

DREDGED MATERIAL RESEARCH PROGRAM



TECHNICAL REPORT D-78-6

PREDICTION OF HEAVY METAL UPTAKE BY MARSH PLANTS BASED ON CHEMICAL EXTRACTION OF HEAVY METALS FROM DREDGED MATERIAL

by

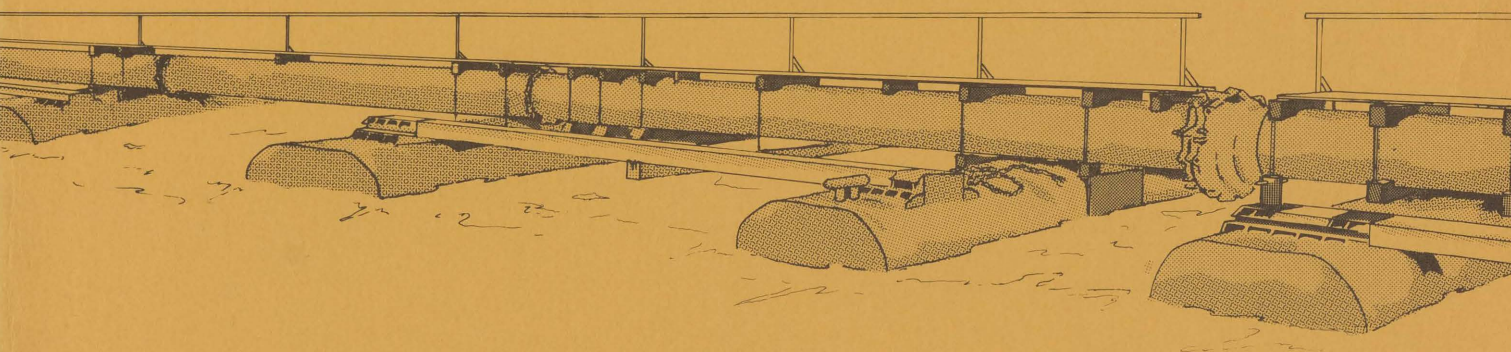
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Prediction of heavy metal uptake by mars



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SUBJECT: Transmittal of Technical Report D-78-6

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1. The technical report transmitted herewith represents the results of Work Unit 4A15A regarding the prediction of heavy 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 part of the Habitat Development Project of the DMRP and is concerned with the development, testing, and evaluation of the environmental, economic, and engineering feasibility of using dredged material as a substrate for marsh development.
2. This work unit reports on two phases of research. The first phase was to determine the extent of heavy metal uptake by marsh plants growing voluntarily at selected dredged material sites along the Gulf and Atlantic coasts. Those studies indicated that uptake of zinc, copper, cadmium, and lead may be of concern in marsh habitat development. In the second phase a chemical extraction procedure was developed to predict heavy metal uptake from a given dredged material, prior to selection of the habitat development alternative.
3. Work Unit 4A15A is one of several research efforts designed by the DMRP to assess the potential for the uptake and mobilization of contaminants through the disposal of dredged material in marsh and estuarine systems. An earlier work unit, 4A15, demonstrated that measurable uptake occurred in marsh plants subjected to various concentrations of heavy metals in hydroponic solution. Other closely related work units are 2A05, which provided a state-of-the-art review of nutrient and heavy metal cycling in marsh-estuarine ecosystems; 4A06, which determined the effects of Eh, pH, and salinity on trace and toxic metal uptake by marsh plants; 4A11H, which compared the water quality and sediment status of a natural and a man-made marsh on the James River, Virginia; 4A11L, which evaluated the uptake of organohalides from contaminated sediments into plant and animal tissues; 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, California (4A18); and Miller Sands, Oregon (4B05). Together these research products will provide the Corps with a comprehensive basis for sound management of potentially contaminated dredged material.



JOHN L. CANNON

Colonel, Corps of Engineers
Commander and Director

1. The first part of the document is a letter from the President of the United States to the Congress, dated January 3, 1862.

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20. ABSTRACT (Continued).

the East and Gulf Coasts of the United States. Marsh plant species studied included Spartina alterniflora, Spartina patens, and Distichlis spicata. Four procedures for the extraction of heavy metals from soil were evaluated including water soluble, ammonium acetate exchangeable, dilute acid extractable, and DTPA extractable.

Results indicated that most marsh plants colonizing dredged material disposal sites sampled in this study contained relatively low concentrations of Zn, Cu, Cd, Pb, Cr, Ni, and Hg. These concentrations were very similar to those reported for natural coastal marshes. There were a few locations, however, in which the concentrations of Zn, Cu, Cd, and Pb in the marsh plants were an order of magnitude greater than the concentrations measured in the majority of marsh plants. The occurrence of these elevated concentrations of heavy metals emphasizes the need for a method to predict heavy metal availability from dredged material to plants.

DTPA extraction of heavy metals gave the best correlations with actual heavy metal concentrations in marsh plants. The other procedures were limited to one or two heavy metals and only one of the three marsh plant species studied. Marsh plant uptake of Zn, Cu, Cd, and, to some extent, Pb and Cr from dredged material can be predicted using a DTPA extraction procedure. Prediction of plant uptake of Ni or Hg was not possible in this study.

Additional verification tests are required to reconfirm and better substantiate the accuracy of the prediction equations developed in this study. Additional research is recommended to improve and expand the prediction equations developed in this study to include dredged material containing higher concentrations of heavy metals and placed under different disposal conditions, such as flooded and upland. Prediction of heavy metal availability in dredged material under various disposal conditions will enhance the ability of CE District personnel to dispose of dredged material in an environmentally compatible manner.

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SUMMARY

Development of techniques for environmentally acceptable marsh creation with dredged material is one of the major goals of the Dredged Material Research Program (DMRP). Movement of contaminants from dredged material is one of the potential problems associated with this and other goals of the DMRP. An understanding of heavy metal and other contaminant movement and the development of a capability to predict this movement are essential for the establishment of meaningful regulatory criteria and for environmentally wise decisions about marsh creation by U. S. Army Corps of Engineers (CE) District personnel.

This report describes a field and laboratory study designed to establish the extent of heavy metal absorption and uptake by marsh plant species from dredged material and to develop a predictive technique using chemical extraction of heavy metals from dredged material to predict the concentration of heavy metals in marsh plants subsequently grown on the dredged material.

Extensive field sampling of marsh plants and dredged material from CE disposal sites was conducted along the East and Gulf Coasts of the United States. A wide range of environmental conditions from natural to heavily industrialized areas were sampled.

Results indicated that most marsh plants colonizing dredged material disposal sites sampled in this study contained relatively low concentrations of Zn, Cu, Cd, Pb, Cr, Ni, and Hg. These concentrations were very similar to those reported for natural coastal marshes. There were a few locations, however, in which the concentrations of Zn, Cu, Cd, and Pb in the marsh plants were an order of magnitude greater than the concentrations measured in the majority of the marsh plants. The occurrence of these elevated concentrations of heavy metals emphasizes the need for a method to predict heavy metal availability from dredged material to plants.

Four procedures for the extraction of heavy metals from soil were evaluated, including water soluble, exchangeable, dilute acid

extractable, and DTPA extractable. DTPA extraction of heavy metals gave the best correlations with actual heavy metal concentrations in marsh plants. The other procedures were limited to one or two heavy metals and only one of the three marsh plant species studied.

The results of the study indicate that marsh plant uptake of Zn, Cu, Cd, and to some extent Pb and Cr from dredged material can be predicted using a DTPA extraction procedure. Prediction of plant uptake of Ni or Hg was not possible in this study.

In order to evaluate the potential of a sediment or dredged material to contaminate marsh plants with heavy metals, it is recommended that the sediment or dredged material be subjected to a DTPA extraction test as described in this report. The resulting extraction solution should be analyzed for Zn, Cu, Cd, Pb, and Cr. By substituting the concentration of each of these heavy metals into the appropriate prediction equation presented in this report, the plant content of each heavy metal can be predicted. These predicted values can then be evaluated as being potentially hazardous or harmless. This procedure should have great practical significance to CE District personnel who plan and evaluate dredged material disposal alternatives.

While this study did develop equations that have good potential for predicting plant uptake of Zn, Cu, Cd, Pb, and Cr, additional verification tests are required to reconfirm and better substantiate the accuracy of these equations.

Additional research is recommended to obtain information about plant uptake of heavy metals in sediments and dredged material containing heavy metals in concentrations in excess of the amounts found in this study. The prediction equations presented in this report are suitable for dredged material in which the concentration of heavy metals falls within the range of those sampled in this study. Therefore, to improve and expand their predictive capability, more data at higher concentration ranges are required. Additional research is required to relate the influence on heavy metal availability to marsh plants of placing dredged material in different disposal environments

such as flooded or upland. Prediction of heavy metal availability in dredged materials under various disposal conditions will enhance the ability of CE District personnel to dispose of dredged material in an environmentally compatible manner.

PREFACE

This investigation was conducted as part of the Corps of Engineers' Dredged Material Research Program (DMRP). The DMRP is sponsored by the Office, Chief of Engineers (DAEN-CWO-M), and was formally authorized by letter, "Study Program for Disposal of Dredged Material," dated 27 December 1971.

The study was conducted during the period July 1975 to September 1977 at the U. S. Army Engineer Waterways Experiment Station (WES) by Dr. C. R. Lee, Messrs. R. M. Smart, T. C. Sturgis, and R. N. Gordon, Sr., and Ms. M. C. Landin of the Ecosystem Processes Branch, Ecosystem Research and Simulation Division, Environmental Effects Laboratory (EEL). Assistance was received from Dr. J. W. Barko and Mr. I. F. Behr III. This research was conducted under the direction of Dr. R. T. Saucier, Special Assistant, EEL, and Dr. H. K. Smith, Project Manager, Habitat Development Project, DMRP. The study was under the general supervision of Dr. R. L. Eley, Chief, Ecosystem Research and Simulation Division, and Dr. John Harrison, Chief of EEL. Technical consultants for the study were Dr. C. B. Loadholt, Professor of Biometrics, Medical University of South Carolina, and Dr. N. R. Page, Head of Agricultural Chemical Services, Clemson University.

Directors of WES during the study and the preparation and publication of this report were COL G. H. Hilt, CE, and COL John L. Cannon, CE. Technical Director was Mr. F. R. Brown.

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PREDICTION OF HEAVY METAL UPTAKE BY MARSH PLANTS BASED ON
CHEMICAL EXTRACTION OF HEAVY METALS FROM DREDGED MATERIAL

PART I: INTRODUCTION

Background

1. Development of techniques for environmentally acceptable marsh creation with dredged material is one of the major goals of the Dredged Material Research Program (DMRP) of the U. S. Army Corps of Engineers (CE). Movement of contaminants from dredged material is one of the potential problems associated with this and other goals of the DMRP. An understanding of heavy metal and other contaminant movement and the development of a capability to predict this movement are essential for the establishment of meaningful regulatory criteria and for environmentally wise decisions about marsh creation by CE District personnel.

2. In the marsh ecosystem, plants die and decay and their constituents are flushed into adjoining lakes or estuaries in either particulate or dissolved form. In addition, plants are consumed by a host of organisms such as insects, waterfowl, and small animals. It is, therefore, extremely important to know whether or not a given plant that might be used in creating a marsh is able to absorb heavy metals from the environment. Extensive research is presently being conducted to determine the heavy metal uptake and content of a large number of agricultural crops. Unfortunately, the extent to which nonagricultural plants absorb heavy metals is neither as well known nor as extensively studied.

3. In addition to a knowledge of the potential of a plant to absorb heavy metals under particular environmental conditions, techniques of predicting absorption based on chemical characterization of the substrate need to be developed. Such techniques have been and are currently being developed to predict the potential uptake of nutrients

and heavy metals by agricultural plants. Similar techniques must be developed for nonagricultural plants, especially those used in habitat development on potentially contaminated materials. While most agricultural soil test techniques have been developed on well-drained, aerated soils, similar or modified techniques can probably be used for predicting heavy metal absorption by marsh plants. Thus, the basic approach for studying heavy metal uptake in plants can be similar, at least in philosophy, whether the plant is growing in the marsh ecosystem or in an agricultural environment.

Literature Review

Role of marsh plants in the mobilization of heavy metals from sediments

4. Nutrient movement or cycling within the salt marsh ecosystem has been under investigation for a number of years. However, only since the early 1970's has heavy metal uptake from sediments by plants been studied. The importance of Spartina alterniflora in mobilizing heavy metals from sediments and conveying them into estuarine food chains has been discussed by Williams and Murdoch,¹ Pomeroy et al.,² Rhan,³ Banus et al.,^{4,5} and Dunstan et al.^{6,7} These reports relate the importance of Spartina alterniflora's contribution to the movement of certain heavy metals through the marsh ecosystem. Banus⁴ reported that lead was taken up by S. alterniflora in concentrations that ranged from 5.4 to 23.2 ppm and that with increased production of standing crop through nitrogen additions to a marsh, substantial amounts of lead could move from the marsh into the estuary via tidal action. S. alterniflora was also reported to play a large role in the transfer of mercury through a salt marsh environment.^{3,6} Remobilization of Hg by the root systems of S. alterniflora was shown to be an effective way of transferring mercury into the food web.³ Windom⁸ has estimated the total Hg taken up by S. alterniflora in Georgia estuaries to be approximately 0.7 mg/m²/yr. Not only did S. alterniflora take up Hg from

sediments, but Hg was released to the surrounding water from the plant's leaves.³

5. There are other reports in the literature that suggest a minor role of S. alterniflora in mobilizing other heavy metals from sediments into food chains.

6. Williams and Murdoch¹ suggested that the role of S. alterniflora in transporting Zn into estuarine food chains was of little consequence because of the low leaf content of Zn (10 ppm). The total uptake of Zn was reported to be 6 kg/km^2 , which was thought to be low when compared to both terrestrial monocots and submerged grasses.

7. Dunstan et al.⁷ data suggest a minor role of S. alterniflora in contributing Cd and Cu from sediment into estuarine food chains. Uptake of Cd and Cu from six important river systems was found to be $1.4 \times 10^3 \text{ kg/yr}$ and $10.4 \times 10^3 \text{ kg/yr}$, respectively. These values accounted for only 3 percent of the total amounts of these metals that flowed through the river systems.

