

# Uranium, Vanadium, and Molybdenum in Saline Waters of California

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## ABSTRACT

Analyses of saline water samples from large salt water bodies, agricultural drainage and evaporation ponds, and soil water extracts were used to determine the extent of elevated uranium (U), vanadium (V), and molybdenum (Mo) in agricultural environments of the San Joaquin Valley. Saline water samples and soil extracts were pretreated by chelation and solvent extraction to separate and concentrate, U, V, and Mo for analyses. Mean concentrations of U, V, and Mo were considerably elevated in agricultural drainage and evaporation ponds of the San Joaquin Valley compared to saline waters of Salton Sea and Mono Lake. Relatively high correlation coefficients were observed between U, Mo, and salinity.

THE United States Geological Survey, in cooperation with the U.S. Fish and Wildlife Service and the U.S. Bureau of Reclamation, recently published the results of a detailed study of two National Wildlife Refuges (NWR) grouped within about 24 km (15 miles) of each other on the south side of Tulare Lake Bed, southern San Joaquin Valley (Schroeder et al., 1988). The purpose of the study was to determine if chemical contamination in drainage water from agricultural irrigation pose a threat to wildlife on or near the NWR, and to ascertain if more detailed studies are warranted. They found elevated levels of U, V, Mo, and other trace elements in an agricultural evaporation pond near Kern NWR. They identified U as high (250–360  $\mu\text{g/L}$ ) in pond water with bottom material from the same pond containing  $6.6 \pm 3.7$  mg/kg. Uranium was determined by a direct fluorometric method with the authors' comment that "Sensitivity of the method is typically reduced in saline waters by quenching of U fluorescence; hence, reported concentrations should be considered minimum estimates" (Schroeder et al., 1988).

Deverel and Millard (1988) suggest that Mo, V, and other trace elements are probably present as dissolved oxyanions in alkaline waters of the western San Joaquin Valley. Uranium is an oxyphile element often concentrated in petroleum and associated brines (Ran-kama and Sahama, 1950).

The objective of the present study was to provide a preliminary assessment of U and geochemically associated V and Mo distribution in saline waters and soil solutions of the San Joaquin Valley, CA.

## MATERIALS AND METHODS

### Study Area

The San Joaquin Valley constitutes the southern two-thirds of the Central Valley of California and represents approximately 3.4 million ha of valley floor. The following

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description of the Central Valley is taken from Schroeder et al. (1988). The Central Valley is a northwestward-trending asymmetric trough bounded by granitic, metamorphic, and marine sedimentary rocks, and filled with as much as several kilometers of sediment. Near the close of the Late Cretaceous Epoch, tectonic movements elevated the Coast Ranges on the west side of the Valley and created the ancestral Central Valley as a restricted trough of deposition lying between the emerging Coast Ranges and the Sierra Nevada to the east.

Within the San Joaquin Valley are 27 salt water evaporation ponds of varying sizes up to 720 ha (1800 acres), which are fed by subsurface drainage from surrounding irrigated lands (Westcot et al., 1988).

*The California Water Atlas, 1978–79* (Kahrl, 1979) gives the following description of two large salt water bodies. Salton Sea is an unnatural body of water formed when a man-made diversion channel from the Colorado River flooded out of control in 1905 and filled the Salton Sink in the Imperial Valley. It covers about 1036 km<sup>2</sup> and has been maintained by surface inflow from saline irrigation water. Mono Lake is a saline body of water covering about 260 km<sup>2</sup> to the east of the Sierra Nevada.

Saline water samples were collected from 62 agricultural drainage waters and evaporation ponds in the San Joaquin Valley. Samples were collected from two cells of Kesterson Reservoir in the San Joaquin Valley and from Salton Sea and Mono Lake.

Nine surface benchmark soils collected from the west side of the San Joaquin Valley for an earlier study by Bradford et al. (1971) were analyzed as part of the current study.

Soil extracts (1:1) and water samples were buffered by the addition of ammonium acetate and U, V, and Mo chelated by the addition of an aqueous solution of ammonium pyrrolidine dithiocarbamate. Samples were then extracted three times with chloroform and the extracts combined and evaporated to dryness. The residue was then dissolved in nitric acid, evaporated, and made to a small volume for analysis with inductively coupled argon plasma optical emission spectroscopy (ICAP-OES).

