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Evaluation of toxicity, bioavailability and speciation of lead, zinc and cadmium in mine/mill wastewaters

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ABSTRACT

The toxicity of common compounds of lead, cadmium and zinc was evaluated in waters similar to that found in the world's largest lead producing area in Missouri. Static, acute toxicity tests were performed using fathead minnows (*Pimephales promelas*) and water fleas (*Daphnia magna*) respectively. Test organisms were subjected to varying amounts of sulfide, carbonate, chloride and sulfate salts of lead, zinc and cadmium mixed in hard, alkaline waters typical to this region. Median lethal concentrations were calculated using nominal versus measured metal concentrations. Measured metal concentrations included four different metal fractionation (extraction/filtration) techniques at different pH levels which included "dissolved", "available", "easily dissolved" and "total" metals. Most consistent correlations between mortality and metal concentrations were found with the "Total" or "Nominal" values. The "Easily Dissolved" metals which corresponded to acid soluble criteria did not effectively represent toxicity and bioavailability of metals. A metal speciation model, MINTEQA2, was used to predict the concentrations of the dissolved metal species at the pH levels commonly seen in the toxicity test vessels. MINTEQ model results suggested that analysis of metals in aqueous environment is better understood when examining speciation characteristics and would likewise be a better mechanism to develop site-specific water quality criteria for metals.

Keywords: Lead mining, lead cadmium and zinc speciation, bioavailability, MINTEQ model.

INTRODUCTION

The aquatic toxicity of metals is a complicated phenomena involving interactions between the environment and the metal pollutants of concern. Predicting the toxic effect that metals have in natural waters requires evaluating the bioavailability of the metal pollutants. The term "bioavailability" reflects the premise that for some heavy metals organisms may be exposed to less than the total amount present in their habitat (Schmitt *et al.*, 1987). The extent to which heavy metals react with and affect biological components is immensely influenced by the physicochemical factors of the specific environment. Many chemical characteristics of the water are important in defining both the chemical species of the metal present and physiological status of the organism being tested.

Earlier studies to determine the toxicity of lead (Pickering and Henderson, 1966; Davies *et al.*, 1976), cadmium (McCarty and Houston, 1976; Sunda, 1978; Calamari and Alabaster, 1980; Borgman, 1983; Sherman *et al.*, 1987;), and zinc (Sprague, 1964; Mount, 1966; Sunda and Guillard, 1976; Bradley and Sprague, 1985) have recognized that water quality characteristics such

as pH and hardness markedly affect bioavailability and toxicity. Further investigations suggested that evaluation of the toxic bioavailability of metals is dependent on the chemical complexation and speciation (Black *et al.*, 1973; Vuceta and Morgan, 1978; Stumm and Morgan, 1981; Davis *et al.*, 1992, 1993).

In recent years, increasing effort has been made to relate toxicity to some fraction of the trace metal concentration obtained by differential extraction or solubilization procedures (Florence, 1982). Some analytical procedures, often offering little information about exact chemical speciation, have produced a number of arbitrary defined fractions termed "total", "total recoverable", "dissolved", and "acid soluble" metals (USEPA, 1985; 1986).

The lack of precise and definitive information about the various chemical species of lead, cadmium and zinc which might be present, or the relative toxicity of various compounds of these metals have frustrated the development of appropriate and adequate water quality standards that are reflective of the different types of ecosystems. In addition, there is no ideal analytical measurement available for expressing aquatic life criteria for metals of lead, cadmium and zinc. It is clear that

water quality criteria based on total metals will be unnecessarily stringent for one type of environment and underprotective for other environments having different physicochemical properties (Babich and Stotzky, 1980; 1983). Consideration of total metal concentration alone can be misleading since uncomplexed metal ions (Cd^{2+} , Zn^{2+} , and Pb^{2+}) are apparently more readily assimilated by organisms than are complexed forms. Likewise, exclusive use of a dissolved fraction to regulate industrial effluents could result in underestimating the potentially toxic metals present in particulate form. It is therefore evident that the effects of chemical speciation such as; inorganic complexation, chelation, precipitation, and adsorption of metals should be taken into account to compensate for the toxic variability when developing guidelines for aquatic life criteria. Water quality criteria and effluent guidelines imposed through the NPDES permitting process should probably take into consideration site-specific environmental conditions when evaluating potential toxicity of vagrant metals.

