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Journal Article

WWRC-84-15

In

Environmental Toxicology
and Chemistry

Volume 4
1985

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CHEMISTRY AND AQUATIC TOXICITY OF RAW OIL SHALE LEACHATES FROM PICEANCE BASIN, COLORADO

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(Received 1 August 1984; Accepted 7 December 1984)

Abstract—Leachates were collected during the period of 1981 to 1983 from several depths in two surface piles of raw, mined oil shale in the Piceance Basin of northwest Colorado. Although both piles were subject to similar climatic conditions, the composition of major inorganic ions in the leachates differed considerably because of different shale compositions. Acute toxicity to *Daphnia magna* and fathead minnows (*Pimephales promelas*) occurred when leachate conductivity exceeded 7,000 to 8,000 $\mu\text{mhos/cm}$ and total dissolved solids exceeded 6 to 7 g/L (0.6 to 0.7% salt). *D. magna* were more sensitive than fathead minnows in acute toxicity tests, and *D. magna* 48-h LC50 values were as low as 13% of full-strength leachate. The lowest no observed effect concentration determined in *D. magna* 21-d chronic toxicity tests was 0.9% of full-strength leachate. Because of interactions among the major ions, the contributions to toxicity by trace elements and organic compounds in the oil shale leachates could not be differentiated from contributions by MgSO_4 , the major toxicant. This study demonstrated that toxic mechanisms occurring within complex chemical mixtures cannot always be identified on the basis of single-compound toxicity values, and that reconstituted mixtures of principal chemical components are useful in identifying toxicants and their interactions with other mixture constituents.

Keywords—*Daphnia magna* *Pimephales promelas* Acute toxicity Chronic toxicity
Field leachates

INTRODUCTION

Recent efforts to stimulate domestic energy production have included the development of synthetic fuels from oil shale. Much of this effort has been focused in northwestern Colorado, where large deposits of oil shale are located in the Green River Formation. Although oil shale development is in a temporary hiatus, several potential environmental problems need to be studied before commercial synfuel facilities are developed. In this article, we address the potential toxicity of leachates from raw oil shale.

Most oil shale companies plan to produce shale oils using above-ground retorting technologies. During above-ground processing, raw shale will be mined and temporarily stored in large surface piles before being retorted. Previously proposed development and operation plans have included raw shale storage piles ranging in size from 0.3 to 5 million tons, depending on process type and shale

quality [1]. These run-of-mine shale piles may contain particles ranging in size from silt and clay to boulders, between which water can easily percolate and leach fragmented shale during snowmelt and rainfall. Currently, reliable estimates of potential leachate volume, chemical composition and transport to surface water or groundwater are not available.

Early studies of raw shale leachates generated in laboratory columns suggested that federal drinking water criteria for some inorganic ions and metals could be exceeded [2], and that total dissolved solids levels might also be high [2,3]. However, no studies to date have characterized the chemistry of raw shale leachates generated in the field or determined their toxicity. This is especially important because laboratory leaching may not duplicate field conditions. In this article, we present results of chemical analyses and aquatic toxicity tests on leachates collected from two raw shale piles in the Piceance Basin of northwestern Colorado. Not only does this study provide information pertinent to the development of a new

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energy industry, it also provides a unique analysis of chemical and toxicological characteristics of leachates generated under natural conditions.

MATERIALS AND METHODS

Study sites

Experimental piles of raw, mined shale were built by Rio Blanco Oil Shale Company on Federal Oil Shale Lease Tract C-a in the spring of 1980 and by Cathedral Bluffs Shale Oil Company on Federal Oil Shale Lease Tract C-b in the fall of 1980. Located approximately 25 km apart in the Piceance Basin of northwestern Colorado, the shale piles at both sites are approximately 2,100 m above sea level. Average annual precipitation is approximately 30 cm at Tract C-a and Tract C-b; snow-melt and heavy rains usually occur during March, April and May.

Raw shale leachates

At Tract C-a, three leachate collectors were buried at depths of 1.5, 3.0 and 4.6 m in the experimental shale storage pile. Raw shale extracted from the R-5 zone, within the kerogen-rich Mahogany Zone of the Green River Formation, was used to build the pile during the period of 18 to 22 May 1980. Potential shale oil yields from the R-5 zone are estimated to be 30 to 40 gal/ton. At Tract C-b, leachate collectors were buried at depths of 3.0, 4.6 and 6.1 m. There, raw shale from the B Groove, an interval of lean oil shale (0 to 5 gal/ton estimated yield) at the base of the Mahogany Zone, was placed over the collectors during the period of 8 to 10 December 1980.

Each collector was a 3.05 m \times 3.05 m sheet of impervious material, contoured so that intercepted percolation flowed into a drain pipe (Fig. 1). Collectors were constructed by first preparing a sand bed on which a continuous sheet of polyethylene was placed; the foundation for the sand bed was natural ground graded to form a small pad for the collector. A hole was cut in the polyethylene so that the outer drain pipe could be raised through the sheet from below. The polyvinylchloride (PVC) outer drain pipe [3.8 cm (1.5 in.) in diameter] served dual functions as a conductor pipe for the inner drain tube and as a drain pipe for percolate collected on the polyethylene sheet. Inside the outer drain pipe, a Teflon inner drain tube was connected to a Teflon funnel that projected upward through the polyethylene sheet. Concrete was placed around the PVC pipe and supported the Teflon funnel. Then a Teflon screen was fitted in the funnel, and a thin layer of gravel was spread over the concrete and funnel. Finally, the polyethylene sheet was covered with 76-cm-wide Teflon sheets that were overlapped to minimize leakage.

Directly above the Teflon filter, holes were drilled through the Teflon sheet so that percolate collected on the Teflon sheet flowed into the funnel, then into the inner drain tube and eventually to Teflon collection bottles located in a small shelter at the toe of the shale pile. As shown in Figure 1, a hole was formed in the concrete around the funnel to allow leachate collected between the Teflon and polyethylene sheets to flow into the outer drain pipe. This additional leachate was collected in a polyethylene bottle so that the total vol-

