portion was analyzed for sodium (Na), calcium (Ca), magnesium (Mg), As, Mo, and B using an Applied Research Laboratories Model 3510 inductively coupled plasma (ICP) spectrophotometer and for Se using a Turner Model III fluorometer following the HNO₃/ HClO₄ digestion and 2,3-diaminonaphthalene (DAN) fluorophore procedure described by Wang et al. (1994). The unacidified sample was analyzed with a Shimadzu high-performance liquid chromatograph (HPLC) equipped with a conductivity detector for sulfate (SO₄) and chloride (Cl) ions and a UV-vis detector for nitrate (NO₃) ion. An additional 20 trace elements were also analyzed by ICP, but concentrations were typically low and are not reported here.

Time-Dependent Evapoconcentration Factor. The concentration of the reference chloride solute, C_{Cl} , increases as a result of evapoconcentration of the pond waters. Therefore, an ECF value can be obtained by calculating the ratio of the Cl concentration at some time t to the Cl concentration at some prior time t_0 :

$$\mathbf{ECF}(t) = C_{\rm Cl}(t) / C_{\rm Cl}(t_0) \tag{1}$$

The calculated ECF can then be applied to evaluate the predicted concentration of a solute, x, at time t, assuming nonreactive behavior and knowing the concentration of solute x at time t_0 :

$$C_{\text{pred }r}(t) = \text{ECF}(t)C_{r}(t_{0})$$
(2)

The ECF(t) variable is termed the "time-dependent evapoconcentration factor" because its value depends only on the specification of the times t and t_0 .

The predicted concentration, $C_{\text{pred},x}(t)$, is then compared to the measured solute concentration, $C_{\text{obs},x}(t)$. For a very reactive solute, the measured concentration would be much less than predicted. A nonreactive solute would have similar measured and predicted values.

The formulas can be applied to the time periods of interest and for which data are available to ascertain (1) whether reactivity or conservancy characteristics change or may be generalized, (2) whether hazardous levels of toxic elements might be obtained through continuing evapoconcentration, (3)whether mediation of trace element levels is possible through salinity level control, and (4) the response of the evaporation pond environment to the buildup of solution constituents.

Two conditions are necessary for the formulations to be true: (1) the trace element to chloride ratio in the inflow water must be constant over the time interval, and (2) the trace element to chloride ratios in the inflow water and the receiving waters should be equal. These conditions can be expressed respectively by the following relationships:

 $([TE]/[Cl])_{inflow,t_1} \stackrel{?}{=} ([TE]/[Cl])_{inflow,t_2}$

and

$$([TE]/[Cl])_{inflow,t} \stackrel{?}{=} ([TE]/[Cl])_{nth cell,t}$$
(4)

(3)

If these conditions are met, the final ratio will reflect the effect of evapoconcentration alone. However, because field conditions cannot be expected to behave ideally, these conditions are assumed to be met for approximation purposes. Calculations not reported here indicate that the conditions are met to our satisfaction (factor of 2 criterion) in the cases of B and Mo. The criterion for validating the assumption for Se and As needed to be larger, about a factor of 10. Examination of the field data shows that B, Mo, and Se concentrations in the pond waters generally increase as chloride concentration increases, but not necessarily in direct proportion to the increase in Cl. The behavior of As is not so easily established relative to chloride because As levels are near the analytical detection limits; changes are as likely to be from analytical uncertainties as from chemical reactivity. The results, despite nonideal behavior, can still be used to generalize accumulation characteristics because buildup or losses from sources other than evapoconcentration are also of critical concern in evaporation pond management.



Figure 3. Annual cycle ECF analysis of As, B, Mo, and Se for the periods November 1986 to November 1987 and November 1987 to November 1988.



Figure 4. Overall ECF analysis of As, B, Mo, and Se for the period November 1986 to November 1988.

The evapoconcentration calculation was applied to annual cycle and 2 year cycle time periods, where the term "cycle" is used to refer to cases in which the start season is the same as the end season. For the annual cycle, two periods are used, each from a different 12 month period. Studying a variety of time periods, shorter and longer than those selected, may be necessary for total pond management.