Industrial effluents from mines, mills, and smelters within the New Lead Belt, located in Southeastern Missouri, contain various amounts of lead, zinc and cadmium in a variety of site-specific chemical forms. Most of these metals occur as particulate matter, or finely divided insoluble sulfides, or metal complexes bound to clays and other minerals. In this area, ground waters as well as surface receiving streams are characterized by high pH and hard alkaline conditions. Dissolved organic complexing agents are generally lower in abundance than inorganic ligands, especially bicarbonates and carbonates. Moreover, it is likely that the inorganic complexes, especially carbonates, will predominate even in the presence of organics in such waters (Borgman, 1983).

There are several computer models now available that may offer considerable assistance in our understanding of complex chemical behavior and toxicity of heavy metals. MINTEQA2 (MINTEQ) was developed by EPA's Environmental Research Laboratory located in Athens, Georgia (Brown and Allison, 1987). It is a thermodynamic equilibrium model that computes aqueous speciation, adsorption, precipitation and/or dissolution of solids. For a defined set of environmental conditions, it will quickly predict the major metallic species and transformations likely to occur. Previous attempts have indicated useful applications of MINTEQ to characterize streams in the New Lead Belt (Schlachter, 1989).

This study was initiated as a continuation of interests regarding the environmental impacts of the lead mining industry and to better define the toxic effects of heavy metals within the context of hard, alkaline ground and surface waters of this region. In addition, the correlations between demonstrated toxicities of various compounds of lead, zinc, and cadmium in alkaline waters and simultaneous analytical data for metal concentrations observed in various fractions extracted by pH adjustment and filtration of the bioassay medium were also examined. The predictive capabilities of MINTEQ were used to identify the various species of dissolved fractions of

lead, cadmium, and zinc that may exist under the conditions specified in the toxicity tests.

MATERIALS AND METHODS

Static acute toxicity tests were conducted with fathead minnows (*Pimephales promelas*) and daphnia (*Daphnia magna*) by using finely ground, reagent grade salts of sulfide, carbonate, chloride, and sulfate of lead, cadmium and zinc. Monocultures of both test organisms were obtained from the U.S. Department of Interior National Fisheries Research Laboratory, Columbia, Missouri. Cultures were propagated and maintained according to the procedures outlined by the Environmental Protection Agency (US EPA, 1985). Five to 10 concentrations of each metal compound were prepared for initial range finding tests. Each test, with appropriate controls, was performed in duplicate, using ten organisms in each test vessel. Definitive tests were subsequently performed using six to 18 metal salt concentrations. Definitive tests and controls were also done in duplicate, with 10 test organisms per vessel. Survival of test organisms in controls was always >90%. Toxicity tests involving fathead minnows were of 96-hour duration and utilized neonates <24 hours old. Tests with neonate daphnids, <24 hours old, were of 48-hour duration.

Dechlorinated Rolla, Missouri, tap water was used for culturing and toxicity testing for fathead minnows. Extreme sensitivity of neonate daphnids to low concentrations of chlorine necessitated the use of non-chlorinated Rolla well water for culturing and toxicity studies using these organisms. Aliquots of lead salts were weighed and added directly to water to create the desired suspensions/solutions. For zinc and cadmium salts, stock suspensions were made in appropriate water and aliquots were transferred during vigorous stirring to maintain even suspension. In tests with fathead minnows, final suspensions were adjusted to an initial pH 7.7 by the addition of small amounts of reagent grade nitric acid (HNO_3) or sodium bicarbonate (NaHCO_3). For *D. magna*, adjustments of initial pH was only required in those tests involving lead chloride (PbCl_2) or lead sulfate (PbSO_4). Suspensions containing large amounts of PbCl_2 and PbSO_4 required considerable quantities of NaHCO_3 , which created significant changes in ionic strength. Confounding of toxicity tests by increased ionic strength due to neutralization of acidic lead chloride and lead sulfate solutions was inevitable with both minnows and daphnids.

Test solutions/suspensions involving fathead minnows were allowed to equilibrate for 24 hours prior to separation of aliquots for bioassays and chemical fractionation. Fractionations were performed on aliquots taken at the beginning and end of each bioassay. Various fractions of test suspension aliquots were obtained in the following manner:

"Dissolved Metals" (D) were determined by filtration through Gelman GN-6, Metrice 0.45 μm membrane filter. The filtrate was acidified to pH <2

with reagent grade nitric acid and taken for metal analysis.

