Evaporative Concentration of Trace Elements in a Multicell Agricultural Evaporation Pond

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Evaporation ponds in California's San Joaquin Valley dispose of saline agricultural drainage waste water by evaporation. The waters comprise mainly Na, Cl, and SO_4 but also may contain low levels of As, B, Mo, and Se. Evaporative concentration is of concern because Se bioaccumulation at Kesterson Reservoir, CA, has led to toxicosis in birds and fish. This project utilizes water quality data compiled from environmental monitoring of a multicell evaporation pond to observe accumulation characteristics of trace elements in pond waters. An evapoconcentration factor (ECF) is calculated from chloride concentrations and is assumed to reflect conservative behavior. Trace elements whose concentrations increase by the ECF are characterized as conservative, while others are labeled reactive, indicating the role of dissipation mechanisms. Conservative behavior characterizes B, while As is highly reactive. Both types of behavior are shown by Mo. Selenium was intermediately reactive, which may be due to a rate-limited removal mechanism.

INTRODUCTION

Agricultural evaporation ponds have been a recent introduction into the San Joaquin Valley of California as part of a salinity management strategy to relieve salt loading of surface and subsurface waste waters (Kruse et al., 1990). The waste waters contain a variety of inorganic constituents brought into solution by weathering, leaching, and agricultural activity (Biggar et al., 1984). The presence of such inorganic constituents is intensified because the valley is essentially one large hydrologic basin with a single outlet at the north end, which means that all water in the basin flows to a fairly small area before reaching the discharge point.

Agricultural evaporation ponds have been constructed as an alternative procedure to the use of drainage canals for transporting and disposing of waste water. However, the containment of this waste water has serious environmental implications, as seen at Kesterson Reservoir (U.S. Bureau of Reclamation, 1986; White et al., 1991). Problems that have resulted relate to the hazardous levels to which certain trace elements, especially selenium, have risen (Burau, 1985; Weres et al., 1989) and the exposure and toxicity of these elements to fish and waterfowl (Davis et al., 1988). Hence, an assessment of environmental toxicant buildup due to evaporative concentration is necessary to ensure secure proliferation of evaporation ponds for disposal of saline agricultural waste water.

This study describes and applies a method for determining the persistence of As, B, Mo, and Se relative to the buildup of salinity in the waters of a multicell evaporation pond. The analysis provides a means of assessing the impact of progressive evapoconcentration on accumulation characteristics of trace elements. It also provides an interim evaluation of the chemical reactivity in terms of immobilization–remobilization behavior in lieu of detailed mechanistic studies. Such information regarding toxic waste management is useful for management of current ponds, planning of future ponds, and looking in hindsight at possible trends in trace element accumulation that may be related to present and potential toxicity problems.

MATERIALS AND METHODS

Multicell Evapoconcentration Factor (MCECF). In cases in which the evaporation pond comprises several sequentially linked cells that are differentiated by the salinity of the water contained in each, the reactivity of a solute can be ascertained by presuming that chloride ions behave conservatively across all cells of the pond. This assumption of conservative behavior holds well so long as sodium chloride salts do not form, which does not occur until evaporation of the water is complete. An evapoconcentration factor (ECF) for multicell ponds, termed the "multicell evapoconcentration factor" (MCECF), may be expressed as

$$MCECF(n) = C_{Cl}(n)/C_{Cl}(m) \qquad (1)$$

where m and n are indices to the different pond cells. Thus, all differences in salinity are related to the concentration in an arbitrarily fixed reference cell, the mth cell. Typically, m refers to the inflow water because it (i) is the principal source of dissolved constituents; (ii) represents the least saline of all waters considered, which usually forces the inflow MCECF to be 1 and all other MCECFs to be greater than or equal to 1 by nature of the cell flow progression; and (iii) represents the original water composition before any evapoconcentration-driven reactions have occurred. In the absence of a steady inflow, $m = 1$ might be used because the first cell receives all external input and hence contains the least saline water, and it is more straightforward to think of conservation in reference to the earliest cell when reactivity in sequential locations is observed.

The MCECF is then used to calculate an estimated concentration based on the concentration in inflow water

$$C_{pred,x}(n) = MCECF(n)C_{obs,x}(m) \qquad (2)$$

where $C_{pred,x}(n)$ is the predicted concentration of solute x in cell n and $C_{obs,x}(m)$ is the observed concentration of solute x in cell m.

