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# The Biogeochemistry of Heavy Metals in Polluted Lakes and Streams at Flin Flon, Canada, and a Proposed Method for Limiting Heavy-Metal Pollution of Natural Waters

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**ABSTRACT** / The biogeochemistry of Zn, Cd, Cu, Hg, and Fe in lakes and streams polluted by mine and smelter wastes emitted at Flin Flon, Canada, was investigated. In Schist Lake, a repository for both tailings-pond drainage and sewage, green algal blooms generated by nutrients from sewage promote entrapment of metals in sediments by (1) accumulation of metals from solution by algal seston, with preferential uptake of Zn, the most abundant metal, followed by sinking of the seston; and (2) production of H<sub>2</sub>S during decomposition of dead algae, resulting in sulfide precipitation. Metals are partially resolubilized from seston as it decomposes while sinking. Preferential retention of Cu by sinking seston and by mud promotes Cu enrichment in the mud but the Cu/Zn ratio of mud varies with the Cu/Zn ratio of surface water seston. In bottom muds, partitioning of a metal between sulfide and organic matter is strongly dependent on the stability of the metal sulfide as measured by its standard entropy, the proportion of sulfide-bound metal decreasing in the order Hg > Cd > Cu > Fe > Zn. When sulfide-rich muds were heated under helium, x-ray diffraction revealed abundant well-crystallized ZnS (sphalerite) containing Cd, Hg, and Fe; only poorly crystallized traces of the mineral were detected in unheated mud, however. Cu sulfide failed to crystallize, suggesting interference by sorbed impurities. Metals were concentrated in H<sub>2</sub>S-rich muds and

extraction of muds with various solvents and by electro dialysis showed that sulfide was much more effective than organic matter in suppressing remobilization of metals. Remobilized Cu is probably bound to organic complexing agents. Some extractable complexing agents bind Cu preferentially with respect to Zn and Cd but others preferentially bind Zn and Cd; the complexes, being stable in the presence of free sulfide, may cause some release of metals from sulfide-rich muds in nature.

These results indicate that introduction of sewage together with heavy-metal effluents into settling ponds could be an effective and economic method for limiting heavy-metal pollution of natural waters.

## Introduction

Natural waters contaminated with heavy metals tend to be purified by processes leading to accumulation and immobilization of the metals in bottom sediments. Among the more effective mechanisms for achieving this result are (1) the scavenging of metals by plankton blooms and other suspended particles, followed by deposition of the metal-bearing particles on the bottom (Nicholls and others 1959, Goldberg 1965, Martin 1970, Morris 1971, Hallberg 1972, Spencer and others 1972, Andelman 1973, Gibbs 1973, Knauer and Martin 1973, Craig 1974, de Groot and Allersma 1975) and (2) the binding of metals by sulfide and organic matter in fine-grained anaerobic bottom sediments (Miller 1950, Rankama and Sahama 1950, Krauskopf 1956, Hutchinson 1957, Manheim 1961, Szalay 1964, Goldberg 1965, Manskaya and Drozdova 1968, Thomas 1972, Jernelöv and Lann 1973, Rashid 1974, Nissenbaum and Swaine 1976, Ramamoorthy and Rust 1976), although these mechanisms are not equally effective for all heavy metals. Serious consideration has been given to the possibility of applying these processes to the problem of preventing or alleviating heavy-metal pollution of natural waters (Szalay 1964, Fagerström and Jernelöv 1971, Feick and others 1972, Vosjan and van der Hoek 1972, Jernelöv and Lann 1973, Leland and others 1974, Rowland and others 1977) but there is still an urgent need for highly efficient, economic methods for removal of metals from water. Our efforts to find practical solutions to the problem would doubtless be furthered by additional research on the biogeochemistry of heavy metals in aquatic environments, with emphasis on factors related to the solubility and biologic availability of the metals.

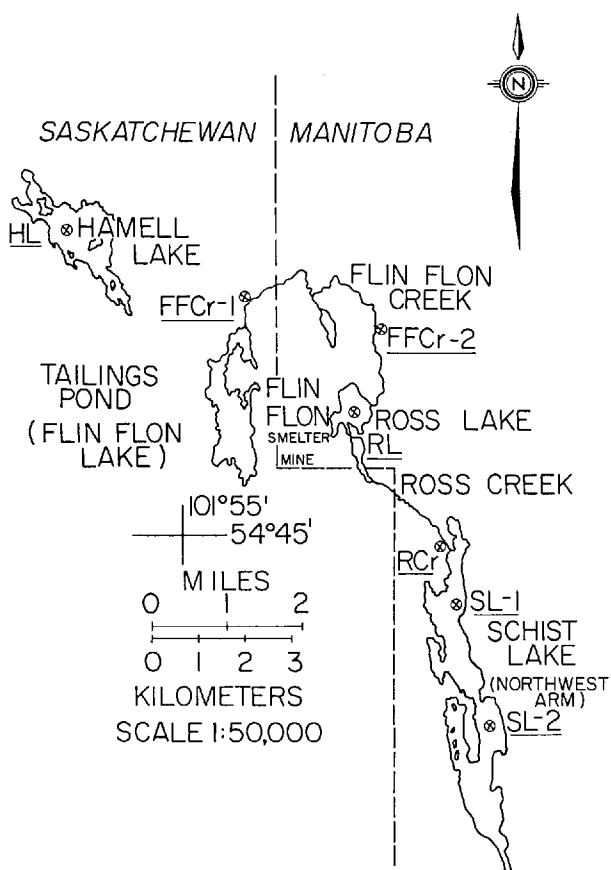
The work reported here was an investigation of heavy-metal biogeochemistry in lakes and streams in the vicinity of Flin Flon, Manitoba (Canada), where surface waters are polluted with zinc, cadmium, copper, and other metals as a result of mining and smelting operations conducted by the Hudson Bay Mining and

Smelting Co. (Rowley 1975, Crowe 1973). The study area selected offers the advantage that plankton blooms, sulfide production, and organic complexing in both the presence and the virtual absence of sulfide may all be observed there.

## Materials and Methods

Samples of mud and water were collected from lakes and streams in and around Flin Flon on June 1 and 2, 1976 (Fig. 1). Metals accumulate in the tailings pond, which is drained by Flin Flon Creek (FFCr). The creek flows through a marsh and empties into Ross Lake (RL). This lake, in turn, is drained by Ross Creek (RCr), which receives municipal sewage effluent near its origin at the south end of RL (Rowley 1975), upstream from the RCr sampling station, and then flows into the northwest arm of Schist Lake (SL). Hamell Lake (HL) in the woods near Flin Flon receives airborne fallout from the smelter but is not connected with the tailings pond and receives no sewage.

**Figure 1.** Map of Flin Flon and environs, showing location (x) of sampling stations.



Surface water was collected by hand in acid-rinsed polyethylene jugs at each site, and "hypolimnion" water was collected by van Dorn bottle at a depth of 15 m at station SL-2. A temperature profile measured at SL-2 revealed a thermocline extending from a depth of 10 m to the bottom (at 18 m). Bottom mud was collected from FFCr-2 (in the marsh), RL (at 3m), SL-1 (at 12 m), SL-2 (at 18 m), and HL (at 6 m) with an Ekman dredge. The mud from FFCr-2, RL, SL-1, and SL-2 was black to dark brown and smelled of  $H_2S$  but the HL mud was medium brown and odorless. Plankton was sampled by pouring surface water through 10  $\mu m$  and 73  $\mu m$  nets. The conductivity and temperature of the water were recorded with a YSI-33 meter and the pH values of the water and mud were measured with a Fisher Accumet-150;  $E_h$  measurements were made by means of platinum and calomel electrodes.

Water samples were filtered with 0.45  $\mu m$  Millipore filters precleaned with dilute HCl and hot water and leached with cold water. Aliquots of filtered water were dialyzed in a Pope multiple dialyzer, and the dialyzed and undialyzed portions were analyzed chemically. Organic carbon (org. C) was determined by Beckman-915 and -215A analyzers and, following wet-ashing with  $H_2SO_4$ ,  $H_2O_2$ , and ultraviolet (UV) radiation (Stainton and others 1974), the water was analyzed for zinc (Zn), cadmium (Cd), and copper (Cu) by Perkin-Elmer-403 atomic absorption (AA) spectrophotometer, for iron (Fe) by AA or by the colorimetric o-phenanthroline method, for phosphorus (P) by the colorimetric molybdate method, and for nitrogen (N) by the colorimetric chloramine-T method. Sulfate ( $SO_4$ ) was determined by the automated procedure of Stainton and others (1974). Total suspended matter and plankton samples were digested with hot  $HNO_3/H_2O_2$  (4 : 1) and analyzed for Zn, Cd, Cu, and Fe. The analytic data for plankton must be regarded as approximations only, as it was not possible to effect a clear-cut separation of plankton and nonliving particles.

Mud samples were digested with hot  $HClO_4/HNO_3$  (1 : 3) and analyzed for Zn, Cd, Cu, and Fe by the methods outlined above. Mercury (Hg) in the mud was determined by extraction with hot  $HCl/HNO_3$  (3 : 1) followed by flameless AA performed with a Perkin-Elmer-403 unit. The mud was analyzed for org. C and N by Carlo-Erba CHN analyzer, and for sulfur (S) by a LECO induction furnace with an automatic titrator. For estimation of sulfide-sulfur ( $S^{2-}$ ), the mud was digested with hot HCl (Berner, 1964) and the expelled  $H_2S$  was trapped in NaOH solution and determined by measurement of the UV absorption maximum for sulfide at 228  $m\mu$  (Armstrong, 1975), which was recorded with a Cary-14 spectrophotometer. "Free  $S^{2-}$ " was estimated by digestion of fresh, wet mud with 0.1N HCl for 10 min, and "metal-bound  $S^{2-}$ " was estimated by digestion of freeze-dried mud with 6N HCl for 30 min.  $Na_2S$  was used as a standard and was carried through the same procedure as the samples. "Free  $S^{2-}$ " probably included some  $S^{2-}$  liberated from relatively labile amorphous metal sulfides, and "metal-bound  $S^{2-}$ " might have included some  $S^{2-}$  liberated from organic sulfides; despite such limitations, however, the methodology employed was found to be useful for quantitative comparisons and yielded results that correlated with other data.

Metal sulfides were also determined both qualitatively and semiquantitatively by a crystallographic method developed by the author on the basis of known physical properties of inorganic sulfides (Jellinek 1968). Freeze-dried mud was heated for 1 hr at 650°C. under helium in a Lindberg electric furnace to promote crystallization of amorphous sulfides, and x-ray diffraction analysis was performed with a Philips diffractometer employing  $\text{CuK}\alpha$  radiation before and after the heat treatment. The height (intensity) of a selected diffraction peak was then measured to estimate the relative abundance of the crystalline sulfide. Because heating may cause the synthesis of inorganic sulfides from metal complexes of organic sulfide compounds (Saxby 1973), the sulfide crystallized by this method may represent both organic and inorganic sulfides, although it seems likely that the inorganic component is quantitatively more important (Berner 1964). Another possible limitation of this method is that sulfides may be synthesized by reaction of metals with native S during heat treatment (Scott 1974).

In order to assess the effect of sulfide and organic matter on remobilization of metals from bottom sediments, freeze-dried mud samples were extracted with 0.5N HCl, 0.5N NaOH, 0.5N  $\text{CaCl}_2$  at pH 7 (cf. McLaren and Crawford 1973; Gibbs 1973), 25% acetic acid (HAc) (Loring and Rantala 1977), and benzene/methanol (1 : 1), and with a Webcell-E electrodialyzer (cf. Kemp and Murdochova 1971); the extracts were then wet ashed and analyzed for Zn, Cd, Cu, and Fe. The solvent extractions were performed for 1 hr in a mechanical shaker, using 0.5 g of mud suspended in 18 ml of solvent, and the extracts were Millipore filtered (0.45  $\mu\text{m}$ ), or centrifuged in the case of the benzene/methanol extracts, prior to analysis. Electrodialysis, which yielded separate cation and anion fractions of sufficiently low molecular size to pass through the dialysis membranes, was performed on 5 g of mud in 500 ml of water at a potential of 50 V and an initial current of 10 A. The extraction was continued until the

current dropped to a low, constant value and the conductivity of the suspension approached one-tenth of its initial value.