8. While the importance of marsh plants in mobilizing certain heavy metals from sediments remains a subject that requires additional research for further substantiation, the above reports and others^{9,10,11} shed some light on heavy metal concentrations that have been found in marsh plants at various coastal locations. The relationship between the plant leaf heavy metal content found in the present study of metal uptake by marsh plants from dredged material and the actual concentrations of each heavy metal reported in available literature will be discussed in more detail later.

Prediction of heavy metal uptake by plants

9. Literature concerning the prediction of heavy metal uptake by marsh plants is scarce. Only three reports were found. Dunstan et al.^{6,7}, in attempting to relate heavy metal concentrations in sediments to marsh plant heavy metal contents, concluded that Cd and Cu concentrations found in S. alterniflora did not directly correlate with the concentration of these metals measured in the sediment by a nitric acid leaching procedure. It was postulated that S. alterniflora was

well buffered against increasing levels of these metals since only a small portion of each metal accumulated in the plant-available fraction of the sediment. The nitric acid leached fraction of sediment heavy metals as measured by Dunstan et al. may contain forms of heavy metals that normally would not be available for plants and therefore would not be a good estimate of plant-available heavy metals.

10. Perhaps the most extensive research conducted on heavy metal availability as related to sediment pH, Eh, and salinity has been that performed by Gambrell et al.^{12,13} at the Laboratory for Wetland Soils and Sediments, Center for Wetland Resources, Louisiana State University. Under laboratory conditions, heavy metal availability in sediment under various pH and Eh conditions and the resultant uptake of heavy metals by S. alterniflora and Distichlis spicata were studied. Gambrell et al.¹³ report that plant uptake of Cd was increased generally under oxidized conditions at both acid and neutral pH values of 4.5 and 7.5. Mercury concentrations in marsh plants were increased at lower salinities and higher pH (7.5) conditions. Both exchangeable (2N NaAc) and DTPA extractable heavy metals were evaluated and correlated with marsh plant heavy metal contents. Exchangeable (2N NaAc) Hg and Cd correlated well with Hg and Cd contents of S. alterniflora while DTPA extractable Cd correlated well with Cd contents of D. spicata.

11. Gambrell et al.¹³, in reviewing available information on marsh plant uptake of heavy metals, also concluded that there was a serious gap in our understanding of the factors affecting the plant availability of heavy metals in the marsh ecosystem. An extensive review was conducted by Gambrell et al.¹³ of the agricultural literature to relate factors affecting heavy metal availability in agricultural soils and sludge-amended soils. To complement Gambrell's review of literature, the present study reviewed literature that reports the prediction of heavy metal uptake by plants.

12. While few reports involving prediction of heavy metal uptake by marsh plants are available, the prediction of crop responses to available nutrients in agricultural soils has been studied at length for many years. Numerous soil extraction and testing procedures have

been developed to determine the availability of nutrients for crop production. Soil testing and subsequent fertilizer supplementation have become routine for the maximization of crop production in the United States.

13. A review of the available literature concerning extraction of minor elements from agricultural soils revealed potential extraction procedures that may have application to extraction of similar heavy metals in marsh ecosystems. The relationships between soil Zn and plant availability have been more extensively studied than any of the other heavy metals or minor elements. This interest in soil zinc resulted from the occurrence of widespread zinc deficiency in a number of agricultural crops. As early as 1936, agricultural researchers in the United States started extensive studies on the reactions of zinc in soils and the relative availability of soil zinc to plants. Jones et al.¹⁴ studied the compounds formed when zinc was applied to soils and the response of plants to the relative concentrations of these compounds. While most of the interest was to correct zinc deficiencies observed in plants, plant response to excessive amounts of applied zinc (345 kg/ha) was also reported. From 1936 to the present time, research has been conducted to better estimate the plant-available fraction of zinc in soils. Some of the more notable reports are those by Hibbard,¹⁵ Shaw and Dean,¹⁶ Stewart and Berger,¹⁷ Wear and Evans,¹⁸ and Trierweiler and Lindsay.¹⁹

14. In these reports, various fractions of soil zinc were discussed as potential indicators of plant-available zinc. These fractions included water soluble;^{14,15} exchangeable using 1N NH_4Cl ,^{14,15} 1N NH_4Ac ,¹⁶ or 2N MgCl_2 ;¹⁷ dilute acid using either 0.01N HCl ,^{15,16,18} 0.05N HCl plus 0.025N H_2SO_4 ,¹⁸ or 0.1N HCl ;^{17,18,19} and chelate extractable using either dithizone,^{16,17,19} 0.05M EDTA ,^{18,19} or 0.005M DTPA .^{20,21}

15. Other minor elements such as copper and manganese have been studied along with zinc in a few reports. Lindsay²⁰ reported that DTPA extractable Cu and Mn correlated well with plant-available soil Cu and Mn. Follett and Lindsay²² further reported that DTPA extraction was

useful to monitor availability of Cu and Mn in fertilized as well as unfertilized soils.

16. There is limited information from agricultural research in the United States relating the extraction from soil of nonessential heavy metals such as lead, nickel, cadmium, chromium, and mercury to plant uptake. Canadian researchers, however, have reported good agreement between plant contents of Pb and Ni and exchangeable soil Pb and Ni extracted with 1N NH_4Ac (pH 7.0).^{23,24} John et al.²⁵ correlated soil Cd extracted with 1N NH_4Ac with Cd content of radish and lettuce tops.

17. Bates et al.²⁶ found that water soluble Cd and Ni correlated well with Cd and Ni contents of swiss chard. Schueneman and Ellis²⁷ in the United States reported a linear relationship between 1N NH_4Ac extractable Cr and the amount of Cr applied to soil. A significant growth reduction of crops occurred at an application of 100 ppm of Cr. There is no available literature on the relationship between levels of Hg extracted from agricultural soils and the plant content of Hg.

18. The information from the above-mentioned studies was considered in combination with recently published information on heavy metal availability and potential toxicities to crops grown on sludge-amended soils.^{28,29,30}

19. Sewage sludge research has resulted in modifications to a number of the previously mentioned soil extraction procedures to adapt them to excessive rather than deficiency levels of heavy metals. Bingham et al.^{31,32,33} evaluated both water soluble and DTPA extraction procedures to relate extractable Cd to plant growth and content of Cd. Both water soluble and DTPA extraction procedures gave results that agreed well with plant content of Cd. The shaking time of the original DTPA procedure of Lindsay²⁰ was increased from 2 to 24 hours. The additional shaking time was thought to allow a better equilibrium of chelate extractable Cd with soil organically bound Cd. The water soluble paste extraction was also allowed to shake for 24 hours before filtering.

20. Based on the above reports and conversations with a number

of the authors of these reports, four potential extraction procedures were selected for evaluation of their ability to predict heavy metal uptake by marsh plants from dredged material.

Selection of soil
extraction procedures

21. Water soluble. The water soluble extraction procedure of Bingham et al.^{32,33} was selected because of the apparent success in relating results obtained with a 24-hour shaking time to plant content of Cd under both flooded and nonflooded soil conditions. Gambrell et al.¹³ emphasized the importance of Eh on Cd availability, which should have been extremely different under the flooded and non-flooded soil conditions of the experiments of Bingham et al.³³ However, a 24-hour water extraction produced results that correlated well with plant Cd content. In addition, water soluble Ni has been shown to correlate well with plant Ni contents²⁶ and therefore may have potential application in the marsh ecosystem.

22. Exchangeable. Based on the reports of Canadian researchers^{23,24,25} and Schueneman and Ellis,²⁷ the exchangeable extraction procedure using 1N NH_4Ac was selected with the modification of adjusting the pH of the extraction solution to the pH of the sediment.³⁴ While both 2N NaAc ¹³ and 2N MgCl_2 ¹⁷ appeared to have potential, the higher salt contents have caused salt buildups on the atomic absorption spectrophotometer burner, resulting in burner problems. In addition, Gogan³⁵ reported that 2N MgCl_2 was incapable of extracting measurable levels of Zn from calcareous soils.

23. Dilute acid extractable. There are numerous reports of the successful use of a dilute acid extraction (0.1N) for predicting the capacity of a soil to supply nutrients and minor elements such as Zn and Mn.^{17,18,36,37,38} Extraction with higher concentrations of acid (1N) has been reported as not indicating plant-available soil Cd but rather removing nearly all of the soil Cd.²⁵ The combination of 0.05N HCl plus 0.025N H_2SO_4 has been widely used in state soil testing laboratories in the southern region of the United States to indicate major nutrients, Zn, and Mn availability to crops. The ability of

existing soil testing laboratories to perform this procedure makes the double acid extraction an appealing procedure from the practical aspect of CE District utilization.

24. Chelate extractable. The DTPA extraction procedure of Lindsay and Norvell²⁰ as modified by Bingham et al.^{32,33} was selected. The 24-hour shaking period appeared to successfully relate soil Cd availability to plants under flooded or nonflooded conditions.³³ DTPA was shown to correlate extractable soil zinc and yield response extremely well on calcareous soils.³⁵ Therefore, a DTPA extract should have good potential in relating zinc, cadmium, and copper availability to plants in a marsh ecosystem.

Contribution of
airborne particulates
to contamination of plant leaves

25. Considerable information has been published on the significance of airborne heavy metal particulates with regard to plant leaf accumulations of certain metals. Lagerwerff³⁹ reported that plants grown 200 m from a busy highway could have more than 40 percent of their leaf content of Pb, Cd, and Zn due to aerial contamination. Banus et al.⁴ estimated an annual deposition of Pb in Great Sippewassett Marsh of 11.2 mg Pb/m²/yr. They compared this value to annual averages of 40 mg Pb/m²/yr for urban areas and 2 mg Pb/m²/yr for rural areas.

26. It would appear that in attempting to predict plant uptake of certain heavy metals, airborne particulate deposits should be removed from plant leaf surfaces, especially in highly urbanized or industrialized areas. In all of the literature reviewed and discussed previously, the investigators either did not wash plant leaves or rinsed the plant leaves in distilled water before acid digestion for heavy metal analysis. Differences from one area to another could quite possibly be due to the differences in airborne particulate desposition rather than differences in plant uptake of metals from the sediment. There is a definite need to clarify the significance of airborne particulate deposition with regard to the heavy metal contents of marsh plants at various coastal locations reported previously. Research by

Elias and Patterson⁴⁰ revealed that over 75 percent of the lead adsorbed to certain plant leaf surfaces was located in the waxy cuticle. Washing leaves with methanol, distilled water, 1N HCl, and finally distilled water removes the airborne lead without destroying the plant leaf epidermal cells. It would appear that in research attempting to predict heavy metal uptake by plants from soils or sediments precautions should be taken to minimize airborne particulate contamination. Unsuccessful attempts to correlate soil extractable heavy metals with plant heavy metal content may have been confounded by airborne particulates if plant leaves were not washed adequately.

Purpose and Scope

27. This study was the second step to evaluate the ability of marsh plants to take up heavy metals from dredged material. A previous greenhouse hydroponic study⁴¹ indicated that certain marsh plants were able to absorb and take up certain heavy metals rapidly from hydroponic solutions. Based on these results, a field survey and sampling study was designed with two phases. The objectives of Phase I: Prediction Development were to:

- a. Establish the extent of heavy metal accumulation by marsh plant species from dredged material under field conditions.
- b. Develop predictive equations and correlations between various extraction and analysis procedures for dredged material and the heavy metal accumulation by plants grown on the dredged material.

The objective of Phase II: Verification was to confirm and improve the developed predictive equations and correlations by additional field tests.

28. Due to time and funding constraints, the field sampling was limited to three estuarine marsh plant species, Spartina alterniflora, Spartina patens, and Distichlis spicata. These species are commonly widespread and took up heavy metals rapidly from hydroponic solutions⁴¹ and therefore would be expected to be potential heavy metal accumulators

when grown on contaminated dredged material. Locations sampled were limited to the East and Gulf Coasts of the United States. A wide range of environmental conditions was sampled. Sampling sites included dredged material disposal areas located near industrial and urban areas, in harbors, turning basins, bays, and rivers, as well as natural locations with limited or no industrialization. Sampling was limited to those marsh plants colonizing the disposal site. Freshwater marsh species and locations were not included in this study.

Approach

29. The study was conducted in two phases: (a) Prediction Development and (b) Verification. During Phase I, a wide range of environments and dredged material were sampled for both marsh plants and dredged material. These samples were analyzed for heavy metals using modified procedures from available literature. Extraction procedures were evaluated to develop a predictive technique for estimating heavy metal uptake by marsh plants from dredged material. Plant heavy metal contents were correlated with the concentrations of heavy metals extracted from the dredged material. Predictive equations were developed for marsh plant uptake of one or more of the heavy metals zinc (Zn), copper (Cu), cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), and mercury (Hg). Phase II was designed to include additional field sampling to test and verify the predictive equations developed in Phase I.

PART II: DESCRIPTION OF STUDY

Phase I: Prediction Development

Field Sampling

30. Marsh plants were sampled from maintenance dredging disposal sites along the Atlantic and Gulf coastal regions of the United States (Table 1, Figure 1). The marsh plant species studied were S. alterniflora, S. patens, and D. spicata. Two to four samples of each species were obtained whenever present on the site.

31. All samples were obtained between 29 September and 6 November 1975. North Atlantic coastal locations were sampled first, followed by the South Atlantic and Gulf coastal locations. Samples were taken at the end of the growing season, but prior to the onset of dormancy. By sampling at this time, it was anticipated that maximum uptake of heavy metals would have occurred.

32. Different lateral expansion characteristics were exhibited by each species. Therefore, each species had to be sampled somewhat differently. The objective of this sampling program was to obtain mature plants indicative of the current season's growth. Flowers or seed heads were on some of the stems in almost all of the S. alterniflora samples, whereas only a few of the S. patens or D. spicata samples contained flowers or seed heads.

