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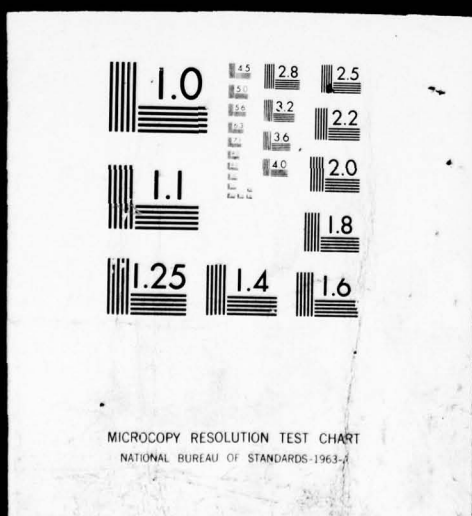
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DREDGED MATERIAL RESEARCH PROGRAM



TECHNICAL REPORT D-77-40

TRACE AND TOXIC METAL UPTAKE BY MARSH PLANTS AS AFFECTED BY Eh, pH, AND SALINITY

by

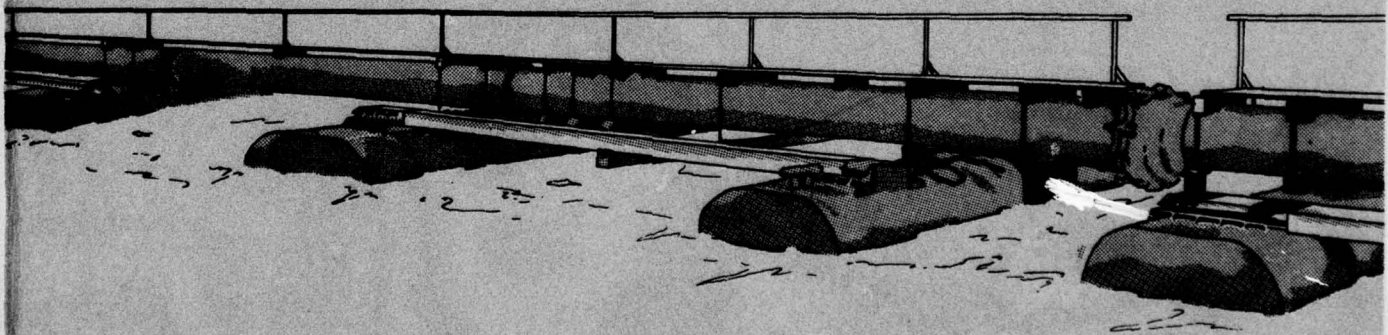
Center for Wetland Resources
Louisiana State University
Baton Rouge, Louisiana 70803

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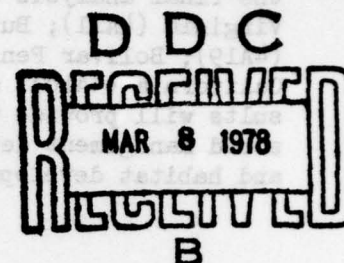
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IN REPLY REFER TO: WESYR

31 January 1978

SUBJECT: Transmittal of Technical Report D-77-40

TO: All Report Recipients



1. The technical report transmitted herewith represents the results of Work Unit 4A06 regarding the effects of Eh, pH, and salinity on trace and toxic metal uptake by marsh plants. This work unit was conducted as part of Task 4A (Marsh Development) of the Corps of Engineers' Dredged Material Research Program (DMRP). Task 4A is a part of the Habitat Development Project (HDP) of the DMRP and is concerned with developing, testing, and evaluating the environmental, economic, and engineering feasibility of using dredged material as a substrate for marsh development.
2. The purpose of this work unit was to determine the effect of substrate physical and chemical conditions on the uptake of trace and toxic metals by marsh plants. It was demonstrated under greenhouse and laboratory conditions that Eh, pH, and salinity do affect the availability to marsh plants of sediment-bound metals. The results of this report suggest that careful consideration should be given to final substrate conditions in the selection of disposal alternatives. Additionally, management practices to reduce metal availability subsequent to disposal appear feasible.
3. Work Unit 4A06 is one of several research efforts designed to assess the potential of the uptake and mobilization of contaminants through disposal of dredged material in marsh and estuarine systems. Closely related work units are 2A05 which provided a state-of-the-art review of nutrient and heavy metal cycling in marsh-estuarine ecosystems; 4A11H, which compared the water quality and sediment status of a natural and man-made marsh on the James River, Virginia; 4A11L, which evaluated the uptake of organohalides from contaminated sediments into plant and animal tissues; 4A15, in which marsh plants were subjected to various concentrations of heavy metals in a hydroponic solution; 4A15A, in which an extraction procedure was developed to predict heavy metal uptake from dredged material; and 4A26, which provided a rapid, inexpensive bioassay technique for predicting contaminant uptake from dredged material under field conditions.

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4. Additional supportive and comparative data will be forthcoming with the final analysis of the results of field studies at Windmill Point, Virginia (4A11); Buttermilk Sound, Georgia (4A12); Apalachicola, Florida (4A19); Bolivar Peninsula, Texas (4A13); Pond No 3, San Francisco Bay, California (4A18); and Miller Sands, Oregon (4B05). Together these results will provide the Corps of Engineers with a comprehensive basis for sound management decisions regarding disposal in marsh-estuarine systems and habitat development on potentially contaminated dredged material.

John L. Cannon

JOHN L. CANNON

Colonel, Corps of Engineers

Commander and Director

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20. ABSTRACT (Continued)

successful methods as well as procedures which were not successful are discussed as are techniques for overcoming many of the experimental difficulties.

In laboratory studies using soil suspensions, Distichlis spicata (L.) Greene, Spartina alterniflora Loisel, and Spartina cynosuroides (L.) Roth were grown in soil suspensions in which treatments included oxidized and reduced conditions at two pH levels and two salinity levels. The effect of these soil physicochemical conditions on plant content of mercury, lead, cadmium, copper, iron, and manganese was studied. Lead and cadmium uptake by Oryza sativa L. was also studied, but over a range of four soil pH levels and six redox (oxidation-reduction) potential conditions.

Greenhouse studies were conducted using Distichlis spicata, Spartina alterniflora, and Sorghum halepense (L.) Pers. in which oxidation-reduction conditions were controlled in unstirred soil material. The plant content of the trace metals studied in the greenhouse generally supported results of laboratory studies where soil suspensions were used as the rooting medium.

In laboratory studies using labeled mercury, the content of this metal in marsh plants tended to be enhanced by decreases in salinity and increases in pH.

Although results with lead were inconclusive in laboratory studies, lead uptake by lowland rice was enhanced as the soil became more acid. In greenhouse studies, an increase in soil oxidation-reduction conditions increased plant lead content, but this was attributed to a redox potential mediated effect on soil pH.

Plant cadmium content responded more to a change in the physicochemical environment of the rooting medium than did other metals studied. The cadmium content of aboveground tissue was consistently and substantially increased with an increase in oxidation conditions in all species in both laboratory and greenhouse studies. Maximum cadmium content occurred under acid, oxidizing conditions except for one species in which an oxidized, weakly alkaline environment favored increased cadmium content.

The effects of physicochemical conditions on the zinc content of plants grown in the greenhouse were studied where the zinc content was found to increase with increasing oxidation conditions.

There was little effect of either pH or oxidation-reduction conditions on the copper content of the species studied.

Two extractants were used on the soil suspensions following harvest to determine the linear relationships between chemical availability and plant content of metals in laboratory studies. Of the metals studied, cadmium generally gave the best linear association between measured uptake and chemical availability, although there were important species differences.

Based on the results of this research, it was concluded that soil and sediment physicochemical conditions do affect the plant availability of trace and toxic metals, and it was recommended that these effects should be considered in selecting environmentally sound disposal methods for contaminated dredged sediments.

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SUMMARY

The purpose of this research was to determine the effects of pH, salinity, and especially oxidation-reduction conditions of the rooting medium on uptake of trace and toxic metals by marsh plants. Previous research conducted by this laboratory determined that pH and oxidation-reduction conditions of a sediment-water system regulated the chemical availability of iron, manganese, zinc, copper, mercury, lead, and cadmium. It was also demonstrated that a change in the physicochemical environment of a sediment-water system would result in transformations altering the chemical form of potentially available metals. A logical and much needed extension of these chemical availability studies was to determine the effects of pH and redox potential (the intensity of oxidation or reduction in soil, sediment, or water systems) on the biological availability of toxic metals. In particular, it is important to understand how these physicochemical parameters may influence uptake of toxic metals by plants which become established on contaminated dredged material applied to upland or intertidal sites.

Because potentially harmful substances such as toxic metals and pesticides tend to accumulate in sediments, there has been much concern over the possible release of sediment-bound contaminants and subsequent adverse environmental effects resulting from dredging and subsequent disposal. In the past, open-water discharge has been used extensively as a convenient and relatively inexpensive means of dredged material disposal. However, land disposal of dredged materials has been increasingly used as an alternate means of disposal where this method is feasible because of potentially adverse effects on benthic and aquatic organisms as well as surface water quality at open-water disposal sites. More recently, research has been directed toward finding beneficial uses of dredged materials where these uses are compatible with environmental quality. For example, land application of dredged material for marsh or habitat creation and agricultural soils improvement

is being explored as a valuable and beneficial alternative to open-water disposal and/or land application for disposal purpose only.

The physicochemical parameters associated with land application of dredged material differ from open-water disposal in one important respect. Gradual drainage and subsequent oxidation of the bulk solid sediment material will likely occur where dredged sediments are deposited above the ground water of the original and surrounding land surface. Although some dissolved chemical components in surface and interstitial waters may respond almost immediately to changes in oxidation conditions, other components of the bulk solid phase may respond very slowly to a change in oxidation-reduction intensity. This may be significant because most potentially toxic substances are associated with the solid phase, and likely changes in oxidation levels over extended time intervals could significantly affect regulatory processes influencing the bioavailability of many toxic materials.

Most studies completed to date on factors influencing the mobilization and immobilization of trace metals in dredged sediments and the environmental impact of dredged material disposal have been more applicable to open-water disposal or to initial drainage from confined disposal sites rather than to long-term drainage from upland disposal sites and plant accumulation of potentially toxic metals from upland areas. These studies have generally indicated little release of toxic metals as a sediment is dispersed in a water column and settles to the bottom. The insignificant release of most biologically active substances reported for many studies of open-water disposal may be due, in part, to little opportunity for changes to occur in some of the physicochemical factors influencing the mobilization of potentially toxic metals bound to the bulk sediment solid phase. It is probable that little change occurs to the pH or oxidation-reduction status of bulk sediment solids discharged into a water column during the relatively short transit time in surface waters before these solids again settle to the bottom of a waterway and become part of the reduced

sediments at the disposal site. However, land application for disposal, habitat development, or agricultural soils amendment may offer considerably more opportunity for significant changes to occur in the physicochemical parameters of the bulk solids and surrounding aqueous micro-environment. Such changes could affect chemical and biological processes regulating toxic metal availability, plant uptake, and subsequent cycling in the environment.

Laboratory studies were conducted to determine the effects of pH, salinity, and oxidation-reduction conditions on mercury, lead, cadmium, copper, iron, and manganese uptake by three marsh plant species: Distichlis spicata (L.) Greene (Saltgrass), Spartina alterniflora Loisel (Smooth cordgrass), and Spartina cynosuroides (L.) Roth (Big cordgrass). The roots of these plants were grown in soil suspensions in sealed vessels where the physicochemical parameters of interest could be accurately monitored and controlled. The pH levels studied were 4.5 and 7.5. Two oxidation-reduction conditions were included--a well-oxidized treatment and a moderate to strongly reduced treatment. Two salinity levels were included for each species simulating saline and brackish conditions for Distichlis spicata and brackish and fresh water conditions for Spartina alterniflora and Spartina cynosuroides. The plants were grown under controlled conditions for 2 weeks and harvested to determine metals content of aboveground tissue. A similar experiment was conducted with Oryza sativa L. (lowland rice) to study lead and cadmium uptake. In the lowland rice experiment, treatments included four pH levels (5, 6, 7, 8) and six redox potential levels (-200, -100, 0, +100, +200, +400 mv), ranging from strongly reduced to well oxidized. Lowland rice is similar to marsh plants in many respects and grows exceptionally well in controlled laboratory uptake vessels. Soil suspensions used in laboratory studies were chemically extracted to compare plant uptake with chemical availability for each metal.

A procedure was developed to study the effects of controlled oxidation-reduction conditions on plant uptake from an unstirred rooting medium under greenhouse conditions. Distichlis spicata, Spartina

alterniflora, and Sorghum halepense (Johnson grass) were grown under strongly reduced, moderately reduced, and well-oxidized conditions, respectively. The pH of the rooting medium was not controlled to enable monitoring of naturally occurring pH changes associated with changes in oxidation-reduction conditions.

There are many difficulties associated with growing plants in systems where physicochemical parameters are controlled. In this research, many of these problems were overcome or minimized. The experimental techniques which were successful, as well as many approaches which were not successful, are presented and advantages and limitations of the developed techniques discussed.

The results of these studies demonstrated that pH, salinity, and redox potential do regulate the plant availability of potentially toxic metals in many cases. The effect of the physicochemical environment of dredged sediments on the biological availability of trace and toxic metals should be considered when selection is made among possible disposal methods for an environmentally sound disposal or productive use alternative.

The following paragraphs will briefly summarize the data from this study to indicate the type of results obtained.

In laboratory studies using soil suspensions, there was no apparent effect of the imposed physicochemical conditions on plant growth during the 2-week uptake studies, and the relative treatment effects were consistently similar whether total metal uptake or tissue concentration was considered. However, increasing oxidation conditions reduced marsh plant growth in greenhouse studies such that opposite results were usually obtained depending on which response was considered.

Both tissue concentration and total uptake are important in evaluating the overall impact of trace metal mobilization from dredged sediments to plants, and data for both uptake and concentration are presented for greenhouse studies in which these responses differed. In this report, however, the treatment effects on plant tissue

concentration will be primarily discussed as an indication of the effects of the physicochemical conditions on transformations of trace and toxic metals in soils and sediments affecting their plant availability.

Mercury concentration in the marsh species studied was enhanced by decreases in salinity and increases in pH. An increase in oxidation conditions tended to increase mercury concentration in two species.

In laboratory studies using soil suspensions, there was little apparent effect of either pH or redox potential on the lead content of marsh species. However, interpretation of lead data was difficult due to the generally greater experimental variability for lead than for other metals.

Lead uptake in lowland rice, a cultivated crop, was enhanced by decreasing pH and little affected by changing oxidation-reduction conditions in laboratory studies. In greenhouse studies, an increase in soil oxidation-reduction conditions increased lead concentration in marsh plants, though generally decreased total uptake because of poorer growth of marsh plants in oxidized soils. The increase in lead content was attributed to a redox potential mediated effect on soil pH.

Plant cadmium uptake responded more to a change in the physicochemical environment than did other metals studied. The cadmium content of aboveground tissue was consistently and substantially increased with an increase in oxidation conditions in all species studied in both laboratory and greenhouse studies. However, total cadmium uptake showed the opposite effect in greenhouse studies of marsh plants due to decreasing plant growth with increasing oxidation conditions. The cause for reduced growth under oxidized conditions is not known for sure. However, the increased chemical availability and tissue concentration of cadmium found under oxidized conditions in soil amended with 50 ppm of this metal may have resulted in some cadmium toxicity to the marsh plants which contributed to reduced yields. Maximum cadmium concentration in plants occurred under acid, oxidizing conditions

except for one species in which an oxidized, weakly alkaline environment favored greatest cadmium concentration.

Plant zinc content was studied in greenhouse experiments where the zinc concentration also increased as the rooting medium became better oxidized.

There was little effect of pH or oxidation-reduction conditions on the copper content of the species studied.

Greatest iron and manganese concentrations in plants occurred under acid, reducing conditions. This is in accord with chemical availability studies and thermodynamically based pH-redox potential diagrams which indicate the strong effect of these physicochemical parameters on the chemical speciation of iron and manganese.

Two extractants were used on the soil suspensions following harvest to determine the linear relationship, if any, between chemical availability and plant availability for the metals studied in the laboratory. The correlations found were species dependent in many cases.

Significant and fairly good linear associations were found between plant content of labeled mercury content and both extractants for Spartina alterniflora and Spartina cynosuroides, but not for Distichlis spicata.

Of the toxic metals studied, cadmium generally gave the best linear association between measured plant content and chemical availability. Soluble plus exchangeable cadmium correlated well with cadmium content in two species in which plant content was enhanced by acid, oxidizing conditions, these conditions being a physicochemical environment that favor maximum chemical availability. Organic chelate extractable cadmium correlated well with the cadmium content of the third species in which uptake responded differently to pH.

Low linear associations were found between chemical availability and plant content of lead and copper with marsh species, though water-soluble lead correlated well with lead uptake by lowland rice.

Based on the results of these studies, it is recommended that the effects of physicochemical parameters on plant availability of toxic and potentially toxic metals should be considered in selecting environmentally sound disposal methods for contaminated dredged sediments. Where an uncontaminated sediment is to be dredged, selection among feasible disposal alternatives can be based on economic, engineering, and social considerations with minimal concern for adverse chemical effects on the environment. However, additional constraints are associated with disposal methods for contaminated dredged sediments due to possible mobilization of sediment-bound toxins to biologically available forms. With chemically contaminated sediments, it should be possible, in many instances, to select from among economically and engineering feasible disposal/use alternatives to minimize adverse environmental effects. Depending on the properties of the contaminated sediments, the nature of the toxic substances and the available disposal methods, a disposal/use alternative can be selected in which the final physicochemical environment of the dredged material will favor minimal release of toxic substances. An example was given for a cadmium contaminated sediment.

Also, knowledge of the effects of physicochemical parameters on toxic metal availability may lead to additional management practices subsequent to disposal which will contribute to reducing toxic metal release to plant available forms.

PREFACE

The objectives of this work were: 1) to develop and refine methods for growing marsh plants in soils and dredged sediments in which salinity, pH, and redox potential (oxidation-reduction conditions) are controlled over the range commonly encountered in nature, and, 2) to determine the effects of these controlled physicochemical conditions on trace and toxic metal uptake by plants.

Previous research in this laboratory indicated that pH and redox potential do affect the chemical availability of trace and toxic metals. A much needed extension of this work was to determine the effects of these parameters on the availability of these metals to plants of the type that may become established on dredged sediments used for habitat development or other upland disposal applications.

The laboratory and greenhouse procedures developed were reasonably successful though the experimental variability in laboratory studies was somewhat greater than normally encountered in conventional plant uptake studies. The results did indicate that different physicochemical environments which may be expected in dredged sediments applied in upland or intertidal situations do influence the availability of trace and toxic metals. In many cases, the treatment effects on plant content of metals were similar to the effects of imposed physicochemical conditions on soluble and exchangeable levels found in previous chemical availability studies. Cadmium was a particularly interesting metal in that pH, oxidation conditions, and salinity were all found to have important bearing on the plant availability of this metal.

This report was prepared by personnel of the Laboratory for Wetland Soils and Sediments, Center for Wetland Resources, Louisiana State University (LSU), Baton Rouge, Louisiana. This investigation was conducted under Contract No. DACW39-73-C-0108 entitled "Productivity and Stress Physiology of Marsh Plants" between the U. S. Army Engineer Waterways Experiment Station (WES) and the Center for Wetland Resources, LSU.

The study forms part of the Dredged Material Research Program (DMRP), Environmental Effects Laboratory (EEL), WES, Vicksburg, Mississippi. The contract was managed by personnel from the Habitat Development Project (HDP) and the Natural Resources Development Branch (NRDB) under the general supervision of Dr. H. K. Smith, Project Manager for the HDP, and Dr. John Harrison, Chief, EEL. The Directors of WES during the conduct of the study were COL G. H. Hilt, CE, and COL J. L. Cannon, CE. The Technical Director was Mr. F. R. Brown.

The principal investigator was Dr. W. H. Patrick, Jr., LSU. Dr. R. P. Gambrell, Ms. Vicki Collard, and Mr. C. N. Reddy also participated in the study.