All chemical analyses were done in duplicate or triplicate; the values recorded are means (for duplicate runs) and medians (for triplicate runs). All chemical data for mud samples were calculated as micromoles per gram of oven-dried (105°C) mud.

In the evaluation of data plots, regression lines, correlation coefficients (r), and significance probabilities (p) were computed by standard statistical procedures.

Particulate matter from the water was examined microscopically to identify the species of phytoplankton and zooplankton in the net samples.

## Results and Discussion

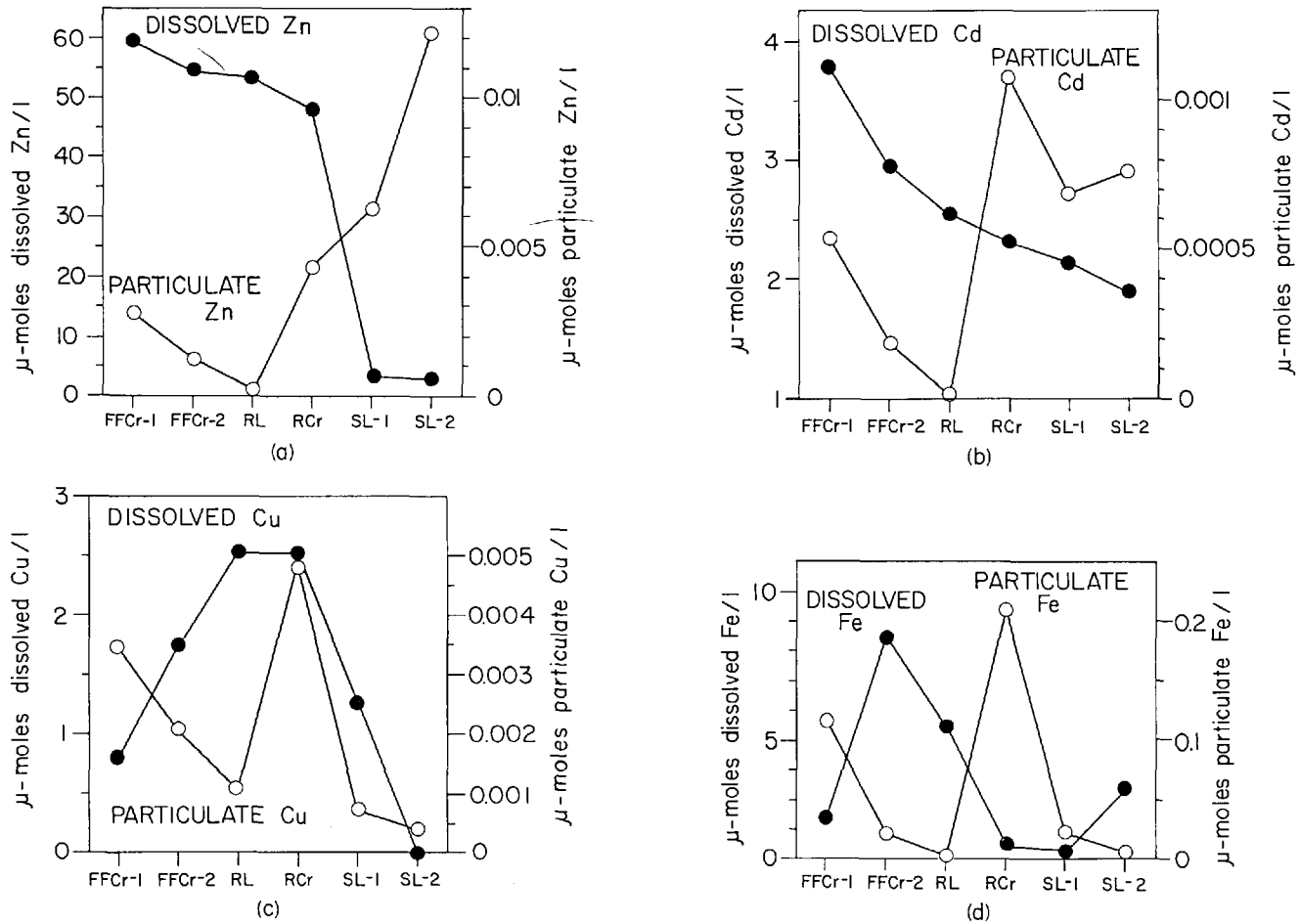
Going downstream from the tailings pond to SL (Fig. 1), the various dissolved and particulate metals in the surface waters show distinctly different patterns of distribution (Fig. 2, Table 1).

Dissolved Zn (Fig. 2a) decreases gradually and progressively downstream as far as the entrance of RCr into SL, presumably owing to dilution, as implied by a corresponding decrease in conductivity (Table 1). As the water enters SL, there is an abrupt and drastic drop in the concentration of dissolved Zn accompanied by a sharp rise in the concentration of particulate Zn. This cannot be accounted for by dilution, and the most plausible explanation appears to be that the plankton in SL accumulate Zn from solution. At both SL sampling sites the sewage outfall from RCr had produced a thick bloom of predominantly green algae, which made up the bulk of the particulate matter, whereas the waters upstream from SL were largely devoid of life (Table 2). Note the increase in pH and dissolved org. C in SL caused by photosynthesis and biologic production, and the corresponding drop in dissolved N and P owing to utilization of these nutrients

Table 1 Chemical Composition of Filtered Water and Suspended Particles, Together with pH and Conductivity of Unfiltered Water\*

Sample	pH	Conductivity ( $\mu\text{mhos/cm}$ )	Filtered water ( $\mu\text{moles/l}$ )								Suspended particles				
			Zn	Cu	Cd	Fe	org. C	N	P	$\text{SO}_4\text{-S}$	g/l	$\mu\text{moles/g}$			
			Zn	Cu	Cd	Fe	org. C	N	P	$\text{SO}_4\text{-S}$	g/l	Zn	Cu	Cd	Fe
FFCr-1	5.20	2,000	59.4	0.79	3.78	1.33	500	36.4	0.639	3,910	0.0130	0.212	0.265	0.0411	9.01
FFCr-2	3.70	2,000	54.4	1.73	2.94	8.47	749	17.2	1.72	3,280	0.0100	0.121	0.205	0.0189	2.14
RL	3.60	1,650	53.4	2.52	2.54	5.43	583	23.6	4.15	2,960	0.00489	0.0810	0.218	0.0026	0.569
RCr	5.30	1,500	48.1	2.52	2.31	0.430	416	30.7	5.59	2,540	0.0143	0.301	0.337	0.0757	14.63
SL-1	8.20	1,300	3.37	1.26	2.14	0.215	1,124	20.0	2.05	3,560	0.0127	0.490	0.0560	0.0539	1.63
SL-2 (epilimnion)	8.60	1,200	2.91	0	1.78	2.36	1,082	21.4	4.83	1,920	0.00796	1.53	0.0487	0.0953	0.819
SL-2 (hypolimnion)	7.25	1,000	10.1	0.79	2.31	0.233	1,207	25.0	7.83	1,620	0.0346	0.409	0.0420	0.0200	0.534
HL	7.20	90	3.52	0	0.178	0.501	916	17.9	11.2	283	0.00484	0.405	0	0	0.997

\*The E<sub>s</sub> of SL-2 water was +925 in the epilimnion but -920 in the hypolimnion.



**Figure 2.** Variation in concentrations of dissolved (●) and particulate (○) Zn (a), Cd (b), Cu (c), and Fe (d) in water, going downstream from FFCr-1 to SL-2.

(Table 1). The relatively high pH of SL water may enhance the uptake of Zn by the particulate matter (O'Connor and Renn 1964). The decrease in dissolved Zn on entering SL is much greater than the increase in particulate Zn, suggesting continuous, rapid removal of particulate Zn by sedimentation. The plankton in SL are apparently able to take up "colloidal" (nondialyzable) Zn (Fig. 3a), but they show a preference for low molecular weight Zn (probably because it can penetrate cell membranes); there is therefore a relative increase in the colloidal fraction of the total dissolved Zn (Fig. 3b). In contrast, the plankton are evidently unable to accumulate colloidal Fe (Fig. 3c).

Another point worth mentioning is that the observed increase in particulate Zn on entering SL cannot be ascribed to nonliving particles of sewage: Although the sewage (RCr) does increase the input of particulate metals into SL (Fig. 2; Table 1), the distribution of particulate Fe (Fig. 2d), which comes chiefly from the

sewage, shows that most of the sewage particles settle out right at the mouth of the stream and do not reach the SL-1 and SL-2 sites.

Cadmium (Fig. 2b) tends to accumulate in SL plankton, but to a much smaller extent than Zn does. Uptake is so minor that there is no discernible decline in the level of dissolved Cd on entering SL other than the slight decline attributable to dilution downstream from the tailings pond. Despite the chemical similarities between Zn and Cd, therefore, the plankton preferentially accumulate Zn. This may be caused by the very high concentration of dissolved Zn relative to dissolved Cd in the water flowing into SL (cf. Knauss and Porter 1954), although biologic selectivity is also a possible explanation (Goldberg 1965, Sparling 1968, Morris 1971, Knauer and Martin 1973, Leland and others 1974, Beveridge and Murray 1976).

Copper (Fig. 2c) behaves differently from either Zn or Cd. From FFCr-1 to RL, dissolved Cu increases at the expense of the

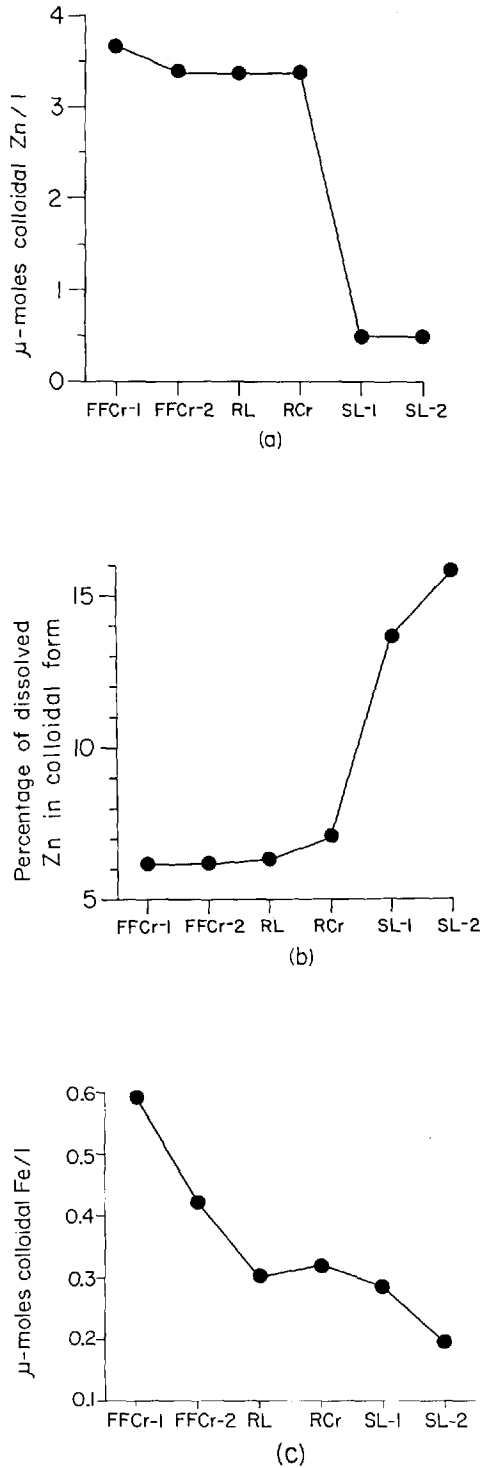


Figure 3. Variation in (a) concentration of colloidal dissolved Zn, (b) percentage of dissolved Zn in colloidal form, and (c) concentration of colloidal dissolved Fe in water, going downstream from FFCr-1 to SL-2.