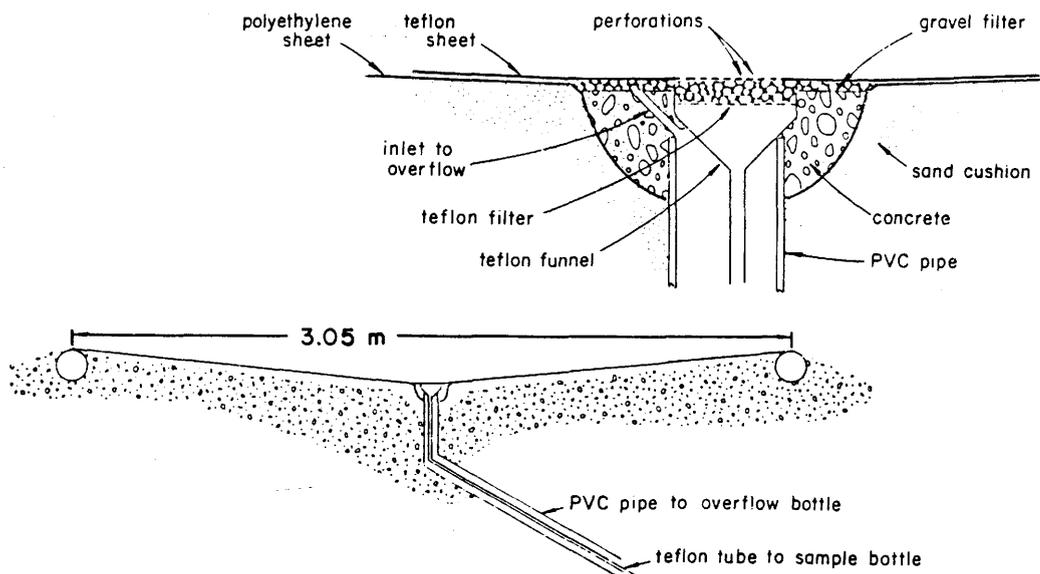


Fig. 1. Diagram of leachate collectors buried in raw shale piles.

ume of water intercepted by the collector could be estimated by summing the volumes collected in the Teflon and polyethylene bottles.

Leachates were retrieved from each field site intermittently from April 1981 until September 1983, usually following periods of snowmelt or intense rainfall. Because of limited, infrequent precipitation at both field sites, leachates were sampled opportunistically. All leachates that drained into the collection system were chemically analyzed at Colorado State University; subsamples of some of these leachates were sent to the University of Wyoming for toxicity testing, depending on leachate volumes available after chemical analyses were completed.

Leachate volumes were measured on-site. Then the collection bottles were transported to Colorado State University, where each sample was divided into three aliquots and prepared for subsequent chemical analyses and toxicity tests, as follows: (a) no pretreatment; (b) filtration through a 0.45- μm acetate filter (Millipore Corp.) under nitrogen pressure; and (c) filtration through a 0.45- μm acetate filter under nitrogen pressure, followed by acidification to pH 2 with HNO_3 .

Pretreated aliquots were analyzed for inorganic constituents at Colorado State University; untreated aliquots collected during 1981 and April 1982 were transported to the University of Wyoming for acute and chronic toxicity tests. Also, major anions (Cl^- , NO_3^- , SO_4^{2-}), major cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+) and dissolved organic carbon (DOC) levels in some of the untreated aliquots were analyzed at the University of Wyoming. All samples were refrigerated at approximately 5°C when they arrived at the respective laboratories.

Precipitation volume was monitored using continuously recording rain gauges located adjacent to each shale pile, but precipitation quality was not chemically analyzed. Recorders were serviced and charts were collected routinely.

Reconstituted leachates

Based on chemical analyses of major anions and cations in the original raw shale leachates, we reconstituted the major ions in four Tract C-a leachates collected during 1981 to determine how much of the acute toxicity was caused by high concentrations of inorganic salts. To prepare these reconstituted leachates, we added CaCl_2 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, NaCl , NaHCO_3 and Na_2SO_4 to distilled water at approximately the same concentrations as they appeared in the original leachates. Before conducting chemical

analyses and toxicity tests, we filtered the mixtures through Whatman No. 4 paper to remove large insoluble particles and refrigerated the filtrates at 5°C.

Inorganic salts

In addition to testing original and reconstituted raw shale leachates we also conducted acute toxicity tests with the following inorganic salts: NaCl , Na_2SO_4 , NaNO_3 and MgSO_4 . The purpose of these tests was to calculate the relative contributions of major salts to the toxicity of original leachates.

Chemical analyses

Routine water quality parameters, including conductivity, alkalinity, hardness, pH and total dissolved solids, were determined by standard methods [4]; ammonia analyses were performed using an ion-selective electrode (Orion Model 407A). For more extensive characterizations, we analyzed major inorganic anions by ion chromatography (Dionex System 10 and Dionex System 14); however, we calculated carbonate and bicarbonate concentrations from pH and alkalinity values. Inorganic cations and heavy metals were quantified using atomic absorption spectroscopy (Varian Model AA-275, Perkin-Elmer Model 403, and Perkin-Elmer Model 560) and inductively coupled plasma emission spectroscopy (Plasmatherm Model HST-2500D). Mercury was analyzed by a cold vapor cell atomic absorption technique [4], and DOC levels were determined using a Coulometrics Carbon Analyzer.

Acute toxicity tests

Static-renewal acute toxicity tests were conducted with *Daphnia magna* and fathead minnows (*Pimephales promelas*) for original leachates, reconstituted leachates and inorganic salts. Stock populations for both species were obtained in 1980 from the U.S. Environmental Protection Agency Environmental Research Laboratory in Duluth, Minnesota, and have since been reared in the University of Wyoming Fish Physiology and Toxicology Laboratory. All acute tests followed standard practices for toxicity testing with macroinvertebrates and fish [5]. In these tests, toxicants were diluted with a mixture of well water and dechlorinated city water (Table 1).

We placed 10 *D. magna* neonates (<24 h old) in each 50-ml test solution for 48 h at 20°C. Similarly, we placed 10 fathead minnow larvae (<24 h post-hatch) in each 50-ml test solution for 96 h at

Table 1. Quality of dilution water used for *Daphnia magna* and fathead minnow toxicity tests

Parameter	Value
pH (units)	8.3 (7.9-8.7)
Alkalinity (mg/L as CaCO ₃)	157 (150-166)
Hardness (mg/L as CaCO ₃)	563 (404-694)
Conductivity (μmhos/cm at 25°C)	942 (600-1,180)
Total ammonia (mg/L)	<0.1
Chlorine (mg/L)	<0.01

Dilution water was a mixture of well water and dechlorinated city water. Parameters are reported as means of values analyzed during all acute toxicity tests, with ranges in parentheses.

17°C. Triplicate beakers were tested for each species at each exposure concentration, and all tests were conducted under a 16-h light:8-h dark photoperiod. Every 24 h, survival and activity levels of test animals were observed. Dead organisms were removed at that time, and survivors were transferred to fresh exposure solutions. Despite the relatively small volumes of leachate and control water in which the *D. magna* and fathead minnows were tested, dissolved oxygen levels remained high (5.8 to 9.7 mg/L) and un-ionized ammonia concentrations were low (≤0.04 mg N/L).

Exposure concentrations in all original and reconstituted leachate tests were 10, 18, 32, 56 and 100% of the full-strength leachate. The limited volumes available for many original raw shale leachates precluded testing at narrower concentration intervals.

We calculated LC50 values (median lethal concentrations) using the trimmed Spearman-Kärber method [6]. To calculate 95% confidence intervals about an LC50 value in this algorithm, partial mortality must occur in at least one exposure concentration. Therefore, since partial mortality was not always observed, confidence intervals are not reported for some leachate LC50 values.

Chronic toxicity tests

Static-renewal, 21-d chronic toxicity tests were conducted with *D. magna* for one Tract C-b and two Tract C-a raw shale leachates. We used the same dilution water for these chronic tests as used in the acute toxicity tests (Table 1).