The predicted and measured data were plotted against each other (Figures 3 and 4) and include a unity ratio line (also referred to as the 1:1 line). Data points that fall close to this line indicate conservative behavior, while those not along the line indicate reactive behavior. Data points that fall in the region above the line indicate a loss of the constituent, while those falling below the line show a net gain in element

 Table 1. Means and Ranges of EC, pH, and Eh Values

 Measured On-Site at Study Sites

	EC	C (dS/m)		pH	Eh(mV)			
	meana	range	mean ^b	range	meanª	range		
pond I								
inflow	8.9	7.8 - 11.1	7.49	7.33-7.83	192	125 - 276		
cell 1	19.2	8.8 - 28.0	8.63	7.49-9.43	119	-132 to 260		
cell 2	24.3	12.9 - 48.3	9.05	8.62-9.40	125	-15 to 182		
cell 3	25.2	14.4-40.0	8.99	8.25-9.42	128	-93 to 243		
pond II								
inflow	10.4	8.4-11.9	7.33	7.11-7.70	179	30-240		
cell 1	12.6	8.4 - 15.7	8.57	7.95-9.29	169	56 - 340		
cell 2	25.0	13.1 - 48.7	8.79	8.18 - 9.28	139	81 - 220		
cell 3	38.3	14.4-109.0	8.86	8.54-9.35	167	100 - 348		
cell 4	27.7	19.8-44.8	8.81	8.44-8.99	154	118 - 207		
cell 5	43.0	25.7 - 84.7	8.84	8.51-9.22	161	109 - 276		
pond III								
inflow	29.7	22.7 - 33.5	7.31	6.71 - 8.13	180	122 - 256		
cell 1	48.8	25.6 - 63.2	8.53	8.09-8.91	152	79 - 240		
cell 2	95.7	35.9-174.7	8.43	7.30-8.96	110	-150 to 187		

^a Arithmetic mean. ^b Geometric mean.

concentration. The gain may arise from (1) nonconservative behavior of Cl at high salinities (e.g., due to evaporite formation) and/or (2) release of soluble trace elements from source/ sinks within the evaporation pond. In addition, fluctuations in the trace element to Cl ratio of input drainage may contribute to the Cl relative gain. In several instances, points may lie along the vertical or horizontal axes. This results from the use of zero values in the database where values were below detection limits (Tanji and Dahlgren, 1990). Points that lie on the horizontal axis are indicative of zero values at the initial time, which lead to predicted zero values at the final time. Those that lie on the vertical axis resulted from situations in which detectable concentrations at the initial time were coupled with nondetectable values at the later time.

RESULTS AND DISCUSSION

Water Quality. Field measurements of EC, pH, and Eh for inflow and pond waters are shown in Table 1. The EC of inflow water is typically lower than that of water already contained in the ponds. Inflow at pond III has an EC about 3 times greater than inflow at the other ponds. In all cases, the EC measured in the area nearest the field drainage inlet most closely resembles the inflow EC. The EC typically increases further away from this inlet, even at pond I despite the unicell design in which water is free to mix. Apparently, complete mixing was somewhat limited at this pond. With the exception of cell 4 which was drained in 1987, a progressive sequence of increasing EC was not observed at pond II. The largest differences between inflow and maximum cell EC are expected during periods of warmer weather. Field-measured evaporation rates, using floating evaporation pans at pond II, ranged from 8.0 mm/day in August 1989 to 2.3 mm/day in November 1989 for a 14 dS/m EC water (Tanji and Dahlgren, 1990). Where the greatest degree of evapoconcentration has occurred, evaporites might be expected to form.

The pH of inflow waters ranged from 6.71 to 8.13, averaging slightly above neutral. Impounded waters tend to have higher pH, up to 9.43, than inflow waters, possibly due to CO_2 degassing. The average Eh values of pond waters indicate that redox conditions are weakly oxidizing (110–179 mV). If one considers the high and low values, there is only a narrow range of redox potentials. A few negative Eh values indicate occasional weakly reducing conditions. Inflow water Eh values on the average were slightly higher, but within a smaller range (179–192 mV).

The evaporation ponds receive agricultural drainage waters that are dominated by Na, Cl, and SO₄ (Table 2A), with pond II input having the highest concentrations of these components. At all ponds, the input cation concentrations follow the trend Na \gg Mg \geq Ca > K. In contrast, the input anion concentrations were found in the order Cl>SO₄ \gg HCO₃ > NO₃ at pond II and in the order SO₄ \approx Cl \gg HCO₃ > NO₃ at ponds I and III.