33. S. alterniflora colonies were generally circular in configuration and ranged from less than 15 cm in diameter to greater than 10 m. In addition to differences in the size of the colony, large differences in the size of the individual plants were observed. S. alterniflora ranged from 1 m in height to over 2 m. Colonies were characterized by a central zone of mature plants including dead stems and decaying plant remains, an outer zone of mature plants without previous year's growth, and a peripheral zone of immature plants (Figure 2). The immature plants of the peripheral zone did not exhibit well-developed root

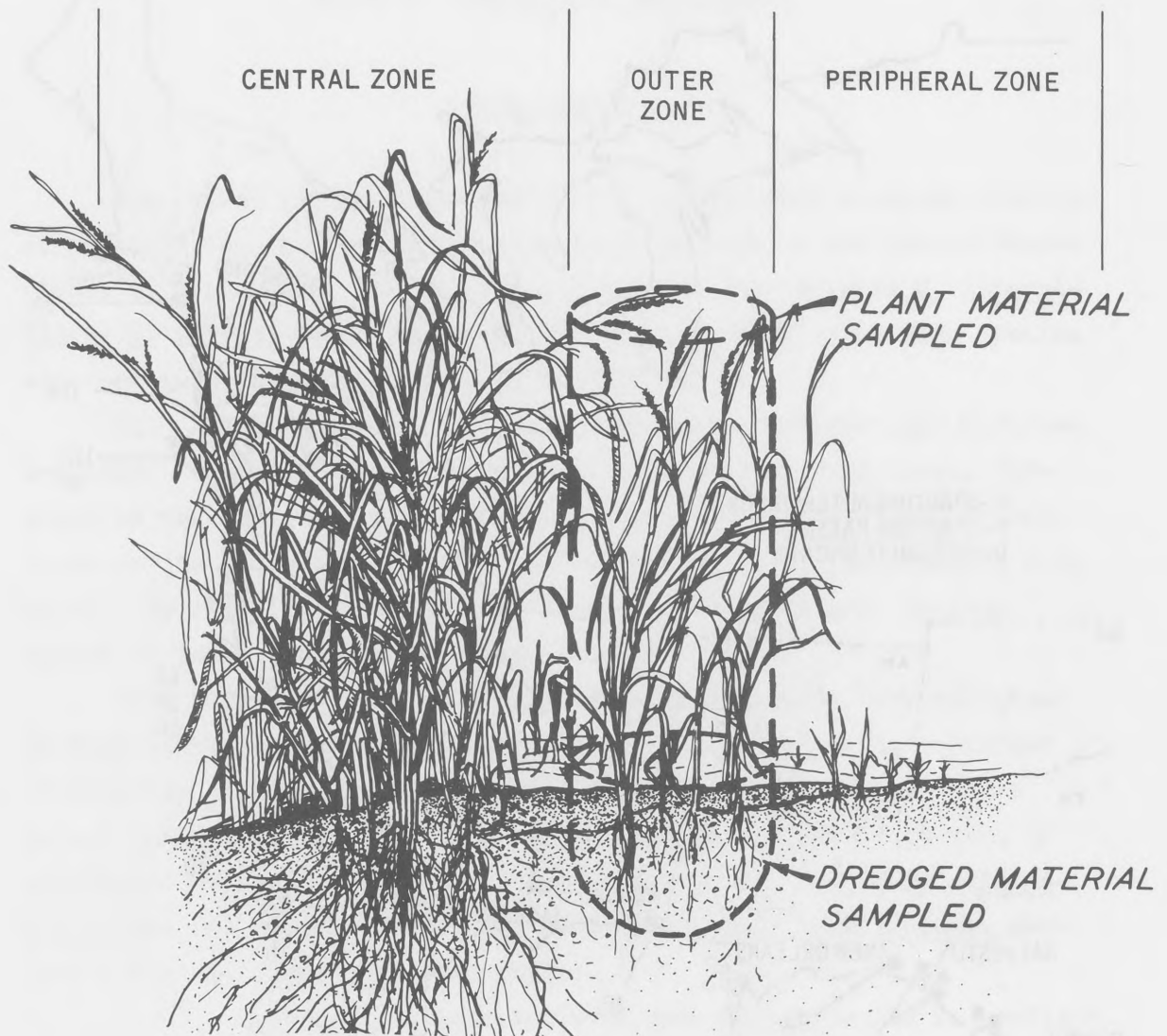


Figure 2. Illustration of typical sample obtained
for Spartina alterniflora

systems and depended to some extent on the transfer of materials from parent plants. No samples were taken from this zone as heavy metal concentrations in these plants may not be related to concentrations in the sediment below. All samples were taken at the outward edge of the mature portion of the colony. These samples did not contain stems from previous years but did exhibit well-developed, but fairly shallow, root systems.

34. Plant roots were excavated to a depth of 15-20 cm below the crown of the plants. Once a plant was removed, aboveground biomass was clipped at 10 cm above the sediment surface and placed in polyethylene bags. Sediment was removed from around plant roots and placed in 1.5-l polyethylene sample bottles. After collecting the sediment sample in this manner, plant roots, with lower stems and rhizomes attached, were placed in plastic bags. All samples were sealed and iced in plastic containers for shipping to the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Miss.

35. S. patens exhibited different growth characteristics than S. alterniflora and, consequently, sampling procedures were modified. Colonies of these plants consisted of dense stands of stems with stolons proliferating new colonies up to 1 m away from the parent plant (Figure 3). Colonies of three distinct ages were apparent. Older colonies consisted of larger basal diameters (10-15 cm) with a considerable amount of dead vegetation. Other colonies consisted of fewer stems and very little dead matter with subsequently smaller basal diameters (5 cm). These latter colonies were assumed to be representative of a single season's growth and all samples were taken from them. Roots were excavated to a depth of 15-20 cm below the crown of the plant. Once a plant was removed, aboveground biomass was clipped at 10 cm above the soil surface. Sediment and plant samples were processed similarly to those for S. alterniflora.

36. D. spicata exhibited still another growth characteristic (Figure 4). Colonies of these plants consisted of a dense central zone containing abundant dead material. The outer zone was characterized by laterally extending stolons up to 1.5 m long and about 0.5 m apart.

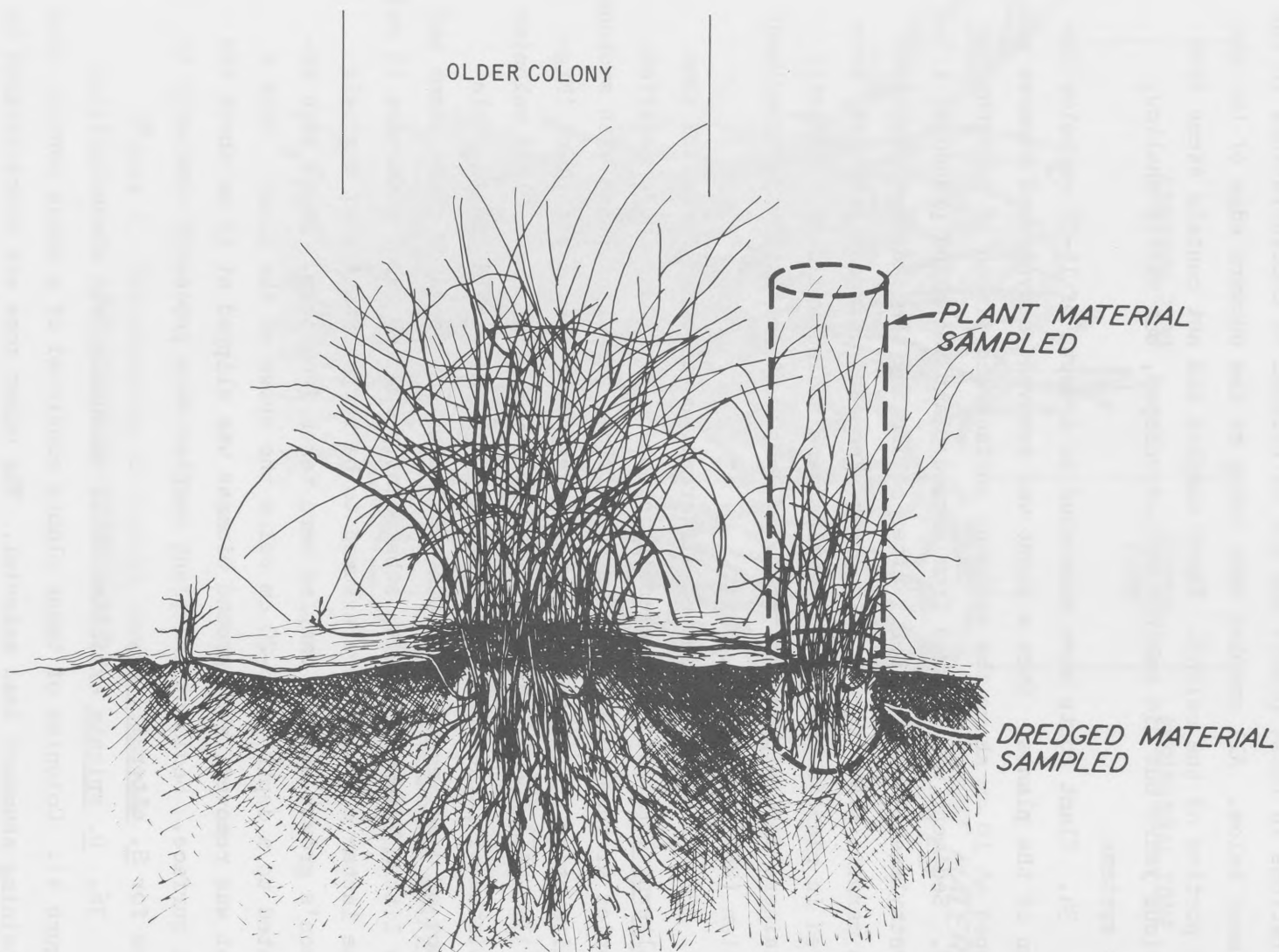


Figure 3. Illustration of typical sample obtained for Spartina patens

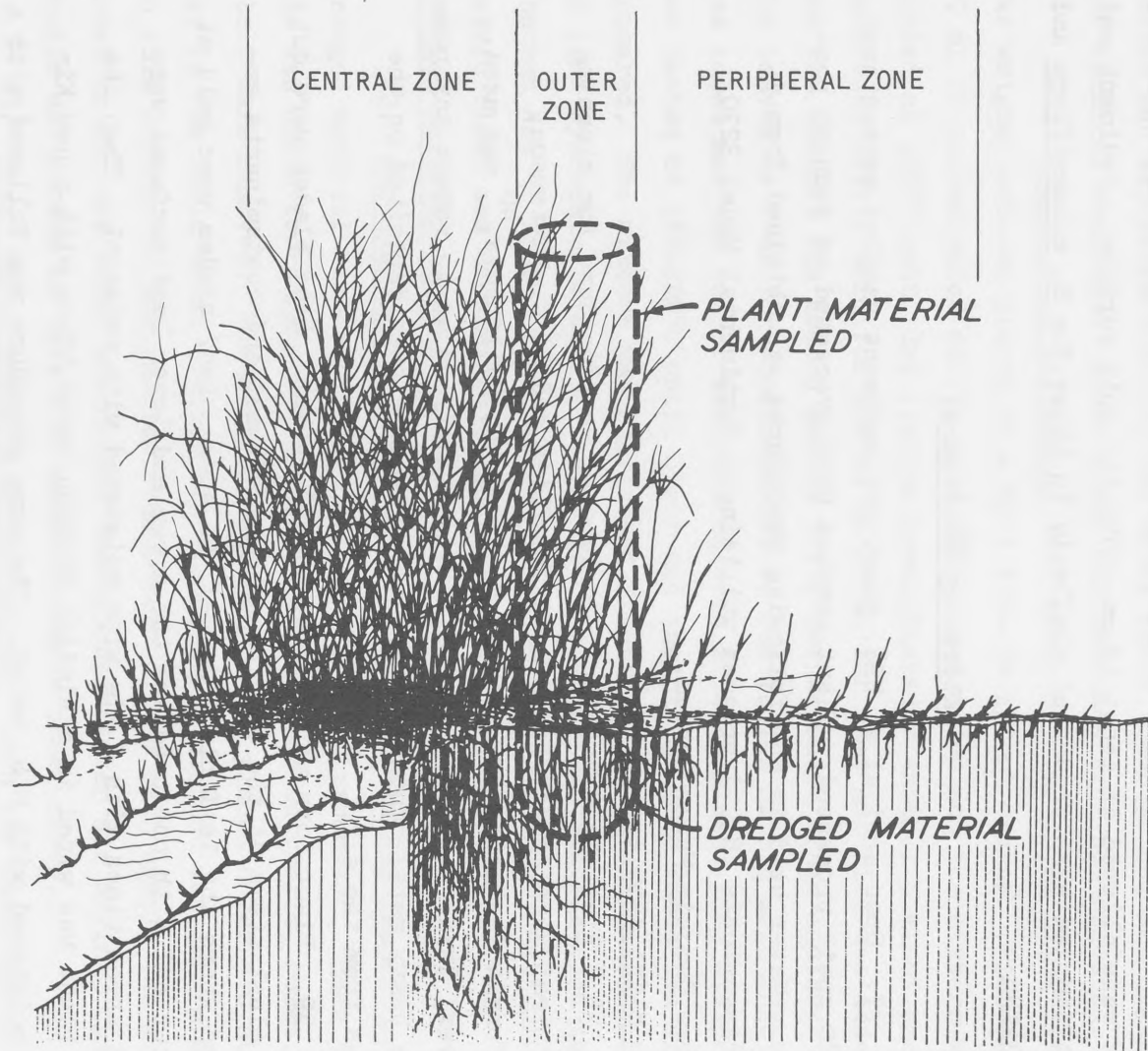


Figure 4. Illustration of typical sample obtained for Distichlis spicata

Numerous plants were observed along the length of the stolons with bare areas between. Samples were taken immediately inward from these where both ground cover and root development were more extensive. These samples did not contain significant amounts of dead material and were thought to be indicative of the current season's growth. Roots were excavated in approximately a 20-cm-square area to a depth of 15-20 cm and stems were clipped at about 10 cm above the soil surface. Sediment and plant samples were processed similarly to those for S. alterniflora and S. patens.

Laboratory Procedures

37. Upon arrival at WES, plant and sediment samples were stored at 5°C until processed. Plant samples were processed as soon as possible. Water used in the following procedures was obtained from a reverse-osmosis (R.O.) process utilizing a Continental Model 3230 Reverse Osmosis Water System.

Marsh plant samples

38. Plant leaf washing. In general, a procedure for cleaning plant leaf surface developed by R. W. Elias and C. C. Patterson, California Institute of Technology, Pasadena, California,⁴⁰ was used. However, their procedure was modified slightly so as to remove any possible heavy metal contaminants that might have been deposited on the leaves from the air.

