The Effects of pH, Redox, and Salinity on Metal Release from a
Contaminated Sediment

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ABSTRACT. A laboratory study was conducted with a brackish marsh
sediment contaminated by several trace and toxic metals to determine
the effect of a range of pH, redox potential, and salinity conditions
on the release of metals to the soluble phase. The purpose of the
study was to provide information on factors affecting the
mobilization/immobilization of metal contaminants under conditions of
various possible remediation alternatives. Substantial amounts of Cd
and Zn were released under moderately acid, oxidizing conditions.
Under the present slightly basic, strongly anaerobic environment of
the marsh sediment, the metals are being effectively immobilized
compared to the release that would occur for some of the metals if the
sediments were excavated and placed under upland conditions where they
would eventually become oxidized and strongly acidic.

1. INTRODUCTION

    In a number of laboratory and greenhouse studies conducted in
this laboratory, the oxidation status of soils and sediments has been
shown to affect the distribution of some trace metals between bound,
unavailable forms and soluble and/or plant-available forms (Gambrell
et al., 1980a,b; Gambrell and Patrick, 1989; Khalid et al., 1981).
Most of these studies were conducted with: 1) uncontaminated
materials, 2) uncontaminated materials spiked to simulate
contamination, or, 3) sludge-amended soils.
    This study presented the opportunity to examine changes in
physicochemical conditions on metal release in a marsh sediment that
had been contaminated by industrial and sewage waste discharges for a
number of years. The possibility exists that some remediative action

will be required at the site. The in situ sediment environment is
strongly anaerobic with a slightly basic pH and low to moderate
salinity levels. Should decisions be made to attempt to clean up the
site or otherwise manage it to contain the contaminants, a very
different set of physicochemical conditions may develop affecting the
mobilization and immobilization of the metal contaminants. Depending
on the alternatives available, moving the material from its present
position to a disposal site could result in changes in the oxidation
status of the sediment as well as pH. Thus the objective of this
study was to determine how changes in pH and redox potential may
affect chemical transformations controlling release of the excess
metals present. For the purpose of this report, release would be an
increase in water soluble levels that may increase bioavailability.

2. MATERIALS AND METHODS

The sediment was collected from a contaminated, brackish marsh in
New Jersey, and stored in sealed containers under refrigeration. When
needed for characterization or experimental purposes, the containers
were opened and mixed under a N_2 or Ar atmosphere to obtain a uniform
and representative aliquot with minimal oxidation.

Three or four replicates of the sediment material were used for
the characterization work. Moisture was determined by oven drying an
aliquot for 24 hr at $105^{\circ}C$ (Peters, 1965). The pH of the original wet
sediment was determined in situ using a calibrated combination pH
electrode. Redox potential was determined by placing three platinum
electrodes in each of four beakers of the sediment and allowing about
24 hr for equilibration. After a day, the readings were made on a
millivolt meter using a saturated calomel reference electrode. To
transform the reported potentials according to electrochemical
convention where potential is expressed based on a standard hydrogen
reference electrode, a factor of 244 mV as added to the uncorrected
reading to obtain redox potentials expressed as Eh. The pH of the
oxidized material was determined by placing a calibrated, combination
pH electrode in a slurry (1:6 solids to water ratio) of the sediment
after continuous stirring under air for 8 d. A check for carbonates
on the original sediment material was made using the method of Nelson
and Sommers (1982). Organic C was measured by a wet oxidation
procedure (Nelson and Sommers, 1982). Acid volatile sulfide in the
sediment material was primarily in the form of precipitated metal
sulfides. This was measured by a modification of the method reported
by Nriagu and Soon (1985) with sulfate measured by ion chromatography.
Oil and grease were measured by Soxhlet extraction with freon (Plumb,
1981) followed by gravimetric analysis. Cation exchange capacity was
measured with a modification of the procedure of Rhoades (1982).
Amorphous iron oxides were measured by the method of McKeague and Day,
(1966). The metals content of the sediment was determined by the hot
nitric acid extraction procedure described by Plumb (1981).

A laboratory study was conducted on the sediment material using
stirred sediment slurries where uniform treatment conditions could be
maintained. The physicochemical treatments include pH levels of 5.0,

6.5, and 8.0 representing weakly acid to slightly basic conditions,
redox potential (Eh) levels of -150, +100, and +400 mV representing
strongly reducing to well oxidized conditions, and salinity levels
were maintained at 2 and 10 parts per thousand (ppt), respectively,
using a commercially available artificial seawater amendment.
Duplicate incubations were conducted and the values reported are
means. The solids content of the slurry was approximately 150,000 mg
L^{-1}. Depending on the desired pH and redox potential combination, a
few days to just over 2 weeks were required to achieve the desired
pH-Eh treatment combinations. Following this, the slurry was
incubated under the selected conditions an additional two weeks before
samples were taken. Aliquots of the slurry were collected,
centrifuged, and filtered through a 0.45 μm filter under an inert
atmosphere to prevent loss of metals due to oxidation and/or
precipitation reactions. The filtrate was acidified while still under
an inert atmosphere, and the soluble (less than 0.45 μm fraction)
metals analyzed by an inductively coupled argon plasma emission
spectrometer. A description of the laboratory microcosm, procedures
for operating them, and sample processing procedures have been
described elsewhere (Gambrell et al., 1977, 1980b).