Table 2 Description of Living and Nonliving Suspended Particulate Matter in Water Samples, Based on Microscopic Examination

Sample	Description of particulate matter	
FFCr-1	Irregular, brownish-yellow nonliving particles	
FFCr-2		Yellowish and colorless non-living particles
RL		Mostly irregular, pale yellow nonliving particles; very sparse plankton population Plankton species present: Chlorophytes: <i>Microthamnion</i> sp. (dominant algal species), <i>Mougotia</i> sp., <i>Scenedesmus acuminatus</i> ; Diatoms: <i>Nitzschia</i> sp.; Others: rotifers and ciliates.
RCr	Mostly irregular, pale yellow nonliving particles (+ bacteria?); no algae were seen	
SL-1	Abundant unicellular green algae together with a fair number of irregular, yellowish nonliving particles Plankton species present: Chlorophytes: The dominant algal species were <i>Golenkinia radiata</i> , <i>Golenkiniopsis parvula</i> , and <i>Scenedesmus acuminatus</i> (all equally abundant); Other chlorophytes: <i>Chlorella vulgaris</i> , <i>Gloeotilia pulchra</i> , <i>Scenedesmus quadricauda</i> , <i>Monoraphidium contortum</i> ; Euglenophyta: <i>Euglena</i> sp.; Diatoms: <i>Asterionella formosa</i> fa. <i>gracillima</i> ; note: no blue-green algae were seen; Zooplankton: <i>Diaptomus</i> sp.; <i>Cyclops bicuspidatus thomasi</i> (S. A. Forbes); <i>Vorticella</i> sp.	
SL-2 (epilimnion)	Similar to SL-1	
SL-2 (hypolimnion)	Brownish nonliving particles plus a few moribund algae; some bacteria and occasional fungi and actinomycetes	
HL	Fair amount of phytoplankton plus nonliving particles Plankton species present: The dominant algal species were the diatoms <i>Tabellaria flocculosa</i> and <i>T. intermedia</i> (in terms of biomass), <i>Synedia acus</i> , and <i>Nitzschia acicularis</i> (in terms of numbers), and the chlorophyte <i>Monoraphidium setiforme</i> (in terms of numbers); Other chlorophytes: <i>Scenedesmus denticulatus</i> , <i>Tetraedron minimum</i> var. <i>tetralobulum</i> , <i>T. limneticum</i> , <i>Coccolathium cambricum</i> , <i>C. microporum</i> , <i>Dictyosphaerium pulchellum</i> , <i>Ankistrodesmus gracilis</i> , <i>Planctosphaeria gelatinosa</i> ; Cyanophyta: <i>Oscillatoria</i> sp., <i>Aphanizomenon flos-aquae</i> fa. <i>gracilis</i> ; Chrysophyceae: <i>Mallomonas pseudocoronata</i> , <i>Dinobryon sociale</i> , <i>Ochromonas</i> sp., <i>Rhizochrysis limneticus</i> ; Heterokonta: <i>Gloeolotryx limneticus</i> , <i>Botryococcus braunii</i> ; Peridinea: <i>Gymnodinium</i> sp.; Zooplankton: <i>Bosmina longirostris</i> (O. F. Müller), <i>Chydorus sphaericus</i> (O. F. Müller), <i>Diaptomus oregonensis</i> (Lilljeborg), <i>Tropocyclops prasinus mexicanus</i> (Kiefer), <i>Cyclops bicuspidatus thomasi</i> (S. A. Forbes) (the latter made up >95% of the >73 µm zooplankton population)	

(nonliving) particulate Cu, probably owing to dissolution caused by a drop in pH (Table 1), which can be explained by oxidation of sulfide minerals (Rowley 1975) as indicated by the high SO<sub>4</sub> content of the water (Table 1). In water entering SL, there is a sharp decline in both dissolved and particulate Cu, suggesting that dissolved Cu is scavenged by particulate matter in the sewage and is rapidly sedimented along with particulate Fe (Fig. 2d) at the mouth of RCr, so that relatively little Cu gets out into the lake. The high pH of SL water may tend to enhance this process (Payne and Pickering 1975).

The highest concentration of dissolved Fe (Fig. 2d) was found at station FFCr-2, where FFCr passes through the marsh. At this locality there is also a maximum in the distribution of dissolved org. C (Table 1), suggesting that the Fe is in the form of organic, probably humic, complexes (Shapiro 1964, 1967, Lamar 1968, Reuter and Perdue 1977) leached out of the bottom mud. None of the other metals shows a maximum at FFCr-2, implying preferential complexing and remobilizing of Fe (cf. Schnitzer 1969).

In both SL-1 and HL surface waters, the >10 μm plankton had higher concentrations of Zn, Cu, and Cd than the >73 μm plankton (Fig. 4, Table 3). We may tentatively infer that the phytoplankton, which are concentrated in the >10 μm fraction, have greater metal-accumulating capabilities than the zooplankton, which are the main components of the >73 μm fraction. If we take the ratio of metal concentration in >10 μm plankton to metal concentration in >73 μm plankton as an index of the enrichment of phytoplankton relative to zooplankton, we find that for Zn the enrichment index is 7.51 in SL-1 but only 2.57 in HL. The enrichment index for Cu, however, is 5.14 in HL but only 3.89 in SL-1. These differences may be related to observed differences in the species composition of SL-1 and HL plankton (Table 2). For Cd, the enrichment index is lower than for Zn or Cu in both SL-1 and HL and is nearly the same in both lakes: 1.22 for SL-1 and 1.28 for HL. Evidently species preferences were of minor importance in the accumulation of Cd by plankton in these lakes.

At station SL-2, epilimnion particulate matter was richer in heavy metals than hypolimnion particulate matter (Fig. 5a, Table 1), suggesting that metals were partially resolubilized from the remains of dead algae sinking to the bottom. Comparison of

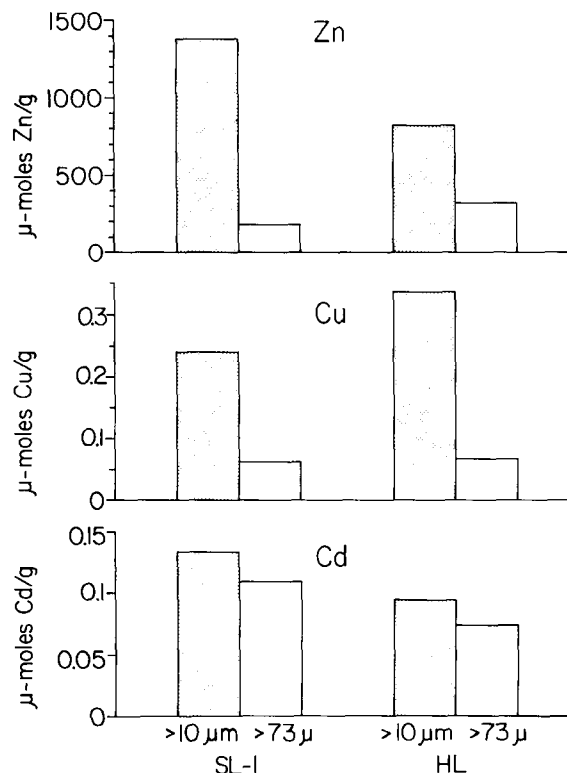


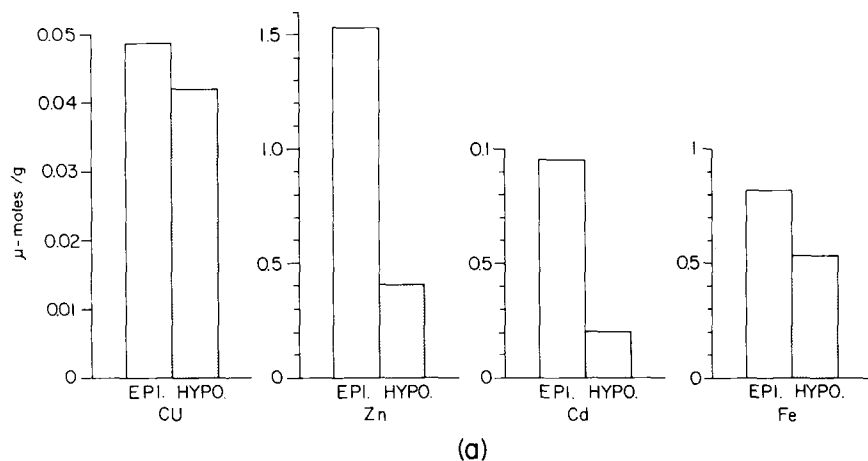
Figure 4. Zn, Cu, and Cd content of >10 μm plankton (gray bars) and >73 μm plankton (white bars) in surface water from SL-1 and HL.

Table 3 Zn, Cd, and Cu Content of >10 μm and >73 μm plankton from SL-1 and HL Surface Water

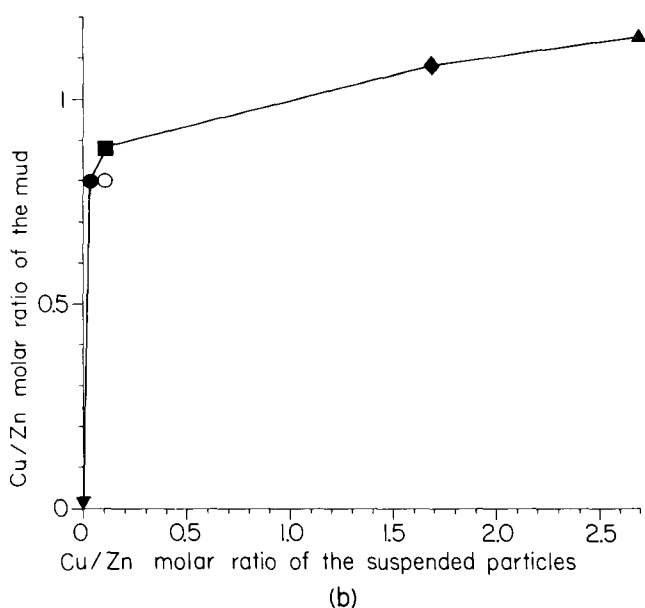
Sample	Size fraction (μm)	g/l	μmoles/g		
			Zn	Cd	Cu
SL-1	>10	0.00091	1,381	0.134	0.237
	>73	0.00058	184	0.110	0.0609
HL	>10	0.00015	820	0.0953	0.337
	>73	0.00013	319	0.0741	0.0656

values for the ratio of metal concentration in epilimnion seston to concentration of the same metal in hypolimnion seston showed that the seston retained Cu preferentially with respect to Zn, Cd, and Fe as it settled out, the order of decreasing retention being Cu > Fe > Zn > Cd.\* Therefore, seston reaching the bottom is enriched in Cu and may foster Cu enrichment of bottom mud. Nevertheless, the Cu/Zn ratio of bottom sediment varies as a function of the Cu/Zn ratio of suspended particles in the overlying surface waters, and differentiation during settling does not seem to make much difference (Fig. 5b), possibly because the waters are so shallow. This apparently demonstrates that the heavy-metal composition of bottom sediment may reflect to a considerable degree the heavy-metal composition of the particulate matter in the overlying water column. However, the data are also consistent with the theories of Hallberg (1972) concerning the influence of redox conditions and the interplay of sulfide and organic complexing agents on the Cu/Zn ratio of bottom sediments. Thus, the FFCr-2, RL, SL-1, and SL-2 muds, which are

\*The order of decreasing electronegativities of the metals is similar (Cu > Fe > Zn = Cd), suggesting that covalent bonding promotes retention of metals by the particulate matter.



(a)



(b)

**Figure 5.** (a) The Cu, Zn, Cd, and Fe content of particulate matter in epilimnion water (white bars) and hypolimnion water (grey bars) from SL-2. (b) The relationship between the Cu/Zn molar ratio of bottom mud and Cu/Zn molar ratio of suspended particles in the overlying surface water (and hypolimnion water included for comparison). Explanation of symbols: ♦, FFCr-2; ▲, RL; ■, SL-1; ●, SL-2 (epilimnion); ◊, SL-2 (hypolimnion); ▼, HL.

highly reducing and contain ample sulfide, have Cu/Zn ratios close to unity (0.796–1.15), whereas the HL mud, which has little or no sulfide, has a Cu/Zn ratio of only 0.0145 (Table 4). In any case, a considerable amount of preferential mobilization or immobilization of metals in bottom sediments or in the water column is necessary to explain the high Cu/Zn values of mud compared with suspended particulate matter at SL-1 and SL-2 (Fig. 5b), unless Cu-enriched particles from the sewage are being transported there along the lake bottom by currents.