39. Plant tops were rinsed in R.O. water. Leaf blades were cut from plant stems at the stem to remove sediment and contaminants embedded where the leaf blade joined the stem. Leaf blades were held at the cut end with one hand and the upper and lower leaf surfaces were wiped three times with a Kim wipe moistened with methanol. Then the leaf blade was wiped in a similar fashion three times with a new Kim wipe moistened with R.O. water. The same procedure was followed with a Kim wipe moistened with a 1N hydrochloric acid. The leaf blade was then again wiped three times with a Kim wipe moistened with R.O. water. The washed leaves were then oven dried at 70°C until constant weights were obtained. Dried plant material was ground into a fine powder in a

stainless steel Wiley mill and stored in polyethylene bottles until acid digested.

40. Plant roots. Randomly selected samples of lower stem, rhizome, and roots were washed thoroughly in a jet of R.O. water to remove as much soil from plant roots as possible. Plant roots were then collected and separated into red and white roots, oven dried, and digested for chemical analysis. Lower stems and rhizomes were not digested.

41. Nitric acid digestion. Two grams of oven-dried plant tissue was weighed out and placed in a tall 100- or 150-ml beaker. Fifteen to 20 ml of concentrated nitric acid (HNO_3) was added and the mixture was heated at 100°C until dry (yellow precipitate). Another 5 ml of concentrated nitric acid for leaves or 20 ml for root material was added and the mixture was heated gently for a few seconds. Then another 5 ml for leaves or 8 ml for root material of red fuming nitric acid (HNO_3) was added and the beaker was covered with a watch glass. The mixture was heated at $180\text{--}200^\circ\text{C}$ until clear and the nitric acid fumes had disappeared. The mixture was cooled and diluted to 30 ml with a solution of 1.2N hydrochloric acid (1:10 HCl). This solution was filtered through Whatman No. 42 filter paper and a long stem funnel into a 50-ml volumetric flask and diluted to 50 ml with 1.2N HCl.

Dredged material samples

42. Handling and storage. Upon arrival at the WES laboratory, dredged material samples were stored at 5°C until processed. Each sample was mixed thoroughly and all large debris such as shells, rocks, etc., were removed. One half of each sample was placed under 5°C storage in the field moist condition. The moisture content was determined on this portion of the sample. The other half of each sample was allowed to air dry under greenhouse conditions. After air drying, the sample was ground to pass a 35-mesh stainless steel sieve.

43. Heavy metal extraction procedures. Both the field moist and the air-dried portions of the dredged material samples were subjected to the following heavy metal extraction procedures.

44. Water paste extract:³² 50 g (oven-dry basis) of dredged material was placed in a 500-ml polycarbonate bottle, and R.O. water was

added for a total water volume of 250 ml to give a soil to solution ratio of 1 to 5. The mixture was shaken for 24 hr and centrifuged at 9,000 rpm ($13,701 \times g$) for 30 min with 5-min acceleration and 30-min deceleration. The supernatant liquid was filtered through No. 42 filter paper on a buchner funnel. Salinity and pH were measured on the filtrate using a refractometer and an orion pH meter, respectively. The filtrate was then acidified to pH 2.0 or less with 1 ml of concentrated nitric acid. It was necessary to change the soil:solution ratio from 1:2 to 1:5 since some dredged material contained enough water initially to give a 1:3 soil:solution ratio and at least 100 ml of extraction solution was required for subsequent chemical analysis.

45. Exchangeable ($1N NH_4Ac$ adjusted to pH of soil):³³ 20 g (oven-dry basis) of dredged material was placed in a 250-ml polycarbonate centrifuge bottle; 50 ml of 2N ammonium acetate adjusted to the pH of the sample was added; R.O. water was then added to dilute to 100 ml. The mixture was shaken for 1 hr and centrifuged at 6000 rpm ($6089 \times g$) for 30 min with 5-min acceleration and 8-min deceleration. The supernatant liquid was filtered through Whatman No. 42 filter paper on a buchner funnel and the filtrate was acidified to pH 2.0 or less with 6 ml of concentrated nitric acid. Ammonium acetate was prepared by mixing 133.3 ml of ammonium hydroxide diluted to 500 ml with R.O. water and 117.50 ml of glacial acetic acid diluted to 500 ml with R.O. water for 1 l of a 2N solution of ammonium acetate.

46. DTPA-extractable ($0.005M DTPA + 0.01M CaCl_2 + 0.1M TEA$):^{20,32} 50 g (oven-dry basis) of dredged material was placed in a 500-ml centrifuge bottle; 125 ml of $0.010M DTPA + 0.020 CaCl_2 + 0.2M$ triethanolamine (TEA) buffered at pH 7.3 was added. R.O. water was added to 250 ml and the mixture was shaken for 24 hr and centrifuged at 9,000 rpm ($13,702 \times g$) for 30 min with 5-min acceleration and 30-min deceleration. The supernatant liquid was filtered through Whatman No. 42 filter paper on a buchner funnel. The filtrate was not acidified, but analyzed within 14 days for heavy metals. DTPA extraction solution was prepared by dissolving DTPA in triethanolamine and diluting to near the proper dilution and adding $CaCl_2$ and completing the dilution with R.O. water.

47. Dilute acid extractable ($0.050\text{N HCl} + 0.025\text{N H}_2\text{SO}_4$):^{36,37}
20 g (oven-dry basis) of dredged material was placed in a 250-ml centrifuge bottle, 50 ml of 0.10N HCl and $0.050\text{N H}_2\text{SO}_4$ extraction solution was added, and R.O. water was added to make a total volume of 100 ml. The mixture was shaken for 5 min and centrifuged at 6000 rpm ($6089 \times g$) for 30 min with 5-min acceleration and 5-min deceleration. The supernatant liquid was filtered through Whatman No. 42 filter paper on a buchner funnel. The filtrate was acidified to pH 2.0 or less with 1 ml of concentrated nitric acid.

Chemical analyses

48. Plant digestion solutions and dredged material extraction solutions were analyzed for Zn, Cd, Cu, Pb, Cr, and Ni using either an atomic absorption spectrophotometer (Perkin Elmer 503 with graphite furnace) or an argon plasma emission multielement spectrophotometer. Mercury was determined using an isotope-zeeman atomic absorption spectrophotometer or the cold vapor method of Hatch and Ott.⁴²

Statistical analyses

49. Descriptive statistics were calculated for all chemical data for both plant and dredged material samples by species and collectively. The analysis of variance was used to estimate variance components and to determine the effect of leaf washing. Chemical data from the plant digestions were correlated with the chemical data from extraction solutions for the respective plant and dredged material samples. Both simple and multiple (or polynomial) regression analyses were performed on the data considering plant chemical data as the dependent variable and soil extraction data as the independent variable. A multiple (or curvilinear) correlation coefficient was calculated at the termination of each stepwise polynomial regression analysis. Significant differences and relationships among the data were tested at the $P = 0.05$ level of significance unless otherwise specified.

Phase II: Verification

Field Sampling and Laboratory Procedures

50. S. alterniflora and D. spicata were sampled in Nueces Bay adjacent to Corpus Christi Bay, Texas. Marsh plants and dredged material sampled in Phase I from this general area were found to contain some of the higher concentrations of Zn and Cd. During the Phase I sampling, considerable air contamination appeared to exist in this area. Marsh plants and dredged materials were sampled and processed identically to the procedures described under Phase I. Twenty-two samples of S. alterniflora and 20 samples of D. spicata were collected. These numbers of samples were collected to give a good indication of the variability occurring within a sampling area of approximately 92 by 92 m.

51. Each leaf sample of S. alterniflora was divided in half. One half was rinsed with R.O. water and the other half was washed according to the plant leaf washing procedure described in Phase I.

52. Additional marsh plant and dredged material samples were collected from a previous greenhouse experiment⁴³ to verify the prediction equations developed in Phase I. Marsh plant leaves and dredged material samples were processed as described under Phase I procedures.

Statistical Analyses

53. Chemical data from the DTPA extraction of dredged material samples were incorporated into the prediction equations developed under Phase I and heavy metal contents were predicted. These predicted values were then compared with the actual content of each heavy metal in the plant samples for each marsh species. This comparison of predicted heavy metal contents with actual observed contents was analyzed for precision and accuracy. Variability in both the DTPA extraction and plant content data was analyzed for standard deviations and coefficients of variation. Significant differences and relationships reported for the data were obtained at the $P = 0.05$ level of significance unless otherwise specified.

PART III: RESULTS AND DISCUSSION

Phase I: Prediction Development

Comparison of Acid Plant Leaf Digestion Procedures

54. Two procedures for digesting plant leaves were evaluated on 20 of the marsh plant samples. The first procedure was the nitric acid digestion described previously. The second procedure is a standard method used by many agricultural scientists. This procedure is similar to the nitric acid digestion with the exception that perchloric acid is substituted for the red fuming nitric acid. Although perchloric acid digestion has been used extensively by Lee,^{44,45,46} a serious explosive hazard exists with hot perchloric acid. Because of this hazard, a comparison was made in which red fuming nitric acid was used in place of perchloric acid for plant digestions. There were no significant differences in the concentrations of Zn, Pb, Hg, and Cu found in marsh plant leaves as determined by the two digestion procedures (Table 2). The red fuming nitric acid procedure gave higher values of Cd and Ni in marsh plant leaves than the perchloric acid procedure. Recovery of Cd and Ni may be poorer in perchloric acid than in nitric acid since the blanks for each procedure did not contain appreciable amounts of Cd or Ni as contamination. The most pronounced difference in these digestion procedures was the excessive amount of Cr found in the perchloric acid digestion. The high values were found to be due to Cr contamination of the reagent grade perchloric acid.

55. These results indicate that red fuming nitric acid can be substituted for perchloric acid for the digestion of plant materials in heavy metal research. The advantage of using red fuming nitric acid instead of perchloric acid is the elimination of potential explosions. As mentioned earlier, the nitric acid digestion procedure was used in this study.

Heavy Metal Contents of Marsh Plants

Zinc

56. Concentrations of Zn in marsh plants were mostly in the range of 10-20 ppm (Figure 5). These values compare well with Zn concentrations of 11 ppm found in natural Louisiana marshes of S. alterniflora as reported by Gosselink et al.⁹ Broome et al.¹⁰ showed Zn concentration of 17 ppm in natural stands of S. alterniflora along the coast of North Carolina. Drifmeyer and Odum¹¹ reported Zn concentrations in S. alterniflora and S. patens of 38.6 and 28.9 ppm, respectively, on dredged material and 20.1 and 21.2 ppm, respectively, in a natural marsh in the same general vicinity in Virginia. Zn concentrations in natural marshes of S. alterniflora near Beaufort, N. C., ranged from 7 to 12 ppm.¹ From these data it would appear that most of the marsh plants growing on the dredged material sampled contained Zn concentrations approximating natural marsh Zn contents. However, there were a few relatively high values (125, 135, and 155 ppm Zn) for S. alterniflora that should be noted.

Copper

57. Marsh plant leaf concentrations of Cu were found to be generally between 2 and 6 ppm (Figure 6). These values agree well with Gosselink et al.⁹ who reported values of 6 ppm of Cu in natural stands of S. patens and D. spicata and 4 ppm of Cu in S. alterniflora. Broome et al.¹⁰ reported 2 to 4 ppm of Cu in S. alterniflora on the North Carolina coast. In the present study, only two samples were found to contain more than 7 ppm of Cu. From these data, it would appear that marsh plants growing on the dredged material sampled did not contain any more Cu than marsh plants growing in a natural marsh.

Cadmium

58. The Cd content of marsh plant leaves was mostly 0.2 ppm or less (Figure 7). There were three samples containing an order of magnitude greater than 0.2 ppm. Dunstan et al.⁷ found an average of 0.61 ppm Cd in natural stands of S. alterniflora along six southeastern U. S. river systems. Cadmium concentrations of 5 ppm or more