3. RESULTS AND DISCUSSION

3.1. Sediment Characterization

    Selected properties of the sediment material are given in Table
I.

    Table I. Selected Physical and Chemical Properties of the
    Sediment Materials.

Property	Mean	Standard Deviation
Moisture, %	64.6	0.0
pH of stored sediment	7.0	0.1
pH of oxidized sediment	3.0	0.0
Redox potential (Eh), mV	-72	78
Organic C, %	10.0	0.9
Carbonate carbon	none detected	
Oil and grease, mg kg^{-1}	13,900	3,960
Cation exchange capacity, cmol(+) kg^{-1}	25.2	0.8
Acid volatile sulfide, mg kg^{-1}	30,000	4,960
Amorphous iron oxides, mg kg^{-1}	11,600	140

    The sediment material was from a brackish marsh and was a
fine-textured material with an appreciable organic matter content.
    Of all the characterization measurements, redox potential may be
the least accurate. One reason for this is that the high acid
volatile sulfides and high total organic matter content should have

rendered the sediment more highly reducing than indicated by these redox potential measurements. Though Harter and McLean (1965), reported sulfide accumulation at redox potentials less than −75 mV, Connell and Patrick (1968) demonstrated the critical potential for sulfate reduction to sulfide and sulfide stability to be closer to −150 mV, a strongly reducing condition. The high oil and grease content of the sediments may have affected the platinum electrodes left standing for 24 hr in the undisturbed sediment. The initial redox potential readings in the continuously stirred microcosms were substantially lower, possibly because of the constant abrasive action of the sediment solids coming in contact with the platinum surface (minimizing a coating effect of the oil and grease).

The acid volatile sulfide content of the sediment was several times higher than those reported for other marshes from the limited information available in the literature. It is possible that discharges of various forms of S from wastewater treatment and industrial sources in the area may have contributed to higher than normal sediment sulfide levels in the anaerobic marsh sediment.

The drop in pH from neutral (7.0) to strongly acid (3.0) conditions upon oxidation of the sediment was a significant finding (Table I). It indicates that should the contaminated material be removed from the marsh and deposited under upland conditions where drainage and subsequent oxidation will occur, the sediment will become strongly acid.

Table II gives the content of selected trace and toxic metals in the sediment material. The values given are the means and standard deviations of four separate extractions. The levels of Cd, Cr, Cu, Pb, and Zn are far above what is normally found in uncontaminated soils and sediments. This was the basis for the concern over how changes in pH and redox potential, which might occur under some possible remediation alternatives, might affect metals release.

Table II. Cd, Cr, Cu, Ni, Pb, and Zn Content of the Sediment Material, $mg\ kg^{-1}$.

Metal	Mean[*]	Standard Deviation
	$mg\ kg^{-1}$	
Cd	27.0	1.6
Cr	660	33
Cu	500	18
Ni	56.7	3.4
Pb	284	16
Zn	2,820	120

[*] N=4

3.2. Metal Release Under Controlled pH and Redox Conditions

The data produced on the effects of imposed pH, redox potential, and salinity conditions on soluble metal concentrations in the

laboratory microcosms should not be interpreted as the concentrations
that currently exist in pore waters under similar physicochemical
conditions, or concentrations that will be present in pore waters
should the sediments be subject in the field to the pH and redox
potential conditions achieved in the laboratory. Metal solubilization
in the microcosms may be promoted by continuous stirring. Also, in an
upland disposal environment, gradual leaching and removal of metals
may keep levels lower than found in the microcosms. The imposed
chemical environments of the laboratory microcosms do reflect the
relative changes in soluble metal levels or mobility that would be
expected to occur, and show the potential for this release if the
sediment chemical environment were changed in the field by disposal or
some other cleanup effort. Because of the possibility that additions
of 1 $\underline{N}$ HCl and NaOH used to control pH may have altered salinity
conditions in the reduced acid (-150 mV, 5.0 pH) and oxidized slightly
alkaline (450 mV, 8.0 pH) treatments, salinity effects are discussed
for the pH 6.5 treatments only where minimal acid or base additions
were required to control pH.

Table III gives the results of the microcosm studies on the
effects of the controlled physicochemical conditions on soluble levels
of Cd, Cr, Cu, Ni, Pb, and Zn in the incubated sediment suspensions.
Table IV presents a statistical evaluation of the treatment effects.