The distribution of free  $S^{2-}$  in bottom sediment going downstream from FFCr-2 to SL-2 (Fig. 6a, Table 4) demonstrates that production of algal blooms by sewage effluent followed by decomposition of dead algae sinking to the bottom is an extremely effective means of generating  $H_2S$ , the concentration of free  $S^{2-}$  being about 100 times greater in SL-1 or SL-2 mud than in FFCr-2 or RL mud. Most of the  $H_2S$  in FFCr-2 and RL mud is

probably generated by bacterial reduction of  $SO_4$  (Table 1) derived from acid mine drainage (Rowley 1975), but the rate of  $H_2S$  production is doubtless limited by low availability of degradable organic matter. In SL the high levels of biologic production combined with an abundant supply of  $SO_4$  (Table 1) may well support luxuriant growth of  $SO_4$ -reducing bacteria (Zajic 1969) as well as bacteria that release  $H_2S$  by putrefaction of proteins. The effectiveness of  $H_2S$  (or, at least, of reducing conditions) in trapping metals may be judged by comparing the distribution patterns of free and metal-bound  $S^{2-}$  (Fig. 6a). Although the two curves have essentially the same shape, the curve for bound  $S^{2-}$  has been flattened out, probably by a tendency of metals to be immobilized in sediments upstream from SL. The unexpectedly high free- $S^{2-}$  values obtained for HL mud might have been an artifact, as suggested by the fact that the mud was odorless and relatively light colored.

Table 4 Chemical Data for the Mud Samples

Sample	pH	E <sub>h</sub> (mV)	μmoles/g (oven-dry weight)								"Free" S <sup>2-</sup>	"Bound" S <sup>2-</sup>	I <sup>220</sup> of ZnS
			Zn	Cu	Cd	Hg	Fe	org. C	N	S			
FFCr-2	5.90	-890	203	219	23.7	0.00643	238	10,100	689	493	14.4	75.6	62.1
RL	6.50	-610	210	241	23.9	0.00442	238	8,150	563	2,975	13.7	57.4	32.8
SL-1	6.80	-570	295	260	37.9	0.00894	339	11,200	986	2,945	773	100	76.3
SL-2	6.75	-565	315	251	32.4	0.00579	341	15,400	1,510	4,229	1,390	105	61.0
HL	6.40	-690	69.3	4.90	1.11	0.00045	268	29,700	2,160	479	34.5	8.61	0

The distributions of Zn, Cd, Cu, Hg, Fe, sulfide, org. C, and N in bottom sediments going downstream from FFCr-2 to SL-2 (Fig. 6b, Table 4) all tend to fit the same general pattern, rising from lower values in FFCr-2 and RL to maximum values in SL-1 or SL-2. Not surprisingly, then, the greatest accumulation of metals occurs in sediments that are richest in organic matter and H<sub>2</sub>S. All the metals are more strongly correlated with bound S<sup>2-</sup>

than with org. C (Table 5), but the concentrations of bound S<sup>2-</sup> are too low to account for all of the sedimentary metals except in the case of Hg and Cd (Table 4). Therefore, the metals must be partitioned to varying degrees between inorganic sulfide and organic matter. Other metal-binding agents, such as clay minerals and Fe oxyhydroxides, are probably unimportant. No clay minerals were detected by x-ray diffraction (quartz being the main

Figure 6. Variation in the composition of bottom mud going downstream from FFCr-2 to SL-2. (a) Comparison between "free" sulfide (●) and "metal-bound" sulfide (○) content. (b) Concentrations of metals, organic carbon, nitrogen, "metal-bound" sulfide (○) content. (b) Concentrations of metals, organic carbon, nitrogen, "metal-bound" sulfide, and ZnS as estimated by intensity of 220 diffraction peak after heat treatment.

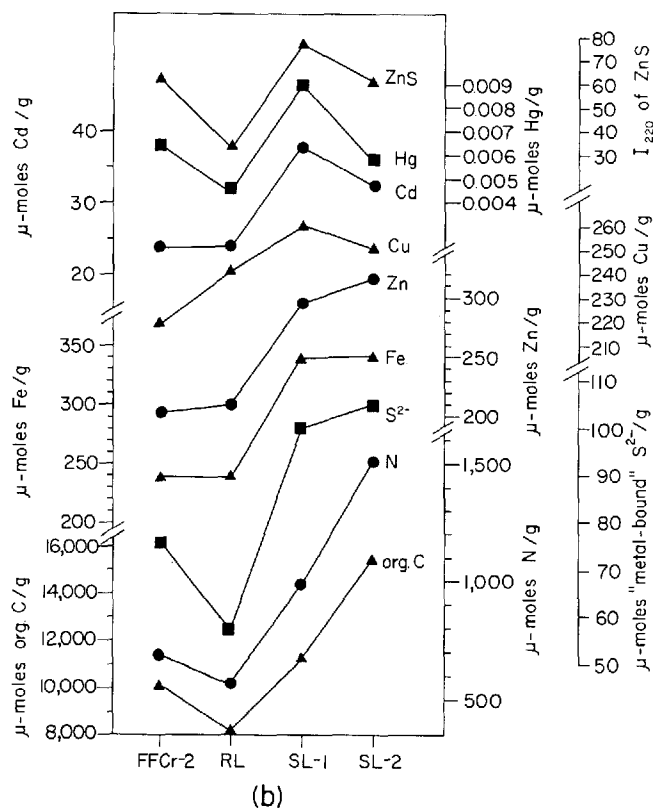
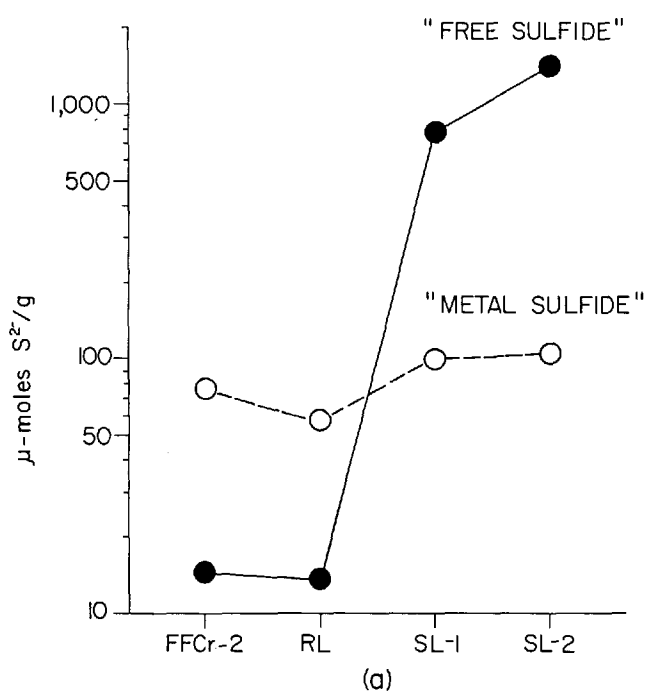




Table 5 Correlation Matrix Representing Degree of Association of Heavy Metals with Metal-Bound  $S^{2-}$ , Crystallized ZnS (as Estimated by  $I_{220}$  Value), and org. C in FFCr-2, RL, SL-1, and SL-2 Mud\*

	$S^{2-}$	ZnS	org. C
Cu	0.593	0.298	0.408
Zn	0.923	0.583	0.844
Cd	0.853	0.739	0.560
Hg	0.638	0.915	0.198
Fe	0.939	0.667	0.795

\*The numbers in the body of the table are correlation coefficients.

detrital mineral) except for some unidentified clay with d spacings of  $\sim 7.69$ – $7.89$  Å and  $\sim 11.3$  Å in SL-1 and SL-2 mud. In any case, we would not expect heavy metals to remain adsorbed to clay and FeOOH in the presence of excess free  $S^{2-}$  (Miller 1950, Weiss and Amstutz 1966, Rickard 1974), whereas organic chelators may compete with  $S^{2-}$  for heavy metals (Eichorn 1956, Hallberg 1972, Rashid and Leonard 1973, Pauli 1975).

The extent to which each metal is partitioned among the inorganic sulfide phase, organic complexes, and other possible forms is difficult to determine in absolute terms; nevertheless, it can be expressed semiquantitatively with the aid of correlation coefficients, and this approach yielded some interesting results. To estimate the affinity of each metal for  $S^{2-}$  relative to organic complexing agents in the FFCr-2, RL, SL-1, and SL-2 sediments, the correlation coefficient representing the association of metal with  $S^{2-}$  ( $r_{S^{2-}}$ ) was normalized with respect to the correlation coefficient for the association of metal with org. C ( $r_{orgC}$ ). When this was done, a startling relationship was discovered (Fig. 7): For all metals, the values of the  $r_{S^{2-}}/r_{orgC}$  ratio show a highly significant positive correlation with the standard entropy ( $S_{298}^{\circ}$ ) values recorded by Mills (1974) for the inorganic sulfides of these metals at 298.15°K (25°C) (for a log–log plot,  $r = 0.993$ ;  $p < 0.001$ ). This not only testifies to the validity of the  $r_{S^{2-}}/r_{orgC}$  ratio as an index of metal partitioning between sulfide and organic matter but also reveals that the partitioning is strongly dependent on the stability of the inorganic metal sulfide, as predicted by thermodynamic calculations (cf. Timperley and Allan 1974). The data indicate that in the bodies of water investigated the proportion of sulfide-bound metal relative to organically bound metal decreases in the order  $Hg > Cd > Cu > Fe > Zn$ .

x-Ray diffraction analysis of heated mud from FFCr-2, RL, SL-1, and SL-2, but not from the sulfide-poor HL mud, yielded sharp, intense peaks for d spacings of 3.13, 1.91, and 1.63 Å, in that order of decreasing relative intensity (Fig. 8). On the basis of both peak position and relative intensity, these peaks may be assigned to sphalerite (ZnS). Unheated mud samples gave only relatively small, broad sphalerite peaks (Fig. 8). We may con-

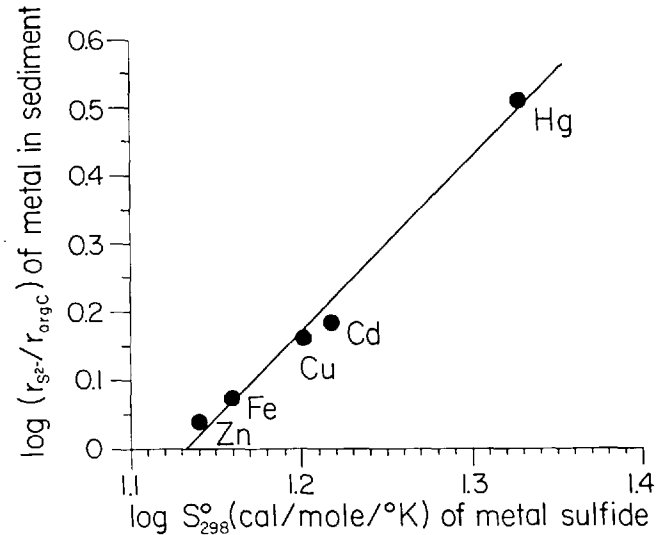
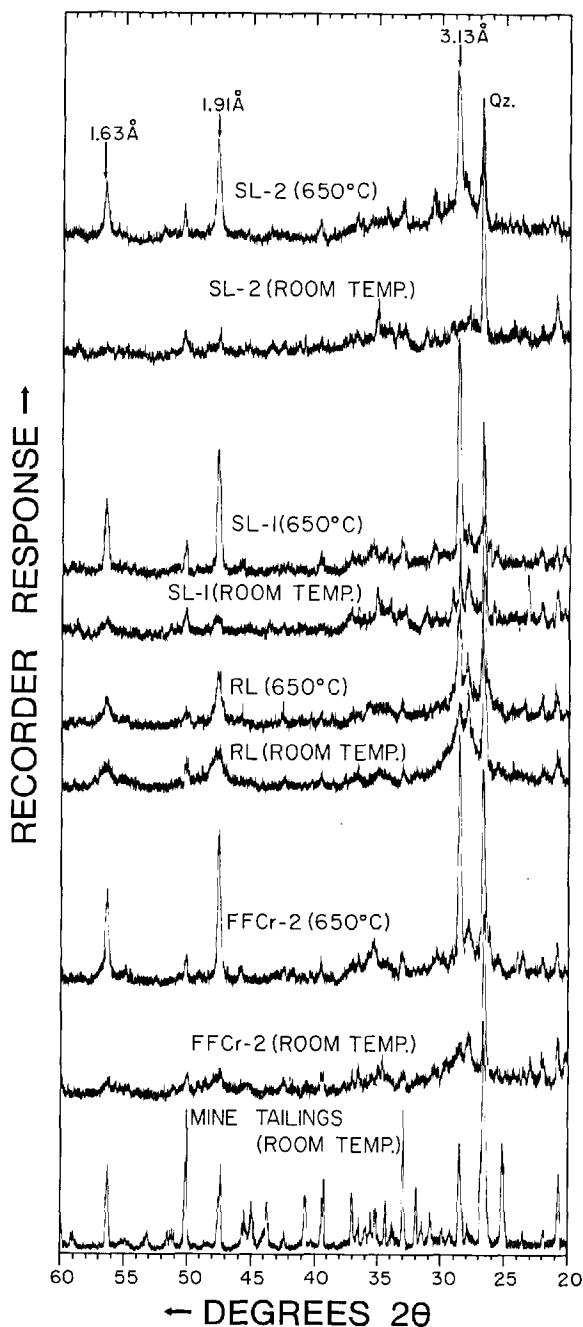


Figure 7. Affinity of each heavy metal for sulfide relative to its affinity for organic matter (as estimated by a ratio of correlation coefficients,  $r_{S^{2-}}/r_{orgC}$ ) in FFCr-2, RL, SL-1, and SL-2 mud plotted against the standard entropy ( $S^{\circ}$ ) of the inorganic metal sulfide.

clude, provisionally, that amorphous to poorly crystallized ZnS is an important constituent of all four muds and that heat treatment greatly improves its crystallinity, thereby making it more readily detectable. No other sulfides were detected, except for traces of pyrite suggested by small reflections at  $\sim 33^{\circ}$  and  $\sim 37^{\circ}$   $2\theta$ .