The same trends in major solute concentrations were observed for the evaporation pond waters (Table 2B) as have been described for the inflow waters. By the nature of the evapoconcentration sequence at the ponds, a much wider range of solute concentrations was found. The high concentrations of these selected components illustrate the high salinity attained by evapoconcentration. Using these measured concentrations of major solute components, the estimated ionic strengths ranged from 0.2 to 2.4 M. In spite of the high solute concentrations, no evaporite minerals were observed to have formed in the ponds. Should speciation of these solutions become necessary, it would be necessary to consider these high ionic strengths and subsequently utilize the appropriate ion activity coefficient models, such as the Pitzer equations (Pabalan and Pitzer, 1990). Use of the semiempirical approaches such as the extended Debye-Hückel equation would be inadequate.

Trace Element Chemistry. The average concentrations and ranges of trace elements (As, B, Mo, and Se) for inflow waters and impounded waters are shown in Table 3. Pond II in the AF region received inflow waters with appreciable levels of As, B, Mo, and Se. Selenium was especially elevated in pond II relative to the other ponds. Pond III, located in the LB region, received drainage water high in As, B, and Mo, while Se levels were extremely low. Pond I, located in the BR region, received input water high in As, moderately high in B and Mo, and lowest in Se levels of the three ponds. These trace element inputs are generally consistent with the geomorphic region characteristics.

The California Department of Health Services (DHS) utilizes regulations in Titles 22 and 23 of the California Administrative Code to impose public health standards on waste waters (Ford, 1988). The hazardous waste criteria applied to pond waters (Table 4) are expressed as soluble threshold limit concentrations (STLC). Under this code, pond waters containing constituents

Table 2. Means and Ranges of Major Cation and Anion Solute Concentrations

	N	a (mM)	С	a (mM)	Mg	g (mM)	K	(mM)	HC	O ₃ (mM)	C	l (mM)	SO	4 (mM)	N	D ₃ (mM)
	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range
(A) Inflow Water																
pond I	96	70 - 117	11.7	10.5 - 13.3	4.6	4 - 5	0.20	0.03-0.41	5.4	2.4 - 6.5	22	13 - 30	48	35 - 58	1.20	0.61 - 1.83
pond II	295	264 - 336	7.6	6.4 - 8.9	21	17 - 24	0.69	0.13 - 1.56	18	16-19	181	151 - 206	83	73-103	0.14	0.03-0.39
pond III	95	61 - 135	2.3	1.6 - 3.1	5.6	3.6 - 8.2	0.15	0.08 - 0.25	13	11 - 15	35	25 - 46	28	18 - 37	0.12	0.03-0.19
(B) Pond Water																
pond I	345	78 - 1775	13	10 - 28	19	4 - 151	1.10	0.06-7.78	5	3 - 24	90	22 - 637	165	40-983	0.96	0.04 - 2.23
pond II	1095	379-5130	8	2 - 21	85	31-413	2.8	0.3 - 14.3	17	10 - 35	760	262-4059	258	100 - 655	0.13	0.04 - 0.45
pond III	269	103 - 724	3.5	1.1 - 29.0	16	6 - 29	0.6	0.1 - 1.3	11	6 - 15	111	40 - 274	94	31-233	0.02	0.01-0.08

Table 3. Means and Ranges of As, B, Mo, and Se Concentrations in (A) Inflow Water and (B) Pond Water

	As $(\mu \mathbf{M})$		Β (μ M)			Μο (μΜ)	Se (µM)		
	mean	range	mean	range	mean	range	mean	range	
				(A) Inflow Wat	er				
pond I	17.66	12.15 - 27.50	46	29 - 68	11.85	9.21 - 15.48	0.04	0.01 - 0.06	
pond II	8.26	2.54 - 12.68	72	35 - 94	8.49	0.80 - 12.01	7.66	0.71 - 10.94	
pond III	14.38	7.61 - 30.70	124	68-160	37.27	18.69 - 86.22	0.17	0.07 - 0.27	
				(B) Pond Wate	er				
pond I	9.67	2.40 - 25.76	992	431 - 1896	19.58	5.63 - 46.07	0.01	0.01 - 0.02	
pond II	6.18	2.27 - 11.14	2138	311-15399	12.82	0.57 - 49.04	13.43	0.98 - 36.28	
pond III	17.07	5.94 - 63.40	4120	916 - 20985	77.47	28.19 - 255.47	0.15	0.07 - 0.38	