## RESULTS AND DISCUSSION

Before the report of U in an evaporation pond in the San Joaquin Valley by Schroeder et al. (1988) was printed, and while we were engaged in laboratory experiments to develop and test a chelation solvent extraction technique to remove and concentrate numerous trace elements from high salt waters, we observed a distinctive amber color develop in the solvent phase of evaporation pond water samples from the San Joaquin Valley. The amber color was not observed in water samples from the Salton Sea and Mono Lake. Subsequent analyses of the solvent phase with (ICAP-OES) revealed elevated levels of U, Mo, and V. High concentrations of U were unexpected, so we repeated the extraction and analyses of the pond water samples and included a blank spiked with U. Spectra were recorded on film during analyses with ICAP-OES. A light amber color appeared in the solvent phase of both samples and the U-spiked blank.

A comparison of spectra from samples and the spiked blank showed perfect matching of position and relative intensity of numerous spectrum lines of U. The sample containing the highest U was diluted 10 $\times$

with distilled water and analyzed directly with ICAP-OES and showed close to the same U concentration as measured following solvent extraction. Extraction of spiked synthetic solution showed 95 to 100% recovery of U, V, and Mo from saline and nonsaline waters.

Final analyses of acidified aqueous extracts of samples were made using ICAP-OES with pneumatic cross flow nebulization.

All of the drainage and evaporation pond water samples were analyzed for U by an independent laboratory (Natural Resources Lab., Golden, CO) using a fluorometric method and compared statistically with the author's analyses using solvent extraction and ICAP-OES. The following equation shows good agreement between the two methods:  $U(\text{fluorometric}) = U(\text{solvent extraction}) \times 1.018 - 0.0451$ .

Table 1 compares concentrations of U, V, and Mo in 62 drainage and evaporation pond waters in the San Joaquin Valley with levels measured by the same technique in two other major salt water bodies in California—Salton Sea and Mono Lake. Mean concentrations of V are about 50 times higher in pond waters compared with the other salt water sources. Differences between mean concentrations of U and Mo in drainage and pond waters compared to Salton Sea and Mono Lake are even greater and approximate three orders of magnitude.

Table 2 shows concentrations of U, V, and Mo in

**Table 1. Concentrations of U, V, and Mo in high salt waters in California.**

	Salton Sea	Mono Lake	Agricultural drainage and evaporation ponds in the San Joaquin Valley, CA	
			Range†	Mean
	mg/L			
U	<0.002	<0.002	0.04–9.90	0.896
V	<0.002 ± 0	<0.001	0.004–0.544	0.087
Mo	0.004 ± 0	<0.001	0.138–23.7	2.85

† Values from 62 samples.

**Table 2. Concentrations of U, V, and Mo in waters associated with a highly saline evaporation pond. "Pond salt solution" was prepared by dissolving a dry sample of pond salt crust in distilled water.**

	Inlet water	Pond water	Pond salt solution
U	0.637 ± 0.053	2.43 ± 0.047	12.44 ± 1.638
V	0.388 ± 0.003	0.224 ± 0.008	0.762 ± 0.062
Mo	2.07 ± 0.012	11.70 ± 0.002	71.78 ± 5.283

**Table 3. Electrical conductance and concentrations of U, V, and Mo in 1:1 water extracts from nine selected benchmark soils.**

Benchmark soil no.:	8	10	21	22	23	32	33	34	49
	Soil extracts								
EC (S/m):	2.450	0.190	0.043	0.040	0.045	0.390	0.147	1.300	0.240
	mg/L								
U	1.78 ± 0.010	<0.02	0.024 ± 0.006	<0.02	<0.020	0.154 ± 0.025	<0.02	0.064 ± 0.028	<0.02
V	11. ± 0.058	0.312 ± 0.001	0.019 ± 0.001	0.007 ± 0.001	0.020 ± 0.001	0.040 ± 0.001	0.033 ± 0.001	0.029 ± 0.002	0.007 ± 0.001
Mo	8.9 ± 0.062	0.109 ± 0.002	0.019 ± 0.000	0.022 ± 0.001	0.016 ± 0.001	0.641 ± 0.002	0.076 ± 0.000	0.316 ± 0.002	0.024 ± 0.000

drain tile water entering a selected pond from agricultural fields, pond water, and a saturated solution of a salt sample from the pond bottom. High concentrations of these elements in inlet water suggests that surrounding soils derived from marine sediments of the coast range are the most likely source.

Concentrations of U, V, and Mo in relation to electrical conductivity of soil solutions are shown in Table 3.

It appears from these data that U, V, and Mo concentrations are elevated in some soils and parent material of the west side of the San Joaquin Valley and tend to be mobile with other salts in the soil solution (Table 4), and finally concentrate as salts on the pond bottom (Table 2). These observations are supported by the results of other studies in the same area. Deverel and Millard (1988) concluded that high Se concentrations seem to coincide with high salinity of Coast Range alluvial deposits, and Schroeder et al. (1988) noted that U and Se are geochemically associated. Cannon (1957) found elevated Se associated with uranium ores.