Ten replicates of a control and five exposure concentrations were started with one *D. magna* neonate (<24 h old) per 100-ml exposure solution. Exposure concentrations were approximately 60, 20, 6, 2 and 0.6% of the 48-h LC50 values. As with the acute toxicity tests, beakers were maintained at 20°C under a 16-h light:8-h dark pho-

toperiod. Daily, we fed the animals a suspension of yeast and trout chow (10 μg/ml final concentration in the exposure beaker). Each daphnid was transferred three times per week to a fresh exposure solution; dead adults, shed exoskeletons and offspring were removed and counted during each transfer. At the end of the 21-d test, we measured the length of surviving adults.

To determine a no observed effect concentration (NOEC) for each test, the following four parameters were calculated: (a) percent adult survival, (b) percentage of adults reproducing at day 21, (c) number of days to first brood and (d) number of young per breeding female. Values for each parameter at each exposure concentration were compared with the control value using Student's *t* test ($\alpha = 0.05$; [7]). The lowest exposure concentration for which results did not differ from the control was designated the NOEC, and was then divided into the 48-h LC50 concentration to calculate an acute/chronic ratio (ACR) for the chronic test.

Statistical analyses

Pearson product-moment correlation coefficients (*r*) for regressions of LC50 values versus chemical parameters were calculated using the MINITAB statistical package on the University of Wyoming computer system [8]. Because logarithmic transformations of toxicity values did not increase the correlation coefficients, only correlations between sets of untransformed data are reported. The significance of correlation coefficients was tested according to the method of Sokal and Rohlf [7], using the equation

$$t_s = r \sqrt{\frac{n-2}{1-r^2}}$$

where *n* is sample size. Computed *t_s* values were then evaluated for statistical significance at *n* - 2 degrees of freedom, using critical values of Student's *t* distribution [9].

RESULTS

Raw shale leachates

Except for the periods of January to April 1981 and July to September 1981, Tract C-b received equal or higher cumulative precipitation than did Tract C-a (Fig. 2). From July to November 1982, cumulative precipitation at Tract C-b was 3 to 5 cm (11 to 31%) greater than at Tract C-a; otherwise, between-tract differences were relatively small.

At both sites, leachate flow lagged approximately 5 to 10 d behind precipitation events.

Usually, more leachate was collected at Tract C-b (Fig. 3), where leachate volumes were relatively constant percentages of the incident precipitation volume (12% at 3.0 m, 16% at 4.6 m and 18% at 6.1 m). Tract C-a leachate production varied considerably (9 to 23% of incident precipitation volume at 1.5 m, 3 to 23% at 3.0 m and 5 to 11% at 4.6 m), and was only higher than at Tract C-b in the 1.5-m and 3.0-m collectors during 1983 [10]. In fact, not enough leachate was collected from the 3.0-m collector at Tract C-a during 1981 and early 1982 to conduct chemical analyses and toxicity tests.

The conductivity and pH of Tract C-a and C-b leachates measured in the field are shown in Figures 4 and 5, respectively. At Tract C-a, pH values were similar among the three collectors and ranged from 6.8 to 8.2. However, leachate conductivities differed considerably between collection depths. After initial increases during April and May 1981, mean conductivities were 18,300 $\mu\text{mhos}/\text{cm}$ for the

1.5-m collector and 30,600 $\mu\text{mhos}/\text{cm}$ for the 4.6-m collector.

Tract C-b pH values ranged from 7.4 to 8.4, and the 3.0-m leachates were usually 0.1 to 0.5 units higher in pH than the 4.6- and 6.0-m leachates. Although this range of pH values is similar to Tract C-a values, Tract C-b leachates were usually 0.5 to 0.8 units higher in pH than Tract C-a leachates during 1982 and 1983. Mean conductivity at Tract C-b (6,950 $\mu\text{mhos}/\text{cm}$), however, was much lower than at Tract C-a. At Tract C-b, conductivity was similar at all depths [10].

Tables 2 and 3 present detailed chemical analyses of leachates collected from the 4.6-m depth of the Tract C-a raw shale pile and from the 6.1-m depth of the Tract C-b raw shale pile, respectively. Leachates collected at these depths often exhibited the highest levels of parameters analyzed at each site.

In general, pH values recorded in the laboratory were 0.5 to 1.5 pH units higher than field measure-

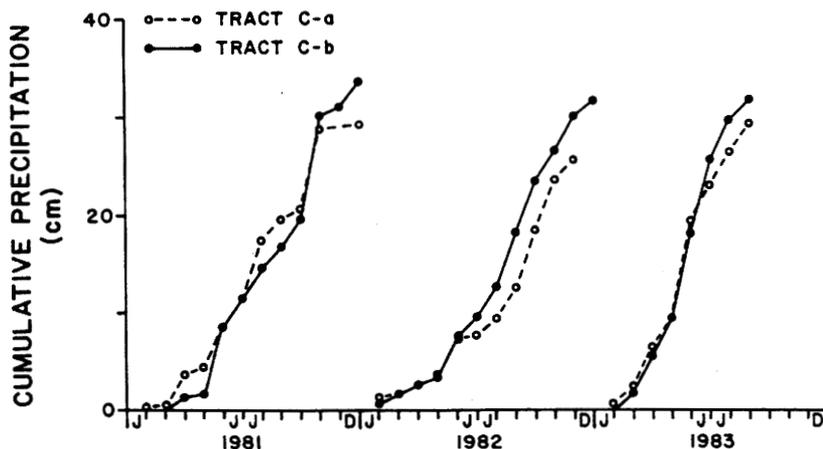


Fig. 2. Precipitation at Tracts C-a and C-b from 1981 to 1983.

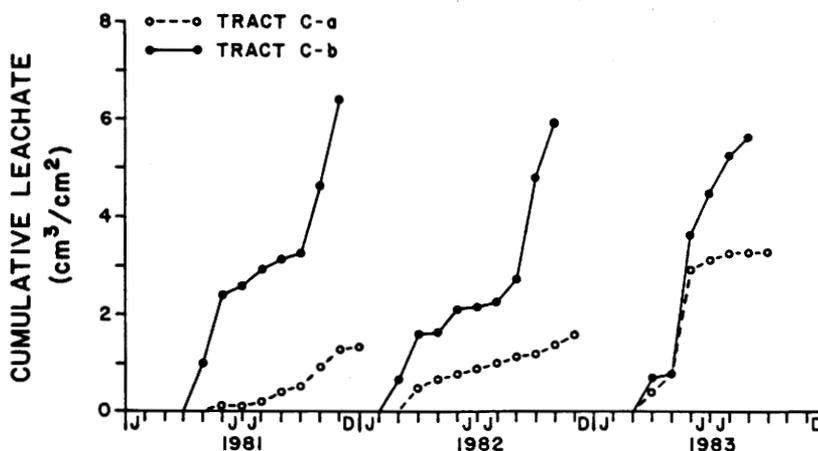


Fig. 3. Leachate collected at 4.6-m depth in Tract C-a and C-b raw shale piles from 1981 to 1983.