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INTRODUCTION

Background

Toxic heavy metals, some nutrients, oils and grease, and organic pesticides have historically moved into waterways from land drainage and uncontrolled waste disposal. Because these potentially harmful substances tend to accumulate in sediments, there has been much concern over the possible release of sediment-bound contaminants and subsequent adverse environmental effects resulting from dredging and dredged material disposal (Lee, 1976; Smith, 1976). In the past, open-water dumping has been used extensively as a convenient and relatively inexpensive means of dredged material disposal. However, because of the potentially adverse effects of open-water disposal on benthic and aquatic organisms and surface water quality, land disposal of dredged materials has been increasingly used as an alternate means of disposal where this method is feasible. More recently, research has been directed toward finding beneficial uses of dredged materials where these uses are compatible with environmental quality. For example, land application of dredged material for marsh or habitat creation and agricultural soils improvement are being explored as valuable and beneficial alternatives to open-water disposal and/or land application for disposal purposes only (Lee, Engler, and Mahlock, 1976).

The physicochemical parameters associated with land application of dredged material differ from open-water disposal in one important respect. Gradual drainage and subsequent oxidation of the bulk solid sediment material will likely occur where dredged sediments are deposited above the ground water of the original and surrounding land surface. Although some dissolved chemical components in surface and interstitial waters may respond almost immediately to changes in oxidation-reduction conditions, other components of the bulk solid phase may respond very slowly to a change in oxidation-reduction intensity. This may be significant because most potentially toxic substances are associated with the solid phase, and likely changes in oxidation levels over extended

time intervals could significantly affect regulatory processes affecting the bioavailability of many toxic materials.

Most studies completed to date on factors influencing the mobilization and immobilization of trace metals in dredged sediments and the environmental impact of dredged material disposal have been more applicable to open-water disposal or to initial drainage from confined disposal sites than to long-term drainage from upland disposal sites and plant accumulation of potentially toxic metals from upland areas. These studies have generally indicated little release of toxic metals as a sediment is dispersed in a water column and settles to the bottom (Chen *et al.* 1976; May, 1973, 1974; U. S. Army Corps of Engineers, 1974; Windom, 1972, 1973). The insignificant release of most biologically active substances reported for many studies of open-water disposal may be due, in part, to little opportunity for changes to occur in some of the physicochemical factors influencing the mobilization of potentially toxic metals bound to the bulk sediment solid phase. It is probable that little change occurs to the pH or oxidation-reduction status of bulk sediment solids discharged into a water column during the relatively short transit time in surface waters before these solids again settle to the bottom of a waterway and become part of the reduced sediments at the disposal site. However, land application behind diked enclosures for disposal or for habitat development may offer considerably more opportunity for significant changes to occur in the physicochemical parameters of the bulk solids and surrounding aqueous micro-environment affecting chemical and biological processes regulating trace metal availability, plant uptake, and subsequent cycling in the environment.

Literature Review

Plant and Soil/Sediment Factors Affecting Trace Metal Availability

Several chemical and biological processes affected by pH and oxidation-reduction conditions occur in sediment-water systems which

influence the bioavailability of toxic heavy metals. Net release or net immobilization is dependent on a complex interaction among the various regulatory processes, some of which are briefly described below.

The formation of heavy metal sulfide precipitates in reduced soil and sediment environments is known to be an important process limiting the mobility and availability of many metals (Engler and Patrick, 1975; Krauskopf, 1956; Morel et al., 1975). Land application methods for dredged material disposal or for productive uses may result in the gradual oxidation of these sulfide compounds, releasing some of the potentially toxic metals initially bound as sulfide to more available chemical forms than would occur with open water disposal.

Metal adsorption or coprecipitation with colloidal hydrous oxides of iron and manganese is another important process limiting the available levels of trace metals where these hydrous oxides are found (Goldberg, 1954; Jenne, 1968; Krauskopf, 1956; Lee, 1973; Lockwood and Chen, 1973). This process is strongly influenced by a change in the oxidation-reduction condition of a soil or sediment-water system. In proportion to the levels of trace metals present in dredged sediments, large amounts of chemically reactive ferrous iron and manganous manganese are usually found in anaerobic sediments (Brannon et al., 1976; Gambrell et al., 1977). Oxidation of iron to colloidal hydrous oxides active in scavenging trace metals is thought to be rapid when reduced ferrous iron is introduced into an oxidized environment (Windom, 1972). Thus, if land applied dredged sediments are subjected to gradual drainage and subsequent oxidation, this process may irreversibly adsorb some of the toxic heavy metals. The pH of a soil or sediment-water system also affects the formation and stability of these hydrous oxides.

Metal complex formation with organics is another important process affecting the availability of trace metals. Both quantitative and qualitative changes in large molecular weight humic materials will likely occur if a reduced soil or sediment becomes oxidized (Patrick and Mikkelsen, 1971; Tusneem and Patrick, 1971). Such changes may

lessen the natural chelating capacity of insoluble sediment organics, possibly releasing some potentially toxic metals to more bioavailable forms (Gambrell et al., 1977). Where open-water disposal is used, significant oxidation of organics in dredged material probably does not have time to occur before the dredged sediment settles to the bottom of a waterway and again becomes reduced sediment at the disposal site. However, if dredged material applied to land becomes drained, time of exposure to an oxidized environment is not a limiting factor, and some of the bulk material, particularly in the surface horizons, may become well oxidized. The pH of a sediment-water system also influences the stability of metal-organic complexes (Schnitzer and Skinner, 1966; 1967) as well as the quantities of trace and toxic metals bound to the soluble organics (Verloo and Cottenie, 1972).

Land application may also alter the pH of the dredged material affecting the mobility of trace metals. Reduced soils and sediments are reported to be near neutral in pH (Gambrell, Khalid, and Patrick, 1976; Patrick and Mikkelsen, 1971). Due to redox potential mediated chemical changes of certain inorganic constituents (principally iron), oxidation of reduced noncalcareous soils and sediments will likely result in a moderate pH reduction (Ponnamperuma, 1972). An increase in acidity may enhance mobility of some toxic heavy metals. A substantial decrease in dredged sediment pH to strongly acid levels may occur where an initially reduced sediment material containing several hundred ppm total sulfides becomes oxidized. As a consequence of sulfide oxidation, a weak sulfuric acid solution may form, resulting in "cat clays" with pH levels as low as 2 to 4. Such a strong acid environment will almost certainly mobilize considerable quantities of most toxic heavy metals and probably alter normal soil microbial processes and plant root metabolism. Sub-surface reduced horizons may also be affected as the weak sulfuric acid solution formed leaches downward with percolating rain water.

The pH of a sediment-water system is an important factor affecting metal oxide, hydroxide, and carbonate formation. An increase in pH to

near neutral or alkaline levels and/or an increase in the oxidation-reduction status of a soil tend to favor the formation of these compounds which limit the availability of many metals.

Redox potential-pH diagrams illustrating the influence of some of the regulatory processes controlling the speciation of metals in simple aqueous systems are available in the literature for mercury (Hem, 1970), cadmium (Hem, 1972), zinc (Hem, 1972), and lead (Stumm and Morgan, 1970). Such diagrams can be developed for simple aqueous systems consisting of a limited number of inorganic elemental components and are characterized by distinct redox potential-pH boundary conditions between the various possible chemical forms. In recent years these thermodynamic calculations have been expanded to describe metal chemistry in more complex aqueous systems which include both organic and inorganic chemical constituents. Although such studies are useful in identifying regulatory mechanisms affecting metal solubility and availability, they are limited in that these models of simple aqueous systems cannot approach the complexity of natural sediment-water systems due to the qualitative diversity and quantitative variability of the chemically reactive constituents present in natural systems. For example, metal coprecipitation or adsorption to hydrous oxides cannot be included in these diagrams because little is known of the thermodynamics of the reaction mechanisms. Also, the effects of pH and redox potential on heavy metal complex formation with insoluble humic materials cannot accurately be computed and does not fall within neat, well defined stability boundaries as indicated in simple aqueous inorganic systems (Hem, 1970). Thus the plant availability of sediment-bound toxic metals cannot be accurately modeled using a thermodynamic approach.

Many plants, and marsh plants in particular, are noted for their ability to permit movement of molecular oxygen from the atmosphere through leaf and stem tissue into roots. From the roots, oxygen may diffuse out into the soil. Thus the oxidation-reduction conditions in the rhizosphere may differ substantially from the bulk soil or sediment material and affect the chemical form and plant availability of

sediment-bound metals. The rhizosphere of these marsh plants is reported to be better oxidized than the surrounding soil (Fukui, 1953; Gotoh and Tai, 1956). The rhizosphere of many upland plants is reported to be more reduced than the surrounding soil material, likely due to oxygen demand for root respiration (Brar, 1972), root secretions of readily metabolized organic substances (Stefanson, 1972), and the lack of morphological structures permitting rapid atmospheric oxygen diffusion into the roots.

Waid (1975) has shown that soil organisms may respond to the oxidation-reduction environment of the rhizosphere to produce metal solubilizing substances. Aerobic rhizospheres may stimulate production and exudation of iron solubilizing organic chelates in response to iron deficiency in aerobic soils. Though some metal selectivity was suggested based on coordination positions in distinguishing between divalent and trivalent metals, it is likely that plant exudates may solubilize most divalent metals to some extent. Conditions in the rhizosphere influencing the production of these metal chelating exudates would be particularly important in dredged sediments contaminated with toxic metals.

Influence of pH and Redox Potential on Heavy Metal Uptake by Plants

In recent years, there have been numerous published reports in the agricultural and environmental literature on toxic heavy metal uptake by crop plants grown on contaminated or sludge-amended soils. The following literature discussion on the effects of pH and redox potential on trace metal uptake is taken primarily from literature pertaining to agricultural crops since much less is known about factors influencing metal uptake by marsh plants from wetland soils or dredged sediments. A strong pH influence on trace metal availability to plants is supported by the agricultural literature where an increase in acidity usually favors plant uptake of metals.

Relatively little is known about the influence of oxidation-reduction intensity on the plant availability of soil and sediment-bound

toxic metals to either crop or marsh plants. This is a potentially serious gap in the understanding of the factors affecting the plant availability of toxic metals.

Agricultural soils amended with sewage sludge are usually found to be more productive than unamended soils. However, yield reductions are frequently noted with excessive application rates of sludge containing toxic materials (Lunt, 1959), particularly when the sludges are acid forming or are applied to acid soils (Page, 1974; Peterson et al., 1971). Heavy metal toxicity to crop plants is thought to be contributing to the observed yield reductions in many instances.

Heavy metal uptake by barley seedlings grown on topographically associated soils having pH levels of 5.9 and 7.9 was reported to be greater from the acid soil than from the mildly alkaline soil, though both soils received equivalent sludge applications (Dowdy and Larson, 1975).

Cunningham, Keeney, and Ryan (1975) also noted a pH effect on plant uptake of several metals from sludge-amended soil. A high lime (pH 7.8) sludge material containing abnormally high levels of zinc, copper, chromium, and nickel did not adversely affect crop yields, while comparative rates of more acid sludge did reduce yields because of metal toxicity.

Lunt (1959) reported higher yields from crop plants grown on soils receiving alkaline sludge than from plants grown on a sludge-amended soil of pH 5.0. It was suggested that the greater availability of toxic metals in the acid soil contributed to the depressed yields.

Jones et al. (1975) noted that the zinc content in corn leaves grown in sludge-amended soils was substantially increased below pH 6.3, while no increases in the leaf zinc content were noted where the soil pH was above 7.

Several investigators have reported that liming reduced the foliar lead content of plants grown on lead-contaminated soils (John and VanLaerhoven, 1972; Cox and Rains, 1972). MacLean, Halstead, and Finn (1969) suggested that a greater complexing capacity of the soil organic

matter as pH increased accounted for reduced plant availability of lead in limed soils. Zimdahl and Foster (1976) noted that liming decreased the uptake of lead by corn and reduced lead translocation within the plant. Numerous others have reported an inverse relationship between plant uptake of lead and pH (Griffeth, 1919; Page and Ganje, 1972; John and VanLaerhoven, 1972; MacLean, Halstead, and Finn, 1969; Miller, Hassett, and Koeppel, 1975; Arvik and Zimdahl, 1974).

The plant availability of cadmium is also reported to increase as soil pH is decreased (Miller, Hassett, and Koeppel, 1976; Lagerwerff, 1971; John, VanLaerhoven, and Chuah, 1972).

Cadmium availability has also been found to be strongly influenced by soil cation exchange capacity (John, VanLaerhoven, and Chuah, 1972; Haghiri, 1974). It is likely that the lower plant cadmium uptake observed as soil organic matter content and pH are increased is due in part to the increased CEC resulting from these soil changes. Gambrell *et al.* (1977) have shown that exchangeable cadmium levels are strongly influenced by redox potential in weakly and moderately acid sediment-water systems.

In an extensive literature review on the fate and effects of trace elements in sewage sludge applied to agricultural soils, Page (1974) concluded that pH was one of several factors affecting trace element concentrations in higher plants. Data were presented indicating a reduction in soil pH would increase the plant availability of zinc, copper, and nickel.

Lagerwerff (1972), reporting the data of James and Lagerwerff, indicated that mercury uptake by peas grown from seed treated with a mercurial fungicide was slightly greater from acid than from neutral soils. However, little to no pH differences were noted for peas which were not treated with the fungicide, and there were no apparent significant effects of pH on the mercury content of wheat from mercury-treated or control seed.

There are numerous publications reporting the effects of soil pH on uptake of trace and toxic metals by agricultural plants grown on

sludge-amended soils. However, very limited information is available on the effects of soil oxidation-reduction conditions on toxic metal uptake by agricultural plants. There are essentially no published reports on the effects of soil pH and oxidation-reduction conditions on trace and toxic metal uptake by marsh plants.

Weeraratna (1969) reported that manganese uptake by rice from wetland soils was greater under flooded conditions than under unflooded conditions. Flooding reduced manganese uptake from an upland soil compared to unflooded conditions, but this was thought to result from increased iron availability and subsequent iron toxicity to plants grown in the flooded, upland soil. Where manganese availability was increased by flooding, it was attributed to the increased levels of soluble manganese in reduced (flooded) soils.

Clark, Nearpass, and Specht (1957) also reported that manganese availability to rice was increased by submerged soil conditions.

Mandal (1962) reported on yield and the nitrogen, iron, and manganese content of rice as a function of the oxygen content of the atmosphere overlying the floodwater. The anaerobic and semianaerobic (0 and 10% oxygen) treatments resulted in greater accumulation of both metals in the shoot tissue than was found in the semiaerobic and aerobic treatments. The aerobic treatments were thought to favor the stability of the sparingly soluble oxides and hydroxides of these metals which reduced their plant availability.

Jones and Etherington (1970) reported the effects of waterlogging on the uptake of iron and manganese by two marsh species (Erica cinerea L. and Erica tetralix L.) in a study to determine factors favoring the establishment by E. tetralix on wetter sites. Waterlogging enhanced the leaf manganese uptake of E. cinerea L., and both species accumulated significantly more iron from waterlogged soils than from the control treatment in both shoot and root tissue.

Kothny (1973) reported that the plant availability of mercury is decreased in reducing soils (negative redox potential). Suggested mechanisms of mercury retention by soils under anaerobic conditions

included insoluble complex formation with soil organics and sulfide.

Mikkelsen and Brandon (1975) reported that zinc deficiency in rice is observed to be more severe in submerged soils than in surface irrigated soils, especially when crop residues are undergoing active decomposition. Though no direct reference is made to the effects of flooding and residue decomposition on soil redox potential, it is probable that the zinc deficiency problems noted were related to the oxidation-reduction conditions of these soils.

Jugsujinda (1975) found that the uptake of iron, manganese, and zinc was strongly influenced by redox potential and pH in a laboratory study in which these parameters were controlled. Labeled iron uptake was high under anaerobic conditions at low pH. Labeled manganese uptake was considerably greater under reduced conditions at both pH 5.5 and 7.5. Zinc uptake was reduced as pH increased in incremental units from 5.0 to 8.0. Aerobic soil increased zinc uptake over anaerobic soils at each pH level studied.

The lower zinc content of plants grown under anaerobic conditions compared to aerobic conditions was attributed to the formation of insoluble zinc sulfide and possibly to the production of more stable, metal-organic complexes under anaerobic conditions.

In a literature review, Lucas and Knezek (1972) reported mixed effects of poor aeration on zinc availability to plants have been found. However, much of the available literature indicates zinc is less available to plants in anaerobic soils (Mikkelsen and Brandon, 1975; International Rice Research Institute, 1970; Jugsujinda, 1975).

Kirkham (1975) reported cadmium accumulation in barley roots grown on sludge-amended soil was inversely proportional to the cadmium retained in sludge crusts, which, in turn, depended on sludge application frequency. Though no redox potential measurements were made, processes affected by redox potential seemed to be involved as it was stressed that application frequency strongly influenced the wetting and drying cycles in the upper soil layer and sludge crust.

Bingham et al. (1976) reported on the γ -leaf content of cadmium, copper, iron, manganese, and zinc in rice grown under flooded and

nonflooded conditions in a soil amended with 1 percent sewage sludge enriched with variable levels of cadmium. Grain yield was reduced at 17 $\mu\text{g Cd/g}$ under nonflooded conditions, while 320 $\mu\text{g Cd/g}$ did not adversely affect grain yield under flooded conditions. Leaf cadmium levels were slightly greater under nonflooded management. In this study, the leaf content of iron and zinc were increased by a factor of about 0.5 to 2 under flooded conditions, while flooding increased manganese content about 20-fold. The leaf copper content was little affected by soil flooding.

These authors attributed the increased plant tolerance and reduced availability of cadmium in flooded soils to precipitation of cadmium sulfide. However, they do not explain why sulfide precipitation failed to reduce zinc availability under flooded conditions. Gambrell *et al.* (1977), working with four river and coastal sediments, reported that the chemical availability of cadmium is enhanced by sequential oxidation of sediment-water systems above the critical potential for sulfide stability. Increased cadmium release from sediment organics with increasing oxidation intensity apparently contributed to the higher levels of cadmium in soluble and exchangeable forms.

Ito and Iimura (1975) reported the cadmium content of rice plants increased only slightly with increasing cadmium additions to submerged soils in pot experiments. However, under oxidizing conditions, the cadmium content of rice plants increased markedly with cadmium additions. Cadmium concentration in the soil solutions ranged from approximately 0.1 $\mu\text{g Cd/l}$ in the submerged soil to 10 $\mu\text{g Cd/l}$ in the drained soil.

Reddy and Patrick (1977) reported that an increase in the redox potential of a Mhoon soil suspension increased cadmium uptake by lowland rice to a considerable extent. In this study, lead uptake was enhanced by lowering the pH, but redox potential had little influence on lead uptake.

Purpose, Scope, and Experimental Approach

From the literature, it is apparent that the various processes affecting the mobilization and immobilization of metals in soils and

sediments are influenced by both redox potential and pH. Also, there is a considerable amount of published information indicating the importance of pH on metals' availability to agricultural plants, as well as limited information on the effects of oxidation-reduction conditions on crop and other upland plants. Currently, there is essentially no information available regarding the effects of pH and redox potential observed together, and especially coincidental changes in these parameters, on the mobilization of sediment-bound toxic heavy metals to plant available forms.

This topic is of increasing interest as upland disposal/use alternatives for amending agricultural soils, creating marsh, or developing habitat for wildlife are being considered and implemented more and more as an alternative to open-water disposal. Under most conditions, upland disposal will result in some increase in the oxidation-reduction conditions of typically reduced sediments.

The purpose of this research is to study the effects of pH and oxidation-reduction conditions on trace and toxic metal uptake by marsh plants which may become established on upland applied dredged sediments. Such studies should contribute to selecting and managing dredged and fill material disposal alternatives to minimize the release of metals to plant available forms and subsequent sediment-derived toxic metal cycling in the environment.

Physicochemical parameters such as pH and redox potential which affect nutrient and toxin availability cannot be accurately monitored or controlled in a field situation. Upland soils are noted for their physical, chemical, and biological heterogeneity, especially when considered on a microscale. Presumably, this lack of uniformity would soon apply to dredged sediments under upland or intertidal conditions. Also, it is well established that plant roots strongly influence the chemical and biological properties of the rhizosphere such that the rhizosphere environment differs markedly from that of the bulk soils.