 Table 4. Hazardous Waste Criteria: Soluble Threshold

 Limit Concentrations (STLC)

constituent	STLC (µM)	constituent	STLC (µM)
arsenic	$\begin{array}{c} 67^a \\ 6476^b \end{array}$	molybdenum	3648 ^a
boron		selenium	13 ^a

 a Title 22, California Administrative Code. b Title 23, California Administrative Code.

exceeding the relevant STLC must be stored or disposed of in Class I impoundments. The water quality data show that inflow waters met the STLC standards and, therefore, were allowed to be discharged into the evaporation ponds, which do not qualify as Class I impoundments. In contrast, certain elements in pond waters approached or exceeded the STLC standards. Pond waters at pond I were maintained well below STLC standards. The desiccating pond waters approached or exceeded California's soluble threshold limit concentration for hazardous wastes in regard to B (6476 μM STLC) and Se (13 μM STLC) in pond II and maximum concentrations of B and As (67 μM STLC) in pond III. Due to the mean concentration of Se exceeding the STLC in several cells, pond II has recently been ordered closed by the Central Valley Regional Water Quality Control Board. At pond III, the high ends of the observed As and B concentrations were close to or exceeded their respective STLC standards. The Central Valley Regional Water Quality Control Board has ordered closure of pond II due to the public health hazard posed by elevated Se levels. Of particular concern was the bioaccumulation and biomagnification of Se in the aquatic food chain for migratory and resident birds attracted to pond II. With respect to exposure to waterfowl at the ponds, synergistic toxic effects should also be considered: B may enhance Se toxicity, whereas As may alleviate it (Davis et al., 1988).

Chloride-Based Evapoconcentration Factors. The mean values and ranges of evapoconcentration factors calculated for the selected time periods are shown in Table 5. The mean ECF values calculated for pond I did not differ much between the annual and 2 year cycle periods studied, in contrast to the wider 0.8-2.7 range at pond II. The largest ECF at pond I (1.3) was obtained during an annual cycle period, whereas the largest at pond II (4.4) and pond III (1.6) were from the 2 year cycle analyses. Comparing the ECF values of the annual cycle and the 2 year cycle, it is apparent that the salinity at pond I is relatively stable, but that at pond II had almost doubled. It is not possible to speculate about overall salinity buildup at pond III because one of its two cells did not receive regular solution input and as a result became dry very often, whereby solution samples could not be collected.

Annual Cycle Reactivity. The annual cycle analysis (Figure 3) of As shows great variability among and within ponds. For instance, at pond I, the observed As concentration appears to be independent of chloride Table 5. Mean Values and Ranges of Time-DependentEvapoconcentration Factors Calculated for Various TimePeriods

	mean	minimum	maximum
pond I			
season to season	0.7	0.6	0.9
four season	1.1	0.6	1.9
annual cycle	1.0	0.4	1.3
2 year cycle	0.9	0.5	1.2
pond II			
season to season	0.8	0.6	1.2
four season	1.2	0.8	1,7
annual cycle	1.7	0.8	2.8
2 vear cvcle	2.7	1.5	4.4
pond III			
season to season	0.9	0.9	1.0
four season ^a		1.2	1.2
annual cycle ^a		1.3	1.3
2 vear cycle^{b}			1.6

^a No mean value because only two ECF values were calculated. ^b No mean or minimum values because only one ECF value was calculated.

concentration, whereas at pond III the relation appears positive. The data at pond II, in contrast to the others, show a reversal of the results between the two periods, each of which falls at opposite extremes. During the first period, negligible amounts of As were predicted, whereas significant amounts were detected; during the second period, As estimates were positive but observed values were all insignificant.

Boron concentrations, consistent with the other periods discussed so far, fall along or slightly above the 1:1 line. The Mo results also lie on or above this line but differ from B in that the first cycle concentrations are grouped at higher levels than those of the second cycle. At pond II, Se is also similar to the patterns previously mentioned.

Overall (2 Year Cycle) Reactivity. Except for B, the trends in the 2 year cycle analysis (Figure 4) do not reflect those of the annual cycle analyses. The As trend is similar to that for the second annual cycle analysis, whereas Mo and Se levels were overestimated. Previously, Mo was also overestimated, but markedly less so, and Se was significantly underestimated.