The criterion for characterizing solutes as reactive or nonreactive also follows that for each cell in the multicell evaporation pond the predicted concentration, $C_{pred,x}(n)$, is compared to the observed concentration, $C_{obs,x}(n)$.

Data Analysis The MCECF data analysis procedure is applied to five consecutive four-season periods and one eight-season period that includes all of the seasons in the shorter periods (see Table I). This approach was chosen because, in averaging the data, data from each season are weighted equally. That is, the contribution to the averaged value is in the ratio 1 fall/1

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Table I. Calculated Evapoconcentration Factors

	period					
	2/87–11/87	5/87–2/88	8/87–5/88	11/87–8/88	2/88–11/88	2/87–11/88
inflow	1.0	1.0	1.0	1.0	1.0	1.0
cell 1	1.2	1.2	1.2	1.1	1.2	1.2
cell 2	2.3	2.6	2.9	2.9	3.8	3.2
cell 3	3.9	3.7	4.1	4.1	5.2	4.7
cell 4	2.9	2.3	1.6	—[a]	—[a]	1.2
cell 5	5.9	6.4	6.8	6.4	6.3	6.1
mean	2.9	2.9	2.9	3.1	3.5	2.9
min[b]	1.2	1.2	1.2	1.1	1.2	1.2
max	5.9	6.4	6.8	6.4	6.3	6.1

[a] MCECF cannot be calculated because cell 4 dry at initial time. [b] Minimum value besides that of inflow.

winter/1 spring/1 summer. Using a five-season period, for instance, would bias the data with respect to one of the seasons. An example would be the case of 2 fall/1 winter/1 spring/1 summer, in which both the first and last seasons in this sequence would be fall. A preliminary report on the application of an evapoconcentration factor was presented by Tanji (1989), but it involved only one eight-season period between August 1986 and May 1988.

RESULTS AND DISCUSSION

Chloride-Based Evapoconcentration Factors. Table I contains the calculated evapoconcentration factors obtained for the selected time periods at Peck pond. For any time period, the lowest MCECF was found in cell 1, whereas the highest MCECF was found in cell 5. The highest MCECF value of 6.8 was calculated for cell 5 in the four-season period between August 1987 and May 1988. The MCECF for the eight-season period in cell 5, 6.1, was at the low end of all MCECF values calculated for this cell. This shows that the chloride concentrations, interpreted as an indicator of salinity, may not be continuously increasing and are subject to large changes in the short term that are not accurately reflected in long-term analysis, which would be the procedure used in periodic monitoring. The variability of ECFs is greater in the middle cells, whereas the first and terminal cells show less variation. Note also that the greatest increase in ECF is between cells 1 and 2. This may be because the rate of evaporation is greater at lower salinity; the lowest salinity would be found in cell 1, which is at the beginning of the evapoconcentration sequence.

Arsenic. Results for all periods considered show that As does not accumulate in the water despite a large ECF (Figure 1). This indicates that As is reactive in the pond environment. Dissipation of As from the water column may occur through either volatilization (Huysmans and Frankenberger, 1991) or adsorption onto manganese solid phases (Anderson and Bruland, 1991). Volatilization is a loss, while adsorption is an immobilization process. This distinction is important in selecting pools from which As could be returned to the water column. Arsenic may exist in several oxidation states, and thus this indication of reactivity may also be valence-dependent. It is unlikely that the predominant oxidation state will vary within the pond solution phase over time, because the overall pond redox condition is stable and pH varies only slightly. Therefore, the characterization of As as reactive is consistent over all the periods and locations considered at this pond but may not necessarily be applicable to other pond environments. Note that concentration values go to zero in cell 4 for the periods November 1987 to August 1988 and February 1988 to November 1988 (Figure 1d,e) because that cell was drained to dryness.
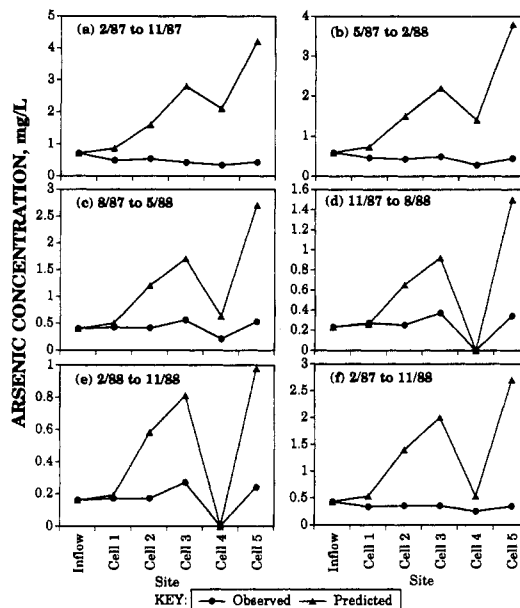