Relative abundance of ZnS in mud was estimated by measuring the intensity ( $I_{220}$ ) of the (220) reflection of sphalerite at 1.91 Å after heat treatment. Intensity ( $I_{220}$ ) was found to correlate significantly with total metal-bound  $S^{2-}$  content (Table 4) (for a linear plot,  $r = 0.953$ ;  $p = 0.01$ – $0.02$ ). This is consistent with the hypothesis that the sphalerite was formed from a preexisting sulfide precipitate and confirms the usefulness of the method for quantitative analysis. Partial loss of organic matter by pyrolysis probably enhanced the peak intensities by causing the inorganic residue to be more highly concentrated, as indicated by the observation that heat treatment produced an approximately 10-fold increase in total Zn concentration accompanied by a 40–67% loss of org. C. However, the use of peak intensities seems to be valid for quantitative comparison of different samples, provided the experimental conditions are uniform.

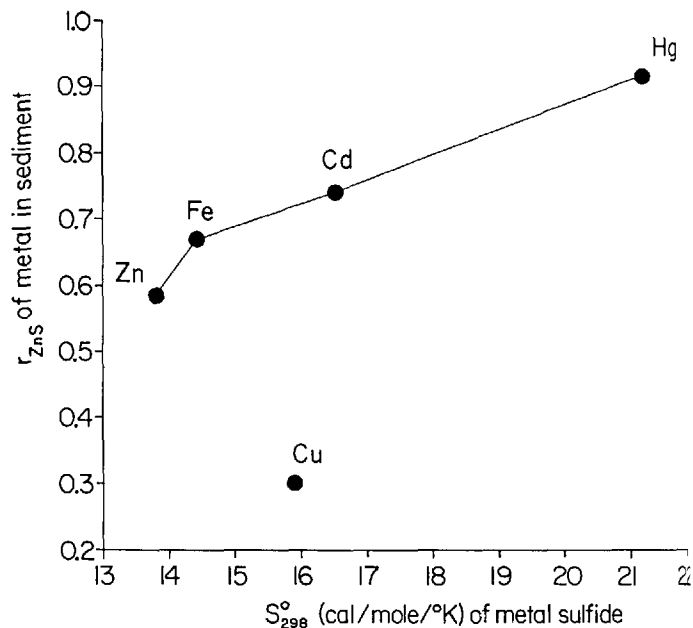
The degree of correlation ( $r_{ZnS}$ ) between ZnS abundance (estimated by  $I_{220}$ ) and the Zn, Cd, Hg, and Fe content of the mud (Table 4 and 5) varies with the standard entropy ( $S_{298}^{\circ}$ ) of the metal sulfide (Fig. 9). This relationship can be explained by isomorphous substitution of Hg, Cd, and Fe for Zn in the sphalerite (Deer and others 1962). The precursor of the sphalerite was probably a coprecipitated mixture of colloidal ZnS, HgS, CdS, and FeS. Note that Cu, which is excluded from the sphalerite



**Figure 8.** X-Ray diffraction patterns of FFCr-2, RL, SL-1, and SL-2 mud before and after being heated at 650°C under helium. Pattern for tailings-pond sediment (unheated) is shown for comparison.

structure (Deer and others 1962), does not fall on the curve with the other metals (Fig. 9).

In view of the striking x-ray data obtained for ZnS, the absence of crystalline Cu sulfide in heated mud samples was unexpected, for the concentrations of Cu in the mud are compa-



**Figure 9.** Degree of correlation ( $r_{ZnS}$ ) between metal concentration and ZnS concentration (estimated by (220) diffraction peak intensity after heat treatment) in FFCr-2, RL, SL-1, and SL-2 mud samples plotted against the standard entropy of the metal sulfide.

table to those of Zn, and  $S^{2-}$  has an even stronger affinity for Cu than for Zn. Chelating agents may have inhibited the precipitation of CuS by preferentially sequestering Cu (Mellor and Maley 1947, 1948, Irving and Williams 1953, Eichorn 1956, Schnitzer 1968, 1969, Hallberg 1972, Pauli 1973, Rashid and Leonard 1973, Rashid 1974, Stevenson 1977) but this possibility is inconsistent with the observation that in the plot of  $r_{S^{2-}}/r_{ORG}$  ratio against  $S_{298}^0$  (Fig. 7) Cu falls on the same curve as the other metals. The most likely explanation for the absence of an x-ray pattern for Cu sulfide would seem to be that impurities—possibly organic metal-binding agents, such as cyanide (Rowley 1975)—interfered with the crystallization of amorphous CuS. The absence of x-ray patterns for CdS and HgS, however, can be attributed to the low concentrations of Cd and Hg in the muds.

The x-ray pattern of a sample of mine tailings (Fig. 8) showed that the x-ray data for FFCr-2, RL, SL-1, and SL-2 mud could not be dismissed as artifacts arising from contamination of the mud by primary sulfide minerals from the ore deposit eroded or accidentally spilled into the bodies of water investigated. In contrast to the unheated mud samples, the unheated mine tailings gave sharp, slender sphalerite peaks, indicating well-crystallized material. Moreover, the tailings contained considerable concentrations of pyrite, pyrrhotite, and chalcopyrite, whereas these minerals were undetectable or (in the case of pyrite) barely detectable in the mud samples even after heat treatment.

Extracts of mud samples (Table 6) yield evidence that sulfide is a highly effective agent for immobilization of heavy metals.

Table 6 Percentages of Total Zn, Cd, Cu, and Fe Extracted from the Mud Samples by 0.5N HCl, 0.5N NaOH, 0.5N CaCl<sub>2</sub>, 25% HAc, and Benzene/Methanol (1 : 1) and Extracted as Cations (+) and Anions (-) by Electrodialysis

Extract	Metal	% extracted from sample indicated				
		FFCr-2	RL	SL-1	SL-2	HL
CaCl <sub>2</sub>	Zn	18.8	17.6	13.2	13.3	58.7
	Cd	24.0	5.44	10.3	22.1	91.0
	Cu	0.316	0.168	0.182	0.474	12.0
	Fe	0.664	0.966	0.416	0.396	1.25
HAc	Zn	18.1	17.3	13.5	13.8	65.5
	Cd	45.6	3.99	18.5	45.7	1.79
	Cu	8.36	0.0838	0.908	2.22	34.1
	Fe	22.4	22.9	17.4	19.1	8.17
HCl	Zn	17.7	16.6	12.4	13.1	59.9
	Cd	43.0	10.8	30.3	43.5	20.5
	Cu	15.2	2.97	8.23	18.0	94.7
	Fe	21.5	21.3	16.2	17.3	22.0
NaOH	Zn	15.8	14.9	11.6	11.9	46.3
	Cd	4.14	1.92	1.31	1.87	20.4
	Cu	7.90	4.49	5.62	8.45	18.2
	Fe	6.14	5.34	1.15	0.848	0.949
Electrodialysis (cations)	Zn	0.0059	0.281	0.24	0.0035	0.013
	Cd	0	0.063	0	0	0.90
	Cu	0.019	0.0685	0.0492	0.031	1.1
	Fe	1.49	3.32	2.33	1.91	0.948
Electrodialysis (anions)	Zn	0.431	1.40	0.226	0.711	1.13
	Cd	0.034	0.063	0.021	0.043	1.8
	Cu	0.0064	0	0.0085	0.0064	0
	Fe	0	0.00042	0	0.00088	0.00037
Benzene/ Methanol	Zn	2.57	4.24	3.34	3.37	2.15
	Cd	0.561	0.331	2.14	1.00	0.450
	Cu	0.103	0.0770	0.0387	0.0310	1.37

The relative effectiveness of sulfide and organic matter in the immobilization of these metals can be judged by comparing data from HL mud, which had the lowest S<sup>2-</sup> content but the highest org. C content, with mud data from FFCr-2, RL, SL-1, and SL-2, which have higher S<sup>2-</sup> concentrations but less org. C (Fig. 10a, Table 4).

When muds were extracted with HCl, HAc, NaOH, and CaCl<sub>2</sub>, it was found that Zn and Cu were much more readily dissolved from the S<sup>2-</sup>-poor HL mud than from the S<sup>2-</sup>-rich FFCr-2, RL, SL-1, and SL-2 muds (Fig. 10b, Table 6). Evidently S<sup>2-</sup>, or S<sup>2-</sup> together with organic matter, is more effective than organic matter alone in preventing remobilization of these met-

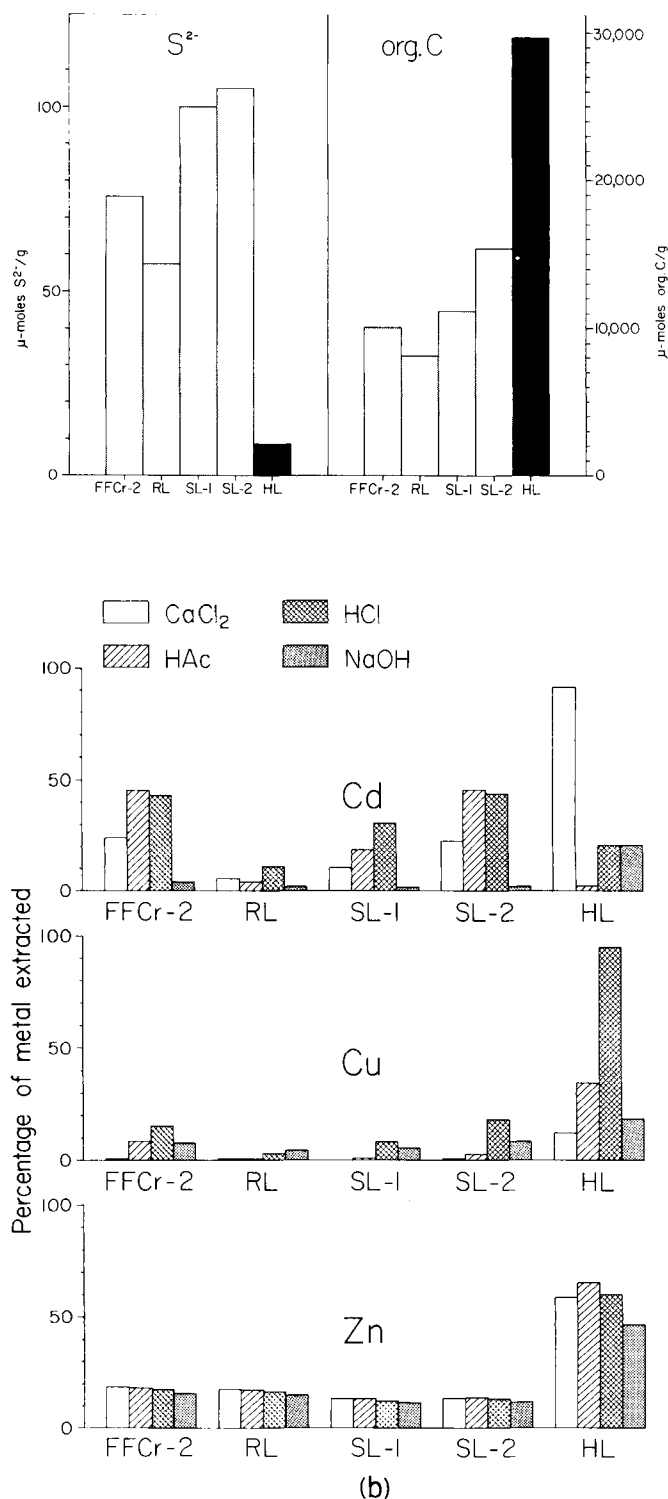
als. In general, Cu was less readily dissolved than Zn, and the difference between the immobilizing effects of the S<sup>2-</sup>-rich and S<sup>2-</sup>-poor environments tended to be more pronounced for Cu than for Zn, especially when the milder extractants (CaCl<sub>2</sub> and HAc) were used. This, together with the preferential retention of Cu by decomposing seston (Fig. 5a, Table 1), may account for the high Cu/Zn ratios in the S<sup>2-</sup>-rich muds (Table 4). In the case of Zn, all four extractants gave remarkably similar results, possibly indicating that all of the solvent-extractable Zn was in the form of loosely sorbed species or was dissolved in interstitial water. (Otherwise we would not expect such a mild reagent as CaCl<sub>2</sub> to dissolve nearly the same quantity of Zn as an aggressive