The presence of oil fields in the Coast Range Foothills gives added support to the likely association of U with these sedimentary formations. Rankama and Sahama (1950) observed that U is enriched in asphaltiferous sandstones as well as in petroleum (100 mg/L) and in associated brines (10 mg/L).

Table 5 shows typical concentrations and/or recommended drinking water limits of U, V, and Mo in natural waters compared with pond waters from the San Joaquin Valley. It should be emphasized that although the concentrations of U, V, and Mo are elevated in pond waters compared with natural waters, the limits set for drinking water do not have significance in this case since the pond water would never be considered for drinking water. Although there are no generally accepted standards for control of radioactive contamination in irrigation water, the Committee on Water Quality (Fed. Water Pollut. Control Admin., 1968) concluded that the United States Public Health Service drinking water standards appear rea-

**Table 4. Correlation coefficients between electrical conductance, U, V, and Mo.**

	Water samples from 62 drains and evaporation ponds			Water extracts from 8 benchmark soils		
	Mo	U	V	Mo	U	V
EC	0.795	0.709	0.210	0.513	0.414	-0.063
Mo	1.00	0.897	0.449	1.00	0.999	0.995
U	0.897	1.00	0.322	0.999	1.00	0.997

sonable for irrigation water. Elevated levels of these elements in pond waters and soil solutions do suggest, however, the possibility that well waters in the area may also contain elevated levels.

Additional problems may arise with evaporation ponds and reservoirs such as Kesterson where biological accumulation of Se through the food chain adversely affects wildfowl (Letey et al., 1986). Rankama and Sahama (1950) make the statement, "It is also known that algae growing in fresh water accumulate uranium." We measured between 500 and 600  $\mu\text{g/L}$  U in saline water from two cells of Kesterson Reservoir. The Canadian Government has suggested a limit of 500  $\mu\text{g/L}$  U for protection of salt fish and wildlife and 100  $\mu\text{g/L}$  U for minimal risk of adverse effects to marine aquatic life (McNeely et al., 1979).

Legumes grown on soils containing concentrations of Mo in excess of 0.01 mg/L in the soil solution frequently contain levels of Mo greater than 5 mg/kg, which is the upper safe limit for cattle (*Bos* sp.) feed (Fed. Water Pollut. Control Admin., 1968; Adriano, 1986). Soil solution concentrations of Mo in excess of 0.01 mg/L in the San Joaquin Valley soils reported in Table 3 are consistent with the well-documented cases of molybdenosis or Mo-induced Cu deficiency reported in dairy cattle in the San Joaquin Valley (Fisher et al., 1976). Molybdenum concentrations in vegetables and grain vary considerably depending on the soil Mo levels, but evidence of deleterious effects on human health is lacking (Crouse et al., 1983).

Crouse et al. (1983) list V as a likely essential element for animals and humans. It is normally found in very low levels in animal and human tissue and at higher levels in some plants. No bioaccumulation has been observed in the human food chain.

The current USEPA (1986) recommended limit of 60  $\mu\text{g/L}$  U in drinking water (Table 5) is based pri-

marily on U chemical toxicity effects on the kidney, as reported by Lagerkvist et al. (1986). Uranium is also known to accumulate in bone. The National Academy of Sciences allowed for contributions of U from sources other than drinking water and estimated a safe upper limit of 35  $\mu\text{g/L}$  in water (USEPA, 1986).

The recommended limits for U in Table 5 are well above the arithmetic average of 2 pCi/L found in over 34 000 surface water and over 55 000 groundwater samples (USEPA, 1986). Approximately 28 000 of these samples were identified as possible drinking water sources. The largest reported concentration was 600 pCi/L. Only a few waters measured in excess of 50 pCi/L.

## CONCLUSIONS

Our data show relatively high concentrations of U, V, and Mo in saline waters of the San Joaquin Valley compared with Salton Sea, Mono Lake, and many other water resources in the USA. There is a high coincidence of U and Mo in saline waters of the San Joaquin Valley and somewhat less coincidence with electrical conductance (Table 4).

Additional research is needed to appraise the significance of high concentrations of U, V, and Mo in an agricultural environment such as the San Joaquin Valley, CA. Questions concerning potential specific and interelement effects on aquatic systems and crop plants need answers. The ultimate disposal of agricultural evaporation pond salt deposits containing U, V, Mo, and other trace elements is a concern of control agencies.

## ACKNOWLEDGMENTS

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## REFERENCES

Table 5. Concentrations and recommended limits of U, V, and Mo in natural waters compared to pond waters of the San Joaquin Valley.