Figure 1. Comparison of observed and MCECF-predicted As concentrations for various four-season periods (a–e) and one eight-season period (f).
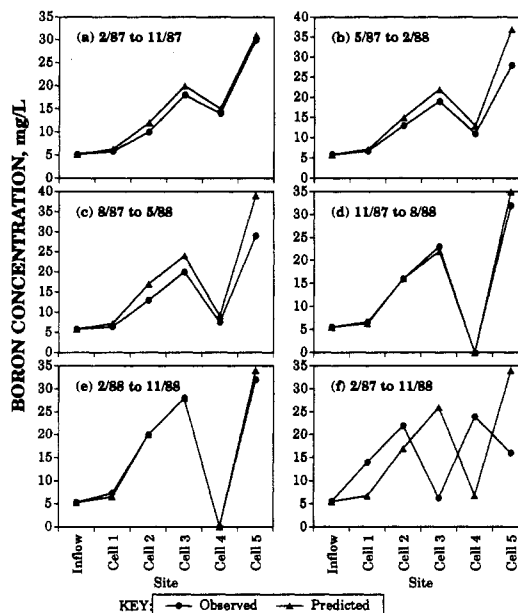

Figure 2. Comparison of observed and MCECF-predicted B concentrations for various four-season periods (a–e) and one eight-season period (f).

Boron. In contrast to As, B is consistently well estimated by the MCECF procedure over all four-season periods (Figure 2). Additionally, the estimated and observed values match extremely well, even at higher concentrations for most of the periods presented. The eight-season analysis (Figure 2f) shows poorer estimation over all cells. This may be a result of averaging the data over a long period of time. The four-season observations indicate that B is extremely nonreactive and is unaffected by increases in the salinity of the matrix. However, the term nonreactive is used only to indicate that B is not removed from the water column. A solute may in fact be highly reactive in solution with no reaction components ever undergoing a removal from the solution phase. For instance, B species may polymerize, but the polymers may remain soluble (Herbel, 1991).

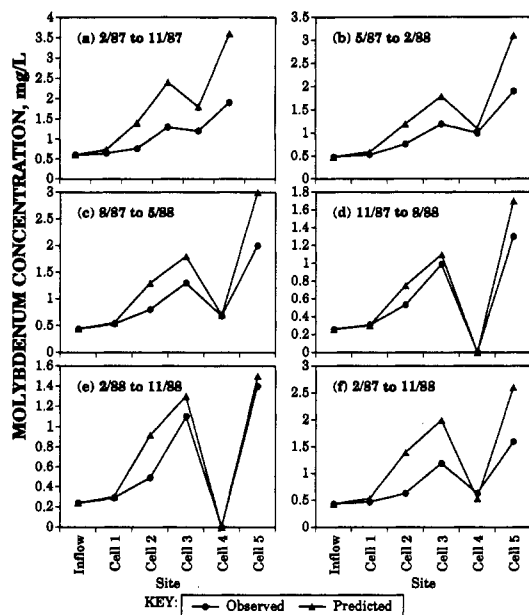**Molybdenum.** Estimated Mo concentrations are not as good as those obtained for B (Figure 3). The observed

Figure 3. Comparison of observed and MCECF-predicted Mo concentrations for various four-season periods (a–e) and one eight-season period (f).