reagent, such as HCl or NaOH). The percentages of Cu extracted with the different solvents showed greater variability, suggesting that Cu was held by a wider range of binding sites representing a considerable range of binding energies. Cadmium, like Zn and Cu, was more readily extracted from HL mud than from the other muds with  $\text{CaCl}_2$  and NaOH, but the reverse was true for HCl and HAc. The reason for this anomaly is not clear, but a possible explanation is preferential binding of Cd by acid-insoluble organics, such as humic acid, in HL mud.

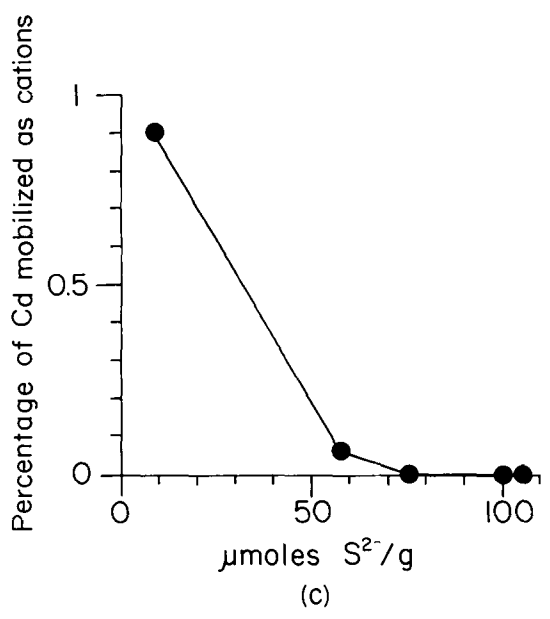
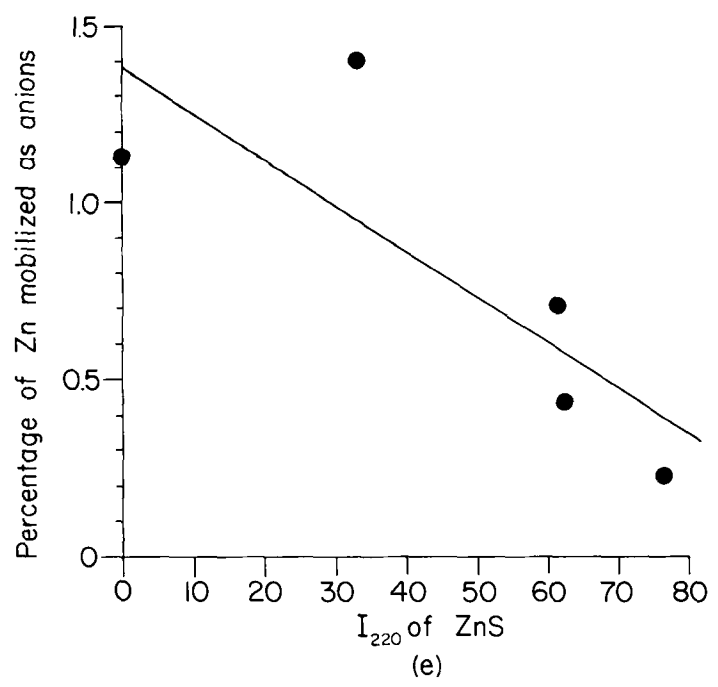
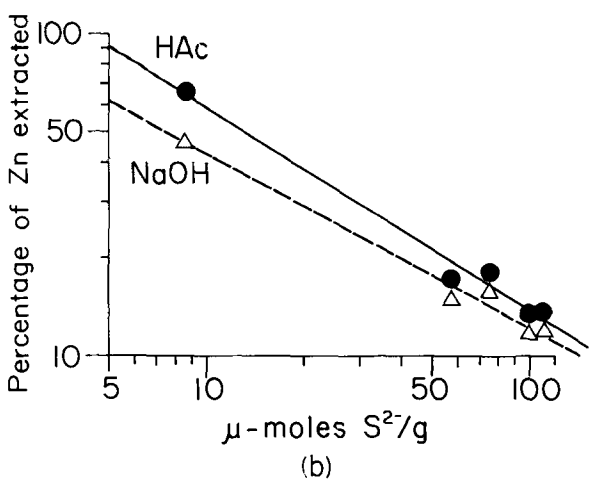
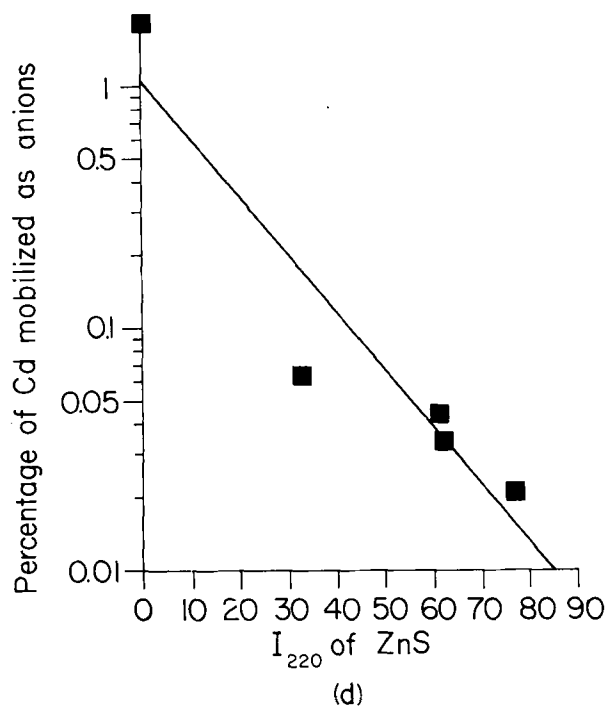
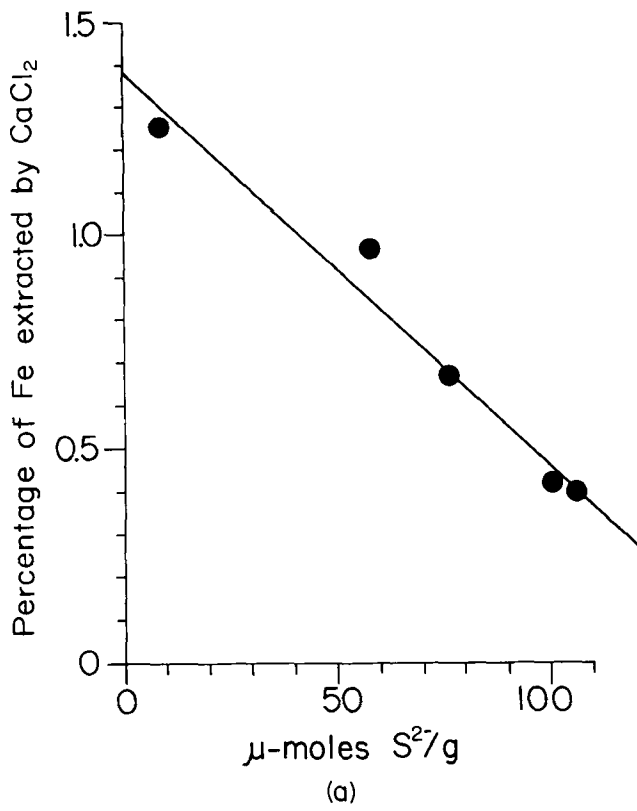
The extractability of Zn from mud by acids, alkali, and  $\text{CaCl}_2$  showed a strong negative correlation with the metal-bound  $\text{S}^{2-}$  content of the mud, and comparable results were obtained for  $\text{CaCl}_2$ -extractable Fe, for anionic species of electro-dialyzable Zn, and for both cationic and anionic species of electro-dialyzable Cd (Fig. 11, a-e). These results can be explained in part by the strong affinity of  $\text{S}^{2-}$  ions for heavy metals and by the very low solubility of the sulfides. However, considering the solubility of ZnS in acid, it was puzzling that HCl and HAc did not dissolve appreciably more Zn than  $\text{CaCl}_2$  did from the  $\text{S}^{2-}$ -bearing muds (Fig. 10b, Table 6). Possibly the ZnS is "protected" by surface coatings and impurities, such as organic compounds (Berner 1964); conversely, organic complexes of metals may be rendered insoluble because they are fixed to ZnS or other sulfides.

Extraction of mud samples yields evidence that certain complexing agents in the mud have preferential affinity for Cu relative to Zn and Cd, or for Zn and Cd relative to Cu, and may form stable, soluble complexes of these metals even in the presence of free sulfide. For example, the extractability of anionic Cu by electro-dialysis actually increases with increasing  $\text{S}^{2-}$  concentration (Fig. 12a, Table 6) and therefore varies inversely with the extractability of anionic Zn and Cd (Figs. 11d, e, and 12b). The observed effect can be tentatively ascribed to an unidentified, low molecular weight, negatively charged complexing agent that is most abundant in the more highly reducing,  $\text{S}^{2-}$ -rich muds and binds Cu preferentially with respect to Zn and Cd. Electro-dialyzable cationic species of Cu, Zn, and Cd, in contrast, showed essentially similar patterns of intersample variation (Table 6), indicating that the cation exchange sites of the mud do not discriminate effectively between the three metals. In contrast to the results obtained for electro-dialyzable anions, the data for benzene/methanol-extractable metals showed decreasing Cu solubilization but increasing Zn and Cd solubilization with increasing  $\text{S}^{2-}$  concentration (Fig. 13, Table 6). Evidently reducing conditions favor production of a lipophilic complexing agent that binds Zn and Cd preferentially with respect to Cu. The similar behavior of Zn and Cd reflects the fact that these two metals belong to the same family of the periodic table and hence are chemically similar.

There are other indications that some complexing agents in mud can bind heavy metals even in the presence of free sulfide. Despite the high concentrations of free  $\text{S}^{2-}$  in SL mud, stoichiometric considerations show that only about 11%, at most, of the heavy metal atoms can be in the form of sulfides (Table 4). Furthermore, the solubility of sediment-bound Cu appears to be controlled by organic matter rather than sulfide. The percentage of Cu extracted by HCl, HAc, NaOH, or  $\text{CaCl}_2$  increases with



**Figure 10.** (a) Total "metal-bound" sulfide and organic carbon content of FFCr-2, RL, SL-1, and HL mud. (b) Percentages of the total Zn, Cd, and Cu extracted from the mud samples by 0.5N HCl, NaOH, and  $\text{CaCl}_2$ , and 25% HAc.