Waters and limits	U	U	V	Mo
	pCi/L	$\mu\text{g/L}$		
<b>Natural waters</b>				
Tap water	(0.011)†	0.032‡	4.3§	
River water	0.005–0.01¶¶	(0.015–0.03)		
Lake water	1.7¶¶	(5.0)		
Groundwater	≤40.¶¶	≤(120)		
Surface water				0.68§§
Evaporation ponds (mean values)¶¶		1070	136	6800
<b>Recommended limits</b>				
Drinking water#	40	60		
Urine limits for renal damage (human)††		250		
For protection of saltwater fish and wildlife‡‡		500		

† Numbers in parentheses are calculated (1 mg U = 330 pCi).

‡ New York City tap water (Berlin and Rudell, 1986).

§ Average U.S. drinking water (Lagerkvist et al., 1986).

¶ Selected agricultural evaporation ponds, San Joaquin Valley.

# Adjusted acceptable daily intake (USEPA, 1986).

†† Berlin and Rudell, 1986.

‡‡ McNeely et al. (1979).

§§ Average U.S. surface waters (Hern, 1970).

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## Effects of Extraction Methods and Sample Storage on Properties of Solutions Obtained from Forested Spodosols

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### ABSTRACT

Soil solutions obtained by three methods from Spodosols at a high-elevation, forested study site were compared. Solutions were extracted by miscible displacement, by centrifugation, and by compressing a soil-packed syringe. Analyses of pH, inorganic anions, total and reactive Al, and organic C showed few differences between miscible displacement and the syringe-pressure methods. However, centrifugation at a relative centrifugal force (RCF) of 9700  $m\ s^{-2}$  consistently produced solutions with significantly higher pH and F-content than did the other methods. Differences after centrifugation also were found in  $C1^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ , but Al, but less frequently. Effect of soil storage time on solutions obtained using the syringe-pressure technique was studied. Both Oa and Bhs horizon samples showed large increases in solution  $NO_3^-$  after 24 h of storage at 3 °C. During 36 d of storage,  $NO_3^-$  levels increased by as much as 10-fold and were accompanied by pH decreases. Measurements in solutions obtained from samples that had been frozen for 36 d were higher than in the original solutions, except for  $NO_3^-$  and pH. Changes with freezing appeared to be related to large increases in soluble organic C. Our results suggest that soil solution samples should be obtained very quickly after sampling of soils and that high-speed centrifuge techniques may give erroneous results. The syringe-pressure method is relatively rapid, simple, and easily performed in the field. However, it may not be practical under dry conditions.

pecially true if the horizon is thin or variable in depth. It is also difficult to collect the solution samples in a timely manner, thus avoiding potential chemical changes as the solution ages. Methods that remove solution by destruction of a soil sample permit comparison between a soil solution and its parent soil. In using such a method, it must be established that the technique for obtaining the solution does not alter its composition.

Three techniques for destructively extracting soil solutions are commonly used: miscible displacement (Adams, 1974), which utilizes a displacing solution to push the soil solution out of a packed column; immiscible displacement by a water-insoluble organic liquid, with gravitational displacement by centrifugation (Mubarak and Olsen, 1976; Whelan and Barrow, 1980; Kinniburgh and Miles, 1983); and extraction of solution already in the soil by centrifugation. The last method has been used with large-volume containers at relatively low speeds (Davies and Davies, 1963; Gillman, 1976) or with 50-mL centrifuge tubes at high speeds (Reynolds, 1984; Elkhatib et al., 1987). Wolt and Graveel (1986) introduced a technique adapted from Adams (1974) by using a mechanical vacuum extractor to simplify the procedure.

These procedures have been compared to one another (Adams et al., 1980; Faber and Nelson, 1984; Wolt and Gravell, 1986; Elkhatib et al., 1987) and have usually given similar results. We used a high-speed centrifugation technique similar to that of Reynolds (1984) to study solutions from forested Spodosols. We frequently found the extracted solution pH to be much higher than the soil pH measured in dilute salt. This prompted the present comparison of methods.

In addition to sampling technique effects, there also is the problem of possible changes resulting from time of soil sample storage before extraction. Although air drying of soil samples has been shown to bring about drastic changes in soil solution chemistry (Bartlett and James, 1980), we tend to assume that storing moist soils in the refrigerator will minimize soil solution changes. However, Edmeades et al. (1985) showed that

**T**HE chemical composition of the soil solution is of interest when studying the reactions of environmental contaminants, the availability of plant nutrients, and other basic soil chemical processes. However, obtaining solutions to study is fraught with problems. Solutions can be sampled either by destructive techniques or by some form of lysimetry. Lysimetry allows repeated sampling with time, but the source of the sampled solution is dependent on flow patterns and moisture levels, and it is difficult to relate the solution to a particular soil horizon. This is es-

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