“Available Metals” (A) were determined by adjustment of pH of an aliquot to pH 4.0, allowing to stand 24 hours, then filtering. Final filtrate was acidified to pH<2 for analysis.

“Easily Dissolved Metals” (ED) were determined by adjustment of pH of an aliquot to pH 1.5–2.0, allowing to stand 24 hours, then filtering.

“Total Metals” (T) were determined on an unfiltered aliquot acidified to pH 1.5–2.0 and subjected to a modified nitric acid digestion procedure as outlined by the EPA (USEPA, 1979).

In toxicity tests utilizing daphnids, at the end of the 48-hour toxicity tests, a separate aliquot from each test vessel was filtered, acidified, and analysed for metals. All acidified samples or filtrates were collected and stored in new acid-cleaned high density polyethylene bottles. Samples were analysed by atomic absorption spectrometry and ICP-Emission spectroscopy at the Environmental Trace Substances Research Center, Columbia, Missouri. Regression analyses were performed for observed mortality versus metal concentrations in the various fractions under comparison. LC50 values, along with standard deviations, were determined by standard probit analysis.

The results of dissolved metal components determined in the laboratory were compared to the MINTEQ model outputs for the dissolved Pb, Zn, and Cd determined for each metal salt. The data for each dissolved metal salt was entered into MINTEQ and run at the pH levels observed in toxicity test vessels. MINTEQ computed the ionic strength and derived the activity coefficient for each compound. Initially, common cation and anion concentrations were determined from the dechlorinated Rolla tap water. The cation and anion concentrations added to the test vessels were entered to the MINTEQ input file for tap water. Additional Na^+ , and CO_3^{2-} were included as inputs where NaHCO_3 was added to high concentrations of PbCl_2 and PbSO_4 solutions.

RESULTS AND DISCUSSION

Results of static acute toxicity tests using the sulfide, carbonate, chloride and sulfate salts of lead, cadmium and zinc performed on fathead minnows and daphnids are displayed in Tables 1, 2, and 3. The LC₅₀ values are shown for fathead minnows in terms of P (nominal concentration), D (Dissolved fraction), A (Available fraction), ED (Easily Dissolved fraction), and T (total extractable metals) as previously defined. For *Daphnia magna*, LC₅₀ values are presented for P and D fractions only. Observed mortality did not consistently correlate well with metal concentrations determined on various fractions. These inconsistencies reflected many methodological difficulties with extraction procedures, especially when working with large amounts of metal compounds, and the effects of varying pH on speciation and solubility. The final pH values in biological test vessels ranged

between 7.5 to 9.1, with the vast majority falling in the narrow range of 8.5 and 8.9.

Figures 1, 2 and 3 compare the predominant dissolved metal components predicted by MINTEQ at pH 7.7, 8.3 and 8.9 which were observed in toxicity test vessels. Even though there were variations in the nominal concentrations of lead, cadmium and zinc that were tested, observed toxic effects showed similar trends depending on the specific anions present. Comparisons were made between the predicted MINTEQ results and with the corresponding acute toxicity test results for the “dissolved” metals salts and are discussed under each metal salt.

Carbonate salts

Carbonate salts of Pb and Zn were generally non toxic to fathead minnows and daphnids (Tables 1 and 2). Cadmium carbonate (CdCO_3) showed some toxic effects to fathead minnows but not to daphnids (Table 3). The intimate contact of the minnows as they positioned themselves near the bottom of the test vessels where there were accumulation of visible particles, and local variations of pH especially as particles were ingested, might have allowed the existence of free cadmium ion (Cd^{2+}) which was suspected to be a highly toxic form. Observed toxic effects appeared to be consistent with the narrow range of stability of CdCO_3 , and possible transition to Cd^{2+} near pH 8. MINTEQ results also showed Cd^{2+} as predominant dissolved species at the specified pH levels (Figure 2). The predicted abundance of carbonate and bicarbonate ions, limited solubility, relative thermodynamic stability of carbonate compounds in the physiological pH range all assured a general ameliorative effect on metal bioavailability and toxicity. At pH levels greater than 8, dissolved lead components did not tend to dissociate into free lead ion (Pb^{2+}), and existed mainly as carbonate species (Figure 1) which was a significant factor in lead bioavailability. MINTEQ results estimated that the carbonates were the predominant species of Zn over pH 8 as shown in Figure 3.