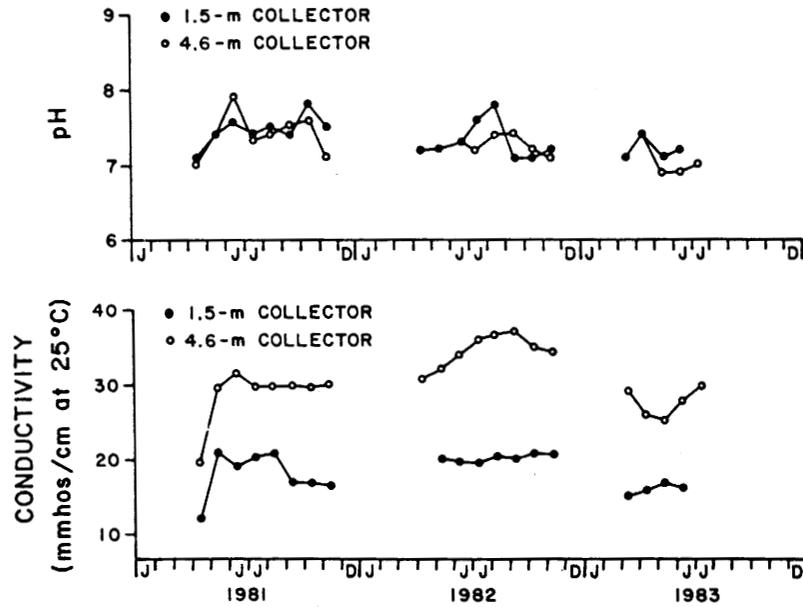


Fig. 4. Conductivity and pH of raw shale leachates measured in the field at Tract C-a from 1981 to 1983.

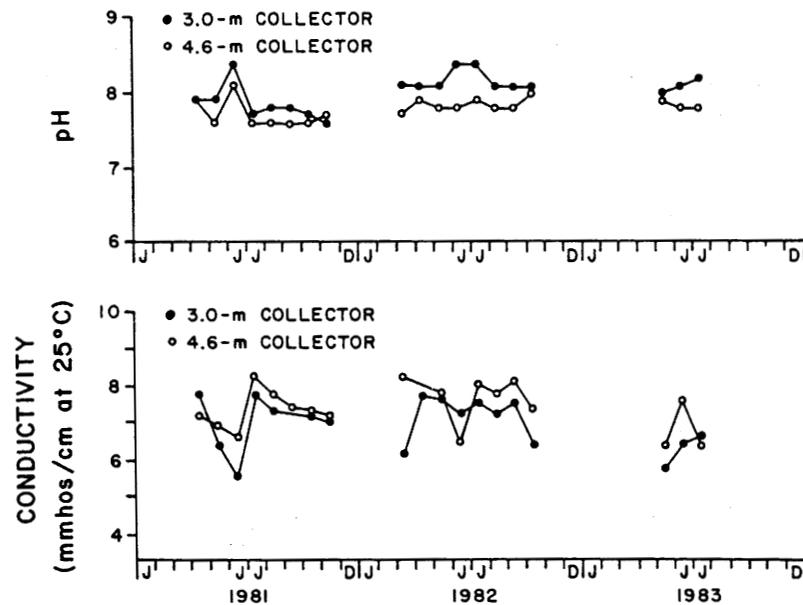


Fig. 5. Conductivity and pH of raw shale leachates measured in the field at Tract C-b from 1981 to 1983.

ments at both sites. However, conductivities of all leachates determined in the laboratory were approximately 1,000 to 5,000 $\mu\text{mhos/cm}$ less than those observed in the field. Ammonia values were initially high in Tract C-a leachates (approximately 10 mg N/L), but eventually decreased to low values at both sites in late 1981. Conductivity values and total dissolved solids levels were high at both sites but were 4 to 15 times greater in Tract C-a leachates than in Tract C-b leachates. Alkalinity was also higher at Tract C-a, although the

highest value recorded (360 mg/L) was relatively low compared with the high dissolved solids and conductivity levels. There was a generally increasing trend in alkalinity, conductivity and total dissolved solids values from April 1981 through December 1982 at both sites.

Trace elements were generally similar between the two sites (Tables 2 and 3). However, cadmium, manganese and nickel concentrations were higher in several Tract C-a leachates, whereas copper and molybdenum concentrations at Tract C-a were

Table 2. Chemical characteristics of Tract C-a raw shale leachates from the 4.6-m collector during 1981 and 1982

Parameter ^a	1981			1982	
	3 April	23 July	10 Sept	19 July	21 Sept
pH (units)	8.8	8.2	7.7	8.5	7.7
Alkalinity (as CaCO ₃)	140	343	312	387	477
Ammonia, total (as N)	10.0	0.26	0.02	0.13	0.10
Conductivity (μ mhos/cm at 25°C)	15,500	25,200	27,600	40,100	38,000
Dissolved solids, total	29,160	60,980	62,040	70,300	71,960
Major anions					
Cl ⁻	302	401	300	327	316
F ⁻	18	21	41	29	42
HCO ₃ ⁻	161	412	379	461	579
NO ₃ ⁻	1,620	2,180	1,485	2,430	2,190
SO ₄ ²⁻	23,360	30,900	37,000	39,800	42,800
Major cations					
Ca ²⁺	592	1,430	530	364	356
K ⁺	11	8	10	16	7
Mg ²⁺	3,980	8,340	8,560	7,690	13,710
Na ⁺	976	1,250	1,220	1,280	1,490
Trace elements					
Al	0.7	<0.02	<0.02	1.26	<0.5
B	0.377	0.510	0.480	1.05	ND
Ba	0.062	0.079	0.080	ND	0.257
Cd	<0.001	<0.001	0.003	0.134	0.143
Cu	0.037	0.042	0.032	0.002	0.010
Fe	<0.001	<0.005	0.012	<0.01	1.75
Li	0.172	0.189	0.197	0.122	0.134
Mn	0.793	2.70	1.97	1.46	0.373
Mo	<0.05	<0.05	<0.05	0.36	ND
Ni	0.290	0.660	0.280	0.660	0.753
P	0.88	0.95	0.59	<0.5	ND
Pb	<0.01	<0.01	<0.01	0.51	0.87
Si	2.3	2.1	1.9	<0.5	ND
Sr	6.8	10.1	8.0	15.4	ND
Zn	0.118	0.330	0.201	0.255	0.311

ND, not determined.

^aValues expressed as mg/L, except as noted.

lower than in Tract C-b leachates. Levels frequently greater than 0.1 mg/L were measured for boron, lithium, manganese, nickel, phosphorus, silicon, strontium and zinc. Concentrations of other metals varied without apparent patterns either within or between years.