Soluble Cd levels were greatest in the sediment suspension at
moderately acid, oxidizing conditions. Soluble Cd increased by a
factor of more than 10 under oxidizing conditions compared to strongly
reducing conditions at all pH levels. Also, there was an apparent
salinity effect on Cd with increased salinity supporting increased Cd
concentrations in solution. Considering the toxic nature of this
metal and low acceptable concentrations in various water quality
criteria guidelines, this oxidation effect should be an important
consideration in any plans for remediating this contaminated sediment.

For Cr in this contaminated sediment, there were no apparent pH
or redox potential effects. Increasing salinity seemed to increase
soluble levels at pH 6.5 where there should have been minimal effect
of pH adjustment on soluble salt levels.

Copper tended to increase with increasing redox potential at all
of the pH treatments with the exception of one unusual value (pH 6.5,
100 mV). However, this trend was not statistically significant. A
strong pH effect on water soluble Cu was not apparent. There may be a
tendency for increasing salinity to increase soluble Cu levels as 8 of
the 9 salinity pairs (experimental treatments differed only by
salinity) showed higher soluble Cu under the higher salinity
conditions.

Soluble Pb was little affected by redox potential except perhaps
at intermediate redox potentials. Lead is tightly bound under
strongly reducing conditions by sulfide precipitation and complexation
with insoluble organic matter, and under well-oxidized conditions Pb
is very effectively immobilized by precipitated iron oxides (Gambrell
et al., 1980b). Soluble Pb was somewhat greater under moderately acid
conditions, but as a result of variability within the data,
significant salinity effects on soluble Pb levels were not observed.

Table III. The Effect of pH, Redox Potential, and Salinity on
Dissolved Metals in the Sediment—Water Suspensions.

Elem.	Sal. ppt	pH 5.0			pH 6.5			pH 8.0		
		−150	100	400	−150	100	400	−150	100	400
						mg L^{-1}				
Cd	2	0.04*	0.14	2.40	bd**	bd	0.36	bd	bd	bd
Cd	10	0.06	0.12	4.50	0.04	0.53	1.15	bd	bd	0.09
Cr	2	0.06	0.16	0.09	0.03	0.02	0.03	0.13	0.20	0.09
Cr	10	0.07	0.15	0.19	0.10	0.29	0.06	0.03	0.03	0.08
Cu	2	0.06	0.12	1.02	0.05	bd	0.20	0.04	0.25	0.77
Cu	10	0.15	0.13	1.54	0.27	6.19	0.41	0.13	0.08	1.21
Ni	2	0.10	1.40	4.00	0.04	0.05	0.68	bd	0.07	0.04
Ni	10	0.11	1.30	4.10	0.11	1.68	0.74	bd	0.04	0.08
Pb	2	0.30	1.15	0.35	bd	0.07	0.14	bd	0.10	0.03
Pb	10	0.35	1.00	0.61	0.10	1.55	0.11	0.06	0.07	0.14
Zn	2	0.10	0.80	415.0	0.40	1.40	34.0	0.40	0.90	0.50
Zn	10	0.10	0.40	493.0	1.90	2.20	42.0	0.10	0.10	0.30

*
** N=2
  Below detection limits

Table IV. General Linear Methods[#] Procedure Applied
to Water Soluble Metals Examining Effects of pH and
redox Potential.

	F value	
Metal	pH	Redox, mV
Cd	147.24**	194.19**
Cr	0.18 ns	1.81 ns
Cu	1.50 ns	2.08 ns
Ni	35.07**	23.55**
Pb	3.87*	4.22*
Zn	145.23**	173.06**

[#]Statistical Analysis System. SAS Institute, Inc., Cary, North
Carolina.
(F—values followed by ** are significant at the 0.01 level; F—values
followed by * are significant at the 0.05 level; F—values followed by
ns are insignificant at the 0.05 level.)

    In studies of Ni with other soils and sediments, we have seen
little evidence of a redox effect on soluble levels (Gambrell et al.,
1983). However, in the current study there was a strong trend for

soluble Ni to increase with increasing redox potential at moderately acid and near-neutral pH levels. There was no consistent trend for salinity effects on soluble nickel.

Total Zn in this sediment material was around 50 to 100 times the levels found in uncontaminated soils and sediments (Fuller and Warrick, 1985). There was a very large effect of pH and redox potential on the levels of soluble Zn in the laboratory chemical availability studies. Very high levels of soluble Zn (greater than 400 mg L^{-1}) were found at pH 5.0 and under well-oxidized conditions. High levels were also found under well oxidized conditions at pH 6.5. Low levels of soluble Zn were found at pH 8.0 at all redox conditions and at moderately and strongly reduced conditions at pH 5.0 and 6.5. These findings were similar to results of previous chemical availability studies on zinc (Gambrell, et al. 1980a,b; Gambrell and Patrick, 1989).