Sulfide salts

The sulfide salts of Pb, Zn, and Cd are very common forms of these metals in natural ore bodies, impressive evidence of their limited solubility and thermodynamic stability over a broad range of pH and low redox potential. These metal sulfides are the most abundant form present in industrial wastes in Missouri’s New Lead Belt. Only 10% of the Pb initially present as lead sulfide (PbS) was brought to the dissolved fraction by adjusting the pH to <4 by adding HNO_3 . Stability diagrams (Richard and Nriagu, 1978) predicted that the sulfides would tend to undergo transformations at redox levels common in streams and rivers, though the rate of transformation are unknown. Practical experience suggests that actual rates of conversions are extremely slow. The appreciable toxicity of cadmium sulfide (CdS) possibly reflected the tendency to form sufficient quantities of reactive Cd^{2+} to reach toxic levels (Table 3). Acute toxic effects of PbS and zinc sulfide (ZnS) were only observed in tests using large amounts of the particulate compounds (Tables 1

Table 1. Acute toxicity of lead compounds to fathead minnows and daphnids.

Metal salt (solubility mg/L) ^a	Fact ^b	Fathead minnows			Daphnia		
		LC50	SD	r ^c	LC50	SD	r ^c
PbS (0.86)	P	4,013	250	0.94	9,958	1,823	0.83
	D	0.915	0.122	-0.53	0.138	0.03	-0.33
	A	403	21	0.94			
	ED	564	27	0.91			
	T	3,655	227	0.94			
PbCO ₃ (1.1)	P	>5,000			>10,000		
PbCl ₂ (9,900)	P	2,918	260	0.77	167	322	0.59
	D	12.5	9.5	0.56	0.168	0.065	0.61
	A	2,823	774	0.20			
	ED	4,333	363	0.54			
	T	3,414	364	0.71			
PbSO ₄ (42.5)	P	3,431	336	0.74	3,166	1,745	0.94
	D	148	739	0.11	0.395	0.051	0.86
	A	6.24	1.67	-0.32			
	ED	60.8	12.0	0.47			
	T	3,221	707	0.62			

^aSolubility data are from *CRC Handbook of Chemistry and Physics*.^bFractions were taken as described in Methods: P = prepared, nominal; D = dissolved; A = available; ED = easily dissolved; T = total.^cr = simple correlation coefficient for regression analyses of mortality vs [metal] in specific fraction.**Table 2.** Acute toxicity of zinc compounds to fathead minnows and daphnids.

Metal salt (solubility mg/L) ^a	Fact ^b	Fathead minnows			Daphnia		
		LC50	SD	r ^c	LC50	SD	r ^c
ZnS (0.65)	P	1,826	529	0.97	>30,000		
ZnCO ₃ (10)	P	>3,000			>30,000		
ZnCl ₂ (4,320,000)	P	43.7	4.7	0.93	47.7	17.4	0.57
	D	2.58	0.24	0.90	0.21	0.022	0.64
	A	38.1	3.6	0.88			
	ED	50.2	5.2	0.93			
	T	47.7	5.0	0.93			
ZnSO ₄ (Very soluble)	P	1.38	1.8	–	29.4	11.9	0.49
	D	0.06	0.01	–	0.62	0.08	0.88
	A	1.83	2.73	–			
	ED	1.37	2.17	–			
	T	1.27	2.01				

^aSolubility data are from *CRC Handbook of Chemistry and Physics*.^bFractions were taken as described in Methods: P = prepared, nominal; D = dissolved; A = available; ED = easily dissolved; T = total.^cr = simple correlation coefficient for regression analyses of mortality vs [metal] in specific fraction.

and 2). It is very likely that these commercial preparations, obtained from hydro metallurgical concentration from ores may contain significant quantities of residual organic reagents which may contribute to observed toxicity. Extremely low levels of filterable, “dissolved” fractions of PbS often showed evidence of contamination. Anomalous data, difficult to avoid during experimental protocol, resulted in variable and quite unreliable LC₅₀ values based on dissolved lead.