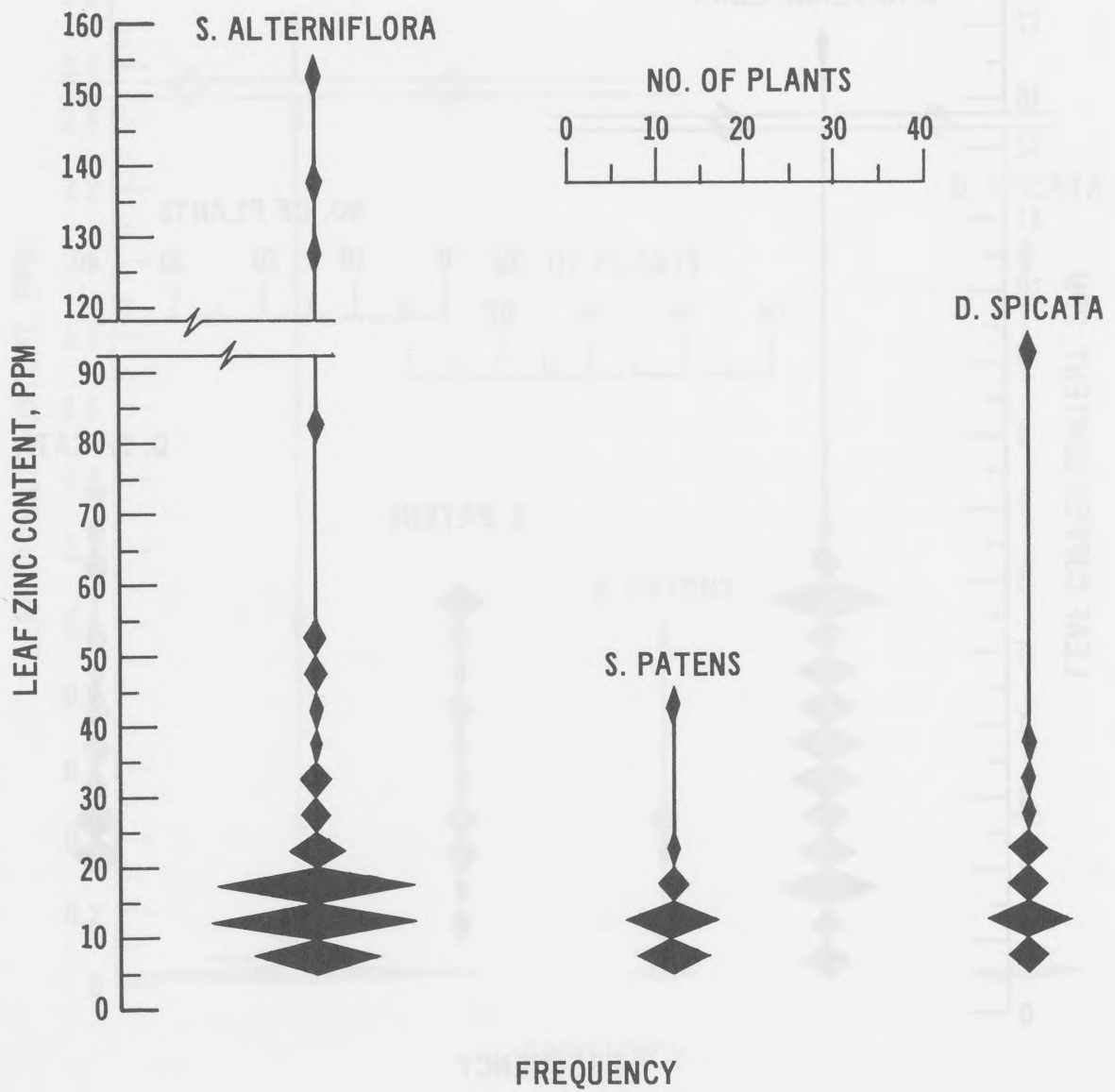


Figure 5. Distribution of zinc concentrations in marsh plant leaves

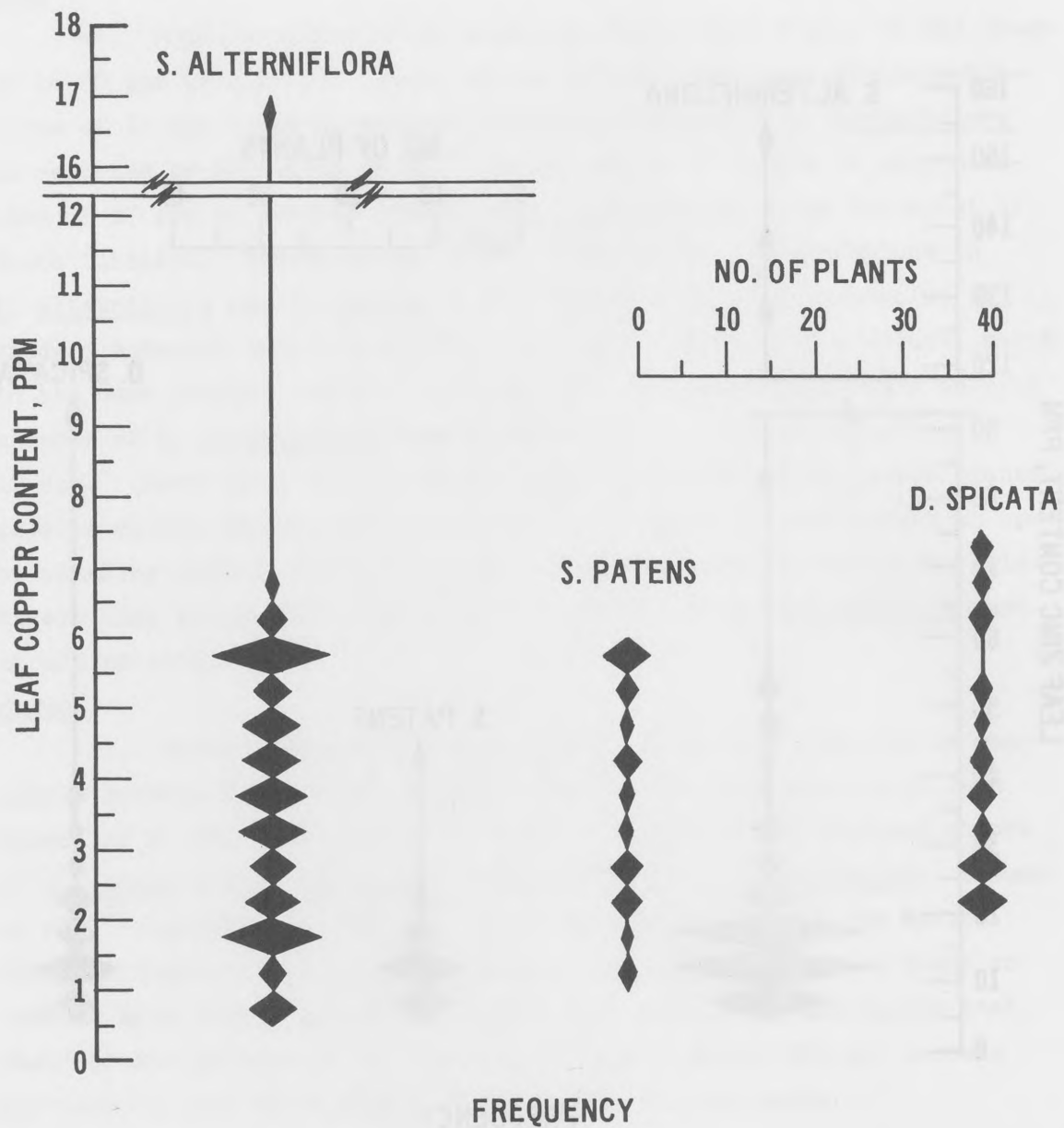


Figure 6. Distribution of copper concentrations in marsh plant leaves

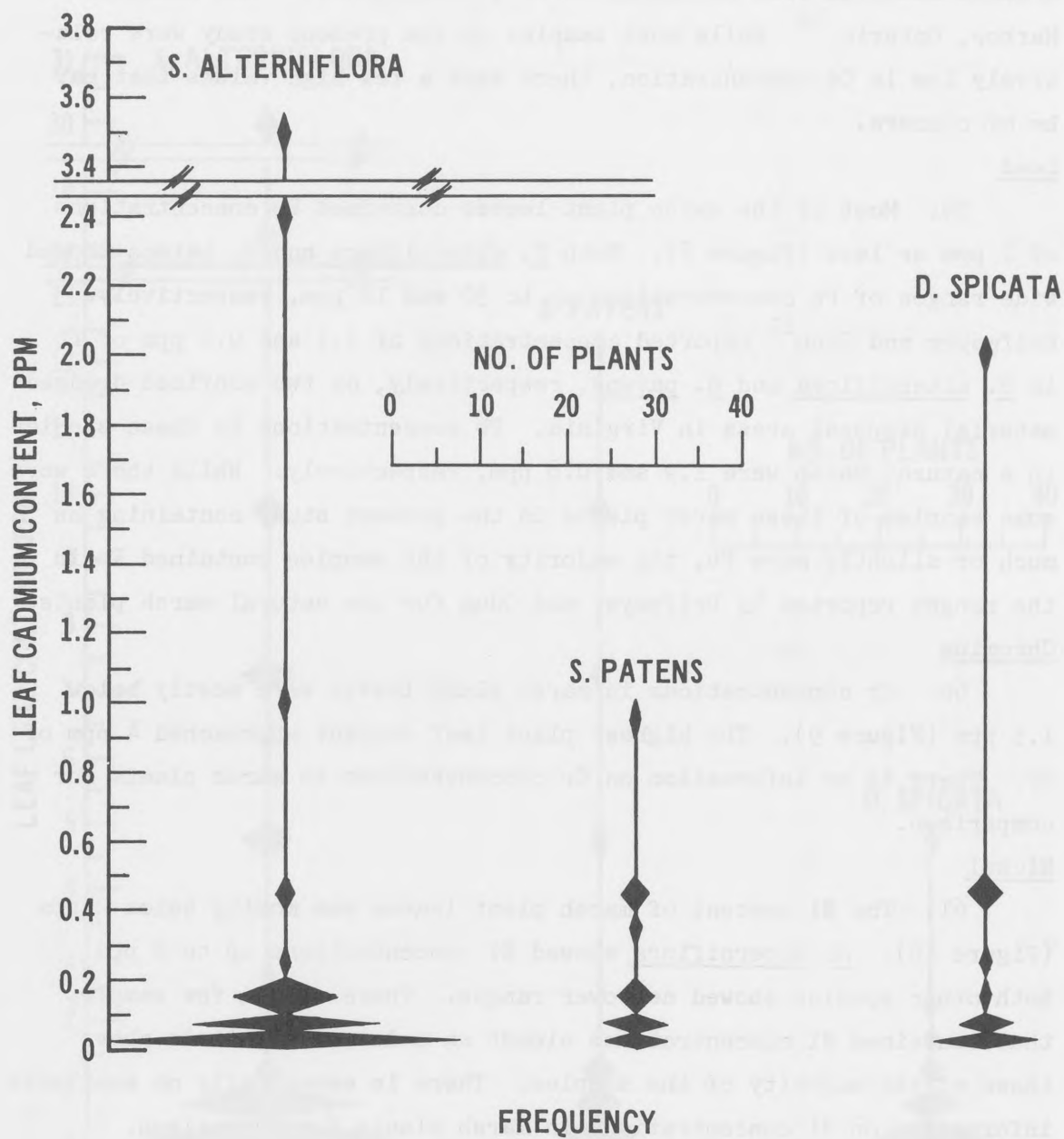


Figure 7. Distribution of cadmium concentrations in marsh plant leaves

have been reported in agronomic crops (lettuce and radishes) grown in dredged material from Rotterdam Harbor, Netherlands,⁴⁷ and Hamilton Harbor, Ontario.⁴⁸ While most samples in the present study were relatively low in Cd concentration, there were a few high values that may be of concern.

Lead

59. Most of the marsh plant leaves contained Pb concentrations of 1 ppm or less (Figure 8). Both S. alterniflora and S. patens showed wide ranges of Pb concentrations up to 30 and 12 ppm, respectively. Drifmeyer and Odum¹¹ reported concentrations of 5.1 and 9.1 ppm of Pb in S. alterniflora and S. patens, respectively, on two confined dredged material disposal areas in Virginia. Pb concentrations in these species in a natural marsh were 1.9 and 0.8 ppm, respectively. While there were some samples of these marsh plants in the present study containing as much or slightly more Pb, the majority of the samples contained Pb in the ranges reported by Drifmeyer and Odum for the natural marsh plants.

Chromium

60. Cr concentrations in marsh plant leaves were mostly below 1.5 ppm (Figure 9). The highest plant leaf content approached 4 ppm of Cr. There is no information on Cr concentrations in marsh plants for comparison.

Nickel

61. The Ni content of marsh plant leaves was mostly below 2 ppm (Figure 10). S. alterniflora showed Ni concentrations up to 8 ppm. Both other species showed narrower ranges. There were a few samples that contained Ni concentrations almost an order of magnitude above those of the majority of the samples. There is essentially no available information on Ni concentrations in marsh plants for comparison.

Mercury

62. Hg concentrations in marsh plant leaves were relatively low and had narrow ranges of 0.0-0.49, 0.0-0.23, and 0.0-0.15 ppm for S. alterniflora, S. patens, and D. spicata, respectively. Dunstan and Windom⁶ reported up to 0.44 ppm Hg in S. alterniflora from eight natural marshes extending from South Carolina to Florida. There appears