4. CONCLUSIONS

Previous studies in this laboratory with spiked sediments and sludge-amended soils have shown that Cd and Zn respond similarly to pH and redox potential conditions. This was also true for this contaminated sediment where a change from near neutral, reduced conditions to moderately acid, oxidizing conditions would apparently cause a large release of Zn and Cd. In this study, Ni responded as did Cd and Zn to pH and redox potential changes.

Under the initial or undisturbed near neutral pH and strongly reducing conditions in the marsh, the sediment chemical environment immobilizes the metal contaminants fairly effectively. Upon oxidation, as would occur upon dredging and unconfined disposal of the contaminated sediment in an upland location, this material would become strongly acid. Oxidation and acidification of these sediments would probably release relatively large amounts of Zn and Cd to water that passes through the material (ie., percolating rainwater). This aspect should be considered in evaluating any remediative actions for contaminated sediments such as those evaluated in the current work.

5. REFERENCES

Connell, W.E. and Patrick, W.H., Jr.: 1968, Science 159,86.

Fuller, W.H. and Warrick, A.W.: 1985, Soils in Waste Treatment and Utilization. Volume I. CRC Press, Inc., Boca Raton, Florida 268 p.

Gambrell, R.P., Collard, V., and Patrick, W.H. Jr.: 1980a, Cadmium
Uptake by Marsh Plants as Affected by Sediment Physicochemical
Conditions. In R.A. Baker (ed.) Contaminants and Sediments, Volume 2:
Analysis, Chemistry, Biology. Ann Arbor Science, Ann Arbor, Michigan.
pp. 425-444.

Gambrell, R.P., Khalid, R.A., and Patrick, W.H., Jr.: 1980b,
Environmental Science and Technology 14,431.

Gambrell, R.P., Khalid, R.A., Verloo, M.G., and Patrick, W.H., Jr.:
1977, Transformations of Heavy Metals and Plant Nutrients in Dredged
Sediments as Affected by Oxidation-Reduction Potential and pH: Part
II. Materials and Methods, Results and Discussion. Contract Report
D-77-4. U.S. Army Engineer Waterways Experiment Station, Vicksburg,
Mississippi. 315 p.

Gambrell, R.P., Landes, S.L., Reddy, C.N., and W.H. Patrick, Jr.:
1983, Soil Physicochemical Parameters Regulating Chemical and
Biological Availability of Trace and Toxic Metals in Sludge-Amended
Soils. Project Completion Report for Research Grant No. R 805789-01,
Municipal Environmental Research Laboratory, U.S. Environmental
Protection Agency, Cincinnati, Ohio. 100 p.

Gambrell, R.P. and Patrick, W.H., Jr.: 1989, Cu, Zn, and Cd
Availability in a Sludge-Amended Soil under Controlled pH and Redox
Potential Conditions. (in) Ecological Studies 74: Inorganic
Contaminants in the Vadose Zone. B.Bar-Yosef, N.J. Barrow, and J.
Goldshmid, eds. Springer-Verlag, Berlin. pp 89-106.

Harter, R.D. and McLean, E.O.: 1965, Agronomy J. 57,583.

Khalid, R.A., Gambrell, R.P., and Patrick, W.H., Jr.: 1981, J.
Environmental Quality 10,523.

McKeague, J.A. and Day, J.H.: 1966, Canadian J. Soil Science 46,13.

Nelson, D.W. and Sommers, L.E.: 1982, Total Carbon, Organic Carbon,
and Organic Matter. (in) Methods of Soil Analysis, Part 2, Chemical
and Microbiological Properties, 2nd Edition. A.L. Page ed. American
Society of Agronomy, Madison, Wisconsin.

Nriagu, J.O. and Soon, Y.K.: 1985, Geochim Cosmochim Acta 49,823.

Peters, D.B.: 1965, Water Availability. (in) Methods of Soil Analysis,
Part 1, Physical Analyses. C.A. Black, ed. American Society of
Agronomy, Madison, Wisconsin.

Plumb, R.H. 1981, Procedure for Sediment Samples/ Metals/ Inorganic
Analysis/ Analytical Methods. (in) Procedures for Handling and
Chemical Analysis of Sediment and Water Samples. Technical Report

EPA/CE-81-1, published by U.S. Army Engineer Waterways Experiment
Station, Vicksburg, MS.

Rhoades, J.D.: 1982, Cation Exchange Capacity. (in) A.L. Page, R.H.
Miller, and D.R. Keeney (eds.) Methods of Soil Analysis. Part 2.
Chemical and Microbiological Properties, 2nd Edition. American Society
of Agronomy, Madison, Wisconsin.