The greatest chemical differences between sites and among the leachates collected at any depth were in the major inorganic anions and cations. Tract C-a leachates were dominated by magnesium and sulfate, which usually constituted greater than 80% of the cations and anions, respectively (Tables 2 and 4). Sodium, calcium, nitrate, chloride, fluoride and bicarbonate were also present, but in relatively low concentrations. The earliest Tract C-a leachates (collected in April 1981) contained

much lower concentrations of all major anions and cations than did leachates collected later (1981 to 1982). Moreover, there were considerably higher concentrations of major ions at the 4.6-m depth than at the 1.5-m depth in the Tract C-a pile (Table 4).

At Tract C-b, sulfate also dominated the major anions (Tables 3 and 4). But magnesium concentrations were lower than sodium concentrations, and approximately equal to those of calcium. As occurred at Tract C-a, the early Tract C-b leachates collected in April 1981 had lower concentrations of major anions and cations than did leachates collected later (1981 to 1982). However, major ion concentrations were similar between depths in the Tract C-b pile [10].

Table 3. Chemical characteristics of Tract C-b raw shale leachates from the 6.1-m collector during 1981 and 1982

Parameter ^a	1981			1982	
	8 April	23 July	10 Sept	6 July	23 Sept
pH (units)	8.9	8.1	8.2	8.1	8.1
Alkalinity (as CaCO ₃)	72	116	126	111	138
Ammonia, total (as N)	0.46	0.08	0.12	<0.10	0.12
Conductivity (μmhos/cm at 25°C)	2,000	6,600	6,800	7,900	6,200
Dissolved solids, total	1,960	6,980	7,310	7,060	6,610
Major anions					
Cl ⁻	5	24	24	18	14
F ⁻	3	10	10	5	5
HCO ₃ ⁻	81	140	151	134	166
NO ₃ ⁻	58	152	127	110	191
SO ₄ ²⁻	1,370	4,010	3,880	4,140	3,880
Major cations					
Ca ²⁺	216	530	770	461	435
K ⁺	1	5	5	8	10
Mg ²⁺	59	249	278	321	310
Na ⁺	235	1,020	1,040	1,910	1,120
Trace elements					
Al	0.80	<0.02	<0.02	1.89	<0.5
B	0.136	0.420	0.440	0.810	ND
Ba	0.109	0.085	0.084	ND	0.257
Cd	<0.001	0.003	0.006	0.032	0.028
Cu	0.299	0.012	0.010	0.023	<0.01
Fe	0.013	<0.005	<0.005	<0.010	0.279
Li	0.037	0.249	0.261	0.189	0.157
Mn	0.059	0.160	0.140	0.521	<0.005
Mo	0.90	0.90	<0.05	1.5	ND
Ni	0.910	0.164	0.151	0.047	<0.05
P	0.24	0.41	0.30	0.15	ND
Pb	0.03	<0.01	0.02	0.20	0.12
Si	3.5	3.2	3.5	1.2	ND
Sr	2.6	8.8	9.1	8.9	ND
Zn	0.037	0.184	0.206	0.110	0.381

ND, not determined.

^aValues expressed as mg/L, except as noted.

In samples tested for acute and chronic toxicity, DOC concentrations ranged from 30 to 50 mg/L for Tract C-a leachates and from 10 to 30 mg/L for Tract C-b leachates [11]. However, we did not characterize individual organic compounds in these leachates.

The acute toxicities of Tract C-a and C-b raw shale leachates are listed in Table 5. Except for one sample (September 1981, combined depths; *D. magna*), no mortalities occurred in Tract C-b leachates. Conductivities of all Tract C-b leachates were between 6,400 and 8,000 μmhos/cm. However, five of the six Tract C-a leachates tested were acutely toxic. *Daphnia* were always more sensitive than fathead minnows (i.e., had lower LC50 concentrations), with several 48-h *D. magna* LC50 values between 10 and 15% of the full-strength

leachate. Tract C-a leachate conductivities ranged between 21,000 and 46,000 μmhos/cm, except for the nontoxic sample collected in April 1981 (5,600 μmhos/cm). Although Tract C-a leachates that had conductivities greater than 8,000 μmhos/cm were acutely toxic, *D. magna* 48-h LC50 values and fathead minnow 96-h LC50 values were not significantly correlated with conductivity or with magnesium and sulfate concentrations (Table 6).

D. magna chronic toxicity tests could be conducted on only the September 1981 and April 1982 combined-depths leachates because of the limited volumes available for all other samples collected during 1981. NOEC values for the Tract C-a samples were 3.0% of the full-strength leachate in September 1981 and 0.9% of the full-strength leachate in April 1982 (Table 5). In both tests, adult survival

Table 4. Concentrations of major inorganic anions and cations in Tract C-a and C-b raw shale leachates for which acute and chronic toxicity tests were performed^a

Leachate	Cations (meq/L)				Anions (meq/L)			
	Mg ²⁺	Na ⁺	Ca ²⁺	K ⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	HCO ₃ ⁻
Tract C-a								
April 1981, 3.0 m	37	9	17	<1	54	4	1	2
May 1981, 4.6 m	601	57	28	<1	768	31	11	3
July 1981, 1.5 m	374	39	33	<1	379	31	5	4
July 1981, 4.6 m	684	54	56	<1	647	35	11	6
September 1981, combined depths	353	60	26	<1	373	20	4	6
April 1982, combined depths	714	74	23	<1	750	30	8	4
Tract C-b								
June 1981, 3.0 m	15	46	27	<1	66	2	<1	3
June 1981, 4.6 m	19	49	22	<1	72	2	<1	3
June 1981, 6.1 m	18	44	28	<1	68	3	<1	2
July 1981, 3.0 m	ND	ND	ND	ND	ND	ND	ND	ND
July 1981, 4.6 m	20	47	26	<1	88	2	<1	2
July 1981, 6.1 m	19	43	25	<1	78	3	<1	2
September 1981, combined depths	22	55	24	<1	81	1	<1	3

ND, not determined.

^aData from refs. 10 and 11.

Table 5. Acute and chronic toxicities of Tract C-a and C-b raw shale leachates to *Daphnia magna* and fathead minnows

Leachate	<i>Daphnia magna</i>			Fathead minnow
	48-h LC50 ^a (% leachate)	21-d LC50 ^b (% leachate)	Acute/chronic ratio ^c	96-h LC50 ^a (% leachate)
Tract C-a				
April 1981, 3.0 m	>100	ND	ND	ND
May 1981, 4.6 m	14 (12.8-15.0)	ND	ND	ND
July 1981, 1.5 m	32 (29.3-36.0)	ND	ND	48 (43.8-53.4)
July 1981, 4.6 m	13 (12.8-14.0)	ND	ND	28 (25.0-32.5)
Sept. 1981, combined depths	14 (12.9-16.2)	3.0 (9.0)	4.7	62 (55.2-69.5)
April 1982, combined depths	13 (12.2-13.6)	0.9 (3.0)	14.4	33 (29.0-37.2)
Tract C-b				
June 1981, 3.0 m	>100	ND	ND	>100
June 1981, 4.6 m	>100	ND	ND	>100
June 1981, 6.1 m	>100	ND	ND	>100
July 1981, 3.0 m	>100	ND	ND	>100
July 1981, 4.6 m	>100	ND	ND	>100
July 1981, 6.1 m	>100	ND	ND	>100
Sept. 1981, combined depths	66 (59.8-71.8)	4.4 (15.0)	15.0	>100

ND, not determined because of limited leachate volume available for toxicity testing.