In this study, marsh plants were grown in soil suspensions in order to: 1) permit good control and monitoring of the physicochemical properties of the rooting medium, 2) ensure the homogeneity of these

properties, and 3) ensure that plant roots are exposed to the same chemical and biological environment imposed by the experiment.

A possible objection to this approach is that plant roots are subjected to an artificial environment which may differ from that of the rhizosphere in an undisturbed soil or dredged material. An attempt was made to compensate for this effect, if any, by comparing uptake results in laboratory studies with results from greenhouse studies where plants were grown in an unstirred rooting medium. In the greenhouse studies, oxidation-reduction conditions could be controlled to some extent, but not to the degree permitted in the laboratory systems.

Despite the possible and probable introduction of some artifacts using the laboratory suspension technique, it is felt this procedure is a valuable tool in characterizing the influence of physicochemical parameters on the plant availability of metals.

MATERIALS AND METHODS

Laboratory Studies with Marsh Species

Rooting Medium

Preliminary efforts to grow marsh plants in suspensions of a salt marsh sediment were not successful. Most plants died soon after transplanting into suspensions of sediment material obtained from a mud flat adjacent to the Southwest Louisiana Canal near Leesville, Louisiana. This sediment material contained greater than 600 μg total sulfide/g sediment solids (oven dry basis) and some free hydrogen sulfide as indicated by the characteristic odor released as this material was disturbed. Plant mortality was attributed to toxicity to hydrogen sulfide or some other chemical constituent present in strongly reduced sediments. Roots suspended in a strongly reduced, stirred sediment-water mixture may not be able to maintain an oxidized environment in the rhizosphere adjacent to the root surface compared to marsh plants grown in undisturbed anaerobic mediums. Thus plants grown in suspensions may be more susceptible to injury where high levels of potential toxins are present. Another difficulty experienced with the marsh sediment material was the inability to reduce the salt content to sufficiently low levels to simulate brackish and freshwater sediments, even after repeated mixing with tap water, settling, and decanting the supernatant.

Because of problems with the salt marsh sediment material and previous successful growth of rice in soil suspensions in this laboratory, a Mhoon silty clay loam was used. This is a Mississippi River floodplain soil. Surface soil material for this study was collected from the Louisiana State University Ben Hur Farm in Baton Rouge. The soil material was air dried, ground, passed through a 20-mesh sieve, mixed well, and stored in polyethylene-lined containers prior to use. This material consisted of 19 percent sand, 46 percent silt, and 35 percent clay. Cation exchange capacity was 21 meq/100 g, and the pH of a 1:1 soil to water paste was 5.2. The total carbon content was 1.2 percent.

The total ammonium-nitrogen, phosphorus, iron, manganese, and zinc contents were 80, 540, 2190, 350, and 40 $\mu\text{g/g}$, respectively.

Processing a soil material by grinding and drying may enhance certain microbial processes when the material is again moistened relative to an unprocessed soil material. However, effects of processing on trace metal uptake, if any, should be reflected equally in all physico-chemical treatments applied to the soil in this study such that soil processing does not invalidate relative treatment effects.

Source of Plant Material

Spartina alterniflora. Two sources of Spartina alterniflora were evaluated. Plants for uptake studies were obtained from seeds germinated in the laboratory and seedlings and culms collected from the marsh near Leesville, Louisiana.

In the laboratory, seeds were soaked in a 1:10 solution of Chlorox and water for 10 minutes to inhibit fungal growth during germination. Seeds were then rinsed and placed in tissue-lined petri dishes. The tissue was kept moist with distilled water and germinated at 33°C in the dark to enhance stem elongation. The seedlings were divided into three groups and transplanted into sand, salt marsh sediment, or Jiffy Mix*. Some seedlings in each rooting medium were placed in the greenhouse and others in a climate controlled growth chamber. The greenhouse daytime temperature ranged from 22 to 32°C and at night dropped to 10 to 16°C. The growth chamber was maintained at 85 percent humidity, 32°C daytime temperature, and 18°C nighttime temperature. In addition to incandescent, fluorescent lighting was used with a photo period of 12 hours light and 12 hours dark. Light intensity was approximately 1,800 foot-candles at plant tops with incandescent lighting contributing 25 percent

*Jiffy mix is a commercially available potting medium comprised of peat moss and vermiculite and supplemented with plant nutrients.

of the total. Half of the seedlings from each potting media was watered daily with tap water, and the remaining half was watered with Hoagland's nutrient solution (Hoagland and Arnon, 1938).

The best growth was observed in the salt marsh sediment followed by Jiffy Mix using no nutrient solution. The seedlings in both sand treatments died after 2 weeks. All seedlings grew slowly, but those grown in the greenhouse were larger and healthier than those grown in the growth chamber. The seedlings in Jiffy Mix were supplemented with nitrogen (50 ppm) and iron (5 ppm) at 2 months. The seedlings grown in the incubator and in the greenhouse were of usable size (about 30 to 45 cm tall and 3 to 8 g fresh weight per plant) for the laboratory study at 4 to 6 months.

Spartina alterniflora culms and seedlings were obtained from the Southwest Louisiana Canal near Leesville, Louisiana at a streamside location from mid-March through mid-April, 1975. These seedlings were about 10 cm tall and weighed 0.3 g. The culms had much thicker stems and were about 15 cm tall and weighed 0.7 g. When pulled from the marsh sediment, the seedlings and culms had a reddish-brown coating on all but the most recently developed roots which were white. The seedlings and culms, plus some water to prevent desiccation, were placed in plastic bags for transport to the greenhouse. At the greenhouse, the plants were rinsed and transplanted into Jiffy Mix or washed marsh sediment. Both the seedlings and culms obtained from the marsh grew faster than those seedlings germinated in the laboratory and grown in the greenhouse. These plants were of adequate size for the laboratory experiments after 3-months growth. When transplanted to laboratory growth vessels, the plants were 30 to 50 cm tall and single plants weighed 3 to 12 g. Marsh plants grew well in both the Jiffy Mix and marsh sediment. Because plants grown in Jiffy Mix could be cleaned of the rooting medium easier with less damage to the roots, Jiffy Mix was selected for growing seedlings to the desired size for use in laboratory metal uptake studies.

Galvanized tubs of 60-l capacity were lined with two layers of 6-mil polyethylene sheeting to prevent zinc contamination from these tubs. Seven kg of Jiffy Mix was added to each tub and kept saturated with tap water. This mixture gave a 15-cm rooting depth. Long roots presented a problem in the laboratory incubation vessels as they became tangled with the magnetic stirring bar causing it to stop. By controlling the depth of the potting media, the problem of roots tangling in the stirring bars was alleviated.

The culms and seedlings grew well in tubs containing Jiffy Mix with varying amounts of water. When the water level was maintained 5 to 8 cm over the growing medium, the stem diameter was maximized, and the leaves were dark green, but the roots were very fragile, and large rhizomes presented a problem in the laboratory incubation vessels. When the rooting medium was kept moist, but not saturated, stem diameter was less, but the stems were still rigid, leaves appeared healthy, and the roots were less fragile. Smaller rhizomes with this treatment made it easier to handle the plants during transplanting. After 3-months growth, it was found that rhizomes or growing culms had punctured both layers of the plastic lining. Subsequent analysis for tissue zinc content indicated the punctured lining resulted in zinc contamination.

Spartina cynosuroides and Distichlis spicata. One-month old Spartina cynosuroides and Distichlis spicata seedlings were provided by Dr. R. T. Parrondo of the L.S.U. Botany and Marine Science Departments. When received, these seedlings were growing in vermiculite in galvanized metal trays. This also precluded meaningful zinc data in laboratory studies with these plants. They were transplanted to Jiffy Mix in plastic-lined tubs until large enough to be used in the laboratory studies. When transplanted to the laboratory growth vessels, the Spartina cynosuroides was 4 to 6 months old, 30 to 50 cm in height, and single plants weighed from 2.0 to 12 g. The Distichlis spicata was 3 to 5 months old, 20 to 28 cm tall, and transplanted clumps weighed 10 to 20 g.

Generalized Procedure for Laboratory Studies

Three-hundred g of air-dried Mhoon soil material was weighed into Pyrex growth vessels. Distilled water (1,200 ml) was added to give a 1:4 soil to water ratio. A homogeneous suspension was maintained by continuous stirring with magnetic stirrers. All soil suspensions were amended initially with 0.45 g of ground green rice straw to give a supplemental organic carbon supply of about 0.5 percent (air-dried weight basis) to ensure a sufficient energy source for anaerobic conditions to develop. A plexiglass cover plate fitted with a closed cell, foam rubber gasket was fastened to the Pyrex vessel to prevent air entry from the laboratory atmosphere to the soil suspension. Holes had been drilled into the plate to accommodate two platinum electrodes, a gas inlet, a rubber septum, a salt bridge connected to a saturated calomel reference electrode, and six plants. The experimental apparatus is illustrated in Figure 1.

In the laboratory systems, an oxidized soil environment was maintained by continuously passing air into the suspension from a compressed air source at a rate of approximately 5 ml/minute. A reduced soil environment was maintained by continuously passing oxygen-free nitrogen through the soil suspensions. The end of the gas outlet tube was immersed in a water trap to prevent oxygen entry. In the absence of oxygen, soils and sediment-water systems naturally tend to become more reduced. Except where noted elsewhere, the soil suspensions were incubated 7 days or until stable reducing and oxidizing conditions were attained. These two treatments resulted in redox potentials of approximately -200 mv for the reduced suspensions and approximately +500 mv for the oxidized suspensions.

Certain species-plant size combinations resulted in an apparent shock effect upon transplanting to the laboratory systems when the suspension was adjusted to desired pH-redox potential-salinity conditions prior to transplanting. To minimize the observed plant stress upon introduction to acid, reduced conditions, it was found that some plants

1. Meter relay
2. Millivolt meter
3. pH meter
4. Air pump
5. Calomel halfcell
- 6,7. Platinum electrodes
8. pH electrode
9. Salt bridge
10. Air inlet

11. Serum cap
12. Plexi-glass plate
13. Thermometer
14. Nitrogen inlet
15. Desiccator lower part
16. Outlet for gases
17. Air trap
18. Stirring bar
19. Magnetic stirrer

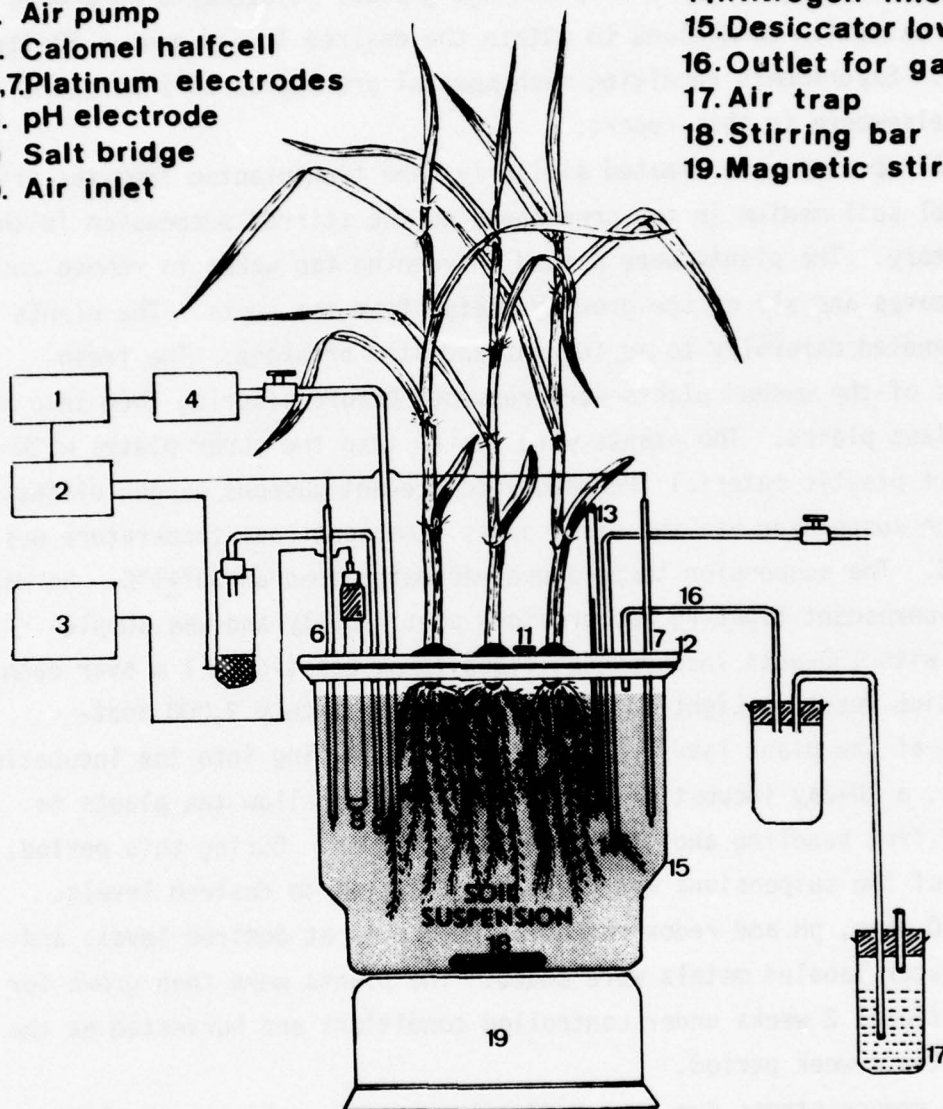


Figure 1. Laboratory System for Plant Uptake Studies Using Soil Suspensions Incubated Under Controlled pH and Redox Potential Conditions.

should initially be transplanted into moderately oxidized, near-neutral soil suspensions. After transplanting, gradual adjustments were made in pH and oxidation conditions to attain the desired levels over a 10-day period. Experiments receiving such special procedures will be designated elsewhere in this report.

All species were treated similarly when transplanted from the artificial soil medium in the greenhouse to the stirred suspension in the laboratory. The plants were washed in running tap water to remove dust from leaves and all of the growing medium from the roots. The plants were handled carefully to avoid root and stem breakage. The fresh weights of the washed plants were recorded before securing them into the plexiglass plates. The plants were sealed into the cover plates with an inert plastic material (Permagum) to prevent gaseous oxygen diffusion into the suspension via the plant ports. Ambient room temperature was $22^{\circ}\pm 1^{\circ}\text{C}$. The suspension temperature was maintained at $30^{\circ}\pm 1^{\circ}\text{C}$. Normal room fluorescent lighting was provided continuously and was supplemented with 150-watt incandescent flood lamps positioned 1 m over each incubation vessel. Light intensity was approximately 2,000 foot-candles at the plant level. Following transplanting into the incubation vessels, a 10-day incubation period was given to allow the plants to recover from handling and transplanting stresses. During this period, the pH of the suspensions was gradually adjusted to desired levels. After 10 days, pH and redox potential were both at desired levels and radiotracer labeled metals were added. The plants were then grown for an additional 2 weeks under controlled conditions and harvested at the end of the 2-week period.

To reduce stress due to a sudden increase in salinity simulating brackish or saltwater systems, the young plants to be used in the laboratory were pretreated in the greenhouse. Saltwater was gradually added to the growing medium commencing 2 weeks prior to transplanting. This pretreatment procedure proved to be very successful and was used for all species.

To confirm and monitor oxidized and reduced conditions in the suspensions, redox potential measurements of each suspension were made daily. Small additions of dextrose (0.25 g), an organic energy source, were occasionally added to all suspensions when there was some difficulty in maintaining sufficiently reduced conditions in any suspension. This sometimes occurred when large plants were growing vigorously.

Suspension pH was also measured daily and adjusted to desired levels as necessary with additions of 2 N hydrochloric acid or 2 N sodium hydroxide. The pH levels in the laboratory uptake studies were maintained at 4.5 and 7.5.

The change in pH from the desired levels during 24 hours were generally greatest during the first few days after pH control was initiated. Maximum change occurred in acid, reduced suspensions which tended to increase in pH and mildly alkaline, oxidized suspensions which tended to become more acid. To minimize possible effects of differing ionic strength on metals uptake due to pH control, sodium chloride was added to suspensions requiring little pH adjustment such that the salinity levels of all suspensions were approximately equivalent. Salinity levels were measured by an electroconductivity meter.

Spartina alterniflora tolerated high salinity levels (15 ppt) well in the greenhouse when the roots were not disturbed. However, if a rhizome or tuber was broken while handling the plants, difficulty in adjusting to the sediment suspensions of this salinity occurred, particularly under reduced conditions at pH 4.5. After transplanting to reduced sediments at pH 7.5, some plants wilted during the first 2 or 3 days, but then recovered and appeared healthy.

Spartina alterniflora transplanted to oxidized suspensions appeared to do well at both pH levels. Young Spartina alterniflora culms taken from the marsh grew well in the greenhouse in the Jiffy Mix, but did not adjust to the laboratory system as well as seedlings.

Spartina cynosuroides tolerated less salt (5 ppt) in the greenhouse. When transplanted to laboratory growth vessels, Spartina

cynosuroides responded well, and mortality rates were much lower than for Spartina alterniflora. Spartina cynosuroides tillered more tightly and did not produce large, tuberous rhizomes as did Spartina alterniflora. Also, this species produced a much more compact and dense rooting system than Spartina alterniflora. As a result of these rooting differences, there were fewer problems associated with roots broken during washing before transplanting and with roots getting caught in the magnetic stirring bar.

It was observed that the larger plants (≈ 1 m tall weighing 25 g) of both species had more difficulty in the laboratory studies than medium sized plants (50 to 65 cm weighing 12 to 15 g). In early trial runs with larger plants, attempts to replace dead plants with plants of the same size were usually unsuccessful.

Distichlis spicata grew in tight clumps rather than as single-stemmed plants. Consequently, this species was hard to wash because of the large number of stems and leaves and the fibrous, dense root system.

Though they had to be handled more for washing, this did not seem to affect the survival of the plants as was found for Spartina alterniflora. This species did well in the laboratory uptake system except under reduced conditions of high salinity and low pH.

After a 10-day adjustment period to the suspensions in laboratory uptake vessels, radiotracers of selected toxic metals were added to the soil suspensions. Details of these additions will be discussed separately with descriptions of each experiment. Following radiotracer additions to the sediment suspensions, the plants were grown in the amended suspensions under conditions of controlled pH and oxidation-reduction conditions for 14 days. After 14 days the plants were harvested.

Plant Harvest and Analysis for Metals Uptake

Fourteen days after amending the suspensions with radiotracer labeled metals, the plants were removed from the laboratory uptake vessels

and washed in tap water to remove soil and dead plant matter. In addition, root tissue was rinsed several times in hydrochloric acid to remove surface adsorbed or precipitated metals. Roots and stem tissue were separated and fresh weights determined. The plant tissue was then dried in perforated paper bags in a forced-draft oven at 60°C for 48 hours after which dry weights of plant tissue were determined. The plant material was then finely cut with stainless steel scissors. Grinding was avoided to minimize contaminating the laboratory with radionuclides contained in plant tissue dust. The cut tissue was placed in plastic bags and each sample thoroughly shaken to mix stem and leaf tissue. A measured aliquot (usually 0.5 to 1.0 g) of cut stem or root tissue was placed in vials to determine gamma activity from the added radiotracers. Gamma emissions were counted on an Ortec solid scintillation (Na I(Tl) crystal) gamma counting system. Specific activity in oven dried plant tissue samples of known weight was determined by comparing sample gamma activity with standards of each radionuclide prepared from the same shipment of each radioisotope.

The remaining plant tissue was digested in a nitric-perchloric acid mixture. Digests were brought to volume in 50-ml volumetric flasks with 6 N distilled hydrochloric acid and stored in acid-rinsed polyethylene bottles at 4°C.

Chemical Extractions of Suspensions

Two chemical extractants of the soil suspensions were made to determine the effects of pH, salinity, and oxidation intensity on selected chemical forms of metals in soils and to compare extractable levels with plant availability of the metals. A combination water-soluble, 1 N sodium acetate extractable (exchangeable) procedure was used, as these chemical forms are thought to represent readily bioavailable forms of metals. Previous studies in this lab indicated that soluble and exchangeable levels of trace metals respond similarly to changes in pH and redox potential (Gambrell et al., 1977). A

diethylenetriaminepentaacetic acid (DTPA) extraction (method of Lindsay and Norvell, 1969) was also used, as this soil extraction procedure and some modifications of this procedure have been found to correlate with trace metal uptake in agricultural crop plants.