**Figure 11.** Percentages of Zn, Cd, and Fe liberated from FFCr-2, RL, SL-1, SL-2, and HL mud by solvent extraction and electro dialysis plotted against total "metal-bound" sulfide (S<sup>2-</sup>) or ZnS diffraction peak intensity (I<sub>220</sub>) (measured after heat treatment). (a) 0.5N CaCl<sub>2</sub>-extractable Fe vs. S<sup>2-</sup>, (b) 25% HAc (●) and 0.5N NaOH (Δ) extractable Zn vs. S<sup>2-</sup>, (c) electro dialyzable cationic Cd vs. S<sup>2-</sup>; (d) electro dialyzable anionic Cd vs. I<sub>220</sub> of ZnS; (e) electro dialyzable anionic Zn vs. I<sub>220</sub> of ZnS.

increasing org. C (Fig. 14), suggesting that the degree of remobilization of Cu depends on the concentration of soluble organic complexing agents in the mud.

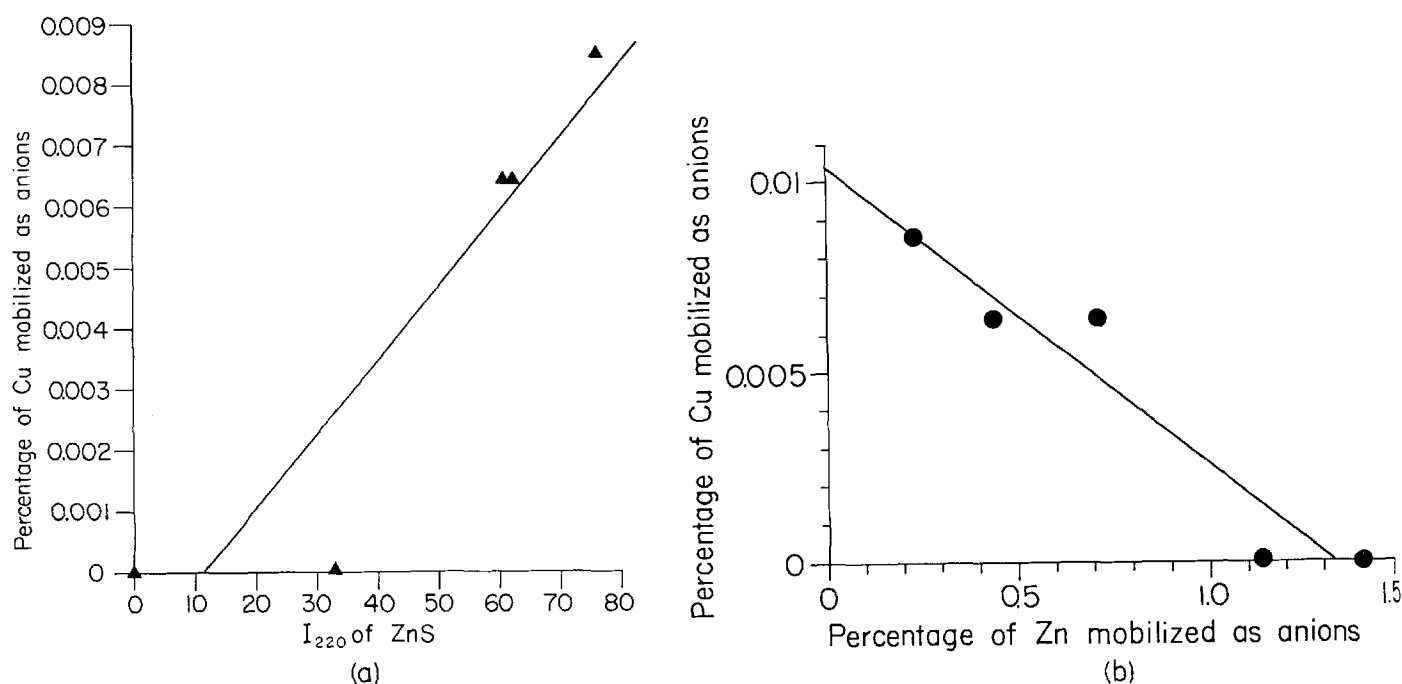
These results demonstrate that complexing agents may to some extent cause release of heavy metal from sulfide-rich muds into the overlying water despite the strong tendency of these metals to precipitate as highly insoluble sulfides. The solubilized metals may be largely in the form of bisulfide, polysulfide, and humic complexes (Gardner 1974, Fagerström and Jernelöv 1972).

In summary, the data presented here demonstrate that algal blooms produced by fertilization of a lake with sewage or other sources of available nutrients may act as extremely effective agents for concentrating heavy metals in bottom sediments. By continually accumulating metals and then sinking through the water column, the algae perform the function of a "conveyor belt" for rapid transfer of metals to the bottom. Sedimentation of metals may also be enhanced as a result of sorption by sewage particles and elevation of the ambient pH owing to photosynthesis, which would thereby promote more efficient sorption by particulate matter (any carbonate precipitation caused by photosynthetic activity would also promote this process). In the case of Hg, the elevated pH would give the added advantage of causing the conversion of toxic, water-soluble monomethyl Hg to relatively harmless, volatile dimethyl Hg (Fagerström and Jernelöv 1972). Above all, production of H<sub>2</sub>S and reducing conditions by putrefaction of algal organic matter, together with SO<sub>4</sub> reduction,

on the floor of the lake would tend to immobilize metals and trap them in the mud as insoluble sulfides or as a network of interconnected sulfide gels and organic complexes. The observed lowering of metal solubility by sulfide is consistent with the claim that sulfide protects aquatic organisms from heavy-metal poisoning by rendering the metals biologically unavailable (Temple and LeRoux 1964, Fagerström and Jernelöv 1971, Vosjan and van de Hoek 1972, Jernelöv and Lann 1973). In the case of Hg, this is accomplished not only by precipitation of metal sulfide but by volatilization of methyl Hg (Fagerström and Jernelöv 1972, Rowland and others 1977). Certain complexing agents interfere with sulfide precipitation, but the formation of stable complexes may in itself, be a powerful means of rendering metals relatively nontoxic (Fogg and Westlake 1955, Steeman-Nielsen and Wiium Andersen 1970, Milanovich and others 1975).

The results of this investigation suggest that deliberate stimulation of algal blooms, with attendant H<sub>2</sub>S production, in small lakes or settling ponds serving as disposal sites for toxic metal wastes may be an effective, economic method for preventing heavy-metal pollution of natural waters. As in Schist Lake, the metals would be largely trapped and immobilized as sulfides or as a sulfide-organic complex in the bottom sediments, and the waters draining the disposal site would be relatively free of heavy-metal contamination. Several connected settling ponds arranged in series could be an especially efficient means of purifying metal-bearing industrial effluent. Of course, maximum

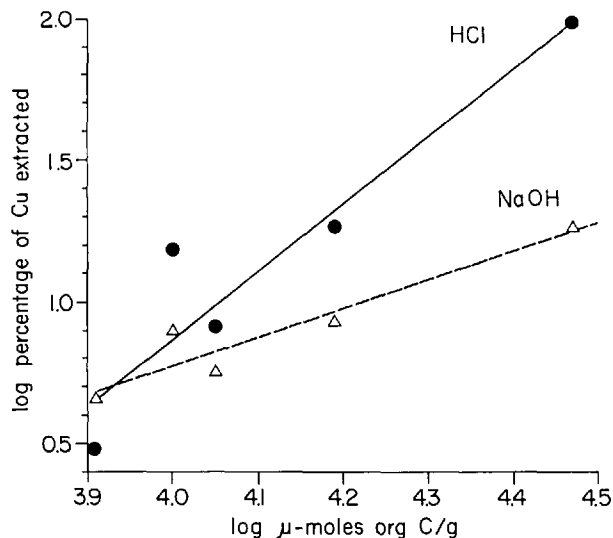
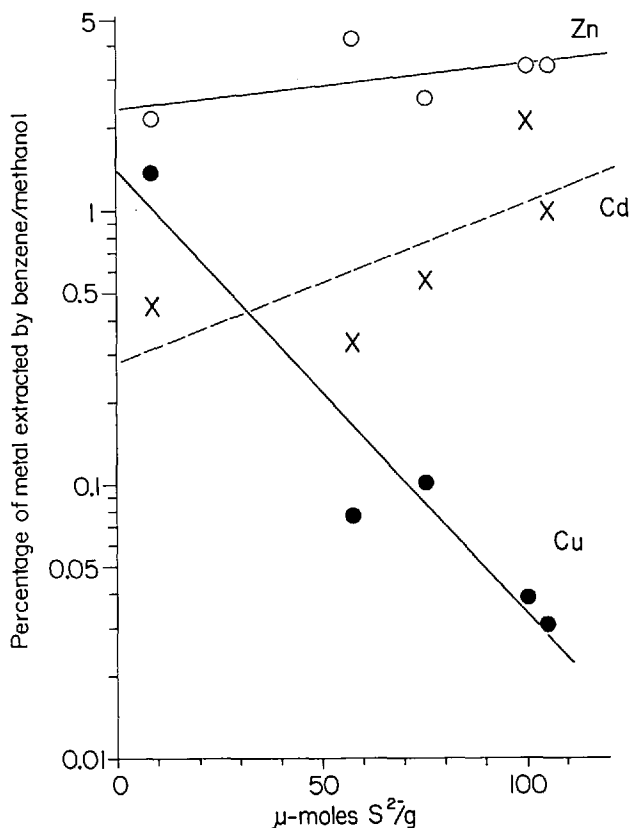
**Figure 12.** (a) Percentage of Cu mobilized as anions by electro dialysis of FFCr-2, RL, SL-1, SL-2, and HL mud plotted against ZnS diffraction peak intensity ( $I_{220}$ ) (measured after heat treatment). (b) Relationship between anionic Cu and Zn extracted from mud samples by electro dialysis.



efficiency would be achieved only if permanently anaerobic conditions could be maintained. Sewage from the nearest community would be a cheap, convenient, and virtually limitless source of available P and N for the algal bloom, although orthophosphate and other inorganic fertilizers could be used instead. In addition, sulfate could be used to stimulate  $\text{SO}_4$ -reducing bacteria. There is no difficulty in promoting  $\text{SO}_4$  reduction, for  $\text{SO}_4$ -reducing bacteria tolerate a wide range of sedimentary conditions and can utilize a variety of carbon sources, including sewage (Zajic 1969, Trudinger and others 1972). Manipulation of the species composition of the algal bloom by adjustment of the nutrient content (for instance, the P/N ratio) of the water might be desirable in order to take advantage of species preferences for particular metals.

Comparable mechanisms for immobilization of heavy metals have been considered by other workers (Feick and others 1972, Jernelöv and Lann 1973), but the technique proposed here has the advantage of being relatively inexpensive and makes use of a waste product (sewage) that is always readily available and must be disposed of anyway. An added economic incentive for development of this method is that eventually the sediments of the

**Figure 13.** Percentages of Zn (○), Cd (×), and Cu (●) extracted from FFCr-2, RL, SL-1, SL-2, and HL muds by benzene/methanol plotted against total "metal-bound" sulfide.



**Figure 14.** Relationship between the percentages of Cu extracted from FFCr-2, RL, SL-1, SL-2, and HL mud by 0.5N HCl (●) and 0.5N NaOH (Δ) and the organic carbon content of the mud.

settling ponds might be mined as secondary sources of heavy metals. Possibly modifications of the method could be used to restore lakes already polluted with toxic metals.

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**REFERENCES**

Andelman, J. B., 1973, Incidence, variability, and controlling factors for trace elements in natural, fresh waters, in Singer, P. C. (ed.), Trace metals and metal-organic interactions in natural waters: Ann Arbor, Mich., Ann Arbor Science, pp. 57-87.