Figure 4. Comparison of observed and MCECF-predicted Se concentrations for various four-season periods (a–e) and one eight-season period (f).

accumulation of Mo with cell progression is reflected in the MCECF estimation. In addition, the gap between estimated and observed Mo concentrations appears to lessen over time, especially for cell 5. As expected, the eight-season analysis (Figure 3f) results in an average of the trends observed for the shorter periods. From these observations, it would appear that Mo is not easily categorizable as either reactive or nonreactive. It would also be too simplistic to call it "intermediately reactive" because the results show gradual changes with time. Thus, it may be more accurate to describe Mo as alternately reactive and nonreactive, though the periodicity of the alternation is not clear. This behavior would be consistent with complexation on organic material (Tanji, 1989), whereby Mo may be regenerated from the breakdown of an organic complex.

Selenium. The accumulative trend shown by Mo is similarly displayed by Se (Figure 4). The Se trend is also far short of the estimated values but differs from Mo in that the gap between estimated and observed values is maintained over time. The eight-season analysis (Figure 4f) results in a trend similar to those seen in the four-season periods. The term intermediately reactive is suitable for Se. It is possible that the removal reactions are rate-dependent and that, were the input of Se discontinued, the removal of Se would go to completion, barring equilibrium conditions being reached. Long et al. (1990) observed time-dependent Se immobilization at Kesterson Reservoir and determined that immobilization ranged from 66% to 108% over a period of 7–10 months. If, for instance, adsorption of Se was the major sink mechanism, the adsorptive capacity of the substrate may eventually become saturated, which would lead to a greater rate of Se accumulation in the water. Adsorption on oxide mineral surfaces is a strongly favored reaction mechanism if Se exists as the selenite ion, SeO_3^{2-} (Balistrieri and Chao, 1987, 1990; Hayes et al., 1987). However, there is probably a wide range of reactions affecting Se in the ponds, so the effect may not be acute. Other reactions that may play a dissipative role include reduction to elemental Se (Oremland et al., 1989), reduction to Se^{2-} and formation of selenides (Masscheleyn et al., 1990), microbial transformation and volatilization of methylated Se (Franken-
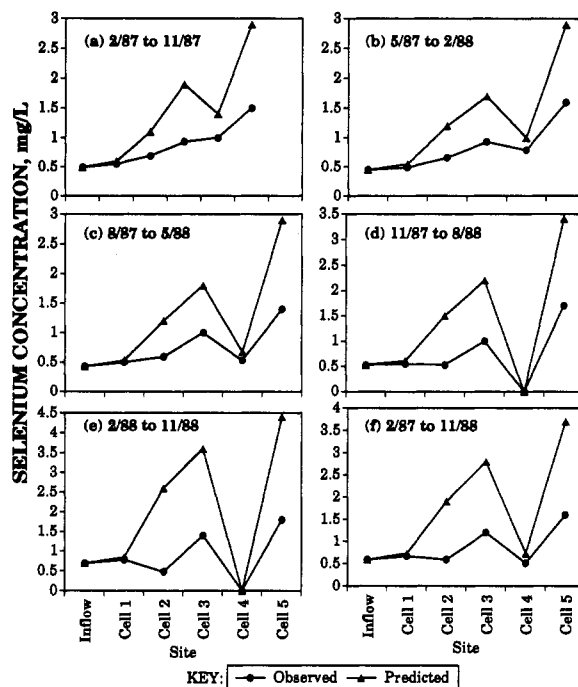
berger and Karlson, 1989), and complexation to organics such as humic acid (Fio and Fujii, 1990).

Conclusions. The fate of trace elements in multicell evaporation ponds can be investigated in a general manner through the use of chloride-based evapoconcentration factors. The application of the method to four trace elements observed at Peck pond indicates a diversity of reactive behavior. At one extreme, As is highly reactive in the sense that it readily leaves the solution phase. At the other extreme, B is conservative, with concentrations increasing in direct proportion to the increases in Cl levels. The behavior of Mo appears to alternate between reactive and nonreactive, but the periodicity of this behavior is not clear. Intermediate reactivity is shown by Se, suggesting that the removal mechanism is rate-limited, unlike As, whose removal is highly efficient.

The method can be further applied to data for other elements for which other general reactivity information is required. In addition, the method can be used in estimating values for management practices, especially in the case of conservative species such as B. The method could also be used on a continuing basis to monitor changes in reactivity or conservancy to bring attention to possible losses that pose new hazards to the environment.

ABBREVIATIONS USED

ECF, evapoconcentration factor; MCECF, multicell evapoconcentration factor.

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