The extractions were conducted in gas-tight 500-ml polycarbonate centrifuge bottles under an oxygen-free, nitrogen atmosphere. A silicone rubber serum cap was sealed into each centrifuge bottle cap to allow additions of suspension samples and transfer of chemical extractants under anoxic conditions. Prior to suspension additions, the sealed centrifuge bottles were purged with oxygen-free nitrogen.

A suspension sample of approximately 120 ml was collected from the laboratory uptake vessels with a large capacity plastic syringe equipped with a small glass pipette and injected into tared centrifuge bottles containing 100 ml of deoxygenated 2 N sodium acetate adjusted to pH 4.5 or 7.5, depending on the suspension pH treatment. The centrifuge bottles were then reweighed to determine the quantity of suspension present. The sample and extract quantities were selected such that the final concentration of sodium acetate was near 1 N. The extractant and soil suspension were shaken on a mechanical shaker for 2 hours, then centrifuged for 20 minutes at 6,000 rpm in a Dupont Sorvall Superspeed Centrifuge equipped with a GS-3 head. The supernatant solution was transferred under a nitrogen atmosphere through a 0.45- μ membrane filter. The water-soluble plus exchangeable extract was collected in a receiving flask containing EDTA, or sufficient distilled 16 N nitric acid to lower extract pH to approximately 2 for sample preservation. The soluble plus exchangeable extract was stored in polyethylene bottles at 4°C until analyzed for trace metals.

Fifty-five ml of the DTPA extractant (method of Lindsay and Norvell, 1969) was added to the residual solids in the centrifuge bottles to give an extractant to soil ratio of approximately 2:1. This extraction was conducted as described previously for the soluble plus exchangeable fraction, except that only refrigeration was used as a sample

preservative. Following the DTPA extraction, the residual solids were oven dried to determine the precise weight of solids in each suspension sample.

Five-ml aliquots of soil-chemical extracts were pipetted into vials for determining gamma radiation activity for samples amended with labeled mercury, lead, and cadmium. Mercury was measured only by radio-tracer techniques. Labeled lead and cadmium were also measured by radiotracer techniques. In addition, added plus indigenous lead and cadmium in soil extracts and plant tissue digests were measured by flameless atomic absorption spectrophotometry.

Where sample matrix effects for lead and cadmium contributed to background levels greater than could be compensated for by deturium arc background correction, soil extracts were digested to near dryness in distilled 16 N nitric acid and brought to 50-ml volume with 6 N hydrochloric acid. Iron, manganese, and copper were measured by flame atomic absorption methods.

To minimize metal contamination, all laboratory glass and plastic-ware was washed with detergent in hot water, rinsed several times with tap water, twice with 4 N distilled nitric acid, and three times with glass distilled water prior to use.

Summary of Laboratory Procedures for Individual Uptake Experiments

Experiment A

Plants. Spartina alterniflora culms were taken from the marsh near the end of the growing season in July, 1975. They were 33.0 to 63.50 cm in height and weighed from 1.5 to 6.2 g each fresh weight. These culms were grown in the greenhouse in Jiffy Mix for 8 weeks until a healthy root system developed and then transferred to the incubation vessels.

Soils. The soil suspensions were preincubated 5 to 7 days with 0.45 g green rice straw prior to transplanting. During this time, those suspensions continuously purged with nitrogen reached redox

potentials of -280 mv at pH 7.5 and -80 mv at pH 4.5. Those suspensions continuously purged with air reached redox potentials of +630 mv at pH 4.5 and +360 mv at pH 7.5. Twenty-four days after transplanting (10 days for plants to adjust to the suspensions and 14 days for uptake after addition of labeled metals to the suspensions), the redox potentials for the reducing treatments were +20 mv at pH 4.5 and -225 mv at pH 7.5. The redox potentials under oxidizing conditions were +600 mv at pH 4.5 and +450 mv at pH 7.5.

Salinity Level. An attempt was made to study the effects of high and low salt levels on the uptake of lead and mercury by Spartina alterniflora. The high salt treatment was achieved by gradual addition of sodium chloride over a period of 10 days to a concentration of approximately 20,900 $\mu\text{g/ml}$ or 2.090 percent sodium chloride (21 ppt). Due to the addition of 2 N sodium hydroxide and 2 N hydrochloric acid for pH control, the final salinity level varied from 20,800 $\mu\text{g/ml}$ (20.8 ppt) to 23,000 $\mu\text{g/ml}$ (23 ppt). The low salt treatment consisted of no electrolyte additions other than the acid or base needed to control pH. The low salt treatments consisted of 1600 $\mu\text{g/ml}$ to 2000 $\mu\text{g/ml}$ or 0.169 to 0.20 percent sodium chloride. Half of the incubation vessels in this experiment received a high salt level. All plants in high salt treatments died before the planned harvest date.

Metals. 5 $\mu\text{g Pb/g}$, labeled with 0.2 $\mu\text{Ci } ^{210}\text{Pb/g}$.
1 $\mu\text{g Hg/g}$, labeled with 0.2 $\mu\text{Ci } ^{203}\text{Hg/g}$.

Replications. Lead and mercury were added to the same vessels. Two replications of each incubation vessel containing the heavy metals with the two salt treatments under aerobic or anaerobic conditions at pH 4.5 or 7.5 were carried out.

Extractions. One-hundred ml of 2 N sodium acetate adjusted to suspension pH and 120 ml of the soil suspension were shaken 2 hours then centrifuged 20 minutes at 6000 rpm. The supernatant was filtered through a 0.45- μ membrane filter into a receiving flask containing EDTA for sample preservation. A 0.005 N DTPA extraction on the residual

solid phase was conducted as described above except that no preservative was added to the filtrate. All extracts were refrigerated at 4°C until analyzed for metal content.

Experiment B

Plants. *Spartina cynosuroides* seedlings obtained from the Botany Department of Louisiana State University were grown in Jiffy Mix for 12 weeks, at which time these plants averaged 40 cm in height and weighed approximately 2.8 g (fresh weight).

Soils. The soil suspensions were preincubated until redox potentials in the reduced treatments were -20 mv at pH 4.5 and -118 mv at pH 7.5. The redox potentials of oxidized suspensions were +640 mv at pH 4.5 and +470 mv at pH 7.5. At harvest, 24 days after plant introduction, redox potentials of oxidized suspensions were +690 mv at pH 4.5 and +500 mv at pH 7.5. The redox potentials of reduced suspensions at pH 4.5 were +332 mv and -158 mv at pH 7.5.

Salinity Level. This was a low salt study with no sodium chloride added. At the end of the study, the salinity contents of reduced suspensions were 2400 µg/ml at pH 4.5 and 1300 µg/ml at pH 7.5. The salt contents of oxidized suspensions were 2150 µg/ml at pH 4.5 and 1900 µg/ml at pH 7.5.

Metals. 5 µg Pb/g labeled with 0.2 µCi ^{210}Pb /g.
1 µg Cd/g labeled with 0.2 µCi ^{109}Cd /g.
1 µg Hg/g labeled with 0.2 µCi ^{203}Hg /g.

Replications. Replications for this study are as described for Experiment A. Lead and mercury were added to the same vessel and replicated twice, and cadmium was added to separate vessels and replicated twice.

Extractions. Soil chemical extractions were conducted as described for Experiment A.

Experiment C

Plants. *Spartina cynosuroides* seedlings were grown in the

greenhouse in Jiffy Mix for 5 to 6 months, at which time the average fresh weight was 8 g and average height was 90 cm. Five days prior to transplanting to laboratory uptake vessels, the solution phase of the potting soil was adjusted to 5000 $\mu\text{g/ml}$ sodium chloride.

Soils. The soil suspensions were preincubated as described in Experiment A. Prior to transferring the *Spartina cynosuroides* to incubation vessels, the redox potentials of reduced suspensions were -200 mv at pH 4.5 and -230 mv at pH 7.5. Redox potentials of the oxidized suspensions were +530 mv at pH 4.5 and +390 mv at pH 7.5. At the end of this experiment, the redox potentials of the reduced suspensions at pH 4.5 were +100 mv and -280 mv at pH 7.5. The redox potentials of the oxidized suspensions were +530 mv at pH 4.5 and +450 mv at pH 7.5.

Salinity Level. In this study, a medium salt level was simulated. The salt concentration was gradually increased by the addition of sodium chloride from 6.8 to 7.2 ppt or 6800 to 7200 $\mu\text{g/ml}$.

Metals. 5 μg Pb/g labeled with 0.2 μCi $^{210}\text{Pb/g}$.
1 μg Cd/g labeled with 0.2 μCi $^{109}\text{Cd/g}$.
1 μg Hg/g labeled with 0.2 μCi $^{203}\text{Hg/g}$.

Replications. Treatments were replicated as described for Experiment B.

Extractions. Soil chemical extractions were conducted as described for Experiment A.

Experiment D

Plants. *Distichlis spicata* was seeded in December, 1975 and grown in saturated Jiffy Mix for 3 months. Two weeks prior to transferring the plants to incubation vessels the watering solution of the potting soil was adjusted to 5000 $\mu\text{g/ml}$ sodium chloride. When transplanting to the incubation vessels, these plants were 24 cm tall and average fresh weight was 4 g per plant.

Soils. The soil suspensions were preincubated as described in Experiment A. Before transplanting, the redox potential values for the

reduced treatments were -150 mv at pH 4.5 and -240 mv at pH 7.5. The redox potential values for the oxidized treatments were +525 mv at pH 4.5 and +400 mv at pH 7.5. At the end of the study, the redox potential values of reduced suspensions were +50 mv at pH 4.5 and -100 mv at pH 7.5. Under oxidized conditions the redox potential values were +500 mv at pH 4.5 and +430 mv at pH 7.5.

Salinity Level. A high salt level was simulated in this experiment. The final salt concentration was 13,700 $\mu\text{g/ml}$ sodium chloride.

Metals. 5 μg Pb/g, labeled with 0.2 $\mu\text{Ci/g}$ $^{210}\text{Pb/g}$.

1 μg Cd/g, labeled with 0.2 $\mu\text{Ci/g}$ $^{109}\text{Cd/g}$.

1 μg Hg/g, labeled with 0.2 $\mu\text{Ci/g}$ $^{203}\text{Hg/g}$.

Replications. Treatments were replicated as described for Experiment B.

Extractions. Soil chemical extractions were conducted as described for Experiment A, except that, instead of EDTA, acid was used as a preservative for the sodium acetate extraction.

Experiment E

Plants. Distichlis spicata seedlings grown in the greenhouse after 4 months weighed approximately 16 g and averaged 36 cm in height.

Soils. The soil suspensions were preincubated as described in Experiment A. Before transplanting, the redox potential for the reduced treatments were +15 mv at pH 4.5 and +107 mv at pH 7.5. The redox potential for the oxidized treatments were +322 mv at pH 4.5 and +364 mv at pH 7.5. All of the plants in the reduced treatments died before the end of the 10-day acclimation period. The oxidized soil-plant systems were switched to reducing conditions, and these soil suspensions became reduced by purging with nitrogen gas. These plants were switched because they had become adjusted to the stirring environment, and there was a limited supply of Distichlis spicata of the same age and size. Replacement plants in new soil suspensions were prepared for oxidized treatments. At the end of the study, the redox potentials of the reducing

treatments were -40 mv at pH 4.5 and -230 mv at pH 7.5. Under oxidizing conditions, the redox values were +577 mv at pH 4.5 and +392 mv at pH 7.5.

Salinity Level. This study was conducted with a medium salinity level with a final concentration of 8700 $\mu\text{g/ml}$ sodium chloride.

Metals. 5 μg Pb/g, unlabeled material
1 μg Cd/g, labeled with 0.3 $\mu\text{Ci/g}$ $^{109}\text{Cd/g}$.
1 μg Hg/g, labeled with 0.3 $\mu\text{Ci/g}$ $^{203}\text{Hg/g}$.

Replications. Each treatment was replicated four times. Labeled mercury and cadmium and unlabeled lead were added to each suspension as indicated above.

Extractions. Soil chemical extractions were conducted as described in Experiment D.

Experiment F

Plants. In this study, Distichlis spicata plants were transplanted to a reducing, medium salinity soil suspension adjusted to pH 4.5. These plants averaged 20.8 g each and 40 cm in height. Spartina alterniflora plants collected from the marsh in April, 1976 weighed 19 g each,

Soils. The soil suspensions were preincubated for 7 days. The redox potentials of the reducing suspensions were +30 mv at pH 4.5 and -258 mv at pH 7.5. The redox potentials of the oxidizing suspensions were +540 mv at pH 4.5 and +465 mv at pH 7.5. At harvest, 24 days after the introduction of the plants, the redox potentials of the oxidizing suspensions were +290 mv at pH 7.5. The redox potentials of the reducing suspensions were +45 mv at pH 4.5 and -300 mv at pH 7.5.

Salinity Level. In this study a medium saline environment was simulated. The salt concentration was gradually increased by the addition of sodium chloride to 7200 $\mu\text{g/ml}$.

Metals. 5 μg Pb/g unlabeled material.
1 μg Cd/g labeled with 0.2 μCi $^{109}\text{Cd/g}$.
1 μg Hg/g labeled with 0.2 μCi $^{203}\text{Hg/g}$.

Replications. The Distichlis spicata grown in pH 4.5 reducing conditions was replicated twice. The Spartina alterniflora grown in pH 4.5 or pH 7.5 reducing conditions was replicated using three incubations of each treatment. Spartina alterniflora grown in oxidizing conditions at pH 4.5 and 7.5 was replicated four times.

Extractions. Soil chemical extractions were conducted as described in Experiment D.

Laboratory Studies with Low¹ Rice (*Oryza sativa*)

The soil used in this study was Crowley silt loam from the Rice Experiment Station, Crowley, Louisiana. Five-hundred g of air dry soil, which had been amended with finely ground rice straw (0.4 percent on an oven dry soil basis), was placed in a glass desiccator base (Pyrex 412230) with 2000 ml of glass distilled deionized water. No supplemental cadmium or lead was added. The mixture was kept in suspension with a magnetic stirrer. The treatments studied were all combinations of six redox potentials (-200, -100, 0, +100, +200, and +400 mv) and four pH levels (5, 6, 7, and 8). The redox potential of the soil suspension was continuously monitored and controlled by an automatic addition of air when the redox potential decreased below the preset value. The pH was controlled manually by the addition of either acid or alkali. A detailed description of the system used in this study to grow plants in soil suspensions under conditions of controlled redox potential and pH is reported elsewhere (Patrick, Williams, and Moraghan, 1973; Reddy, Jugsujinda, and Patrick, 1976).

After incubating the soil suspension at a selected redox potential-pH combination for 14 days, 30-day old rice seedlings that had been growing in a nutrient solution were transferred to the soil suspension. The composition of the nutrient solution which was used for growing the rice seedlings and the technique of transferring rice seedlings from the nutrient solution to an incubated soil suspension was described by Reddy *et al.* (1976). The rice seedlings were grown for 10 days in soil suspensions of controlled redox potential and pH. At the end of the 10-day

growth period, root and shoot portions of the plants were harvested separately, washed thoroughly with tap water, and rinsed twice with 0.1 N HCl (Arkley, Munns, and Johnson, 1960) and three times with glass distilled deionized water. The plant tissue was then dried in a draft oven at 70°C until constant weights were obtained. Stainless steel scissors were used to cut the plant material into fine pieces, and 1 g of shoot tissue and 0.5 g of root tissue were digested separately with reagent grade concentrated nitric acid and a nitric-perchloric acid mixture (Jackson, 1958). Metal content of reagent blanks was measured to compensate for reagent contamination. The digested plant material was analyzed for cadmium and lead by flameless atomic absorption spectrophotometry (Perkin-Elmer Model 2100 HGA, Perkin-Elmer Model 360 Spectrophotometer equipped with background corrector).

At the time the plants were sampled, 100 ml of soil suspension was transferred under a nitrogen atmosphere to sealed 500-ml polycarbonate centrifuge bottles fitted with serum caps which had been previously purged with nitrogen gas. The soil suspension was centrifuged at 5000 rpm for 20 minutes and filtered under a nitrogen atmosphere through a 0.45- μ membrane filter. The samples were preserved with EDTA to maintain cadmium and lead in a soluble form until analysis. Water-soluble cadmium and lead were also analyzed using a flameless atomic absorption spectrophotometer.

Greenhouse Studies

A greenhouse study was conducted to determine the effects of soil or sediment oxidation conditions on uptake of trace metals by plants from an undisturbed soil material. In this report, the term undisturbed refers to typical greenhouse experiments in which plants are grown in soil material added to pots. Specifically, distinction is made between continuously stirred soil suspensions in the laboratory and conventional experimental methods of growing plants. This approach was thought to better simulate physical conditions of a natural rooting environment.

As little published information is available on procedures of studying the effects of oxidation on metal uptake by plants, the primary objective was to attempt to develop a satisfactory experimental approach for this type of study in undisturbed (not stirred suspensions) soil material. Assuming a successful method could be developed, an additional objective was to qualitatively confirm conclusions obtained from laboratory studies using soil suspensions.

The Mhoon soil selected for this study has been described previously in this report. The moist soil material was sieved through a 5-mm mesh screen, then thinly spread on greenhouse benches to air dry. After air drying, 22.3 kg of this soil was added to a 120-l metal drum. To this soil was added 454 g of finely ground Mhoon soil amended and well mixed with 1.85 g lead nitrate and 3.16 g cadmium nitrate, such that when mixed, the 22.7 kg of Mhoon soil material would contain 50 µg/g each of added lead and cadmium. Amendments were made to this agricultural soil to increase the availability of these metals to the marsh plants used in the study to facilitate their detection in plant tissue by atomic absorption techniques. The 120-l drums were turned on a large capacity roller mixer for 8 hours to ensure uniform mixing of the added metals. Six kg of the metals amended, air-dried soil was weighed into each of 18 ceramic pots which were 20 cm in diameter and 30 cm tall.

Plant Establishment

The plant species included in this study were Spartina alterniflora, Distichlis spicata, and Sorghum halepense (Johnson grass).

The Spartina alterniflora culms were collected from the marsh near Leesville, Louisiana during early April, 1976 and grown in Jiffy Mix in the greenhouse until transplanted into the potted Mhoon soil on June 7, 1976. The plants were approximately 40 cm tall at transplanting. Ten culms were transplanted to each of six pots.

Distichlis spicata plants were separated as much as possible without excessive root damage from their characteristic aggregate groupings and transplanted to the soil.

Approximately 1 cm of surface soil from each of 6 pots was removed and 3 g of Sorghum halepense seeds uniformly distributed over the exposed soil surface. The removed soil was then replaced and packed lightly.

Soil moisture in all pots was maintained near saturation levels for 5 days to favor germination of the Sorghum halepense seed and establishment of the Spartina alterniflora and Distichlis spicata transplants. Then, each pot was fertilized with 250 ml of a Hoagland's solution to provide secondary and trace nutrients. In addition, each pot received ammonium sulfate equivalent to 224 kg/nitrogen per ha. For 4 additional days, each pot was maintained at approximately "field moisture capacity" by daily additions of water adjusted to allow a minimum excess moisture drainage through the bottom holes of each pot. Ten days after seeding and transplanting Spartina alterniflora and Distichlis spicata, control was begun to regulate oxidation intensity in the soil material. Control of oxidation conditions was delayed until June 30 for pots growing Sorghum halepense to give seedlings time to become established.

Control and Monitoring of Oxidation-Reduction Potential

Oxidation-reduction intensity (redox potential) was measured daily on each of four platinum electrodes positioned 5 to 8 cm beneath the soil surface in each pot. The electrochemical cell was completed with a flexible salt bridge which was moved from pot to pot during measurements. Unlike soil suspension studies in which replicate electrodes usually agree very closely, the redox potential measurements from four electrodes in each of the greenhouse pots showed considerably more variability, especially in reduced soils. This was attributed to possible nonuniform oxidation-reduction conditions expected in the rhizosphere. For example, a platinum wire electrode adjacent to a root may be responding to a different chemical environment than would be found in soil a few mm away from any active roots. Therefore, the average value of four electrodes was considered representative of oxidation conditions in the soil. In undisturbed soil systems, gradual electrode "poisoning" (Bailey and Beauchamp, 1971) may have occurred. It was found that cleaning the

electrodes at about 10-day intervals minimized the variability within a given pot.