The variable acute toxicity occurring at very high concentrations was difficult to interpret using the

MINTEQ predictions (Figures 1 and 3). Conditions placed on MINTEQ input data file did not allow oxidation of sulfide ions and formation of other resulting complexes. Dissolved components that would be responsible for toxicity were Sn²⁺, SO₄²⁻ or H₂S which might have been present at higher concentrations upon oxidation of sulfide salts.

Sulfate salts

Lead sulfate (PbSO₄) is moderately soluble in water, but may exist in solution or fine suspension as the non-dis-

Table 3. Acute toxicity of cadmium compounds to fathead minnows and daphnids.

Metal salt (solubility mg/L) ^a	Fact ^b	Fathead minnows			Daphnia		
		LC50	SD	r ^c	LC50	SD	r ^c
CdS (1.3)	P	0.336	0.053	0.84	0.161	0.044	0.11
	D	0.108	0.007	0.82	0.011	0.002	0.15
	A	0.153	0.015	0.89			
	ED	0.222	0.028	0.88			
	T	0.354	0.057	0.85			
CdSO ₃ (Insoluble)	P	2,658	2,469	0.88	>20,000		
CdCl ₂ (1,400,000)	P	0.126	0.021	0.62	22.6	6.2	0.66
	D	0.067	0.005	0.66	0.008	0.001	0.76
	A	0.138	0.020	0.63			
	ED	0.230	0.041	0.78			
	T	0.237	0.044	0.76			
CdSO ₄	P	0.144	0.019	0.88	3.83	0.73	0.80
	D	0.072	0.009	0.71	0.027	0.002	0.68
	A	0.243	0.058	0.69			
	ED	0.298	0.046	0.67			
	T	0.272	0.035	0.70			

^aSolubility data are from *CRC Handbook of Chemistry and Physics*.

^bFractions were taken as described in Methods: P = prepared, nominal; D = dissolved; A = available; ED = easily dissolved; T = total.

^cr = simple correlation coefficient for regression analyses of mortality vs [metal] in specific fraction.

sociated PbSO₄, anglesite. This non-ionic species is stable over a broad pH range from 1 to 6. The addition of large quantities of PbSO₄ to water, in order to arrive at toxic levels, caused a marked decrease in pH. Neutralization to pH 7.7 with NaHCO₃ caused significant increases in ionic strength, undoubtedly contributing to observed mortality. Varying amounts of Pb appeared in the dissolved fraction, resulting in poor correlation of this fraction with mortality (Table 1). Controls with comparable concentrations of NaHCO₃, neutralized with HNO₃ also showed considerable mortality. Daphnids appeared to be more sensitive to this combination of PbSO₄ and increased ionic strength than the fathead minnows. MINTEQ predicted Pb²⁺ as one of the predominant species at pH 7.7 (Figure 1). However, the concentration of Pb²⁺ decreased with increasing pH, leading to carbonate species being the predominant form. Another possible relationship could be noted between the observed toxicity and presence of various sulfate bound dissolved metal complexes. However, wider ranges of pH, observed for tests solutions of lead sulfate, implied that toxicity or toxic variability might be attributed to altering concentrations of dissolved metals consisting of lead ions and/or lead-sulfate bound complexes.

The sulfate salts of Zn and Cd are very soluble and apparently dissociate at or near physiological pH. These salts are very toxic. MINTEQ predicted that at pH 7.7, the ionic cadmium and zinc were the major species (Figures 2 and 3). As pH increased, the presence of carbonate and bicarbonate ions offered some amelioration, especially for zinc, however the narrow range of stability of the carbonate species of zinc and particularly cadmium permitted persistence of Zn²⁺ and Cd²⁺. Therefore, the LC₅₀ values for zinc sulfate (ZnSO₄) and cadmium

sulfate (CdSO₄) were orders of magnitude lower than those observed with carbonate forms (Tables 2 and 3). It was likely that toxicity of these salts would be affected significantly by modest changes in pH.