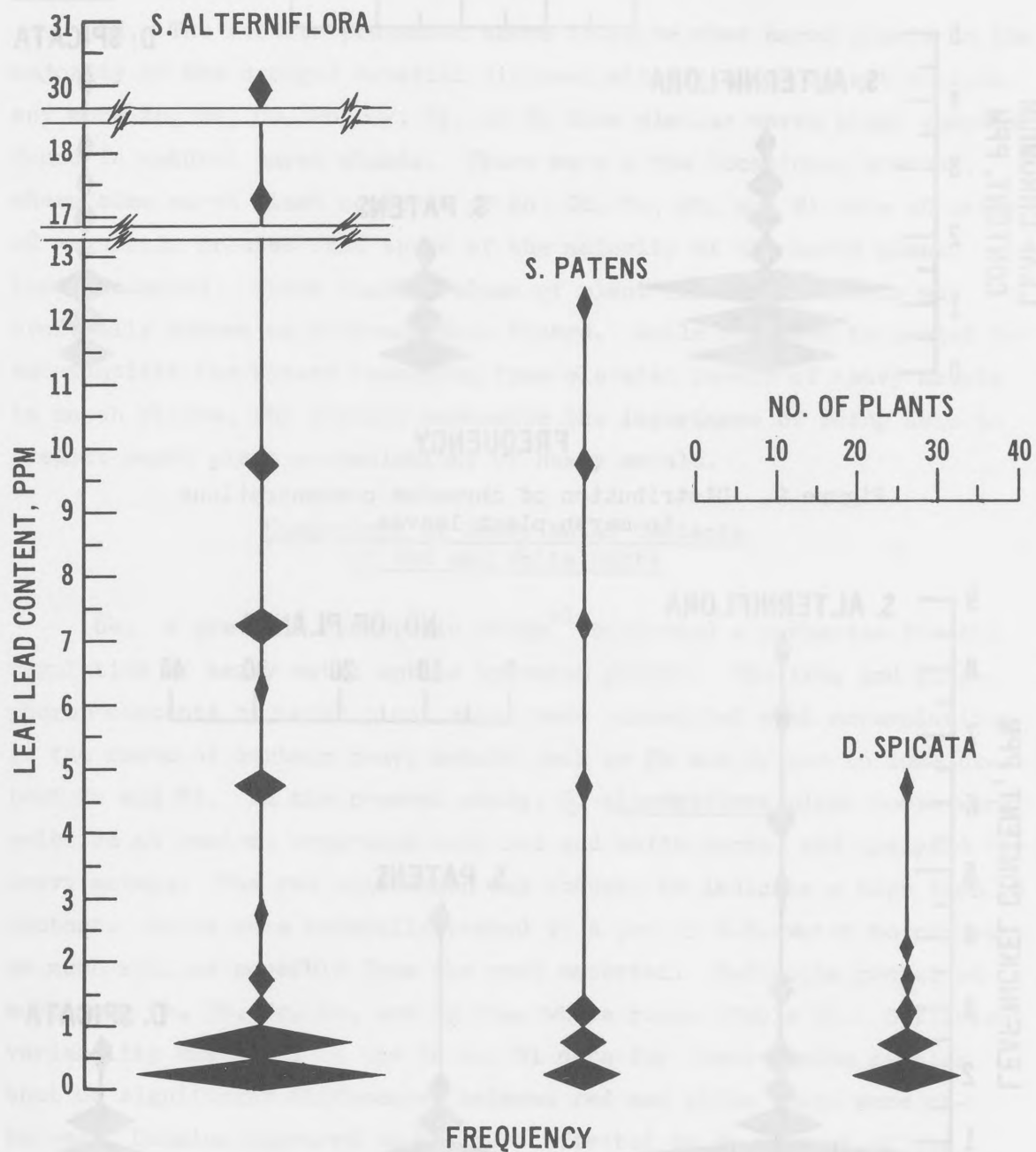


Figure 8. Distribution of lead concentrations in marsh plant leaves

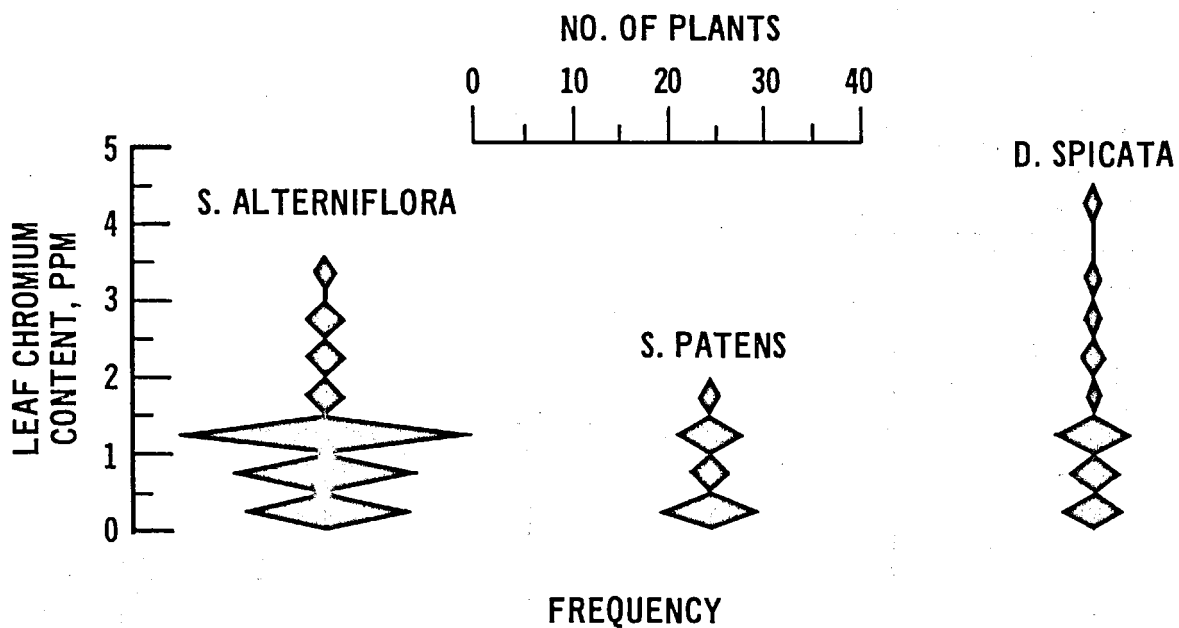


Figure 9. Distribution of chromium concentrations in marsh plant leaves

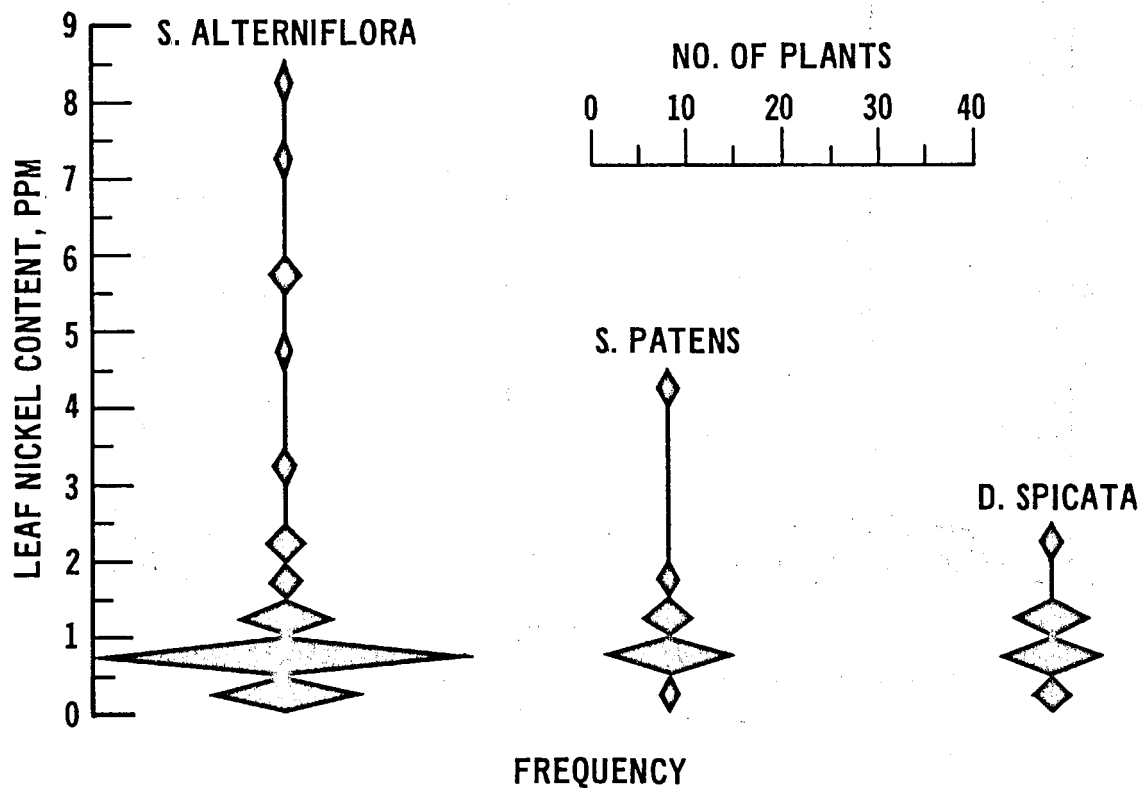


Figure 10. Distribution of nickel concentrations in marsh plant leaves

to be as much Hg in marsh plants on dredged material as that found in a natural marsh.

Summary

63. The results presented above indicate that marsh plants on the majority of the dredged material disposal sites sampled do not contain any more Zn, Cd, Cu, Pb, Cr, Ni, or Hg than similar marsh plant species found in natural marsh stands. There were a few locations, however, where some marsh plant contents of Zn, Cd, Cu, Pb, and Ni were an order of magnitude greater than those of the majority of the marsh plant leaves sampled. These higher values of plant leaf heavy metals may eventually become an environmental hazard. While research is needed to substantiate the hazard resulting from elevated levels of heavy metals in marsh plants, the results emphasize the importance of being able to predict marsh plant accumulations of heavy metals.

Comparison of Heavy Metal Contents of Red and White Roots

64. A previous hydroponic study⁴¹ suggested a mechanism for the regulation of heavy metal uptake by marsh plants. The iron and phosphorus contents of marsh plant roots were correlated with accumulations in the roots of certain heavy metals such as Pb and Cr and to some extent Zn and Ni. In the present study, S. alterniflora plant roots were selected at random, separated into red and white roots, and analyzed for heavy metals. The red coloration was thought to indicate a high iron content. Roots were carefully washed in a jet of R.O. water to remove as much soil as possible from the root material. Red roots contained much more Fe, Pb, Cr, Cu, and Hg than white roots (Table 3). Sufficient variability was found in the Zn and Ni data for these random samples that no significant differences between red and white roots were obtained. Cadmium appeared to be least affected by Fe content of the roots, a finding that agrees well with the results of the hydroponic study.⁴¹

Extractable Heavy Metals from Dredged Material

65. Each field moist dredged material sample was subjected to each of the four extraction procedures. Twenty of the dredged material samples were air-dried and subjected to each of the four extraction procedures. The concentration ranges of each heavy metal extracted from the field moist samples by each procedure are presented in Table 4 as a point of reference. Further discussion of these data will be incorporated in the discussion of the correlations obtained.

66. Air-drying the dredged material before extraction generally increased the concentration of heavy metals for each extraction procedure. DTPA extraction of all heavy metals except Hg increased considerably after the dredged material was air-dried (Table 5).

67. Salinity and pH data were measured on the water paste extract and are presented in Table 6 for reference. Samples had a wide range of salinity and pH.

Correlations Between Plant Content and Extractable Heavy Metals

68. Simple and multiple correlation coefficients were determined and regression analyses were performed for the heavy metal concentrations in the marsh plant leaves and the concentrations of heavy metals extracted from the dredged material. Data used in these analyses are tabulated in Appendices A and B. Initially the three marsh plant species were analyzed collectively to obtain overall correlations between plant heavy metal contents and extractable heavy metals. However, subsequent correlations performed on each marsh plant species separately improved a number of the correlations. All tests for significance were conducted at the $P = 0.05$ level of significance.

Water soluble

69. There were very few significant correlations between plant heavy metal content and the water soluble concentration of that heavy metal extracted from dredged material (Table 7). The most notable correlations were found within each species. A significant multiple

correlation was found between water soluble Hg and plant leaf Hg in S. alterniflora ($r = 0.57$). A significant linear relationship was found between water soluble Ni and plant leaf Ni in S. patens ($r = 0.55$). Bates et al.²⁶ report a relatively similar correlation between water soluble Ni and plant Ni content. Water soluble Cu showed a significant linear relationship to plant leaf Cu in D. spicata ($r = 0.49$). There was no significant correlation for Zn, Pb, Cr, and Cd. While Bingham et al.³³ found good correlations between water soluble Cd and plant Cd contents for rice grown under flooded and nonflooded conditions, their research was limited to one soil. Additional research was recommended to verify the correlation of water soluble Cd to plant Cd content for a number of different soils. Since the present study sampled a wide range of different dredged materials and no significant correlations for plant Cd uptake were found, the use of water soluble Cd to predict plant uptake of Cd may be limited to certain soil types and not be applicable to a wide range of soils.

Exchangeable NH_4Ac

70. There were few significant correlations between plant heavy metal content and the exchangeable concentration of that heavy metal extracted from dredged material (Table 8). No significant correlations were obtained when all species were considered together. While S. alterniflora and S. patens showed only two significant correlations, D. spicata showed a highly significant multiple correlation of plant leaf Zn and Cd content and exchangeable Zn and Cd extracted from dredged material. These high correlations for Cd in D. spicata agree well with the correlations of 1N NH_4Ac extractable Cd with plant Cd content reported by John et al.²⁵ Exchangeable Cu showed a significant multiple correlation with plant leaf Cu ($r = 0.54$). Exchangeable Ni, Pb, and Cr did not relate well to plant contents of these metals as reported by MacLean et al.,²³ Halstead et al.,²⁴ and Schueneman and Ellis.²⁷ These investigators added various amounts of each heavy metal to a soil and then evaluated 1N NH_4Ac extractable concentrations with regard to plant heavy metals contents. The dredged materials sampled

in the present study contained Ni, Pb, and Cr that may have been in forms other than exchangeable and therefore very few significant correlations were obtained. These data indicate that the exchangeable ammonium acetate procedure is limited to only one species, D. spicata, for predicting plant uptake of Zn, Cd, and Cu.

Dilute acid extractable

71. There were very few significant correlations of plant heavy metal contents and dilute acid extractable heavy metals (Table 9). Dilute acid extractable Zn was not related to plant Zn content as reported by Coffman and Miller.³⁸ However, Coffman and Miller applied Zn to soil and then evaluated the relationship of dilute acid extractable Zn to plant Zn content. Concentrations of dilute acid extractable Zn ranged from 0.3 to 1.7 ppm in Coffman and Miller's research. The range of dilute acid extractable Zn in the present study was from 0.1 to 64.8 ppm Zn. Dilute acid extractable Zn may relate well to plant Zn contents at low levels of soil Zn around the deficiency range; however, at higher levels of soil Zn, correlation of plant Zn contents to dilute acid extractable Zn may not exist. Acid extractable Cu showed a significant correlation with marsh plant leaf Cu contents when all three plant species were grouped together, and also for S. alterniflora and S. patens individually (Table 9). Acid extractable Pb showed significant multiple correlations with plant Pb content for all species and for S. alterniflora (Table 9). A linear correlation was obtained for plant Pb content of S. patens. There are no reports of dilute acid soil extraction of Pb related to plant Pb contents. The value of dilute acid extraction of heavy metals appears to be limited to low levels of heavy metals in soils or to Cu and to some extent Pb in dredged material.