Three oxidation-reduction levels were studied with two replications for each species-oxidation intensity combination. Maximum reduction was achieved and maintained by keeping the soil in pots 1 and 2 of each species submerged under 2 to 4 cm of water. Maximum oxidation was maintained by adding approximately 300 ml of water to pots 5 and 6 daily and allowing excess water, if any, to drain through an opening at the base of each pot. Openings at the base of pots 3 and 4 were connected by a valve and tubing to a water reservoir where head height was equal to the soil surface.

Oxidation intensity was maintained at an intermediate level by manually opening and closing the valve to each pot depending on redox potential which was measured twice daily. This procedure for control is described in more detail in the next section. When the redox potential exceeded desired levels, the valve was opened from 1 to several hours until the soil became wet and was then closed. Using this system, redox potential generally followed a 4-day cycle in which it would increase above desired levels, water would be added, and within 24 hours, the soil would begin to become more reducing, reaching a minimum after about the end of the second day. Then a gradual increase was observed to or just above the selected level after which water would again be added.

Unlike the laboratory studies where both pH and redox potential can be closely controlled, no pH control was attempted in the greenhouse experiments. Since soil and sediment pH are influenced to a considerable extent by chemical and microbiological processes affected by oxidation intensity, it was expected that pH levels would differ for each oxidation treatment, and soil samples were taken for pH measurements twice during this study.

While the laboratory study is applicable to the range of pH-oxidation conditions commonly encountered in nature, the greenhouse study more closely approximated the relationship between pH and redox potential conditions associated with the principal methods of dredged material

disposal. Open water disposal or utilization for marsh or habitat creation within an intertidal zone generally results in a reduced sediment environment. Habitat development, agricultural soils amendment, or other upland disposal methods such as confinement behind dikes at elevations well above the natural water table may result in gradual drainage and subsequent oxidation.

Oxidation intensity treatments were begun on June 18, 1976 for Spartina alterniflora and Distichlis spicata. Oxidation intensity control was begun on June 30 for Sorghum halepense to give these seedlings time to grow to approximately 20 cm before initiating control. A summary of harvest dates, cutting heights, and yield at harvest is indicated in Table 1. Sample preparation and analyses were conducted as previously described for laboratory studies.

Preliminary Efforts to Develop Methods for Studying Marsh Plant Uptake of Trace Metals from Unstirred Soil Materials

There is little information in the literature on the effect of soil oxidation intensity on metal uptake by plants and even less published on methods for conducting controlled experiments to study this phenomenon. Consequently, one of the objectives of this research was to attempt to develop a method to study metals uptake from undisturbed soils or sediments in which oxidation intensity could be varied. The following paragraphs describe these efforts, briefly discussing procedures that did not work, as well as those that did. The greenhouse procedures finally adopted for this study represent a reasonably successful approach developed within the time restraints of this project.

To regulate oxidation intensity of undisturbed soil and sediment material, control of oxygen availability within the material is required. Most surface soils and sediments contain considerable levels of indigenous residual organic material which serves as an energy source for microbial activity. Oxygen is the preferred electron acceptor for microbial respiration, and a high oxygen demand usually exists in surface soils and sediments. Where oxygen demand is considerable, oxygen availability

Table 1

Dry Matter Production, Cutting Height, and Soil pH in Greenhouse Trace

Metal Uptake Studies for *Distichlis spicata*,

Spartina alterniflora, and *Sorghum halepense**

Species	Oxidation-reduction conditions	First harvest			Second harvest			
		Soil pH	Upper stem** Dry matter	Upper stem** Cutting height	Soil pH	Upper stem Dry matter	Upper stem Cutting height	Lower stem† Dry matter Cutting height
		--g----	----	----cm--		--g----	----cm--	----cm--
<u><i>Distichlis spicata</i></u>	Reduced	6.5	8.5	27	6.9	6.9	27	15.9
	Intermediate	5.6	6.6	27	5.8	3.8	27	9.2
	Oxidized	5.6	3.9	27	6.2	2.6	27	9.8
<u><i>Spartina alterniflora</i></u>	Reduced	6.6	10.1	36	6.9	9.2	36	38.4
	Intermediate	6.0	6.5	36	6.2	5.7	36	18.0
	Oxidized	5.8	1.8	36	6.0	1.0	36	18.2
<u><i>Sorghum halepense</i></u>	Reduced	6.6	21.0	36	7.0	7.4	36	19.3
	Intermediate	5.6	15.8	36	5.9	9.3	36	21.0
	Oxidized	4.8	3.5	36	5.1	12.9	36	15.7

*Soil pH and dry matter harvested are means of duplicate pots.

**Mostly leaf tissue with some stem.

†Mostly stem tissue.

may be regulated by controlling the rate of oxygen resupply or transport from the overlying atmosphere into the soil or sediment material. Oxygen transport through the interconnected pore space of well-drained soils by gaseous diffusion is rapid, and oxygen deficiencies of the bulk soil material generally do not occur. Oxygen transport through quiescent interstitial water of flooded soils and sediments by aqueous diffusion is extremely slow, and oxygen deficiencies accompanied by strongly reduced or anaerobic conditions occur readily in these systems. Thus the experimental approach used to regulate oxidation intensity was to control oxygen resupply rate by controlling the water content of the soil material.

Initially, a salt marsh sediment was obtained from a mud flat adjacent to a stand of Spartina alterniflora in the Southwestern Louisiana Canal near Leesville, Louisiana.

In greenhouse pots, this material supported vigorous marsh plant (Spartina cynosuroides) growth when maintained in a saturated state, and a strongly reduced rooting environment was confirmed by redox potential measurements. Attempts to oxidize the rooting environment by removing excess water by gravity flow through an opening in the bottom of the pot and by plant transpiration resulted in considerable irreversible shrinkage of the soil and development of a dry, impervious surface which apparently retarded water reentry into this material. Also, redox potential measurements from permanently placed electrodes indicated the interior of this material was still strongly reduced despite the shrunken, dry exterior appearance. Work with the unamended sediment was terminated when it became apparent the drained pots with marsh sediments may not simulate aerobic conditions in short-term studies.

To minimize sediment shrinkage within the pot and to improve water permeability with minimum effects on sediment chemical properties, the sediment material was mixed with an equal volume of washed, coarse sand into which Spartina cynosuroides was transplanted and the previous study repeated. This time some improvement was noted in shrink-swell tendencies, apparent water permeability, and plant growth under attempted

oxidized conditions, though the improvement was not to the degree desired. It was felt that further increases in the proportions of sand might improve the physical properties of the marsh sediment and make a study of an oxidized rooting environment feasible, but after two attempts, this material was dropped.

A third start was made, as previously described, using a sandy loam material containing 1.5 percent organic matter collected from the bank of the Mississippi River near St. Gabriel, Louisiana.

Though the physical properties of this alluvial soil were suitable for the greenhouse studies, marsh species transplanted into this sediment material appeared yellowed and stunted at all oxidation levels. Subsequent tests revealed a pH of 8.3, which may have contributed to trace nutrient deficiencies.

The Mhoon soil previously described for the laboratory studies was used in the next study. Both physical and chemical properties of this soil were found suitable for growing marsh plants under controlled oxidation conditions in the greenhouse.

Initially, an attempt was made to achieve automatic redox potential control at six different levels, ranging from strongly reduced to well oxidized. Millivolt meters continuously monitored redox potential from four electrodes in each pot. The recorder output from the meters was connected to meter relays which were wired to solenoid valves regulating water entry into the base of each pot from an adjacent constant height reservoir. Whenever the redox potential decreased above a preset potential, the valve opened adding water to the pot. However, the soil in the pots tended to become saturated with some surface water accumulation before oxygen became sufficiently limiting to microbial populations for redox potential to decline. Then the redox potential would often decrease well below the preset level before evapotranspiration removed excess water permitting gaseous oxygen entry into the soils. Evapotranspiration was particularly limiting during the winter and early spring months even though the greenhouse was heated to 21°C.

Due to the oscillating redox potential cycles over periods of 3 to 5 days and time constraints, it was decided to try and obtain replicated uptake studies at three general oxidation-reduction levels, as previously described, instead of six levels with automatic control.

RESULTS AND DISCUSSION

In the laboratory studies, there were no consistent trends indicating treatments affected total harvested weight of plants. For these studies, the relative treatment effects were consistently similar whether total uptake or concentration was considered. However, this was not true for greenhouse studies in which treatments had a marked effect on biomass production. In the greenhouse studies, the mildly acid, oxidized soil conditions resulted in poorest growth of marsh plants (Distichlis spicata and Spartina alterniflora) and a mixed growth response with Johnson grass (Sorghum halepense) depending on the harvest. In greenhouse studies, maximum tissue concentration of metals was usually associated with treatments which have been found to favor enhanced chemical availability of these metals in sediments (Gambrell *et al.*, 1977), and this was generally supported by the laboratory studies. But opposite treatment effects were frequently noted in greenhouse studies depending on whether tissue concentration or total uptake was considered. Therefore, both concentration and uptake data will be presented for greenhouse studies to illustrate this effect.

It was not determined why biomass production of marsh plants was adversely affected by oxidized conditions in greenhouse studies using undisturbed soil, but was little affected or unaffected in laboratory studies using soil suspensions as the rooting medium. Two possibilities include limited moisture and metal toxicity. Limited moisture may have been a contributing factor to the reduced growth noted in the most oxidized treatment, but this seems unlikely as water was added daily and the excess was observed to drain through an opening in the bottom of each pot. Limited moisture was not a factor in the reduced growth noted in the intermediate treatment where the soil remained very moist for the duration of the experiment.

The tissue concentration of cadmium in the two marsh species was similar to levels which have been reported to decrease growth of

Distichlis spicata and Spartina alterniflora (Lee, 1976). Thus cadmium toxicity may have been a contributing factor and growth may have been less affected had the soils received a smaller cadmium amendment. If cadmium toxicity did contribute to decreased biomass production due to greater tissue cadmium concentrations in oxidized treatments, this would suggest tissue concentration of metals is more indicative of plant availability of soil or sediment-bound metals than total uptake.

Tissue concentrations of metals in the greenhouse and laboratory studies generally responded similarly to experimentally imposed pH and oxidation-reduction conditions. Tissue concentrations will be the primary response discussed in this report as it is believed this parameter is an indication of the relative treatment effects on the plant availability of trace and toxic metals.

The intent of this study was to identify the effects of physico-chemical parameters on the plant availability of sediment-bound metals using representative plant species. Thus, trace metal concentration in plant tissue is stressed as an indication of the effects of the experimental treatments on plant availability in these relatively short-term laboratory studies. Precise determination of total metal uptake potentially available for biocycling for specific contaminated dredged material disposal projects involving habitat development or other up-land application methods would require long-term field studies.

Metal Uptake Studies with Marsh Species

Mercury

The effect of pH and oxidation-reduction conditions on mercury uptake was determined using radiotracer techniques in laboratory studies with Distichlis spicata, Spartina alterniflora, and Spartina cynosuroides. Specific activity of mercury-203 in plant tissue was transformed to μg mercury/g oven dry plant tissue based on amendments to soil suspensions of $0.2 \mu\text{Ci}$ ($0.3 \mu\text{Ci}$ in Experiment E) mercury-203 + $1 \mu\text{g}$ unlabeled mercury (as $\text{Hg}(\text{NO}_3)_2$) per g oven dry soil solids. For

example, a specific activity of 0.1 μCi mercury-203 per g plant tissue would be equivalent to 0.5 μg labeled mercury per g plant tissue. This plant mercury content would represent labeled mercury added to the soil and not indigenous soil mercury. Thus the reported plant mercury content represents that mercury taken up from the labeled mercury added to the soil.

Distichlis spicata. The effects of pH and oxidation-reduction conditions on the labeled mercury content of Distichlis spicata are indicated in Table 2. With this species, there was a decrease in mercury content at the higher salinity level at every pH-oxidation level combination. At both salt levels, mercury content increased with increasing pH and oxidation intensity. Maximum mercury uptake occurred under weakly alkaline, oxidized conditions.

Spartina alterniflora. As observed with Distichlis spicata, a reduction in mercury content was associated with an increase in salinity (Table 3). Mercury concentration was insufficient at the medium salt treatment to show possible pH and redox potential treatment effects. At the low salt level there was probably an increase in mercury uptake with oxidation intensity at pH 4.5, while treatment effects, if any, were not apparent at pH 7.5 due to considerable experimental error.

Spartina cynosuroides. The experimental error at the low levels accumulated in aboveground tissue may have masked treatment effects on mercury uptake by Spartina cynosuroides. However, as generally observed for Distichlis spicata and Spartina alterniflora, there was a consistent increase in the mercury content of this species with an increase in pH (Table 4).

Lead

The effect of pH and oxidation-reduction conditions on lead uptake was determined using radiotracer techniques and flameless atomic absorption in laboratory studies of Distichlis spicata, Spartina alterniflora, and Spartina cynosuroides. Flameless atomic absorption was used to

Table 2
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Mercury in Distichlis spicata Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Hg content, $\mu\text{g/g}$ -----			
medium	Hg-203	0.004 [†] <u>+0.003[‡]</u>	0.013 <u>+0.012</u>	0.005 <u>+0.002</u>	0.027 <u>+0.012</u>
high	Hg-203	0.001 <u>+0.000</u>	0.006 <u>+0.002</u>	0.003 <u>+0.002</u>	0.011 <u>+0.000</u>

[†]Mean.

[‡]Standard deviation.

Table 3
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Mercury in Spartina alterniflora Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Hg content, µg/g -----					
low	Hg-203	0.010 [†] <u>+0.003[‡]</u>	0.022 <u>+0.007</u>	0.119 <u>+0.093</u>	0.018 <u>+0.011</u>
medium	Hg-203	0.001 <u>+0.000</u>	0.001 <u>+0.000</u>	0.001 <u>+0.001</u>	0.001 <u>+0.000</u>

[†]Mean.

[‡]Standard deviation.

Table 4
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Mercury in *Spartina cynosuroides* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Hg content, µg/g -----					
low	Hg-203	0.002 -----*	0.004 [†] +0.001 [‡]	0.016 +0.021	0.026 +0.019
medium	Hg-203	0.011 +0.013	0.004 +0.001	0.044 +0.026	0.021 +0.015

[†]Mean.

*Lost one sample.

[‡]Standard deviation.

measure lead uptake in greenhouse experiments with Distichlis spicata, Spartina alterniflora, and Sorghum halepense.

Distichlis spicata. Insufficient radiotracer lead was found in Distichlis spicata grown for 2 weeks in laboratory suspensions to evaluate the effects of pH and redox potential on labeled lead uptake.

Generally, there was little effect of either pH or oxidation conditions on measured lead content in this species in laboratory studies (Table 5). In the greenhouse, increasing oxidation intensity also had little effect on the lead content of the aboveground tissue (Table 6), but total uptake decreased substantially with an increase in oxidation levels because of decreased plant growth under oxidized conditions.

Spartina alterniflora. There was no discernible response of lead content in Spartina alterniflora to pH changes and oxidation intensity in laboratory studies (Table 7). In the greenhouse experiment, the lead content consistently increased in upper and lower stem tissue as oxidation intensity increased (Table 8) though total uptake was least under oxidized conditions due to poor growth. Since soil oxidation was accompanied by an increase in acidity, Table 1, pH effects cannot be excluded in the increase in tissue lead content. Thus the observed oxidation effects may have been due to secondary effects of redox potential mediated changes in soil acidity.

Spartina cynosuroides. In the laboratory studies, lead uptake by aboveground Spartina cynosuroides tissue was little affected by changes in pH or oxidation intensity (Table 9). The apparent greater uptake measured under reduced conditions in the low salt treatment was accompanied by considerable experimental error and was not evident in the medium salt treatment.

Sorghum halepense. The lead content of Sorghum halepense grown in undisturbed soil material in the greenhouse generally increased as oxidation intensity increased (Table 10). Again, the reduction in pH accompanying soil oxidation may have contributed to the increase in lead availability. Measured pH ranged from about 7 in reduced soil material

Table 5
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Lead in Distichlis spicata Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Pb content, µg/g -----					
medium	soil + labeled Pb [§]	4.75 [†] +3.98 [#]	4.54 +0.52	2.58 +0.67	3.01 +0.74
high	labeled Pb	0.004 +0.002	0.003 +0.000	0.003 +0.002	0.012 +0.007
	soil + labeled Pb [§]	2.19 +0.29	2.52 +1.00	2.42 +1.58	4.61 +1.63

[§]By atomic absorption.

[†]Mean.

[#]Standard deviation.

Table 6
The Effect of Oxidation-Reduction Conditions on the
Lead Content of Distichlis spicata in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake
First harvest, upper stem	1.38 [†] $\pm 0.56^\ddagger$	11.7 ± 4.3	0.79 ± 0.08	5.2 ± 0.8	0.95 ± 0.13	3.7 ± 0.7
Second harvest, upper stem	1.82 ± 0.39	12.8 ± 4.2	1.84 ± 0.19	7.1 ± 3.3	2.14 ± 0.23	5.6 ± 2.2
Second harvest, lower stem	1.76 ± 0.31	28.2 ± 7.3	1.87 ± 0.16	17.2 ± 2.0	1.47 ± 0.60	13.6 ± 1.9

[†]Mean.

[‡]Standard deviation.

Table 7

The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Lead in *Spartina alterniflora* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Pb uptake, μg -----					
low	labeled Pb	0.002 [†] <u>+0.001[#]</u>	0.002 <u>+0.000</u>	0.000 <u>+0.000</u>	0.004 <u>+0.001</u>
	soil + labeled Pb [§]	4.33 <u>+3.49</u>	1.76 <u>+0.29</u>	1.61 <u>+0.48</u>	2.33 <u>+0.32</u>
medium	soil + labeled Pb [§]	1.50 <u>+0.98</u>	2.26 <u>+0.68</u>	1.90 <u>+0.57</u>	2.00 <u>+1.08</u>

[†]Mean.

#Standard deviation.

[§]By atomic absorption.

Table 8

The Effect of Oxidation-Reduction Conditions on the
Lead Content of *Spartina alterniflora* in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake
First harvest, upper stem	1.06^{\dagger} $\pm 0.10^{\#}$	10.8 ± 4.5	1.92 ± 0.08	12.5 ± 2.5	2.22 ± 0.21	4.0 ± 2.2
Second harvest upper stem	1.01 0.02	9.2 ± 0.8	1.58 ± 0.22	9.1 ± 2.2	2.36 -----*	2.3 -----*
Second harvest, lower stem	0.80 ± 0.00	30.8 ± 1.0	1.34 ± 0.13	24.8 ± 19.6	2.38 ± 0.02	43.3 ± 10.7

† Mean.

$^{\#}$ Standard deviation.

*Lost one sample.

Table 9
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Lead in *Spartina cynosuroides* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Pb content, $\mu\text{g/g}$ -----					
low	labeled Pb	0.035 -----*	0.013 [†] <u>+0.003[‡]</u>	0.026 <u>+0.016</u>	0.004 <u>+0.004</u>
	soil + labeled Pb [§]	5.24 -----*	1.46 <u>+0.46</u>	6.95 <u>+6.51</u>	1.02 <u>+0.02</u>
medium	labeled Pb	0.004 <u>+0.004</u>	0.044 <u>+0.057</u>	0.008 <u>+0.004</u>	0.005 <u>+0.002</u>
	soil + labeled Pb [§]	1.54 <u>+1.09</u>	1.14 <u>+0.04</u>	1.35 <u>+0.05</u>	1.62 <u>+0.42</u>

[†]Mean.

*Lost one sample.

[‡]Standard deviation.

[§]By atomic absorption.

Table 10
The Effect of Oxidation-Reduction Conditions on the
Lead Content of Sorghum halepense in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake	$\mu\text{g Pb/g}$ Content	$\mu\text{g Pb}$ Uptake
First harvest, upper stem	2.06 [†] $\pm 0.04^*$	43.2 ± 1.0	1.98 ± 0.40	31.6 ± 9.5	2.60 ± 0.32	9.1 ± 0.3
Second harvest, upper stem	0.53 ± 0.08	3.9 ± 0.4	0.36 ± 0.04	3.4 ± 1.9	0.96 ± 0.74	12.9 ± 10.7
Second harvest, lower stem	0.52 ± 0.02	10.0 ± 0.2	1.23 ± 0.09	26.0 ± 6.2	1.86 ± 0.30	29.4 ± 5.7

[†] Mean.