Chloride salts

The chloride salts of Pb, Zn, and Cd are quite soluble. The addition of sufficient lead chloride (PbCl₂) to the test vessels altered the quality of the suspension medium. Alkalinity decreased with increased metal concentrations because of considerable precipitation of PbCO₃. This resulted in reduction of the pH levels. Neutralization with NaHCO₃ increased ionic strength, similar to the situation with PbSO₄. Toxicity might be attributed to the test organisms' succumbing to toxic lead or merely the high ionic strength. Daphnids appeared to be more sensitive to this combination of PbCl₂ and increased ionic strength than fathead minnows. In the fractionation procedure, prior to analysis for metal concentration, adjusting the pH of PbCl₂ suspensions with HNO₃ to less than 2 might have allowed the metals to dissociate and pass through the 0.45 µ filter. The behavior of zinc chloride (ZnCl₂) and cadmium chloride (CdCl₂) were quite similar to the sulfate salts of these metals. MINTEQ results showed the presence of significant levels of dissociated metal ions for dissolved cadmium chloride which contributed to the toxicity (Figure 2). For zinc chloride, the carbonate species were stable within a narrow pH range between 8.3 to 9 (Richard and Nriagu, 1978). At pH levels outside this range, zinc existed as Zn²⁺ or hydroxide species which contributed to the low LC₅₀ values in experiments with chloride salts. Under the toxicity test conditions, zinc chloride was less toxic than cadmium chloride (Tables 2 and 3)

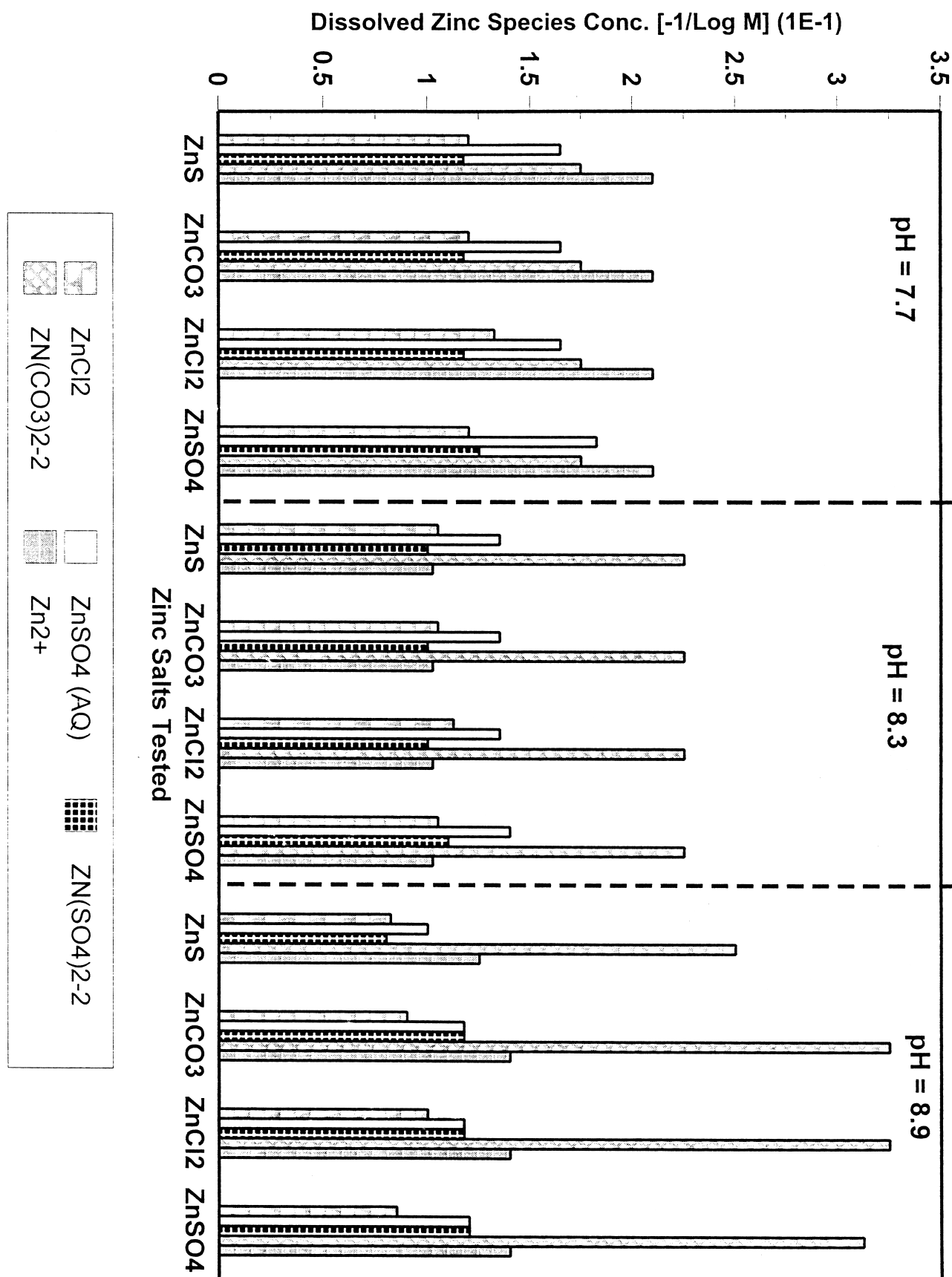
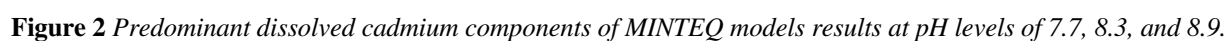