^a95% confidence intervals about LC50 values in parentheses.

^bNumbers in parentheses indicate next highest concentration tested above the no observed effect concentration (NOEC).

^cAcute/chronic ratio = (48-h LC50/21-d NOEC).

and production of young were the most sensitive parameters [11]. LC50 values (48-h) were approximately the same in the September 1981 and April 1982 leachates (14 and 13%, respectively), and ACRs (LC50/NOEC) were 4.7 and 14.4. As a chemical comparison, the more toxic April 1982

Tract C-a leachate contained approximately twice as much magnesium and sulfate as did the September 1981 leachate (Table 4).

For the Tract C-b September 1981 leachate, the reproductive-level NOEC was 4.4% of the full-strength leachate (Table 5). Again, adult survival

Table 6. Correlation coefficients for *Daphnia magna* and fathead minnow LC50 values versus magnesium and sulfate concentrations and conductivity in original and reconstituted Tract C-a raw shale leachates

Correlation	Correlation coefficient (<i>r</i>) ^a	
	Original leachate	Reconstituted major ions
<i>Daphnia magna</i>	(<i>n</i> = 5)	(<i>n</i> = 4)
48-h LC50 vs. [Mg ²⁺]	-0.597	-0.946
48-h LC50 vs. [SO ₄ ²⁻]	-0.605	-0.996 ^b
48-h LC50 vs. conductivity	-0.161	-0.944
Fathead minnow	(<i>n</i> = 4)	(<i>n</i> = 4)
96-h LC50 vs. [Mg ²⁺]	-0.924	-0.975 ^c
96-h LC50 vs. [SO ₄ ²⁻]	-0.872	-0.895
96-h LC50 vs. conductivity	-0.882	-0.957 ^c

^aSample sizes (*n*) in parentheses.

^b0.05 > *p* > 0.01.

^c*p* < 0.01.

and production of young were the most sensitive parameters [11]. Since the 48-h LC50 was 66%, the ACR was 15.0. Total ionic content of this Tract C-b leachate was approximately one-fifth that of the September 1981 Tract C-a combined-depths leachate (Table 4).

Inorganic salts

Because acute toxicity occurred only in leachates with conductivities greater than 7,000 to 8,000 $\mu\text{mhos/cm}$, we conducted acute toxicity tests with four inorganic salts to determine if they were a major cause of the observed toxicities. For *D. magna* and fathead minnows, MgSO₄ was much more toxic than Na₂SO₄, NaNO₃ and NaCl (Table 7). *D. magna* were always more sensitive than fathead minnows. Based on these MgSO₄ LC50 values and calculated concentrations of MgSO₄ present in the Tract C-a raw shale leachates at their LC50 values, more than enough MgSO₄ toxic units were present to account for the observed toxicity in all leachates except the September 1981 combined-depths sample tested with *D. magna* (0.70 toxic units of MgSO₄ were present at the *D. magna* LC50 concentration for the September 1981 combined-depths leachate; 1.16 to 1.72 toxic units of MgSO₄ were present at the four other *D. magna* LC50 concentrations, and 1.30 to 1.96 toxic units of MgSO₄ were present at the four fathead minnow LC50 concentrations).

Table 7. Acute toxicities of four inorganic salts to *Daphnia magna* and fathead minnows

Salt	48-h <i>D. magna</i> LC50 (mg/L) ^a	96-h fathead minnow LC50 (mg/L) ^a
Na ₂ SO ₄	8,600 (8,390-8,770)	15,200 (14,470-15,940)
NaNO ₃	8,100 (7,850-8,290)	15,300 (14,460-16,200)
NaCl	6,500 (6,270-6,670)	11,400 (10,890-11,850)
MgSO ₄	4,300 (4,100-4,570)	7,900 (7,690-8,150)

^a95% confidence intervals about LC50 values in parentheses.

Reconstituted leachates

To further test whether major ions could account for the toxicity of Tract C-a leachates, we reconstituted the major anions and cations in four of the five toxic leachates, adding no trace elements or organic compounds. Analyzed concentrations of these ions in the original and reconstituted leachates were similar, except for the magnesium concentrations in the May 1981 4.6-m leachate (601 meq Mg²⁺/L in the original leachate versus 691 meq Mg²⁺/L in the reconstituted leachate) and the sodium concentrations in the September 1981 combined-depths leachate (60 meq Na⁺/L in the original leachate versus 9 meq Na⁺/L in the reconstituted leachate [11]).

In all cases, the reconstituted leachate LC50 values were greater than or equal to the original leachate LC50 values (Table 8). There was no consistent pattern of toxicity for either species; *D. magna* LC50 values were equal for two of the original and reconstituted sample pairs (May 1981 4.6-m depth and July 1981 1.5-m depth), but these differed from each other by 54 and 114%, respectively, for the two other original and reconstituted sample pairs (July 1981 4.6-m depth and September 1981 combined depths). Relative differences between fathead minnow LC50 values for original and reconstituted leachate pairs ranged from 18 to 52%, and were only significant for the July 1981 1.5-m depth and the September 1981 combined-depths leachates. As observed for the original leachates, fathead minnows were always less sensitive than *D. magna* to the reconstituted leachates.

Acute toxicities of reconstituted leachates correlated much better with levels of chemical parameters than did acute toxicities of the original raw shale leachates (Table 6). For example, fathead minnow toxicities for reconstituted leachates were significantly correlated with conductivity and magnesium concentration (*p* < 0.05), while *D. magna*

Table 8. Acute toxicities of original and reconstituted Tract C-a raw shale leachates to *Daphnia magna* and fathead minnows

Leachate	48-h <i>D. magna</i> LC50 (% leachate) ^a	96-h fathead minnow LC50 (% leachate) ^a
May 1981, 4.6 m		
Original	14 (12.8–15.0)	ND
Reconstituted	13 (12.7–13.7)	44 (39.8–47.6)
July 1981, 1.5 m		
Original	32 (29.3–36.0)	48 (43.8–53.4)
Reconstituted	31 (27.2–36.2)	73 (65.5–81.8)
July 1981, 4.6 m		
Original	13 (12.8–14.0)	28 (25.0–32.5)
Reconstituted	20 (18.1–22.8)	34 (30.2–38.7)
September 1981, combined depths		
Original	14 (12.9–16.2)	62 (55.2–69.5)
Reconstituted	30 (27.4–33.7)	73 (70.7–76.2)

ND, not determined because of limited leachate volume available for toxicity testing.

^a95% confidence intervals about LC50 values in parentheses.

toxicities for reconstituted leachates were highly correlated with sulfate concentration ($p < 0.01$).