* Standard deviation.

to near 5.0 in the oxidized treatment (Table 1). Thus the treatment effect on lead content may have been due to a change in oxidation conditions, pH, or a combination of these factors.

Cadmium

The effect of pH and oxidation-reduction conditions on cadmium uptake was determined in laboratory studies using radiotracer techniques and flameless atomic absorption for Distichlis spicata, Spartina alterniflora, and Spartina cynosuroides. In the greenhouse experiments, flameless atomic absorption was used to determine uptake in aboveground tissue by Distichlis spicata, Spartina alterniflora, and Sorghum halepense.

Distichlis spicata. Table 11 indicates that concentration of radiotracer cadmium increased in this species with increasing oxidation levels. While there was little or no apparent effect of pH under reduced conditions, labeled cadmium concentration was enhanced by increasing pH in oxidized suspensions. Maximum radiotracer concentration at both salt levels occurred under mildly alkaline, oxidized conditions.

Cadmium uptake responses as measured by atomic absorption techniques were very similar to changes in pH and oxidation conditions found for labeled cadmium uptake (Table 11). Comparison of uptake by radiotracer and atomic absorption techniques indicated that most of the cadmium in aboveground tissue was derived from the indigenous soil cadmium rather than the 1- μ g cadmium/g soil (oven dry basis) added with the cadmium-109. Nevertheless, unlike results for lead, plants grown in soil suspensions amended with cadmium usually contained a slightly greater cadmium content than did plants grown in unamended suspensions in the same experiment. Thus data from both cadmium-amended and unamended soils are given in Table 11. For Distichlis spicata, cadmium concentration was consistently enhanced at pH 7.5 by increasing oxidation intensity at both salt levels. This contrasts somewhat with previous studies conducted in this laboratory in which the chemical availability of cadmium was always greatest under acid, oxidizing conditions (Gambrell et al., 1977). As will be subsequently discussed, cadmium uptake by Distichlis

Table 11
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Cadmium in *Distichlis spicata* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Cd content, µg/g -----					
medium	labeled Pb	0.012 [†] <u>+0.015[‡]</u>	0.009 <u>+0.004</u>	0.004 <u>+0.007</u>	0.131 <u>+0.047</u>
	soil + labeled Cd [§]	0.42 <u>+0.18</u>	0.42 <u>+0.07</u>	0.36 <u>+0.11</u>	1.58 <u>+0.49</u>
high	labeled Cd	0.006 <u>+0.001</u>	0.145 <u>+0.040</u>	0.001 <u>+0.000</u>	0.416 <u>+0.294</u>
	soil + labeled Cd [§]	0.38 <u>+0.06</u>	1.46 <u>+0.02</u>	0.48 <u>+0.01</u>	2.42 <u>+1.33</u>
	soil Cd [§]	0.57 <u>+0.18</u>	0.92 <u>+0.25</u>	0.42 <u>+0.06</u>	1.05 <u>+0.27</u>

[†]Mean.

[‡]Standard deviation.

[§]By atomic absorption.

spicata responded differently to pH and oxidation-reduction conditions compared to Spartina cynosuroides and Spartina alterniflora.

In the greenhouse experiment using an undisturbed rooting medium amended with 50 µg cadmium/g solids, cadmium concentration in plant tissue was also found to increase substantially with an increase in oxidation intensity (Table 12). However, because of the decrease in biomass production at the most oxidized level, total cadmium uptake was not greatest in the oxidized treatment. As previously discussed, the reduced growth under oxidized conditions may have been caused by a moisture stress or cadmium toxicity.

Spartina alterniflora. In laboratory studies with Spartina alterniflora at low salt levels (an unnatural salinity situation for this species), the aboveground tissue concentration of cadmium was not affected by changes in pH and oxidation intensity. At medium salt levels, cadmium uptake was greatest under acid, oxidizing conditions, as measured by both atomic absorption and radiotracer techniques (Table 13). As found for Distichlis spicata, indigenous soil cadmium seemed to be the primary source of metal in the plant tissue.

Greenhouse experiments confirmed the laboratory studies as the cadmium content increased with increasing oxidation intensity. The concurrent decrease in pH accompanying increasing soil oxidation may have contributed to the increased cadmium concentration in the plant. The considerably greater cadmium content in the greenhouse experiment was probably the result of adding 50 µg cadmium/g soil in the greenhouse study, compared to either no cadmium additions or 1 µg/g additions in the laboratory study (Table 14). As noted for Distichlis spicata, cadmium content increased with increasing oxidation conditions, but total cadmium uptake was markedly decreased in upper stem tissue due to less growth under oxidized conditions.

Spartina cynosuroides. Cadmium accumulation by Spartina cynosuroides responded similarly to Spartina alterniflora in laboratory studies at controlled pH and redox potential (Table 15). Maximum

Table 12

The Effect of Oxidation-Reduction Conditions on the
Cadmium Content of Distichlis spicata in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake
First harvest, upper stem	6.0 [†] $\pm 1.0^*$	50 ± 7	10.0 ± 2.6	66 ± 20	10.2 ± 0.8	40 ± 2
Second harvest, upper stem	6.8 ± 1.0	47 ± 13	16.5 ± 5.5	66 ± 44	22.3 ± 1.4	57 ± 13
Second harvest, lower stem	21.0 ± 1.8	335 ± 58	30.5 ± 1.2	281 ± 20	25.0 ± 1.2	245 ± 55

[†]Mean.

*Standard deviation.

Table 13
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Cadmium in *Spartina alterniflora* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Cd content, $\mu\text{g/g}$ -----			
low	soil Cd ^s	0.29 [†] <u>+0.08[‡]</u>	0.20 <u>+0.02</u>	0.25 <u>+0.02</u>	0.24 <u>+0.05</u>
medium	labeled Cd	0.002 <u>+0.002</u>	0.240 <u>+0.048</u>	0.001 <u>+0.002</u>	0.002 <u>+0.001</u>
	soil + labeled Cd ^s	0.27 <u>+0.12</u>	1.68 <u>+0.50</u>	0.39 <u>+0.17</u>	0.32 <u>+0.14</u>

^sBy atomic absorption.

[†]Mean.

[‡]Standard deviation.

Table 14
The Effect of Oxidation-Reduction Conditions on the
Cadmium Content of *Spartina alterniflora* in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake
First harvest, upper stem	6.5 [†] +1.3 [*]	68 +35	13.8 +0.2	90 +16	13.4 +0.8	24 +12
Second harvest, upper stem	8.0 +0.0	74 +8	16.8 +1.4	96 +18	33.4 -----*	32 -----*
Second harvest, lower stem	20.5 +0.6	788 +48	33.6 +2.8	622 +484	36.2 +2.4	652 +112

[†] Mean.

^{*} Standard deviation.

*Lost one sample.

Table 15
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Cadmium in *Spartina cynosuroides* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Cd content, µg/g -----			
low	labeled Cd	0.034 -----*	0.239 [†] <u>+0.029</u> [‡]	0.029 <u>+0.039</u>	0.040 <u>+0.002</u>
	soil + labeled Cd [§]	0.30 -----*	0.66 <u>+0.12</u>	0.23 <u>+0.15</u>	0.33 <u>+0.06</u>
	soil Cd [§]	0.20 -----*	0.57 <u>+0.00</u>	0.18 <u>+0.02</u>	0.32 <u>+0.04</u>
medium	labeled Cd	0.009 <u>+0.003</u>	0.398 <u>+0.249</u>	0.001 <u>+0.001</u>	0.071 <u>+0.018</u>
	soil + labeled Cd [§]	0.27 <u>+0.06</u>	1.68 <u>+1.25</u>	0.46 <u>+0.19</u>	0.80 <u>+0.05</u>
	soil Cd [§]	0.26 <u>+0.01</u>	1.06 <u>+0.28</u>	0.28 <u>+0.03</u>	0.46 <u>+0.07</u>

[†]Mean.

*Lost one sample.

[‡]Standard deviation.

[§]By atomic absorption.

uptake was found under acid, oxidizing conditions at both salt levels studied by radiotracer and atomic absorption techniques.

In the laboratory studies, some increase in cadmium accumulation occurred as the suspension salt content increased, possibly due to the formation of a soluble cadmium chloride complex (Hahne and Kroontje, 1973) and the probable greater plant availability of soluble cadmium.

Sorghum halepense. The effects of three levels of soil oxidation on cadmium concentration in Sorghum halepense from undisturbed cadmium-amended soil material in the greenhouse is shown in Table 16. Cadmium content increased substantially as the soil material became better oxidized, though the secondary effect of decreasing pH may have contributed to the increased availability and plant concentration of cadmium in the greenhouse study. Although content and total uptake increased in upper stem tissue of the second harvest, total uptake decreased at the most oxidized treatment because of poor plant growth.

Zinc

The effect of controlled pH and oxidation-reduction conditions was not determined in laboratory experiments due to some zinc contamination of the plants prior to transplanting to the laboratory growth vessels. Early in this study, seedlings and culms were grown in the greenhouse in polyethylene-lined, galvanized trays until the plants reached a suitable size for the laboratory study. However, in many such trays, tiny holes already present in the polyethylene sheeting or holes caused by root penetration caused the solution in the rooting medium to come in contact with the galvanized metal trays, resulting in high plant-zinc contents prior to initiation of the laboratory study. Though this study was unable to evaluate the effects of controlled physicochemical parameters on zinc uptake due to zinc contamination of the plant material, the authors feel that the elevated zinc content of the plants prior to transplanting to suspensions of controlled pH and oxidation-reduction potential probably had minimal effects on uptake of other trace metals.

Table 16
The Effect of Oxidation-Reduction Conditions on the
Cadmium Content of Sorghum halepense in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake	$\mu\text{g Cd/g}$ Content	$\mu\text{g Cd}$ Uptake
First harvest, upper stem	7.6 [†] +1.3 [‡]	161 +34	8.0 +3.3	130 +65	13.6 +0.2	48 +7
Second harvest, upper stem	8.1 +0.9	61 +9	12.9 +7.7	137 +126	18.2 +2.8	233 +14
Second harvest, lower stem	33.1 +0.4	639 +14	40.5 +6.9	861 +284	48.0 +0.4	756 +18

[†] Mean.

[‡] Standard deviation.

Singh and Lag (1976) have shown that uptake of cadmium, mercury, lead, and arsenic was not affected by the zinc content of simulated zinc-polluted soils. In this study it is doubtful that zinc taken up prior to transplanting to the laboratory uptake vessels affected the trace metal uptake response to controlled pH-oxidation conditions.

The effect of three oxidation levels on zinc content of plants from undisturbed soil materials was studied in the greenhouse on Distichlis spicata, Spartina alterniflora, and Sorghum halepense. With each harvest of all three species, there was a considerable increase in zinc content as the oxidation level increased from reduced to intermediate levels and generally little or no increase in zinc content as the oxidation level was increased further (Tables 17,18,19). This corresponded with results of previous studies in this laboratory on the effects of controlled pH and redox potential on the chemical availability of zinc (Gambrell et al., 1977). In these studies soluble and exchangeable zinc levels increased as redox potential was increased from strongly reducing to moderately reducing levels (across the redox potential stability boundary for sulfide) and showed no further increase with subsequent incremental increases in redox potential (oxidation intensity).

Copper

Distichlis spicata. Laboratory studies of the effect of controlled pH and oxidation conditions on copper uptake by Distichlis spicata were inconclusive due to the similarity of treatment means and moderate experimental error (Table 20). In greenhouse studies, there was a small increase in the copper content of upper stem tissue as oxidation intensity increased (Table 21). The decrease in pH as the soil became oxidized may have been a contributing factor (Table 1).

Spartina alterniflora. Laboratory studies in soil suspensions indicated little effect of pH and redox potential on copper uptake by this species (Table 22). Greenhouse results were similar to those for

Table 17

The Effect of Oxidation-Reduction Conditions on the
Zinc Content of Distichlis spicata in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake
First harvest, upper stem	41 [†] +8 [‡]	346 +59	68 +5	447 +56	66 +2	261 +18
Second harvest, upper stem	38 +1	261 +37	73 +9	282 +136	62 +6	162 +62
Second harvest, lower stem	133 +26	2,090 +241	262 +69	2,420 +715	288 +2	2,840 +755

[†] Mean.

[‡] Standard deviation.

Table 18

The Effect of Oxidation-Reduction Conditions on the
Zinc Content of Spartina alterniflora in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake
First harvest, upper stem	55 [†] +2 [*]	557 +164	97 +10	622 +39	92 +8	166 +88
Second harvest, upper stem	52 +1	479 +44	79 +2	452 +58	126 ---*	121 ---*
Second harvest, lower stem	60 +1	2,310 +118	115 +4	2,090 +1,550	118 +15	2,110 +245

[†] Mean.

^{*} Standard deviation.

*Lost one sample.

Table 19

The Effect of Oxidation-Reduction Conditions on the
Zinc Content of Sorghum halepense in Greenhouse Experiments

Experimental parameter	<u>Oxidation-Reduction Conditions</u>					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake	$\mu\text{g Zn/g}$ Content	$\mu\text{g Zn}$ Uptake
First harvest, upper stem	41 [†] +6*	865 +176	60 +12	945 +95	65 +4	229 +21
Second harvest, upper stem	59 +6	435 +28	93 +5	876 +439	79 +8	1,030 +204
Second harvest, lower stem	139 +28	2,680 +510	157 +30	3,240 +97	134 +21	2,120 +399

[†] Mean.

* Standard deviation.

Table 20
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Copper in *Distichlis spicata* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Cu content, $\mu\text{g/g}$ -----			
medium	soil Cu ^s	14.1 [†]	13.8	15.8	16.0
		<u>+1.9[‡]</u>	<u>+3.0</u>	<u>+5.0</u>	<u>+2.2</u>
high	soil Cu ^s	25.5	20.5	21.0	23.5
		<u>+3.0</u>	<u>+1.9</u>	<u>+1.2</u>	<u>+7.0</u>

^sBy atomic absorption.

[†]Mean.

[#]Standard deviation.

Table 21

The Effect of Oxidation-Reduction Conditions on the
Copper Content of *Distichlis spicata* in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake
First harvest, upper stem	8.0 [†] +1.4 [*]	68 +9	9.0 +0.0	59 +3	10.0 +1.4	39 +7
Second harvest, upper stem	6.0 +0.0	42 +5	11.0 +1.4	40 +10	10.0 +0.0	26 +8
Second harvest, lower stem	8.0 +0.0	127 +11	8.0 +0.0	74 +2	8.0 +5.6	71 +34

[†] Mean.

^{*} Standard deviation.

Table 22

The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Copper in *Spartina alterniflora* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Cu content, $\mu\text{g/g}$ -----			
low	soil Cu ^s	14.1 [†] <u>+0.9[‡]</u>	16.7 <u>+2.8</u>	13.4 <u>+0.0</u>	13.4 <u>+0.0</u>
medium	soil Cu ^s	10.9 <u>+2.2</u>	12.2 <u>+1.6</u>	13.5 <u>+1.3</u>	11.7 <u>+1.0</u>

^sBy atomic absorption.

[†]Mean.

[‡]Standard deviation.

Distichlis spicata in that little change to perhaps a slight increase in copper content may have occurred with increasing oxidation levels in upper stem tissue (Table 23), though total uptake was low under oxidized conditions because of poor plant growth.

The laboratory data for Spartina cynosuroides and greenhouse data for Sorghum halepense were inconclusive (Tables 24,25).

Iron

Plant uptake of iron responded less to changes in pH and oxidation-reduction conditions than one would expect based on chemical availability studies. The probable ability of organisms to synthesize organic chelating substances to solubilize iron in oxidized soils, as suggested by Waid (1975), likely contributes to supplying adequate iron where soil physicochemical parameters favor sparingly soluble ferric oxyhydroxides.

In laboratory studies using stirred suspensions, the response pattern for iron uptake was similar for Distichlis spicata, Spartina cynosuroides, and Spartina alterniflora. For each species at all salt levels, the greatest iron uptake was always found under acid, reducing conditions, which corresponds to the physicochemical environment favoring maximum chemical availability (Tables 26,27,28). The iron levels in remaining pH and oxidation-reduction treatment combinations were generally grouped close together and ranged from slightly less than the acid, reduced treatment levels to approximately one-half of maximum tissue iron concentrations.

Greenhouse studies gave mixed results for iron depending on the species studied. The iron content of Distichlis spicata increased with increasing oxidation-reduction conditions in upper and lower stem tissue at the second harvest, while no consistent oxidation effect was noted in upper stem tissue in the first harvest. The iron content of Spartina alterniflora consistently decreased with an increase in oxidation intensity and a concurrent decrease in pH, while Sorghum halepense gave mixed results depending on the harvest date and tissue sampled (Tables 29,30,31).

Table 23

The Effect of Oxidation-Reduction Conditions on the
Copper Content of *Spartina alterniflora* in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake
First harvest, upper stem	4.5 [†] +0.7 [‡]	47 +22	7.0 +0.0	45 +7	7.0 +2.8	14 +11
Second harvest, upper stem	8.0 +2.8	72 +18	9.0 +1.4	52 +14	11.0 -----*	11 ----*
Second harvest, lower stem	3.0 +1.4	116 +58	6.0 +0.0	108 +77	4.0 +2.8	66 +34

[†] Mean.

[‡] Standard deviation.

*Lost one sample.

Table 24

The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Copper in *Spartina cynosuroides* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Cu content, $\mu\text{g/g}$ -----					
low	soil Cu ^s	22.8 [†] <u>+13.2</u>	18.7 <u>+5.4</u>	13.4 <u>+0.0</u>	15.1 <u>+2.5</u>
medium	soil Cu ^s	13.4 <u>+0.0</u>	18.8 <u>+7.3</u>	15.1 <u>+3.3</u>	17.4 <u>+7.2</u>

^sBy atomic absorption.

[†]Mean.

*Standard deviation.

Table 25

The Effect of Oxidation-Reduction Conditions on the
Copper Content of Sorghum halepense in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake	$\mu\text{g Cu/g}$ Content	$\mu\text{g Cu}$ Uptake
First harvest, upper stem	6.0 [†] +0.0 [‡]	126 +6	5.5 +1.0	87 +20	8.5 +2.1	30 +12
Second harvest, upper stem	5.0 +1.4	37 +9	6.0 +2.8	50 +1	4.0 +2.8	53 +41
Second harvest, lower stem	5.0 +1.4	96 +26	5.0 +1.4	102 +12	3.0 +1.4	48 +24

[†]Mean.

[‡]Standard deviation.

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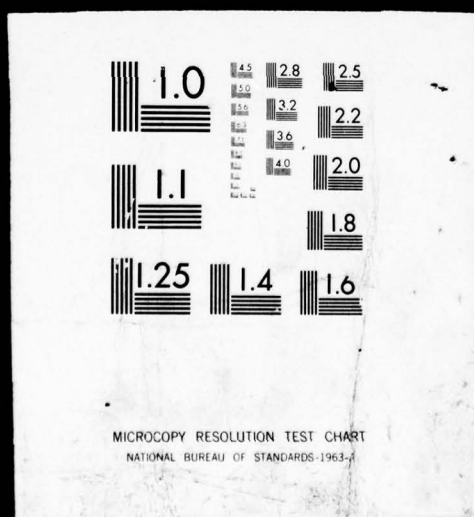


Table 26
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Iron in *Distichlis spicata* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Fe content, µg/g -----			
medium	soil Fe ^s	322 [†]	207	169	172
		<u>+135[‡]</u>	<u>+28</u>	<u>+41</u>	<u>+32</u>
high	soil Fe ^s	730	276	253	327
		<u>+182</u>	<u>+53</u>	<u>+19</u>	<u>+113</u>

^sBy atomic absorption.

[†]Mean.

[‡]Standard deviation.

Table 27
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Iron in *Spartina alterniflora* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Fe content, µg/g -----			
low	soil Fe ^s	312 [†] <u>+50[#]</u>	134 <u>+30</u>	122 <u>+24</u>	145 <u>+45</u>
medium	soil Fe ^s	222 <u>+59</u>	115 <u>+0</u>	115 <u>+0</u>	129 <u>+29</u>

[§]By atomic absorption.