DTPA

72. Field moist. Of the four extraction procedures evaluated, DTPA was the most successful for correlating extractable heavy metals with plant uptake of heavy metals. A high degree of linear correlation was obtained between DTPA extractable Zn and Cd and the leaf content of Zn and Cd when all species were considered together (Table 10, Figures 11 and 12). The aforementioned relationships were improved

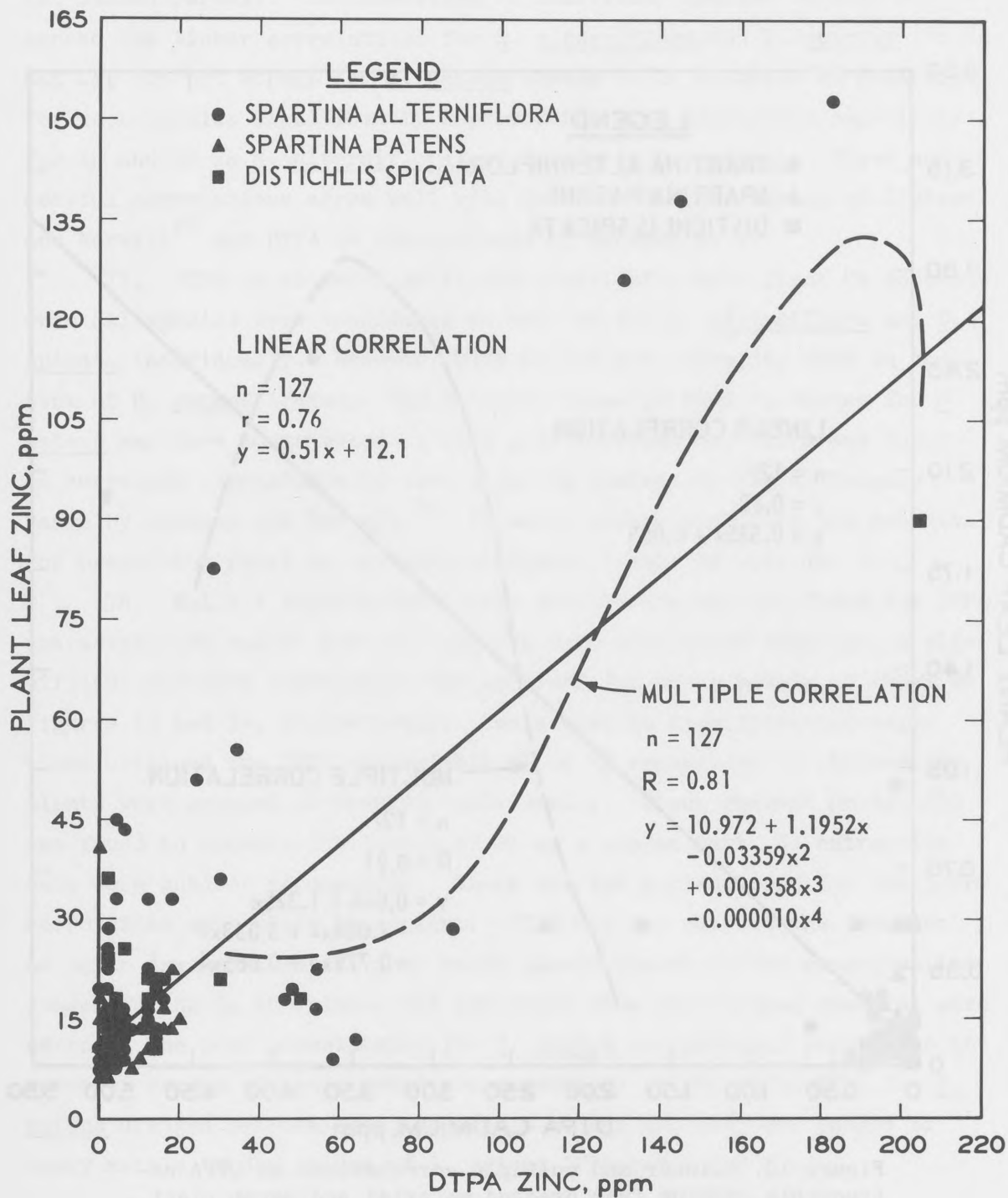


Figure 11. Linear and multiple correlations of DTPA extractable zinc from dredged material and marsh plant leaf zinc content (all species included)

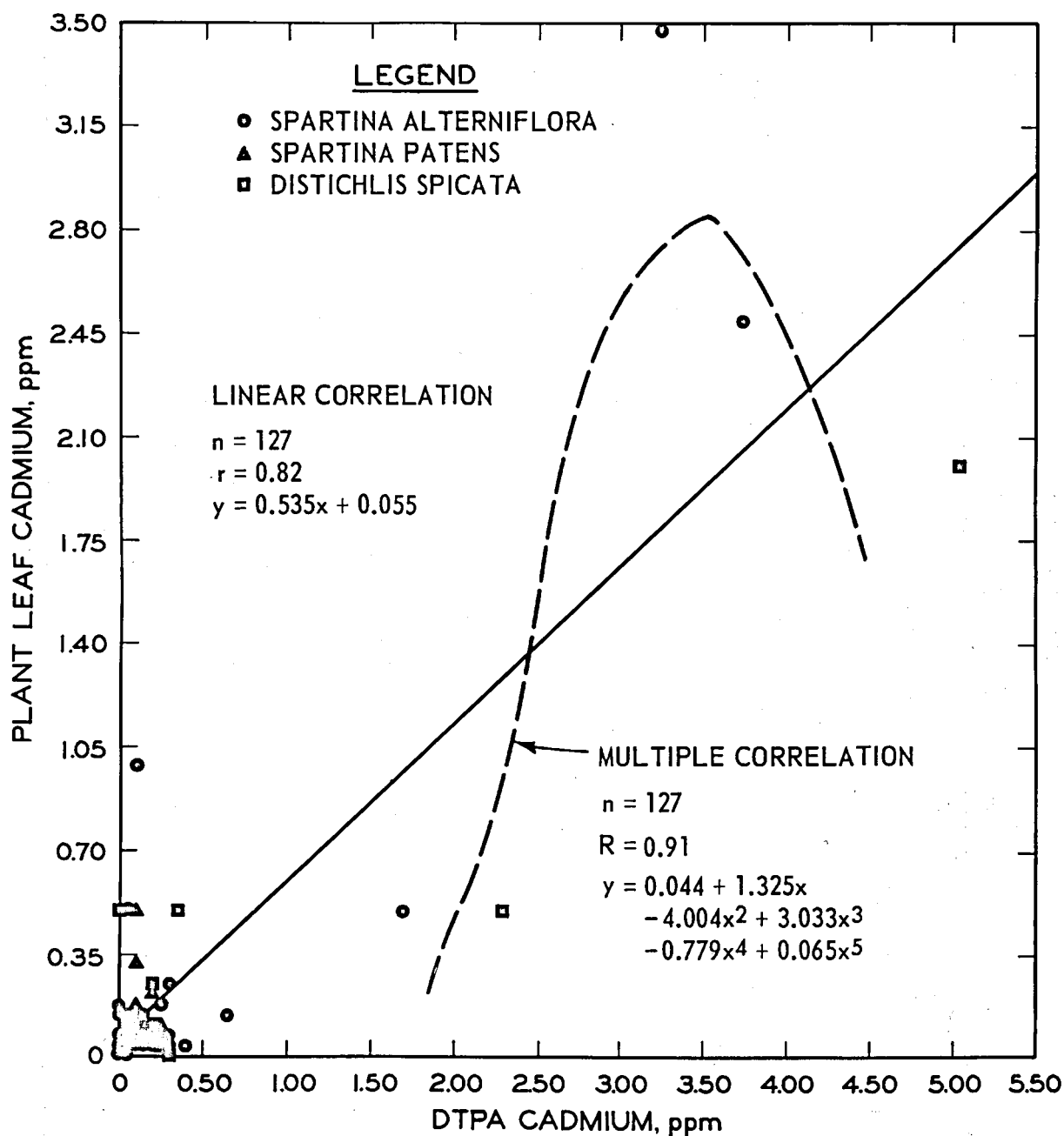


Figure 12. Linear and multiple correlations of DTPA extractable cadmium from dredged material and marsh plant leaf cadmium content (all species included)

by the calculation of multiple correlation coefficients (Figures 11 and 12, dashed curves). Consideration of individual species further enhanced the linear correlations for S. alterniflora and D. spicata for Zn and Cd, but not at all for S. patens (Table 10). Multiple correlations for each species significantly improved the DTPA predictive capability for Zn and Cd in S. alterniflora and for Zn in D. spicata. These successful correlations agree well with the DTPA Zn correlation of Lindsay and Norvell²⁰ and DTPA Cd correlations of Bingham et al.³³

73. DTPA Cu showed significant correlation with plant Cu contents when all species were considered as well as for S. alterniflora and D. spicata individually. However, DTPA Cu did not correlate with Cu content of S. patens leaves. The narrower range of DTPA Cu values for S. patens may have contributed to this poor correlation. DTPA was found to correlate extractable Cu with plant Cu content in the deficiency range by Lindsay and Norvell.²⁰ It would appear that DTPA has potential for predicting plant Cu contents at higher levels of soil Cu.

74. While a significant linear correlation was not found for DTPA extractable Pb and Cr when all species were considered together, a significant multiple correlation was obtained for these metals as shown in Figures 13 and 14, respectively. There were no significant correlations obtained for DTPA extractable Ni or Hg regardless of whether the plants were grouped or treated individually. Since reagent grade DTPA was found to contain low levels of Ni as a contaminant, Ni extraction data were subject to question. There are two explanations for the poor correlation with plant Hg content. DTPA may not extract the fraction of Hg in dredged material that marsh plants absorb or the concentration ranges for Hg in the plants and extracted from the dredged material were narrow. The poor correlations for S. patens are probably related to the narrower ranges of heavy metal concentrations extracted by DTPA for S. patens dredged material samples (Table 4) and the narrower ranges of heavy metals in the leaves of S. patens (Figures 5 and 7).

75. Air-dried. The above correlations were obtained from extraction data of field moist dredged material. Correlations of extractable heavy metals from air-dried dredged material were significant for

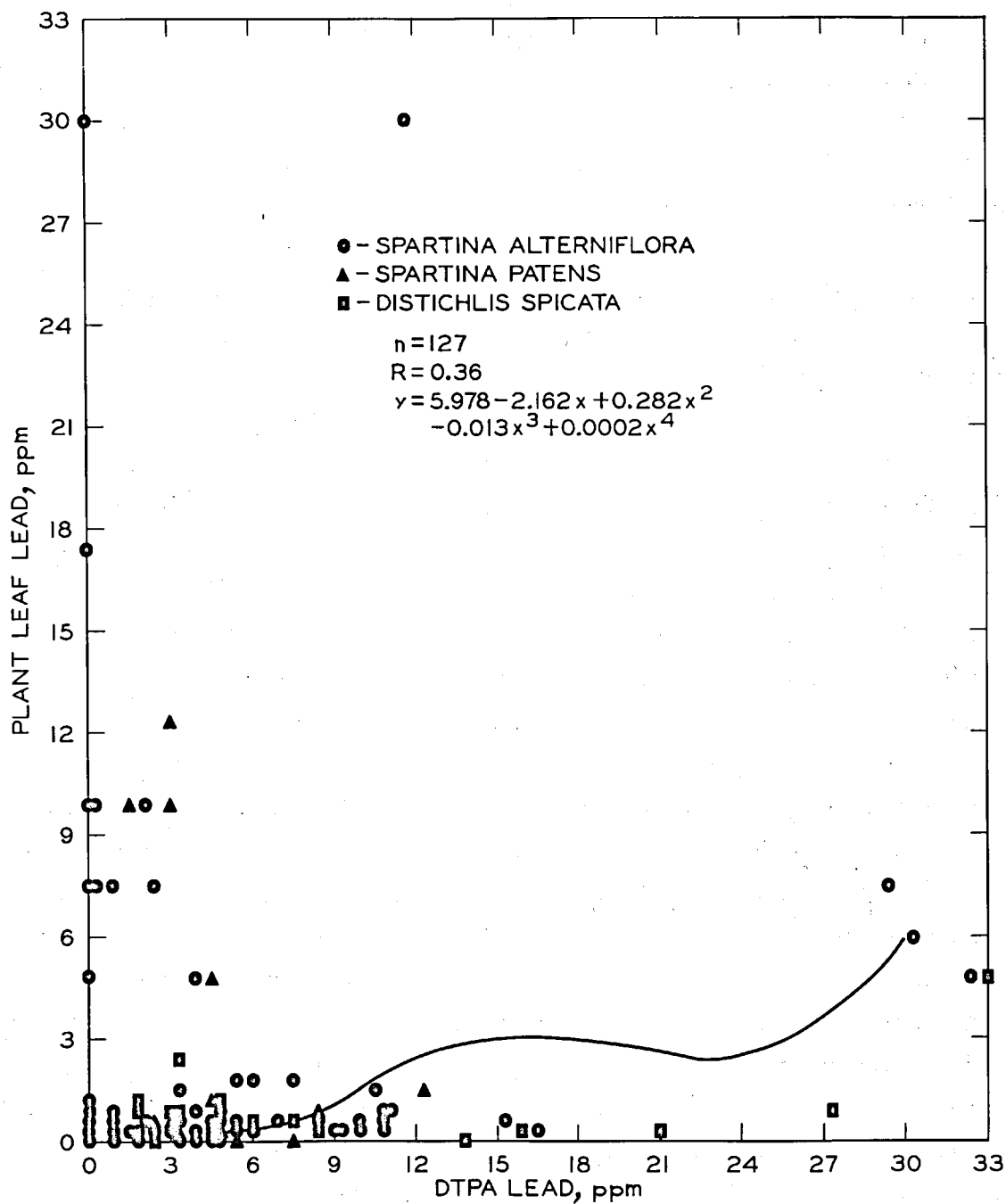


Figure 13. Multiple correlation of DTPA extractable lead from dredged material and marsh plant leaf lead content (all species included)

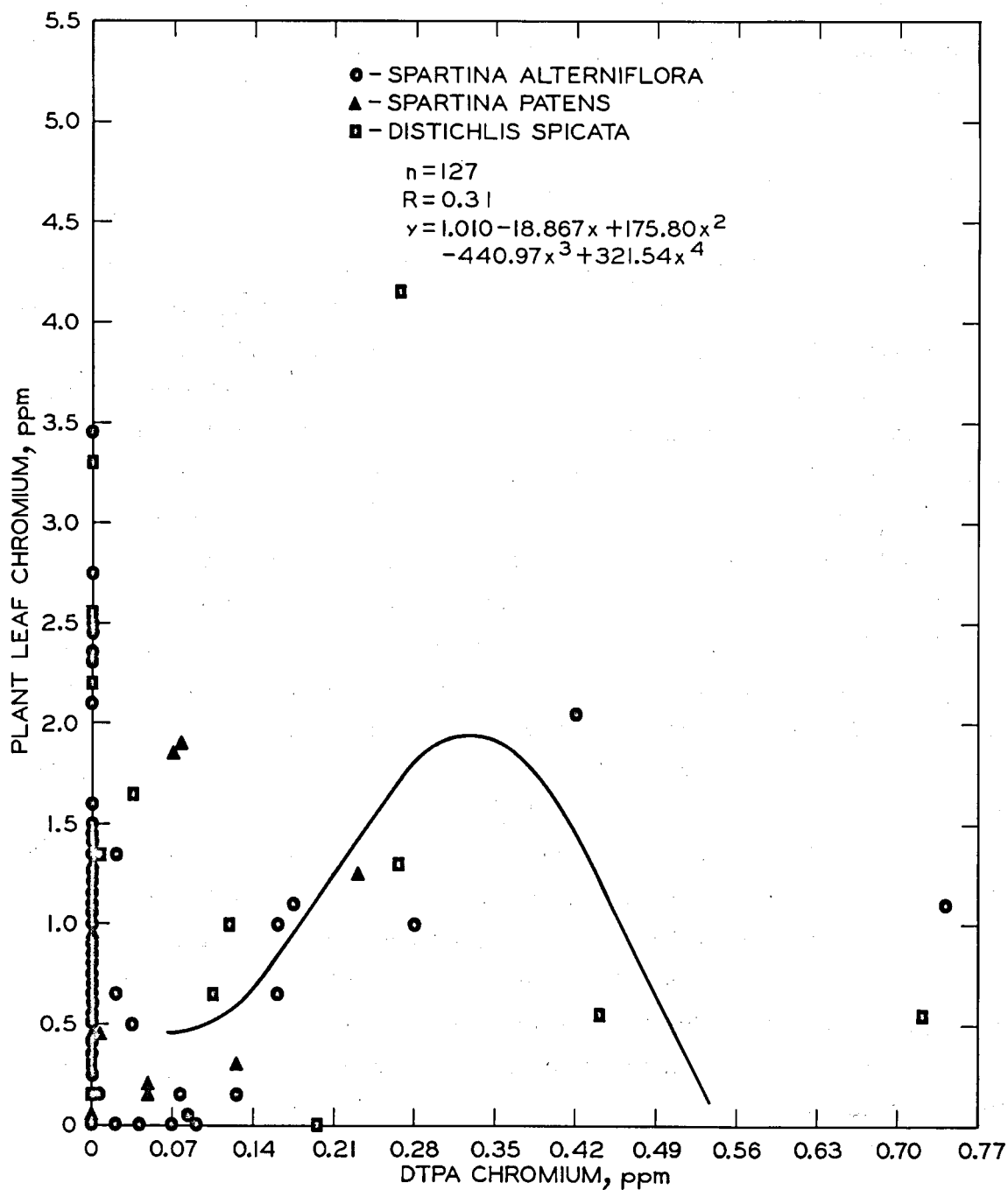


Figure 14. Multiple correlation of DTPA extractable chromium from dredged material and marsh plant leaf chromium content (all species included)

DTPA only; the other extraction procedures showed extremely poor correlations. A comparison of the correlations of plant leaf heavy metal content with the extractable heavy metals in both field moist and air-dried dredged material is shown in Table 11. Good correlations were obtained under both moisture conditions.