Figure 1 Predominant dissolved lead components of MINTEQ models results at pH levels of 7.7, 8.3, and 8.9.



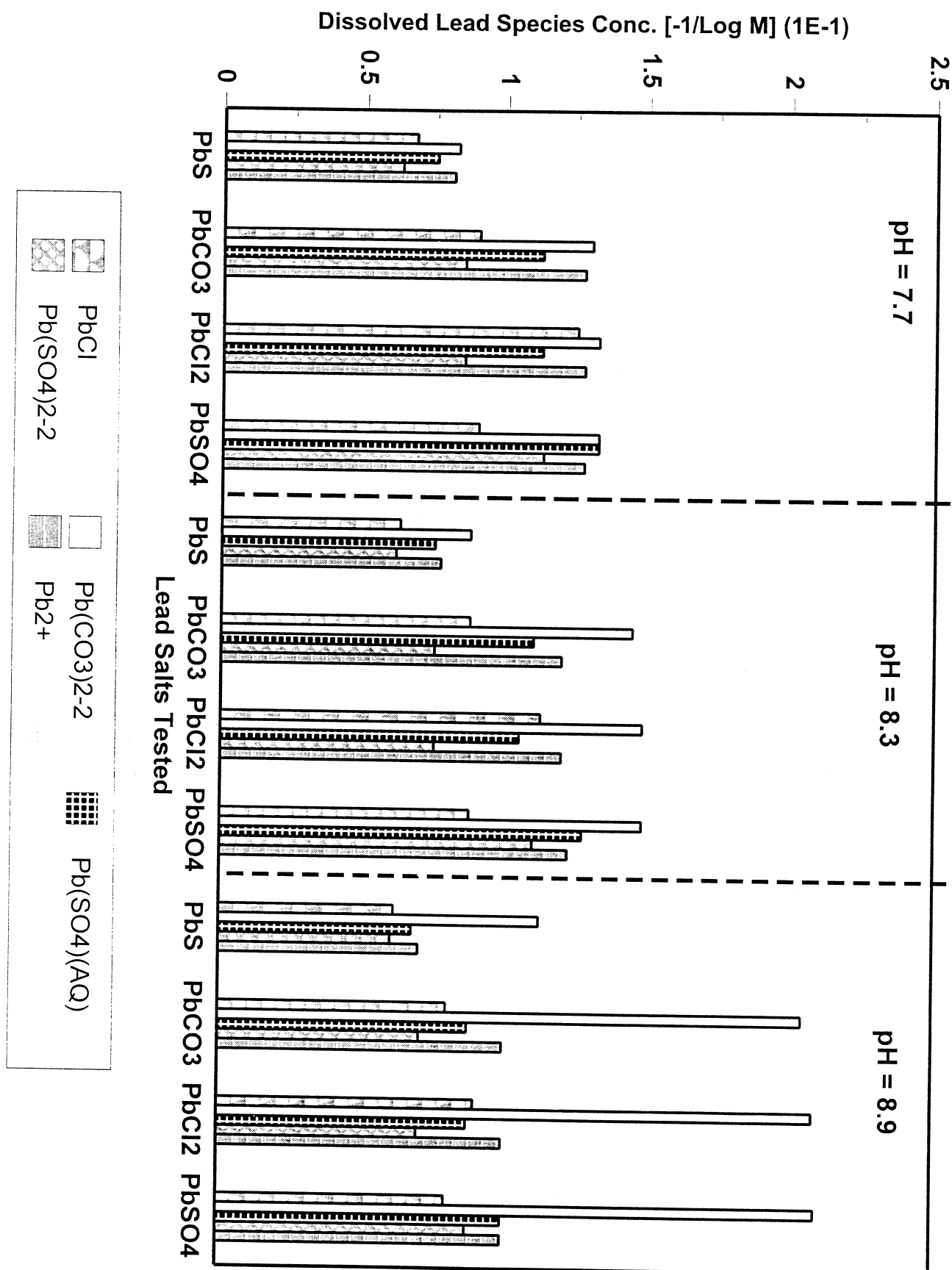


Figure 32 Predominant dissolved zinc components of MINTEQA2 models results at pH levels of 7.7, 8.3, and 8.9.

SUMMARY AND CONCLUSIONS

Static acute toxicity tests using fathead minnows and daphnids showed that various lead, zinc, and cadmium salts were much less toxic in hard, alkaline waters that are typical of the New Lead Belt streams and rivers. Of the various lead compounds tested in this hard, alkaline environment, the carbonates proved to be the least toxic. For fathead minnows, the LC_{50} values for all other compounds were in the same order of magnitude. For daphnids, the sulfide and sulfate salts were less toxic than the chloride salts. Of the various fractions studied, most consistent correlations between mortality and metal concentrations were found with the Total (T) or nominal (P) values. The lead salts varied considerably in their solubility and/or particle size reduction during pH adjustments to 4 or to 2. The carbonate and chloride salts were apparently brought into filterable size range or dissolved by adjusting the pH, while the sulfide and sulfate salts were apparently less affected. In the case of daphnids, toxicity of most lead compounds except the carbonates appeared to be directly related to the solubility of the compound as well as different species that would form at low pH levels.

Of the five zinc salts studied, zinc carbonate was the least toxic. Zinc sulfide demonstrated moderate toxicity for the fathead minnows but not for daphnids. LC_{50} values for the chloride, and sulfate were of the same order of magnitude for daphnids. Limited extraction data available for zinc salts indicated good correlation with mortality data on fathead minnows in all fractions analyzed. Extraction data taken from the daphnid study showed poor correlation with mortality. Separate extraction studies showed that zinc carbonate was effectively brought into solution by adjusting the pH to either 2 or 4. The chloride and sulfate salts showed significantly greater dissolution at pH 2 than at 4, while the sulfide salt was the least affected by pH adjustment and only entered complete solution after digestion with nitric acid. Cadmium carbonate was the least toxic of the five cadmium salts tested. In fathead minnows, the LC_{50} value