- Armstrong, F. A. J., 1975, Spectrophotometric determination of sulfide in water: Water Quality Parameters, ASTM STP 573, American Soc. for Testing and Materials, pp. 14–19.
- Berner, R. A., 1964, Distribution and diagenesis of sulfur in some sediments from the Gulf of California: *Mar. Geol.*, v. 1, pp. 117–140.
- Beveridge, T. J., and R. G. E. Murray, 1976, Uptake and retention of metals by cell walls of *Bacillus subtilis*: *J. Bacteriol.* v. 127, pp. 1502–1518.
- Craig, H., 1974, A scavenging model for trace elements in the deep sea: *Earth Planetary Sci. Lett.*, v. 23, pp. 149–159.
- Crowe, J. M. E., 1973, A pollution survey of Schist Lake, 1969: Manitoba Dept. Mines, Resources, and Environmental Management, Research Branch, Report No. 73-21.
- Deer, W. A., R. A. Howie, and J. Zussman, 1962, Rock-forming minerals, Vol. 5, Non-silicates: London, Longmans.
- De Groot, A. J., and E. Allersma, 1975, Field observations on the transport of heavy metals in sediments, in Krenkel, P. A. (ed.), Heavy metals in the aquatic environment: New York, Oxford, Toronto, Sydney, Braunschweig, Pergamon Press, pp. 85–95.
- Eichorn, G. L., 1956, Coordination compounds in natural products, in Bailar, J. C. (ed.), The chemistry of the coordination compounds: New York, Reinhold: London, Chapman and Hall, pp. 698–742.
- Fagerström, T., and A. Jernelöv, 1971, Formation of methyl mercury from pure mercuric sulphide in aerobic organic sediment: *Water Res.*, v. 5, pp. 121–122.
- Fagerström, T., and A. Jernelöv, 1972, Some aspects of the quantitative ecology of mercury: *Water Res.*, v. 6, pp. 1193–1202.
- Feick, G., E. E. Johanson, and D. S. Yeaple, 1972, Control of mercury contamination in freshwater sediments: Environmental Protection Technology Series, Office of Research and Monitoring, U.S. Environmental Protection Agency (Washington, D.C.), Report No. EPA-R2-077.
- Fogg, G. E., and D. F. Westlake, 1955, The importance of extracellular products of algae in freshwater: *Proc. Intl. Assoc. Theoret. Appl. Limnol.*, v. 12, pp. 219–231.
- Gardner, L. R., 1974, Organic versus inorganic trace metal complexes in sulfidic marine waters—some speculative calculations based on available stability constants: *Geochim. Cosmochim. Acta*, v. 38, pp. 1297–1302.
- Gibbs, R. J., 1973, Mechanisms of trace metal transport in rivers: *Science*, v. 180, pp. 71–73.
- Goldberg, E. D., 1965, Minor elements in sea water, in Riley, J. P., and G. Skirrow (eds.), Chemical oceanography, vol. 1: London and New York, Academic Press, pp. 163–196.
- Hallberg, R. O., 1972, Sedimentary sulfide mineral formation—an energy circuit system approach: *Mineral. Deposita*, v. 7, pp. 189–201.
- Hutchinson, G. E., 1957, A treatise on limnology, vol. 1: New York, John Wiley and Sons; London, Chapman and Hall.
- Irving, H., and R. J. P. Williams, 1953, The stability of transition-metal complexes: *J. Chem. Soc.*, v. 1953, pp. 3192–3210.
- Jellinek, F., 1968, Sulphides, in Nickless, G. (ed.), Inorganic sulphur chemistry: Amsterdam, London, New York, Elsevier, pp. 669–747.
- Jernelöv, A., and H. Lann, 1973, Studies in Sweden on feasibility of some methods for restoration of mercury-contaminated bodies of water: *Environ. Sci. Technol.*, v. 7, pp. 712–718.
- Kemp, A. L. W., and A. Murdrochova, 1971, Electrodialysis: a method for extracting available nutrients in Great Lakes sediments: *Intl. Assoc. Great Lakes Res.*, Proc. 14th Conf. Great Lakes Res., 1971, pp. 241–251.
- Knauer, G. A., and J. H. Martin, 1973, Seasonal variations of cadmium, copper, manganese, lead, and zinc in water and phytoplankton in Monterey Bay, California: *Limnol. Oceanogr.*, v. 18, pp. 597–604.
- Knauss, H. J., and J. W. Porter, 1954, The adsorption of inorganic ions by *Chlorella pyrenoidosa*: *Plant Physiol.*, v. 29, pp. 229–234.
- Krauskopf, K. B., 1956, Factors controlling the concentrations of thirteen rare metals in sea-water: *Geochim. Cosmochim. Acta*, v. 9, pp. 1–32B.
- Lamar, W. L., 1968, Evaluation of organic color and iron in natural surface waters: Washington, D.C., U.S. Geol. Surv. Prof. Pap. 600-D, pp. D24–D29.
- Leland, H. V., E. D. Copenhaver, and L. S. Corrill, 1974, Heavy metals and other trace elements: *J. Water Poll. Contr. Fed.*, v. 46, pp. 1452–1476.
- Loring, D. H., and R. T. T. Rantala, 1977, Geochemical analyses of marine sediments and suspended particulate matter: Environment Canada, Fisheries & Marine Service, Technical Report No. 700.
- Manheim, F. T., 1961, A geochemical profile in the Baltic Sea: *Geochim. Cosmochim. Acta*, v. 25, pp. 52–70.
- Manskaya, S. M., and T. V. Drozdova, 1968, Geochemistry of organic substances (transl. from Russian and edited by L. Shapiro and I. Breger): Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris, Braunschweig.
- Martin, J. H., 1970, The possible transport of trace metals via moulted copepod exoskeletons: *Limnol. Oceanogr.*, v. 15, pp. 756–761.
- McLaren, R. G., and D. V. Crawford, 1973, Studies on soil copper. I. The fractionation of copper in soils: *J. Soil Sci.*, v. 24, pp. 172–181.
- Mellor, D. P., and L. Maley, 1947, Stability constants of internal complexes: *Nature*, v. 159, p. 370.
- Mellor, D. P., and L. Maley, 1948, Order of stability of metal complexes: *Nature*, v. 161, pp. 436–437.
- Milanovich, F. P., D. W. Wilson, and Y. Yeh, 1975, Detoxifying effect of yellow substance on *E. Coli* in media containing copper: *Nature*, v. 253, pp. 460–461.
- Miller, L. P., 1950, Formation of metal sulfides through the activities of sulfate-reducing bacteria: *Contrib. Boyce Thompson Inst.*, v. 16, pp. 85–89.
- Mills, K. C., 1974, Thermodynamic data for inorganic sulphides, selenides, and tellurides: London, Butterworths.
- Morris, A. W., 1971, Trace metal variations in sea water of the Menai Straits caused by a bloom of *Phaeocystis*: *Nature*, v. 233, pp. 427–428.
- Nicholls, G. D., H. Curl, Jr., and V. T. Bowen, 1959, Spectrographic analyses of marine plankton: *Limnol. Oceanogr.*, v. 4, pp. 472–478.
- Nissenbaum, A., and D. J. Swaine, 1976, Organic matter-metal interactions in Recent sediments: the role of humic substances: *Geochim. Cosmochim. Acta*, v. 40, pp. 809–816.
- O'Connor, J. T., and C. E. Renn, 1964, Soluble-adsorbed zinc equilibrium in natural waters: *J. Am. Water Works Assoc.*, v. 56, pp. 1055–1061.
- Pauli, F. W., 1975, Heavy metal humates and their behavior against hydrogen sulfide: *Soil Sci.*, v. 119, pp. 98–105.
- Payne, K., and W. F. Pickering, 1975, Influence of clay-solute interactions on aqueous copper ion levels: *Water, Air, Soil Poll.*, v. 5, pp. 63–69.
- Ramamoorthy, S., and B. R. Rust, 1976, Mercury sorption and desorption characteristics of some Ottawa River sediments: *Can. J. Earth Sci.*, v. 13, pp. 530–536.
- Rankama, K., and Th. G. Sahama, 1950, Geochemistry: Chicago and London, Univ. of Chicago Press.



- Rashid, M. A., 1974, Absorption of metals on sedimentary and peat humic acids: *Chem. Geol.*, v. 13, pp. 115–123.
- Rashid, M. A., and J. D. Leonard, 1973, Modifications in the solubility and precipitation behavior of various metals as a result of their interaction with sedimentary humic acid: *Chem. Geol.*, v. 11, pp. 89–97.
- Reuter, J. H., and E. M. perdue, 1977, Importance of heavy metal–organic matter interactions in natural waters: *Geochim. Cosmochim. Acta*, v. 41, pp. 325–334.
- Rickard, D. T., 1974, Kinetics and mechanism of the sulfidation of goethite: *Am. J. Sci.*, v. 274, pp. 941–952.
- Rowland, I. R., M. J. Davies, and P. Grasso, 1977, Volatilisation of methyl mercuric chloride by hydrogen sulfide: *Nature*, v. 265, pp. 718–719.
- Rowley, W. J., 1975, A study of water pollution in the vicinity of Flin Flon, Manitoba. Part A: Water pollution sources: Environment Canada, Environmental Protection Service (Water Pollution Control Section), NW region, Surveillance Report EPS 5-NW-75-7.
- Saxby, J. D., 1973, Diagenesis of metal–organic complexes in sediments: formation of metal sulphides from cystine complexes: *Chem. Geol.*, v. 12, pp. 241–248.
- Schnitzer, M., 1968, Reactions between organic matter and inorganic soil constituents: 9th Intl. Congr. Soil Sci., Trans., v. 1, pp. 635–644.
- Schnitzer, M., 1969, Reactions between fulvic acid, a soil humic compound, and inorganic soil constituents: *Soil Sci. Soc. Am. Proc.*, v. 33, pp. 75–81.
- Scott, S. D., 1974, Experimental methods in sulfide synthesis, in Ribbe, P. H. (ed.), Sulfide mineralogy (Mineralogical Soc. America short course notes, Vol. 1): Washington, D. C., Mineralogical Soc. America, pp. S-1 to S-38.
- Shapiro, J., 1964, Effect of yellow organic acids on iron and other metals in water: *J. Am. Water Works Assoc.*, v. 56, pp. 1062–1082.
- Shapiro, J., 1967, Yellow organic acids of lake water: differences in their composition and behaviour, in Golterman, H. L., and R. S. Clymo (eds.), *Chemical environment in the aquatic habitat*: Amsterdam, N. V. Noord-Hollandische Uitgevers, Maatschappij, pp. 202–216.
- Sparling, A. B., 1968, Interactions between blue-green algae and heavy metals: D. Sc. dissertation, Sever Institut. of Technology, Washington Univ., St. Louis, Missouri.
- Spencer, D. W., P. G. Brewer, and P. L. Sachs, 1972, Aspects of the distribution and trace element composition of suspended matter in the Black Sea: *Geochim. Cosmochim. Acta*, v. 36, pp. 71–86.
- Stainton, M. P., M. J. Capel, and F. A. J. Armstrong, 1974, The chemical analysis of fresh water: Dept. of the Environment (Canada), Fisheries and Marine Service (Research and Development Directorate), Misc. Special Publ. No. 25.
- Steeman-Nielsen, E., and S. Wium-Andersen, 1970, Copper ions as poison in the sea and in freshwater: *Mar. Biol.*, v. 6, pp. 93–97.
- Stevenson, F. J., 1977, Nature of divalent transition metal complexes of humic acids as revealed by a modified potentiometric titration method: *Soil Sci.*, v. 123, pp. 10–17.
- Szalay, A., 1964, Cation exchange properties of humic acids and their importance in the geochemical enrichment of  $\text{UO}_2^{2+}$  and other cations: *Geochim. Cosmochim. Acta*, v. 28, pp. 1605–1614.
- Temple, K. L., and N. W. Le Roux, 1964, Syngeneses of sulfide ores: sulfate-reducing bacteria and copper toxicity: *Econ. Geol.*, v. 59, pp. 271–278.
- Thomas, R. L., 1972, The distribution of mercury in the sediments of Lake Ontario: *Can. J. Earth Sci.*, v. 9, pp. 636–651.
- Timperley, M. H., and R. J. Allan, 1974, The formation and detection of metal dispersion halos in organic lake sediments: *J. Geochem. Explor.*, v. 3, pp. 167–190.
- Trudinger, P. A., I. B. Lambert, and G. W. Skyring, 1972, Biogenic sulfide ores: a feasibility study: *Econ. Geol.*, v. 67, pp. 1114–1127.
- Vosjan, J. H., and G. J. van der Hoek, 1972, A continuous culture of *Desulfovibrio* on a medium containing mercury and copper ions: *Netherlands J. Sea Res.*, v. 5, pp. 440–444.
- Weiss, A., and G. C. Amstutz, 1966, Ion-exchange reactions on clay minerals and cation selective membrane properties as possible mechanisms of economic metal concentration: *Mineral. Deposita*, v. 1, pp. 60–66.
- Zajic, J. E., 1969, *Microbial biogeochemistry*: New York and London, Academic Press.