DISCUSSION

Although annual precipitation in the oil shale regions of northwestern Colorado is low, episodic snowmelt and rainfall provided enough water for leachates to percolate through raw, mined oil shale piles, at least to a depth of 6 m in this study. Compared with natural recharge rates for Piceance Basin soils, the leachate volumes we collected from Tract C-a and C-b raw shale piles were relatively large (averages as high as 18% of incident precipitation). These high flow rates were probably caused by high permeability of the shale piles and no surface vegetation, both of which tend to minimize runoff and evapotranspiration. However, the piles did not appear to be saturated, since we always observed a 5- to 10-d lag between precipitation events and leachate collection at all depths.

Erratic leachate collection from the Tract C-a pile was probably caused by postconstruction shale settlement that tilted the collectors and reduced their percolate interception efficiency. Although similar settlement may have occurred in the Tract C-b pile, those collectors were probably more efficient because of higher Teflon edges. Presumably, the inefficiency of Tract C-a collectors affected only leachate quantity and not leachate quality.

Chemically, the fragmented raw shale stored in surface piles resides in a hydrogeochemical environment different from the before-mining environment. Many fresh surfaces are exposed to water and air, and shale constituents can be dissolved into waters percolating through the piles. In this study, we observed intrapile, interpile and time-dependent variations in leachate quality. Surprisingly, though, the greatest chemical differences were in major inorganic ions rather than trace elements.

Tract C-a leachates were dominated by magnesium sulfate, whereas Tract C-b leachates tended toward sodium sulfate waters. This was probably due to different mineralogic compositions of the raw shales, since physical characteristics of the piles and climatic conditions at the two sites were similar. Oxidation of pyrite (FeS_2) to sulfate appeared to be the major chemical reaction controlling leachate composition in both piles.

Specifically, concentrations of several major anions (sulfate, nitrate and chloride) in Tract C-a leachates were higher than in Tract C-b leachates. Although sulfate and chloride differences between Tracts C-a and C-b can be explained by different shale compositions and extent of pyrite oxidation, nitrate may represent residue from the explosives used to mine raw shale. If this was the major source, nitrate concentrations should have decreased as the residual explosive was washed from shale particle surfaces. However, throughput volumes by the end of this study were too small to detect the predicted decrease.

The only major cation difference between the two sites was in magnesium. Since concentrations in Tract C-a leachates were usually more than 10 to 20 times higher than in Tract C-b leachates, magnesium did not appear to be controlled by solubility. However, calcium concentrations averaged approximately 30 meq/L at both sites and may have been controlled by CaCO_3 and CaSO_4 solubility [10]. Sodium concentrations varied with collector depth at Tract C-a (20 to 60 meq/L), but were relatively constant at Tract C-b (40 to 50 meq/L). Because of the high solubility of most sodium salts, it is unlikely that sodium levels were controlled by solubility.

As was observed for nitrate, total ammonia levels were initially high at Tract C-a and may have represented residue from mining explosives. Lower, but relatively high, total ammonia levels also occurred in early Tract C-b leachates. However, concentrations at both sites decreased by mid-1981, suggesting that either chemical or bacterial

oxidation within the pile converted ammonia to nitrate.

Although several factors may have contributed to the large differences in major ion concentrations between Tract C-a and C-b leachates, different shale composition is one apparent cause. The Tract C-b pile material was mined from an interval of lean shale that had a greater *in situ* permeability than did the Tract C-a shale. The higher-permeability shale would have been leached more intensively prior to mining, and thus may have contained less pyrite and possibly less dolomite [$\text{CaMg}(\text{CO}_3)_2$].

Most trace element concentrations were too erratic to allow discernment of obvious patterns after only 3 years of leachate collection. Although boron, lithium, manganese, phosphorus, silicon and strontium were frequently high, they probably contributed little to acute toxicity for *D. magna* and fathead minnows. However, nickel and zinc (0.1 to 1.0 mg/L) may have caused some of the observed toxicity, if they were bioavailable (i.e., not complexed to carbonate, sulfate or organic anions).

Concentrations of other metals such as aluminum, barium, cadmium, copper, iron, molybdenum and lead were high only occasionally, and the maximum observed concentrations for these metals exceeded solubility [10]. Three explanations are possible for this. First, leachates percolating from these piles may not have attained chemical equilibrium. Second, metals may have been complexed with organic anions, thus increasing their aqueous solubility. Finally, fine-grained particles may have passed through the 0.45- μm membrane filters and, when the filtrates were subsequently acidified, may have resulted in overestimates of aqueous concentrations of aluminum, iron, manganese and other elements that occur in clay-sized sediments [12]. Additional data would be needed to differentiate among these mechanisms.

DOC levels were slightly higher in Tract C-a leachates, but all measured concentrations were less than 50 mg/L. Although they may not have directly degraded water quality, the presence of organic compounds may have controlled solubility of the major cations, aluminum and other trace elements. Organic anions such as acetate and oxalate would be especially important in this process, but detailed organic analyses were not performed to identify potential organic ligands.

Besides these interpile chemical differences, we also observed intrapile differences at Tract C-a. Leachates collected from the 4.6-m collector always had higher concentrations of major ions

than leachates collected from the 1.5-m collector on the same day. A possible explanation is that longer residence times within the pile increased the amount of ions leached from the raw shale. Yet in the Tract C-b pile, leachates from the 3.0- and 6.1-m depths were chemically similar. These results suggest that raw shale leachates may reach chemical equilibrium at relatively shallow depths, and the differences observed in Tract C-a leachates may have been caused by physical and chemical heterogeneity of the shale used to build that pile. Neither possibility can be confirmed without conducting additional experiments.

Acute toxicities of raw shale leachates appeared to be caused mostly by major inorganic anions and cations. Mortalities only occurred when conductivities exceeded 7,000 to 8,000 $\mu\text{mhos/cm}$ and total dissolved solids levels exceeded approximately 6 to 7 g/L (0.6 to 0.7% salt). All leachates that greatly exceeded these ranges were collected from Tract C-a and contained high magnesium and sulfate concentrations accounting for 80 to 90% of the total cations and anions. Toxicity tests of individual salts with *D. magna* and fathead minnows indicated that on a single-compound basis, the concentrations of magnesium sulfate in Tract C-a leachates were sufficiently high to cause the observed invertebrate and fish mortalities. However, trace elements such as aluminum, nickel and zinc were present at high enough levels to have contributed partly to some of the leachate toxicities, if they were bioavailable.

Since other major anions and cations constituted relatively small percentages of the total ions in Tract C-a leachates, they probably contributed little to the observed acute toxicities. In fact, they may have counteracted some of the high MgSO_4 concentrations, as indicated by the apparently excess MgSO_4 present at leachate LC50s as compared with MgSO_4 single-compound toxicity tests (apparent excesses ranged from 16 to 96% more MgSO_4 present at leachate LC50 concentrations than was needed to account for the observed toxicities). This illustrates that the toxicities of complex inorganic mixtures are difficult to predict accurately *a priori* based on LC50 values of individual constituents and that they should be evaluated using toxicity tests of whole mixtures. Supporting this conclusion, correlations of original leachate toxicity with conductivity levels and magnesium and sulfate concentrations were not significant ($p > 0.05$) for *D. magna* and fathead minnow tests. Therefore, neither conductivity nor magnesium sulfate concentrations could be used as an accurate predictor of acute toxicity, although

threshold toxicity levels were apparently present for both chemical parameters. In fact, based on $MgSO_4$ single-compound LC50 values alone, Tract C-a leachates would have been predicted to be almost twice as toxic as they actually were.