The lack of clear and consistent trends over short and longer periods of time shows that it is necessary in practice to apply the ECF calculations to a variety of time periods. With the exception of B, which consistently displays conservative behavior, it is likely that As, Mo, Se, and other elements to be considered in the future would require ongoing ECF analysis to determine their fate in the water column.

Fate. Chemical forms and reaction mechanisms that may be responsible for trace element losses in the evaporation pond water column have been comprehensively reviewed by Tanji (1989). Since this work did not involve analytical speciation, the principal pathways will be mentioned here to emphasize that the reaction mechanisms controlling trace element fate in the evaporation ponds are complex and differ among trace elements and consequently lead to variable responses in an evapoconcentration scenario.

Volatilization, mainly through methylation, and adsorption are major fate pathways for dissolved As (Anderson and Bruland, 1991) and Se (Frankenberger et al., 1989). Reduction of dissolved Se to insoluble elemental or selenide forms may also be important. Boron may be removed by adsorption or precipitation, while Mo may readily be adsorbed or complexed by organic matter.

The dominance of a particular reaction mechanism is largely determined by the chemical form of the trace element, also termed speciation. The extent to which adsorption plays a role would also be influenced by the nature and quantity of adsorbing surfaces and competing ligands (Davis and Leckie, 1978). Dissolved inorganic As and Se exist in two principal valence states: As(III) and As(V); Se(IV) and Se(VI). With Eh in the weakly oxidized state and pH in the range 7-10, the evaporation pond waters would not necessarily favor a particular oxidation state of As or Se. As an example of the importance of valence state on specific removal mechanisms, selenite (SeO_3^{2-}) forms a strong inner sphere complex at the goethite-water interface, whereas selenate (SeO_4^{2-}) forms a weaker outer sphere complex (Hayes et al., 1987). The adsorption pathway may therefore account for Se removal if selenite were dominant, but would not if selenate dominated. A similar argument can be made for As in which redox condition is highly influential on oxidation state speciation (Aurilio et al., 1994), although redox transformations may be rate-limited.

Dissolved organic forms of As and Se may also be important under appropriate conditions (Anderson and Bruland, 1991; Cutter, 1982), which include a supply of readily substituted organic compounds and the necessary trace element valence state. Organic As compounds contain As(V) while the organic Se compounds predominantly contain Se(-II). In contrast to the species that may exist in different oxidation states, dissolved B may be present in various polymeric forms (Mesmer et al., 1972).

From this study, it is generally observed that B behaves consistently conservatively, whereas As, Mo, and Se exhibit changing trends. This means that the level of B in solution would rapidly reach excessive levels with ongoing salinity buildup. It is also necessary to locate specific reaction sinks for the other elements to determine an approximate time at which that sink may become exhausted and hence lead to a buildup similar to that of B.

Variability in short-term accumulation such as that displayed by Se and As is likely to be a function of seasonal differences in drainage input concentrations as well as evapoconcentration. The results of the analysis on the entire period spanning November 1986 through November 1988 show that As, B, Mo, and Se are noncumulative. In addition, B and Se show only partial removal, whereas As and Mo show practically complete dissipation.

Agricultural evaporation ponds should be considered as only an interim and temporary solution to the management of saline drainage waters containing trace elements of concern.

From this analysis of water quality in the early stages of agricultural drainage disposal at evaporation ponds, it is apparent that the use of isolated cells creates elevated concentrations of trace elements, especially with respect to those elements not subject to immobilization or dispersion. The desired result of managing these waters by salinity has effectively created, in some instances, trace element concentrations in violation of state legal limits. The issue of salt accumulation determining the life expectancy of a pond facility becomes secondary to management of trace elements.

Closed ponds may still require remediation involving soil treatment or burial of dry pond surfaces. Even after the short-term needs for waste water disposal are overcome, evaporation ponds remain only an interim and temporary solution to the management of saline drainage waters. This is principally because of the finite ability to locate repositories for salt deposits after removal from evaporation sites to maintain efficient evaporation. It is not feasible to expect additional ponds to be constructed as this requires the consumption of land that may otherwise be agriculturally productive and hence of greater economic value.

ABBREVIATIONS USED

AF, alluvial fan; BR, basin rim; LB, lakebed; DAN, 2,3-diaminonaphthalene; EC, electrical conductivity; ECF, evapoconcentration factor; HPLC, high-performance liquid chromatograph; ICP, inductively coupled plasma; STLC, soluble threshold limit concentration.

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