for cadmium carbonate was three to four orders of magnitude lower than those found for the other four salts, however, the standard deviation demonstrated great variability in observed mortality. Experimental results indicated the following order of increasing toxicity of cadmium salts to fathead minnows: carbonate < sulfide < chloride < = sulfate. The observed order of toxicity of cadmium compounds seemed to be a function of solubility and the presence of free Cd^{2+} . Extraction data for cadmium salts generally indicated better overall correlation with mortality to fathead minnows than those for lead and zinc salts.

For cadmium compounds and to a lesser extent for zinc compounds, filtration to determine the dissolved metal or the use of some extraction procedure based on pH alteration might prove to be adequate and reliable means of assessing bioavailability or potential toxicity. However, extraction at pH 2 or 4 appear to offer no significant improvement or advantage over simple determination of total metal by nitric acid digestion.

The acid soluble criteria alone did not effectively represent toxicity or bioavailability of metals from a water quality standpoint. This was mainly due to the vast interactions and complexations that can occur at different pH levels due to the presence and quantity of different anions such as sulfates. The presence of sulfates in waters containing lead formed lead sulfate complexes at lower pH levels which was a major inhibitor in effectively measuring acid soluble results. A recommended method of metals analysis and application based on this study would be to apply both dissolved and total water quality standard and use MINTEQ model to determine the appropriate limits for that specific dissolved and total metals concentrations.

Use of the MINTEQ model to depict metal species' concentration is an effective tool and appeared to offer additional reasoning for the behavior of metals based on speciation distribution. Analysis of metals in an aqueous environment is better understood when examining speciation characteristics and would likewise be a good mechanism to develop site-specific water quality criteria for metals. Further work with the model's attributes, including analysis of various redox potentials as MINTEQ inputs, would lead to a better understanding of specific toxicity of metal species.

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