[†]Mean.

[#]Standard deviation.

Table 28
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Iron in *Spartina cynosuroides* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Fe content, µg/g -----					
low	soil Fe ^s	255 [†] +186 [#]	125 +17	214 +131	212 +102
medium	soil Fe ^s	193 [†] +70 [#]	88 +33	97 +27	91 +59

^sBy atomic absorption.

[†]Mean.

[#]Standard deviation.

Table 29

The Effect of Oxidation-Reduction Conditions on the
Iron Content of Distichlis spicata in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake
First harvest, upper stem	125 [†] +35 [*]	1,070 +341	142 +12	932 +124	133 +24	520 +72
Second harvest, upper stem	50 +24	231 +28	50 +24	204 +158	183 +24	463 +78
Second harvest, lower stem	33 +0	529 +45	50 +24	463 +232	183 +24	1,770 +263

[†] Mean.

^{*} Standard deviation.

Table 30
The Effect of Oxidation-Reduction Conditions on the
Iron Content of *Spartina alterniflora* in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake
First harvest, upper stem	175 [†] +35 [*]	1,710 +219	183 +47	1,160 +112	133 +24	246 +149
Second harvest, upper stem	250 +71	4,400 +2,620	166 +47	1,420 +19	66 ---*	66 ---*
Second harvest, lower stem	466 +235	18,000 +9,590	250 +24	4,640 +3,640	33 +47	503 +711

[†]Mean.

^{*}Standard deviation.

*Lost one sample.

Table 31
The Effect of Oxidation-Reduction Conditions on the
Iron Content of Sorghum halepense in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake	$\mu\text{g Fe/g}$ Content	$\mu\text{g Fe}$ Uptake
First harvest, upper stem	83 [†] +24 [‡]	1,760 +572	133 +24	2,120 +583	150 +47	542 +249
Second harvest, upper stem	166 +0	2,220 +616	41 +10	1,850 +1,430	133 +47	888 +688
Second harvest, lower stem	300 +94	5,800 +1,880	183 +71	3,960 +2,110	67 +47	1,060 +775

[†] Mean.

[‡] Standard deviation.

Manganese

Similar to iron, plant manganese levels were expected to respond markedly to changes in pH and oxidation-reduction conditions as chemical speciation of this metal affecting its availability is strongly pH and redox dependent within the range studied in the laboratory. However, as observed for iron, the response to controlled oxidation and/or pH conditions was not consistent and frequently did not respond as expected based on previous studies on chemical availability and thermodynamic considerations.

In laboratory studies with Distichlis spicata, reduced conditions resulted in small increases in manganese content compared to oxidized conditions, but there was little consistent effect of pH (Table 32). Greenhouse studies gave mixed results from the first harvest, but showed sequential reductions in lower and upper stem manganese content with increasing oxidation levels at the second harvest (Table 33).

There was also little apparent treatment effect on manganese content of Spartina alterniflora in laboratory or greenhouse studies or Spartina cynosuroides in laboratory studies (Tables 34,35,36).

Sorghum halepense generally accumulated less manganese under oxidized conditions in greenhouse studies (Table 37).

Lead and Cadmium Uptake by Lowland Rice (*Oryza sativa*, L.)

The total plant uptake of cadmium and content in aboveground tissue generally increased with an increase in redox potential and a decrease in pH, though there was a decline in cadmium uptake as redox potential increased from +200 to +400 mv at pH 5, 6, and 7, as indicated in Table 38. Cadmium was found to be very mobile within the plant. It was readily translocated from the root to shoot tissue once it was absorbed by the plant roots. About 99 percent of total cadmium taken up by rice plants was found in the shoots at all redox potential-pH combinations. The relatively complete translocation of cadmium from root to above-ground plant tissue has important implications as cadmium from contaminated soils and sediments may readily enter food cycles in wetland ecosystems.

Table 32
The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Manganese in Distichlis spicata Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Mn content, µg/g -----			
medium	soil Mn ^s	126 [†]	91	152	89
		<u>+22[‡]</u>	<u>+8</u>	<u>+22</u>	<u>+14</u>
high	soil Mn ^s	205	191	165	153
		<u>+29</u>	<u>+9</u>	<u>+14</u>	<u>+51</u>

^sBy atomic absorption.

[†]Mean.

[#]Standard deviation.

Table 33
The Effect of Oxidation-Reduction Conditions on the
Manganese Content of Distichlis spicata in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Mn/g}$ Content	$\mu\text{g Mn}$ Uptake	$\mu\text{g Mn/g}$ Content	$\mu\text{g Mn}$ Uptake	$\mu\text{g Mn/g}$ Content	$\mu\text{g Mn}$ Uptake
First harvest, upper stem	150 [†] +22*	1,270 +134	117 +2	769 +27	302 +81	1,180 +269
Second harvest, upper stem	182 +45	1,250 +161	117 +33	462 +289	60 +1	155 +48
Second harvest, lower stem	228 +36	3,650 +881	160 +12	1,480 +159	110 +12	1,060 +179

[†]Mean.

*Standard deviation.

Table 34

The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Manganese in *Spartina alterniflora* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Mn content, $\mu\text{g/g}$ -----					
low	soil Mn ^s	121 [†] <u>+17[‡]</u>	112 <u>+17</u>	102 <u>+7</u>	79 <u>+10</u>
medium	soil Mn ^s	159 <u>+48</u>	169 <u>+56</u>	351 <u>+31</u>	143 <u>+31</u>

^sBy atomic absorption.

[†]Mean.

[‡]Standard deviation.

Table 35
The Effect of Oxidation-Reduction Conditions on the
Manganese Content of *Spartina alterniflora* in Greenhouse Experiments

Experimental parameter	<u>Oxidation-Reduction Conditions</u>					
	Reduced		Intermediate		Oxidized	
	$\mu\text{g Mn/g}$ Content	$\mu\text{g Mn}$ Uptake	$\mu\text{g Mn/g}$ Content	$\mu\text{g Mn}$ Uptake	$\mu\text{g Mn/g}$ Content	$\mu\text{g Mn}$ Uptake
First harvest, upper stem	386 [†] +3 [#]	3,900 +1,240	380 +6	2,470 +439	319 +81	600 +401
Second harvest, upper stem	311 +28	2,870 +566	214 +0	1,230 +132	396 ----*	0.380 -----*
Second harvest, lower stem	558 +24	21,400 +246	549 +60	9,480 +6,010	372 +24	6,700 +1,180

[†] Mean.

[#] Standard deviation.

*Lost one sample.

Table 36

The Effect of Salinity, pH, and Oxidation-Reduction
Conditions on Manganese in *Spartina cynosuroides* Shoots

Salt level	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Mn content, $\mu\text{g/g}$ -----			
low	soil Mn ^s	365 [†] <u>+6[‡]</u>	314 <u>+95</u>	241 <u>+41</u>	289 <u>+65</u>
medium	soil Mn ^s	111 <u>+13</u>	282 <u>+24</u>	128 <u>+13</u>	124 <u>+10</u>

^sBy atomic absorption.

[†]Mean.

[‡]Standard deviation.

Table 37
The Effect of Oxidation-Reduction Conditions on the
Manganese Content of Sorghum halepense in Greenhouse Experiments

Experimental parameter	Oxidation-Reduction Conditions					
	Reduced		Intermediate		Oxidized	
	µg Mn/g Content	µg Mn Uptake	µg Mn/g Content	µg Mn Uptake	µg Mn/g Content	µg Mn Uptake
First harvest, upper stem	391 [†] +27 [‡]	8,210 +932	471 +87	7,510 +2,120	336 +45	1,170 +27
Second harvest, upper stem	556 +10	4,140 +228	583 +12	5,440 +2,580	225 +12	2,910 +428
Second harvest, lower stem	575 +72	11,100 +1,490	693 +120	14,700 +4,890	228 +12	3,590 +304

[†]Mean.

[‡]Standard deviation.

Table 38

The Effect of pH and Oxidation-Reduction
Potential on Cadmium Uptake by *Oryza sativa*, L.

Plant tissue	Redox potential ----- mv -----	pH			
		5.0	6.0	7.0	8.0
		Cd, ng/pot			
Stem + leaf	-200	656 [†]	624	492	325
	-100	900	750	799	458
	0	1,010	1,060	825	503
	100	1,390	1,260	1,080	475
	200	2,420	1,930	1,150	479
	400	1,550	1,330	748	740
Root	-200	2.1	2.2	2.1	2.2
	-100	3.4	2.8	3.5	3.3
	0	3.6	4.6	7.0	2.8
	100	4.6	6.6	11.0	2.8
	200	10.0	5.1	14.0	4.0
	400	5.5	10.0	11.0	5.0

[†]Total Cd accumulation in indicated tissue from all plants in experimental unit.

As observed for cadmium, lead uptake in aboveground tissue increased with decreasing pH (Table 39). However, there was little apparent effect of redox potential on aboveground lead content. Redox potential and pH had a pronounced effect on the association of lead with root tissue where increases in pH and redox potential generally reduced root lead.

Correlation between Plant Content and Chemical Availability

Chemical Availability Studies

Following marsh plant harvests from laboratory uptake vessels, all soil suspensions were extracted under an oxygen-free atmosphere with 1 N sodium acetate adjusted to treatment pH levels. Metals recovered by this extractant represent initially dissolved plus exchangeable metal ions. The residual solids were extracted again with 0.005 N DTPA as described by Lindsay and Norvell (1969). The following tables give the average metal quantities extracted for each extractant, pH, and redox potential combination. It is not the intent of this section to present a detailed discussion of the effects of pH and redox potential on the chemical availability of trace and toxic metals as this topic has been covered elsewhere (Gambrell *et al.*, 1977). Therefore, these data were averaged over salt levels and experimental units receiving and not receiving supplemental cadmium and lead, as well as experiments with different plant species. Plant species and age sometimes affected reduction intensity as some plants apparently translocated more oxygen through aboveground tissue into the rooting media than others. Bearing in mind the above factors which in some cases contributed a considerable deviation from the reported means, the purpose of this discussion is to briefly describe the type of chemical availability results obtained. These data give the general effects of pH and redox potential on the chemical availability of these metals as an introduction to the results and discussion of correlation studies between plant content and chemical extractability of metals.

Table 39
The Effect of pH and Oxidation-Reduction
Potential on Lead Uptake by *Oryza sativa*, L.

Plant tissue	Redox potential ----- mv -----	pH			
		5.0	6.0	7.0	8.0
		Pb, µg/pot			
Stem + leaf	-200	10.8 [†]	7.1	6.3	3.5
	-100	12.3	8.8	8.7	5.0
	0	13.5	9.5	7.4	6.0
	100	13.0	11.0	9.3	4.0
	200	13.7	8.7	7.8	4.6
	400	9.6	9.8	7.7	5.2
Root	-200	21.9	27.3	4.1	15.9
	-100	19.9	20.2	5.8	10.0
	0	12.1	9.0	4.4	6.0
	100	5.6	9.5	1.6	2.6
	200	6.8	6.6	1.5	1.6
	400	5.2	4.8	0.9	1.2

[†]Total Pb accumulation in indicated tissue from all plants in experimental unit.

There was considerable variability in the extractable mercury-203 data. Labeled mercury extracted by sodium acetate was greater under reduced than oxidized conditions at each pH level (Table 40). DTPA extractable mercury was consistently enhanced by increasing oxidation levels and increasing pH. Specific activity of labeled mercury was measured on sample aliquots which were not digested in hot, concentrated nitric acid since much of the mercury could have been volatilized by this treatment.

Labeled lead extracted with 1 N sodium acetate was strongly pH dependent. An average of greater than 1 $\mu\text{g/g}$ labeled lead was recovered at pH 4.5, and essentially none was recovered by this extractant at pH 7.5 (Table 41). This pH effect was not apparent for lead measured by atomic absorption techniques (Table 42). Increasing oxidation conditions increased DTPA-extractable lead by both analytical techniques at pH 4.5.

Using radiotracer techniques, maximum sodium acetate extractable cadmium occurred under acid, oxidizing conditions (Table 43). Cadmium measured by atomic absorption was greater under oxidized than reduced conditions, but pH effects were not apparent (Table 44). As found for sodium acetate, DTPA extractable cadmium levels were also greater under oxidized conditions, though total cadmium extracted by this reagent in the sequential fractionation procedure was considerably less.

Dissolved plus sodium acetate extractable copper was little affected by changes in pH or redox potential. An increase in redox potential did consistently result in a small increase in DTPA extractable copper (Table 45).

Maximum dissolved plus sodium acetate extractable iron was recovered under acid, reducing conditions (Table 46), an environment favoring stability of relatively mobile ferrous compounds. Increasing pH and/or oxidation levels markedly reduced the chemical availability of iron.

Dissolved plus sodium acetate extractable manganese was also

Table 40
The Effect of pH and Oxidation-Reduction
Conditions on Extractable Labeled Mercury

Extractant	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Hg, $\mu\text{g/kg}$ -----			
Sodium acetate	Hg-203	12.2 [†]	4.0	10.5	5.2
DTPA	Hg-203	1.3	2.6	5.3	6.4

[†]Mean.

Table 41
The Effect of pH and Oxidation-Reduction
Conditions on Extractable Labeled Lead

Extractant	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Pb, µg/g -----			
Sodium acetate	Pb-210	1.37 [†]	1.03	0.01	0.01
DTPA	Pb-210	0.20	1.49	1.40	1.35

[†]Mean.

Table 42
The Effect of pH and Oxidation-Reduction
Conditions on Extractable Lead

Extractant	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Pb, µg/g -----					
Sodium acetate	combined*	4.03 [†]	3.59	3.09	3.71
DTPA	combined	0.90	2.74	1.50	1.60

^{*}Data sets of Pb amended and unamended studies combined.

[†]Mean.

Table 43
The Effect of pH and Oxidation-Reduction
Conditions on Extractable Labeled Cadmium

Extractant	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
----- Cd, µg/g -----					
Sodium acetate	Cd-109	0.30†	0.63	0.17	0.20
DTPA	Cd-109	0.04	0.11	0.03	0.47

[†]Mean.

Table 44

The Effect of pH and Oxidation-ReductionConditions on Extractable Cadmium

Extractant	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Cd, $\mu\text{g/g}$ -----			
Sodium acetate	combined [‡]	0.18 [†]	0.40	0.22	0.47
DTPA	combined	0.01	0.02	0.02	0.05

[‡] Data sets of Cd amended and unamended studies combined.

[†] Mean.

Table 45
The Effect of pH and Oxidation-Reduction
Conditions on Extractable Copper

Extractant	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Cu, µg/g -----			
Sodium acetate	soil Cu	2.73 [†]	2.35	2.47	2.59
DTPA	soil Cu	0.94	1.56	1.11	1.68

[†]Mean.

Table 46
The Effect of pH and Oxidation-Reduction
Conditions on Extractable Iron

Extractant	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Fe, µg/g -----			
Sodium acetate	soil Fe	1980 [†]	25	227	20
DTPA	soil Fe	288	295	185	27

[†]Mean.

greatest under acid, reducing conditions (Table 47). Increasing pH and/or redox potential reduced the levels of the readily available manganese pools. As for iron, acid and reducing conditions favored the stability of the more mobile, divalent manganous compounds.

In laboratory studies with lowland rice, only total dissolved lead and cadmium in the soil suspensions were measured. Soil suspension samples were centrifuged and the supernatant filtered through an 0.45- μ membrane filter into a receiving flask containing EDTA (ethylenediamine-tetraacetic acid) for sample preservation. The dissolved lead and cadmium in these solution extracts were analyzed by flameless atomic absorption.

Dissolved cadmium increased as redox potential increased and pH decreased (Table 48). Soluble lead consistently decreased with an increase in redox potential and pH in this soil suspension (Table 49).

Correlation Studies

In the previous section, the chemical availability data presented were averaged over a number of experimental parameters and briefly discussed to indicate the type of extract data obtained. For correlation studies, data sets for plant uptake and chemical availability were combined such that comparisons were made for each experimental unit for deriving correlation coefficients. That is, the metal content of above-ground tissue growing in each uptake vessel was paired with the chemical availability data only from that vessel.

Table 50 indicates the correlation coefficients for mercury. With all species, salt, pH, and redox potential treatments included in the model, there was a significant linear association between labeled mercury uptake and labeled mercury extracted by sodium acetate and DTPA (Table 50), though the correlation was low, especially for sodium acetate ($r = 0.272^*$ for sodium acetate, $r = 0.473^{**}$ for DTPA). There were apparent species differences. There was no significant correlation between labeled mercury in aboveground Distichlis spicata tissue, but a fairly good linear association was found between mercury content and

Table 47

The Effect of pH and Oxidation-ReductionConditions on Extractable Manganese

Extractant	Uptake study	pH 4.5		pH 7.5	
		Reduced	Oxidized	Reduced	Oxidized
		----- Mn, µg/g -----			
Sodium acetate	soil Mn	265 [†]	73	128	7
DTPA	soil Mn	13	28	47	8

[†]Mean.

Table 48
The Effect of pH and Oxidation-Reduction Potential on
Water-Soluble Cadmium in Soil Suspensions
Used for *Oryza sativa*, L. Uptake Studies

Redox potential	pH			
	5.0	6.0	7.0	8.0
---- mv ----	----- Cd, µg/l -----			
-200	2.5	2.8	1.8	0.9
-100	2.2	2.5	2.4	1.9
0	4.6	2.7	2.5	2.2
100	5.2	3.0	2.9	2.9
200	5.7	3.7	3.3	3.3
400	5.9	5.5	4.7	3.9

Table 49
The Effect of pH and Oxidation-Reduction Potential on
Water-Soluble Lead in Soil Suspensions
Used for Oryza sativa, L. Uptake Studies

Redox potential	pH			
	5.0	6.0	7.0	8.0
---- mv ----	----- Pb, µg/l -----			
-200	44	41	34	29
-100	41	30	25	23
0	35	27	22	21
100	28	24	20	18
200	25	22	19	17
400	22	15	14	11

Table 50

Correlation Coefficient (r) between Labeled Mercury
Content and Chemical Availability

Experimental parameter	Experimental units in model	Chemical Extractant	
		Sodium acetate	DTPA
Mercury	(59)	0.272*	0.473**
Mercury <u>Distichlis spicata</u>	(26)	0.184	0.232
Mercury <u>Spartina alterniflora</u>	(22)	0.659**	0.497*
Mercury <u>Spartina cynosuroides</u>	(11)	0.671*	0.601*

* Significant at 5% level.

** Significant at 1% level.

both extractants for Spartina alterniflora ($r = 0.659^{**}$ for sodium acetate, $r = 0.497^{*}$ for DTPA) and Spartina cynosuroides ($r = 0.671^{*}$ for sodium acetate, $r = 0.601^{*}$ for DTPA).

A significant ($r = 0.389^{**}$), but low correlation was found between sodium acetate extractable lead and lead content when all species were included in the model (Table 51). However, no significant correlations were found when individual species were considered. Studies with labeled lead also indicated that these two chemical extractants would be of little predictive value for lead in studies of this type (Table 52).

Of the toxic metals studied, cadmium generally gave the best linear association between plant content and chemical availability. There was a somewhat low but highly significant correlation between uptake and sodium acetate extractable labeled cadmium ($r = 0.485^{**}$) and a poor correlation with this extractant where cadmium was measured by atomic absorption ($r = 0.132$) (Tables 53,54) in models in which species and all other treatment effects were pooled. However, results from radiotracer and atomic absorption techniques generally compared well in correlation models in which species and/or salt levels were considered separately.

Sodium acetate extractable cadmium correlated poorly with cadmium uptake by Distichlis spicata, but a good correlation was found with DTPA extractable cadmium ($r = 0.710^{**}$, atomic absorption; $r = 0.644^{**}$, radiotracer). Recall from discussion of uptake experiments that this species apparently responded differently to pH-oxidation-reduction treatments than the other two marsh species studied.

Cadmium uptake by Spartina alterniflora correlated well with sodium acetate extractable cadmium ($r = 0.881^{**}$, atomic absorption; $r = 0.924^{**}$, radiotracer) and poorly with DTPA extractable cadmium.