D. magna ACRs ranged from 4.7 to 15.0 for the three leachates tested. In general, these results could be used to predict a range of potential chronic toxicity values if acute toxicity data only were available for a given leachate. But in making extrapolations from acute to chronic toxicity for these complex mixtures, it must be remembered that (a) the chemical components responsible for the acute toxicity may not be responsible for the chronic toxicity, and (b) relative concentrations of acutely toxic and chronically toxic components may change temporally or spatially in a leachate. Therefore, such extrapolations should be made with caution until results of additional studies become available.

To further test whether the concentrations of major ions alone could account for the observed acute toxicities, we reconstituted the major inorganic anions and cations in four Tract C-a leachates collected during 1981. Without trace inorganic and organic compounds present, acute toxicities of reconstituted leachates were equal to or slightly less than the corresponding raw shale leachate toxicities. Again, this suggests that major anions and cations were the principal toxicants. Toxicity differences between original and reconstituted leachates could have been caused by incomplete dissolution of the added salts, as evidenced by the visible residue filtered from each reconstituted leachate before testing. In turn, this incomplete dissolution of major ions near their solubility limits may have been caused by the absence of trace organics (e.g., acetate or oxalate). However, the chemical compositions of reconstituted leachates were similar to those of the original leachates, indicating that relatively little of the added salts failed to dissolve. Thus, although their individual contributions to the original leachate toxicities might be difficult to evaluate because of the chemical complexity of these waters, toxic trace elements not present in the reconstituted leachates could also have accounted for the toxicity differences.

Correlations of toxicity with conductivity levels and magnesium and sulfate concentrations in reconstituted leachates were significant ($p < 0.05$) for *D. magna* and fathead minnows. This contrasts with the poor correlations for original leachates that contained approximately the same major ion concentrations, and supports our conclusion that

the toxicities of these complex inorganic mixtures are difficult to predict accurately based on concentrations of only the principal toxicants. Furthermore, these results indicate that important interactions between the major ions probably occurred. Correlations of reconstituted leachate toxicity with magnesium and sulfate concentrations explained more than 80% of the variance in fathead minnow tests and more than 89% of the variance in *D. magna* tests. Since much less variance was explained by the same chemical parameters in original leachate toxicity tests with *D. magna*, it appears that interactions of relatively nontoxic chemicals with the principal toxicant may have affected toxicities in original and reconstituted leachates.

The only nontoxic Tract C-a leachate was the earliest leachate collected (during April 1981). This sample was most likely a combination of residual mine water originally present in the raw shale and of snowmelt and rain percolating rapidly through the pile, thus producing a relatively dilute leachate.

Since chemical characteristics and toxicity values for leachates vary considerably between dates of collection and depths within a raw shale pile, safe discharge concentrations for short-term exposures cannot be precisely defined. At this time we cannot distinguish among the possible causes of relatively high salt concentrations in Tract C-a leachates collected from summer 1981 through summer 1983. Factors that could affect salt concentrations and, hence, toxicity include chemical composition of the raw shale, age of the pile, time of year and flow rate of leachate through the pile. Additional laboratory and field leaching studies are needed to determine how these factors contribute to leachate characteristics and whether relatively high- or relatively low-salinity leachates will be produced from run-of-mine shale piles in commercial oil shale facilities.

It is especially important to note that shale leachates can vary between sites for at least two reasons. First, different grades of shale with different mineralogic compositions exist at different levels in the Mahogany Zone of the Green River Formation. Only high-grade oil shale will be stored in run-of-mine piles for future retorting; low-grade shales either will not be mined or may be used for various construction projects on-site. Thus, low-grade shale may be leached by precipitation over periods of years, while high-grade shale will be processed rapidly and will not be extensively exposed to precipitation. Second, average shale compositions can vary horizontally throughout the Piceance Basin. Therefore, the Tract C-a and

C-b leachates tested in this study may not be characteristic of leachates from all high-grade and low-grade oil shales, respectively, in northwestern Colorado.

At this time, the toxic Tract C-a leachates collected during the summer and fall of 1981 and the spring of 1982 should be considered only as worst-case examples, which may not be produced during routine operating conditions. Harmful concentrations for fish or invertebrates would depend on many factors, including (a) commercial facility and raw shale pile designs and leachate containment structures, (b) duration of shale storage above ground, (c) the type of leachate flow from the piles (point-source versus diffuse discharge), (d) effects of soils on leachate quality after the leachate leaves the raw shale pile and before it reaches surface waters, (e) potential flow rates into receiving streams, (f) receiving stream water quality and (g) the aquatic organisms potentially at risk.

In summary, it is difficult to predict quantity and quality of leachates from raw shale that will be stored above ground or used during construction of oil shale facilities. Although conductivity and magnesium sulfate concentration can be used as crude predictors of acute toxicity, interactions with other constituents in these complex chemical mixtures preclude identification of minor toxicants based on single-compound toxicities and only a few leachate samples. The bioavailability of trace elements is especially difficult to characterize because of numerous potential organic and inorganic ligands. However, by testing reconstituted solutions, the principal toxicants and interactions among major constituents can be identified. Considerable time and effort would be required to characterize the chemical complexation and bioavailability of trace elements and to thus attain a more exact explanation of the toxic mechanisms associated with oil shale leachates. This conclusion may apply generally to other complex chemical mixtures, including solid waste leachates, agricultural runoff and municipal and industrial effluents in receiving waters.

Acknowledgement—We thank Rio Blanco Oil Shale Company and Cathedral Bluffs Shale Oil Company for allowing us to conduct these studies on Federal Oil Shale Lease Tracts C-a and C-b, for providing the materials for leachate collection systems, and for assisting with leachate collection and precipitation monitoring. At Colorado State University, Tom Smith helped prepare and analyze leachate samples. Julia Collins, Jim Coyle, Laurie Crosse, Mike Crosse and Joe Fernandez assisted with chem-

ical analyses and toxicity tests at the University of Wyoming. Chuck Bray, Butch Slawson and Jim Johnson provided valuable comments on a draft of the manuscript; and Tim Drever, Laurie Crosse and Mike Crosse helped the UW co-authors understand some of the geochemical mechanisms controlling shale leachate chemistry. This work was performed under Cooperative Agreement No. CR807513 between the U.S. Environmental Protection Agency and Colorado State University and under Cooperative Agreement No. CR808671 between the U.S. Environmental Protection Agency and the University of Wyoming. The University of Wyoming Water Research Center supported J.S. Meyer while part of the manuscript was being prepared.

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