There was also a good correlation ($r = 0.744^{**}$, atomic absorption; $r = 0.850^{**}$, radiotracer) between content and sodium acetate extractable cadmium with Spartina cynosuroides at a medium salt level. For unknown reasons, only the radiotracer procedure gave a similar

Table 51
Correlation Coefficient (r) between Lead Content
and Chemical Availability

Experimental parameter	Experimental units in model	Chemical Extractant	
		Sodium acetate	DTPA
Lead	(86)	0.389**	0.030
Lead <u>Distichlis spicata</u>	(34)	0.226	0.158
Lead <u>Spartina alterniflora</u>	(22)	0.357	0.334
Lead <u>Spartina cynosuroides</u>	(30)	0.077	0.100

** Significant at 1% level.

Table 52
Correlation Coefficient (r) between Labeled Lead
Content and Chemical Availability

Experimental parameter	Experimental units in model	Chemical Extractant	
		Sodium acetate	DTPA
Lead	(31)	0.209	0.034
Lead <u>Distichlis spicata</u>	8)	0.460	0.425
Lead <u>Spartina alterniflora</u>	(8)	0.094	0.342
Lead <u>Spartina cynosuroides</u>	(15)	0.400	0.110

Table 53
Correlation Coefficient (r) between Labeled Cadmium
Content and Chemical Availability

Experimental parameter	Experimental units in model	Chemical Extractant	
		Sodium acetate	DTPA
Cadmium	(55)	0.485**	0.089
Cadmium <u>Distichlis spicata</u>	(26)	0.000	0.644**
Cadmium <u>Spartina alterniflora</u>	(14)	0.924**	0.405
Cadmium <u>Spartina cynosuroides</u>	(15)	0.776**	0.077
Cadmium, high salt <u>Distichlis spicata</u>	(8)	0.000	0.843**
Cadmium, medium salt <u>Distichlis spicata</u>	(18)	0.167	0.843*
Cadmium, medium salt <u>Spartina alterniflora</u>	(14)	0.924**	0.405
Cadmium, medium salt <u>Spartina cynosuroides</u>	(8)	0.850**	0.000
Cadmium, low salt <u>Spartina cynosuroides</u>	(7)	0.941**	0.145

* Significant at 5% level.

** Significant at 1% level.

Table 54
Correlation Coefficient (r) between Cadmium Content
and Chemical Availability

Experimental parameter	Experimental units in model	Chemical Extractant	
		Sodium acetate	DTPA
Cadmium	(86)	0.132	0.016
Cadmium <u>Distichlis spicata</u>	(34)	0.251	0.710**
Cadmium <u>Spartina alterniflora</u>	(22)	0.881**	0.065
Cadmium <u>Spartina cynosuroides</u>	(30)	0.210	0.164
Cadmium, high salt <u>Distichlis spicata</u>	(16)	0.212	0.673**
Cadmium, medium salt <u>Distichlis spicata</u>	(18)	0.173	0.745**
Cadmium, medium salt <u>Spartina alterniflora</u>	(14)	0.934**	0.394
Cadmium, low salt <u>Spartina alterniflora</u>	(8)	0.645	0.281
Cadmium, medium salt <u>Spartina cynosuroides</u>	(16)	0.744**	0.334
Cadmium, low salt <u>Spartina cynosuroides</u>	(14)	0.283	0.118

** Significant at 1% level.

correlation ($r = 0.283$, atomic absorption; $r = 0.941^{**}$, radiotracer) from the low salt treatment.

A significant, but low correlation was found between copper extracted with sodium acetate and content when all species were included in the model ($r = 0.356^{**}$). When individual species were considered, only copper uptake by Distichlis spicata correlated reasonably well with sodium acetate extractable copper ($r = 0.563^{**}$). There was a low but significant linear relationship between DTPA extractable copper and copper content by Distichlis spicata and Spartina alterniflora ($r = 0.362^*$; $r = 0.470^*$, respectively). Models including salt levels did not improve the correlations (Table 55).

Significant but very low correlations existed between sodium acetate and DTPA extractable iron ($r = 0.264^{**}$; $r = 0.233^*$, respectively) with all treatments and species in the model (Table 56). The correlation coefficient for sodium acetate extractable iron and uptake by Spartina cynosuroides was not significant when salt levels were pooled ($r = 0.141$) or considered separately ($r = 0.401$, medium salt; $r = 0.474$, low salt). However, highly significant correlations of 0.840 or greater were found with sodium acetate extractable iron for the other two species at each salt level. A salt effect was apparent for Distichlis spicata, as a good correlation was not obtained when salt treatments were pooled.

The only significant relationships found for manganese were for sodium acetate extractable with uptake by Distichlis spicata when salt levels were considered separately (Table 57).

In uptake studies with lowland rice grown in soil suspensions, there was a highly significant correlation between lead uptake in above-ground tissue and soluble lead in the soil suspensions ($r = 0.857^{**}$) (Table 58). Cadmium uptake also correlated well with water-soluble levels for this species ($r = 0.711^{**}$) (Table 58).

Table 55
Correlation Coefficient (r) between Copper Content
and Chemical Availability

Experimental parameter	Experimental units in model	Chemical Extractant	
		Sodium acetate	DTPA
Copper	(86)	0.356**	0.106
Copper <u>Distichlis spicata</u>	(34)	0.563**	0.362*
Copper <u>Spartina alterniflora</u>	(22)	0.236	0.470*
Copper <u>Spartina cynosuroides</u>	(30)	0.184	0.148

* Significant at 5% level.

** Significant at 1% level.

Table 56
Correlation Coefficient (r) between Iron Content
and Chemical Availability

Experimental parameter	Experimental units in model	Chemical Extractant	
		Sodium acetate	DTPA
Iron	(86)	0.264**	0.233*
Iron <u>Distichlis spicata</u>	(34)	0.184	0.083
Iron <u>Spartina alterniflora</u>	(22)	0.840**	0.522*
Iron <u>Spartina cynosuroides</u>	(30)	0.141	0.164
Iron, high salt <u>Distichlis spicata</u>	(16)	0.879**	0.258
Iron, medium salt <u>Distichlis spicata</u>	(18)	0.844**	0.071
Iron, medium salt <u>Spartina alterniflora</u>	(14)	0.886**	0.782**
Iron, low salt <u>Spartina alterniflora</u>	(8)	0.955**	0.245
Iron, medium salt <u>Spartina cynosuroides</u>	(16)	0.401	0.063
Iron, low salt <u>Spartina cynosuroides</u>	(14)	0.474	0.063

* Significant at 5% level.

** Significant at 1% level.

Table 57
Correlation Coefficient (r) between Manganese Content
and Chemical Availability

Experimental parameter	Experimental units in model	Chemical Extractant	
		Sodium acetate	DTPA
Manganese	(86)	0.110	0.128
Manganese <u>Distichlis spicata</u>	(34)	0.158	0.134
Manganese <u>Spartina alterniflora</u>	(22)	0.080	0.228
Manganese <u>Spartina cynosuroides</u>	(30)	0.176	0.084
Manganese, high salt <u>Distichlis spicata</u>	(16)	0.489*	0.158
Manganese, medium salt <u>Distichlis spicata</u>	(18)	0.581*	0.392
Manganese, medium salt <u>Spartina alterniflora</u>	(14)	0.207	0.315
Manganese, low salt <u>Spartina alterniflora</u>	(8)	0.494	0.044
Manganese, medium salt <u>Spartina cynosuroides</u>	(16)	0.126	0.122
Manganese, low salt <u>Spartina cynosuroides</u>	(14)	0.400	0.408

* Significant at 5% level.

Table 58
Correlation Coefficient (r) between Lead and Cadmium
Uptake by Oryza sativa L. and Water-Soluble Levels

Experimental parameter	Experimental units in model	Total Water- Soluble Levels
Lead Shoot	(24)	0.857**
Lead Root	(24)	0.380
Lead Total	(24)	0.832**
Cadmium Shoot	(24)	0.711**
Cadmium Root	(24)	0.498
Cadmium Total	(24)	0.712**

**Significant at 1% level.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

In an earlier study conducted by this laboratory (Gambrell et al., 1977), it was shown that the pH and oxidation-reduction conditions of a sediment-water system regulated the chemical availability of iron, manganese, zinc, copper, mercury, lead, and cadmium. Furthermore, it was demonstrated that a change in the physicochemical environment of a sediment-water system would induce transformations altering the chemical form of potentially available metals. A logical extension of this work was to determine the effects of pH and redox potential on the plant availability of these metals.

Successful laboratory studies using stirred soil suspensions and reasonably successful greenhouse procedures using an unstirred rooting medium were developed to look at the effects of pH and redox potential on trace and toxic metal content of marsh plants from simulated dredged sediments. The results of these studies demonstrated that pH and redox potential do influence the plant availability of potentially toxic metals, a phenomenon which should be considered when selecting a disposal method for contaminated sediments.

Mercury content was consistently decreased by an increase in salinity in the marsh species studied. The mercury content was greater from a weakly alkaline rooting medium than from a moderately acid suspension. An increase in oxidation-reduction conditions also tended to increase the mercury content in two species, while results for the third species were inconclusive.

There was little apparent effect of either pH or redox potential on the lead content of the species grown in soil suspensions. In greenhouse studies, the lead content of both Spartina alterniflora and Sorghum halepense increased with an increase in oxidation intensity and the concurrent redox potential mediated decrease in soil pH. The observed response with lead may have been the result of increasing oxidation conditions, decreasing pH, reduced plant growth, or a combination of these

factors. Laboratory studies conducted with lowland rice showed that a decrease in pH increased lead uptake while changing oxidation conditions had little, if any, effect. Thus the increase in acidity may have been the primary factor enhancing lead content of marsh plants grown in the greenhouse.

The cadmium content of aboveground tissue was consistently increased with an increase in oxidation levels in all species studied. In three species (Spartina alterniflora, Spartina cynosuroides, and Sorghum halepense) maximum cadmium content was favored by acid, oxidizing conditions. This was also true for lowland rice and corresponded to previous studies on the effect of pH and oxidation-reduction conditions on the chemical availability of cadmium. Distichlis spicata was an exception in that maximum cadmium content always occurred under weakly alkaline, oxidized conditions rather than acid, oxidized conditions. This apparent species difference was confirmed by conducting several experiments with this marsh species.

Zinc was not studied in the laboratory systems. In greenhouse studies with multiple harvest of three species (Distichlis spicata, Spartina alterniflora, and Sorghum halepense), there was a consistent and substantial increase in zinc content as the oxidation level increased, from reduced to intermediate levels and generally no increase in zinc content with a further increase in oxidation-reduction conditions.

There was little effect of pH or oxidation-reduction conditions on the copper content of the species studied.

The greatest iron content for all species in laboratory studies occurred under acid, reducing conditions. This corresponds to the physicochemical environment favoring maximum chemical availability of iron. The iron levels in remaining pH and oxidation-reduction treatment combinations were generally grouped close together and ranged from slightly less than the acid, reduced treatment levels to approximately one-half maximum tissue iron concentrations.

Extracts of the soil material were analyzed for metals content at the end of each uptake experiment to determine the relationship between chemical availability and plant availability of metals in laboratory studies using soil suspensions. A combination water-soluble and 1 N sodium acetate extract was selected because it is thought that these forms represent the most readily available forms. Previous work in this laboratory indicated water-soluble and exchangeable levels of many trace and toxic metals responded similarly to changes in pH and oxidation-reduction intensity. A DTPA extract was selected because of its fairly successful use in predicting plant availability of many trace metals in agricultural soils.

A linear association between chemical availability and plant content was strongly species-dependent in laboratory studies.

Significant and fairly good linear associations were found between the labeled mercury content and both extractants for Spartina alterniflora and Spartina cynosuroides, but not for Distichlis spicata.

Of the toxic metals studied, cadmium generally gave the best linear association between measured content and chemical availability. Sodium acetate extractable cadmium correlated poorly with cadmium content by Distichlis spicata, but a good correlation was attained with DTPA extractable cadmium. This species apparently responded differently to pH-oxidation-reduction treatments than the other two marsh species studied, and this was reflected in its poor correlation with sodium acetate extractable cadmium. Both Spartina alterniflora and Spartina cynosuroides cadmium levels correlated well with sodium acetate extractable cadmium.

Low linear associations were found between chemical availability and plant content for lead and copper with marsh species, though water-soluble lead correlated well with lead uptake by lowland rice.

Based on the results of these studies, it is recommended that the effects of physicochemical parameters on the plant availability of toxic and potentially toxic metals should be considered in selecting environmentally sound disposal methods for contaminated dredged sediments.

Where an uncontaminated or relatively clean sediment is to be dredged, selection among feasible disposal alternatives can be based on economic, engineering, and social considerations with minimal attention given to adverse chemical effects on the environment.

Additional constraints are associated with disposal methods for contaminated dredged sediments. However, it should be possible in many instances to select from among the economically and engineering feasible disposal/use alternatives to minimize adverse environmental effects. Depending on the properties of the contaminated sediments, the nature of the toxic substances, and the available disposal alternatives, a disposal/use alternative can be selected in which the final physicochemical environment of the dredged material will favor minimal release of toxic substances to biologically available forms. For example, a typically reduced sediment material contaminated with cadmium should not be used as an amendment to agricultural soils or otherwise deposited under upland conditions where drainage and subsequent oxidation will result in enhanced cadmium availability to plants and possibly cadmium leaching into groundwater. A reduced, cadmium-contaminated sediment should be disposed of by a method which will maintain its reduced condition, such as by open-water disposal where a subaqueous environment is maintained.

Lead availability may be enhanced more readily by a reduction in pH than by a change in oxidation conditions. Therefore, a lead contaminated sediment should be deposited in an environment which will not result in pH reduction. With lead, the chemical and mineralogical properties of the sediment material may have some bearing on environmentally sound disposal alternatives, as redox potential mediated changes may result in development of considerable acidity in some sediments and little change or perhaps a modest increase in pH with other materials.

Also, knowledge of the effects of physicochemical parameters on toxic metal availability may suggest additional management practices to minimize cycling of trace metals in the environment. For example,

plant availability of sediment-bound lead in upland applied dredged sediments which tend to become acid upon oxidation could be minimized by liming to a depth equivalent to the rhizosphere if upland disposal were the only feasible disposal alternative.

Also, it is recommended that additional work be done to further develop laboratory and greenhouse procedures with stirred and unstirred rooting mediums in order to determine the effects of imposed physico-chemical environments on the plant availability of toxic metals and synthetic organics as well as nutrients.

Though the techniques developed in this laboratory for these studies were reasonably successful, there is a need to make these systems work for all soil and sediment materials and to determine optimum plant size, growth periods, and methods of acclimatization of plants to laboratory systems with controlled rhizosphere environments. Also, the results of this research indicated apparent species differences in the physico-chemical environment favoring maximum metal uptake. Additional work should be done to characterize conditions favoring toxic metal availability to other plant species which may become established on dredged materials. The availability of several species in which metal uptake responds differently to a given physicochemical environment could be a valuable management tool in tailoring plant species with dredged material disposal/use alternatives to minimize release of sediment-bound toxic metals into food chains.

There is a need to refine oxidation-reduction intensity control procedures in greenhouse experiments using unstirred rooting mediums. Ultimately, simplified and standardized laboratory and/or greenhouse procedures for studying plant availability of sediment-bound materials under controlled physicochemical environments may be useful as testing criteria in selecting environmentally sound disposal alternatives for contaminated dredged sediments.

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In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

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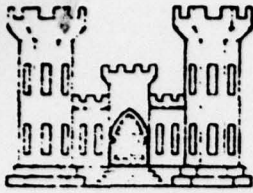
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TRACE AND TOXIC METAL UPTAKE BY MARSH PLANTS
AS AFFECTED BY Eh, pH, AND SALINITY

Technical Report D-77-40
December 1977

1. Names of authors (R. P. Gambrell, V. R. Collard, C. N. Reddy, and W. H. Patrick, Jr.) were inadvertently omitted from Cover and Form 1473, and catalog card at the end of report.
2. Inclosed herewith are corrected pages.





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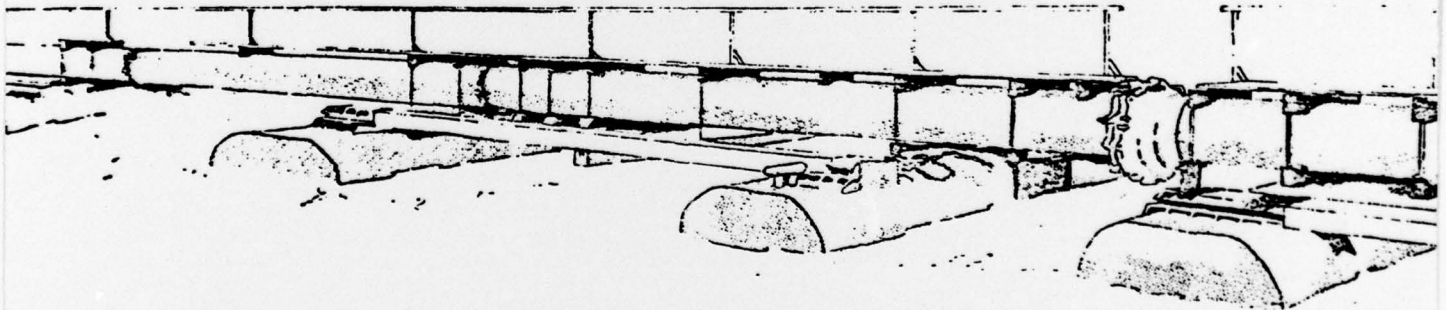
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Center for Wetland Resources
Louisiana State University
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A laboratory study was conducted to develop and refine methods for growing marsh plants under conditions of controlled pH, redox potential (oxidation-reduction conditions) and salinity as well as to determine the effects of these physicochemical conditions in the rooting medium on trace and toxic metal availability to plants. Reasonably successful methods were developed for growing marsh plants in the experimental systems. The (Continued)		

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20. ABSTRACT (Continued)

successful methods as well as procedures which were not successful are discussed as are techniques for overcoming many of the experimental difficulties.

In laboratory studies using soil suspensions, Distichlis spicata (L.) Greene, Spartina alterniflora Loisel, and Spartina cynosuroides (L.) Roth were grown in soil suspensions in which treatments included oxidized and reduced conditions at two pH levels and two salinity levels. The effect of these soil physicochemical conditions on plant content of mercury, lead, cadmium, copper, iron, and manganese was studied. Lead and cadmium uptake by Oryza sativa L. was also studied, but over a range of four soil pH levels and six redox (oxidation-reduction) potential conditions.

Greenhouse studies were conducted using Distichlis spicata, Spartina alterniflora, and Sorghum halepense (L.) Pers. in which oxidation-reduction conditions were controlled in unstirred soil material. The plant content of the trace metals studied in the greenhouse generally supported results of laboratory studies where soil suspensions were used as the rooting medium.

In laboratory studies using labeled mercury, the content of this metal in marsh plants tended to be enhanced by decreases in salinity and increases in pH.

Although results with lead were inconclusive in laboratory studies, lead uptake by lowland rice was enhanced as the soil became more acid. In greenhouse studies, an increase in soil oxidation-reduction conditions increased plant lead content, but this was attributed to a redox potential mediated effect on soil pH.

Plant cadmium content responded more to a change in the physicochemical environment of the rooting medium than did other metals studied. The cadmium content of aboveground tissue was consistently and substantially increased with an increase in oxidation conditions in all species in both laboratory and greenhouse studies. Maximum cadmium content occurred under acid, oxidizing conditions except for one species in which an oxidized, weakly alkaline environment favored increased cadmium content.

The effects of physicochemical conditions on the zinc content of plants grown in the greenhouse were studied where the zinc content was found to increase with increasing oxidation conditions.

There was little effect of either pH or oxidation-reduction conditions on the copper content of the species studied.

Two extractants were used on the soil suspensions following harvest to determine the linear relationships between chemical availability and plant content of metals in laboratory studies. Of the metals studied, cadmium generally gave the best linear association between measured uptake and chemical availability, although there were important species differences.

Based on the results of this research, it was concluded that soil and sediment physicochemical conditions do affect the plant availability of trace and toxic metals, and it was recommended that these effects should be considered in selecting environmentally sound disposal methods for contaminated dredged sediments.

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

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