Conclusions

76. These results indicate that dredged material tested in the field moist or air-dried state can produce significant correlations between extractable heavy metals (from the soil) and plant contents of certain heavy metals such as Zn, Cd, and Cu. Since most agricultural soil testing laboratories test soils in the air-dried state, dredged materials could be air-dried and sent to any one of a number of agricultural soil testing laboratories for heavy metal extraction and testing. While air-drying sediments may be practical for testing in existing agricultural soil testing facilities, extreme difficulty was experienced with the finer clay-textured dredged materials upon air-drying. These materials became extremely hard and required excessive labor to grind and screen the material for laboratory heavy metal extraction. Laboratory extraction of field moist samples was much easier and is recommended for the finer clay-textured sediments.

77. Salinity and pH were also tested separately and collectively with regard to plant heavy metal content. Neither variable improved the aforementioned correlations. It was therefore concluded at the termination of Phase I that DTPA had good potential for predicting marsh plant uptake of Zn, Cd, Cu, and to some extent Pb and Cr. However, prediction of marsh plant uptake of Ni and Hg was not possible from this study.

Phase II: Verification

DTPA Extractable Heavy Metals from Dredged Material

78. The concentration ranges of each heavy metal extracted by DTPA from the verification dredged material samples are presented in Table 12. The values for heavy metals from a previous greenhouse study⁴³ were relatively low, whereas the concentrations of Zn, Cd, and Pb in DTPA extracts reached extremely high values for the Corpus Christi samples. A number of DTPA extract Zn, Cd, and Pb concentrations were above the ranges observed in Phase I sampling. Corpus Christi was selected for verification because high levels of Zn and Cd were observed in Phase I samples. These high concentrations of metals should enable verification and improvement of prediction equations at the higher levels of contamination.

79. Ten randomly selected samples of dredged material were analyzed in triplicate to estimate variation in DTPA extraction data (Table 13). There was considerable variation in DTPA extractable Zn, Cu, Cd, Ni, and Pb within the Corpus Christi location. Laboratory variation in the DTPA extraction data was relatively small for Zn (12.6%), Cu (9.6%), and Pb (7.7%). Variation increased slightly for Cd (17.3%) and Ni (20.4%). Most variation was found for Cr (63.0%). However, the overall concentrations and ranges of these latter heavy metals were lower than those of the former metals, which tends to increase laboratory variation. This is especially true for Cr, which had a mean DTPA extractable concentration of only 8.7 ppb. With this extremely low concentration initially, it is not surprising that laboratory variation of 5.48 ppb, which normally would be considered exceptionally good, appears as 63.0% variation.

Marsh Plant Heavy Metal Contents

80. Marsh plant leaves collected from a previous greenhouse

study⁴³ and from Corpus Christi varied widely in their concentrations of heavy metals (Table 14). The Corpus Christi plant leaves had much higher heavy metal contents than the greenhouse plants. The average concentrations of heavy metal from the Corpus Christi samples were compared with the predicted concentrations using the respective DTPA extraction values as will be discussed in a later section.

Comparison of plant leaf washing techniques

81. Two procedures for preparing plant leaves for heavy metal analysis were evaluated on marsh plant leaf samples. The first procedure was described previously and utilized methanol, R.O. water, and hydrochloric acid. The second procedure involved rinsing the marsh plant leaves in R.O. water only. Most of the reports of marsh plant leaf analyses cited previously involved rinsing the leaves with water only. The Phase I random sampling was not sufficient to establish significant differences between washing procedures except for Ni and Cr (Table 15). The rinse in R.O. water did not remove leaf surface adsorbed Ni and Cr. Phase II sampling included 22 samples of S. alterniflora to enable a more complete evaluation of washing procedures. The R.O. water rinse did not remove Zn and Ni from the leaf surface. There was no difference in Cu and Pb contents of leaves related to the washing procedures. Leaf content of Cd was higher in the washed leaves, which indicates possible Cd contamination from materials used during the washing procedures. Chromium concentration data were not obtained due to analytical instrumentation malfunctioning during Cr analyses.

82. While these data indicate that plant leaf adsorbed metals can significantly affect the concentrations of Zn and Ni observed for plant leaf samples, more research is required to more fully substantiate the magnitude of this contamination. Marsh plants from the Corpus Christi site sampled in the verification phase of this study did not have significant leaf adsorbed Cu or Pb. However, the sampling was conducted following a month of severe rainstorms that could have influenced the amount of leaf adsorbed contamination on marsh plant leaves prior to collection. It would appear that more sampling in areas of

considerable air pollution is warranted. Since the intensity of airborne particulates with heavy metals varies from location to location and from source to source, valid comparisons of the contribution of airborne particulate contamination on marsh plants become complex and difficult to substantiate. The previously referenced heavy metal contents of marsh plants may be confounded by leaf adsorbed heavy metals from airborne particulates. Consideration should be given to an adequate leaf washing procedure for plant leaves to be analyzed for heavy metals if the location of the sampling is known to be influenced by an elevated level of airborne particulate contamination.

Variation in observed heavy metal concentrations in marsh plant leaves

83. Ten randomly selected samples of washed marsh plant leaves were used to estimate the variation in plant leaf heavy metal data by conducting triplicate determinations on each leaf sample. The plant leaf heavy metal content did not vary greatly within the Corpus Christi site for any of the heavy metals except Zn (Table 16).

84. Laboratory variation was extremely low for Zn (5.5%) and Cu (7.6%). There was more laboratory variation in Cd, Ni, Pb, and Cr. Usually the greater percent variation in the data was related to lower concentrations of a heavy metal observed. The values in Table 16 should actually be divided by a dilution factor of 25 to give the concentrations that were determined in laboratory analyses. The actual laboratory variations were therefore in the range of mean concentrations of Zn (4.47 ppm), Cu (0.183 ppm), Cd (0.0079 ppm), Ni (0.0425 ppm), Pb (0.191 ppm), and Cr (0.0421 ppm). Small variations in heavy metal concentrations in the laboratory became magnified by a factor of 25 in relating actual plant concentrations.

Prediction of Plant Leaf Heavy Metal Content

85. Equations developed in Phase I were used to predict the concentration of heavy metals in marsh plant leaves collected in Phase II. Dredged material samples collected in Phase II were extracted with DTPA,

and the DTPA extractable heavy metals were determined. Each DTPA value for a heavy metal was then incorporated into the appropriate prediction equation and the plant leaf content of that heavy metal was predicted. There were extremely wide ranges of plant leaf heavy metal concentrations predicted using individual DTPA values. This extreme variation in plant heavy metal content within the Corpus Christi sampling site can also be seen in the observed values presented in Table 14. Since a number of the Zn, Cd, and Pb DTPA values were above the range used in Phase I to develop the prediction equations, only DTPA concentrations within the range of Phase I values were used to predict the plant leaf concentrations of heavy metals shown in Table 17. Because of this wide variation, comparison of individual predicted and observed leaf heavy metal contents also showed wide ranges in percent deviation of observed values from predicted values. For example, 3 of the 5 samples used to predict S. alterniflora leaf contents of Zn fell within +39% deviation from the observed plant Zn content (Table 17). Predicted plant Cu content showed 16 out of 22 samples falling within +36% deviation from the observed values. While this presentation of the accuracy of the Phase I equations in predicting plant leaf heavy metal contents may relate the variability found in the data, it was thought that perhaps a more practical way to consider the potential of Phase I equations was to compare the average values of the predicted plant leaf heavy metals and the average observed heavy metals content. The average predicted value, average observed value, and percent deviation of the predicted values from the observed values are presented in Table 17.

86. Prediction of plant content of Zn, Cu, and Cr for S. alterniflora was 10.5, 18.1, and 13.0% below the respective observed metal concentration. Prediction of plant uptake of Zn and Cu by D. spicata was 31.6 and 15.1% above the respective observed metal concentration. Prediction of plant leaf Pb content in S. alterniflora was 30.7% above the observed concentration. Prediction of leaf Pb in D. spicata was 93.3% below the observed concentration. Prediction of plant Cd content was extremely poor for both species, being as much as 556 and 438% above the observed Cd concentration in S. alterniflora and D. spicata leaves,

respectively. Even though elevated concentrations of Cd were extracted from the dredged material with DTPA, marsh plants did not take up elevated Cd concentrations. These data indicate the presence of some mechanism for reducing or inhibiting Cd uptake by S. alterniflora at elevated levels of Cd in dredged material.

Verification and Improvement of Prediction Equations

87. Data presented in Table 17 indicate that Phase I equations have potential to predict the uptake of Zn, Cu, Cr, and to some extent Pb in marsh plants grown on dredged material using the DTPA extraction procedure. Prediction of Cd uptake by marsh plants was not good using Phase I equations.

88. Since a number of samples collected at Corpus Christi contained concentrations of certain heavy metals beyond the ranges found in Phase I samples, the data from Phase II samples were added to the data from Phase I and new prediction equations were generated for a wider range of heavy metal concentrations (Table 18). Stepwise multiple regression analyses were tested in addition to polynomial regressions to give additional prediction equations for both leaf Zn and leaf Cd which consider the interaction of DTPA extractable Zn and Cd. The improved equations in Table 18 are based on a wider data base and therefore are substantially stronger than Phase I equations. All correlation coefficients presented in Table 18 are highly significant ($P = 0.01$). Prediction equations under "All Species" include all the data from Phases I and II for all species, collectively. These could be considered generalized prediction equations for marsh plant uptake of selected heavy metals. More specific prediction equations for each species can be used when either S. alterniflora or D. spicata are considered.

89. Additional samples of dredged material and S. alterniflora were collected from a greenhouse study for use in the verification of prediction equations. The concentrations of heavy metals in DTPA extracts of the dredged material and in plant leaves were low (Tables 12 and 14). Because of these low values, incorporation of the DTPA

extractable heavy metals into the prediction equations resulted in very poor predictions for Cd, Pb, and Cr. Average predicted concentrations for plant leaf Zn and Cu, however, were within 14.5 and 18.7% of the average observed plant leaf contents of Zn and Cu, respectively. The average predicted values of Zn and Cu were 16.8 and 2.46 ppm, respectively, which compare well with the average observed values of 19.6 ppm Zn and 3.03 ppm Cu.

90. These results indicate that the equations in Table 18 can predict relatively "normal" or elevated levels of heavy metals in marsh plants, but cannot predict extremely low levels of Cd, Pb, or Cr in marsh plants. However, this study was conducted to develop a technique to predict "normal" and elevated levels of heavy metals in marsh plants rather than extremely low levels of plant leaf heavy metals.

PART IV: CONCLUSIONS AND RECOMMENDATIONS

91. Most marsh plants colonizing dredged material disposal sites sampled in this study contained relatively low concentrations of Zn, Cu, Cd, Pb, Cr, Ni, and Hg. These concentrations were very similar to those reported for natural coastal marshes. There were a few locations, however, that showed marsh plant contents of Zn, Cu, Cd, and Pb that were an order of magnitude above those of the other samples. The occurrence of these elevated plant metal contents emphasizes the need for a method to predict heavy metal availability from dredged material to plants. The results of this study indicate that marsh plant uptake of Zn, Cu, Cd, and, to some extent, Pb and Cr from dredged material may be predicted using the DTPA extraction procedure described in this report. Prediction of plant uptake of Ni or Hg was not possible in this study.

92. Air-drying dredged material increased the amounts of heavy metals extracted with DTPA. Even so, these higher values also correlated well with plant contents of Zn, Cu, and Cd. Since air-drying created great difficulty in processing and screening the finer clay-textured dredged material, DTPA extraction is recommended for use on a field moist sample.

93. In order to evaluate the potential of a sediment or dredged material to contaminate marsh plants with heavy metals, it is recommended that a number of samples of the sediment or dredged material be collected and extracted in the field moist condition with DTPA according to the procedure described in paragraph 46. The resulting extraction solution should be analyzed for Zn, Cu, Cd, Pb, and Cr. The concentrations of each heavy metal should then be incorporated in the appropriate prediction equation given in Table 18, and the plant content of each heavy metal can be predicted. These predicted values can then be evaluated as being potentially hazardous or harmless.

94. Additional verification tests are needed to reconfirm and better substantiate the accuracy of the prediction equations developed in this study. These tests could be performed during ongoing DMRP marsh creation projects and on future District marsh creation projects.

95. While the prediction equations in this report (Table 18) may be suitable for dredged materials that fall in the contamination range of those sampled in this study, additional research is required to obtain information about the plant availability of heavy metals in more highly contaminated sediments and dredged material. Locations of more highly contaminated dredged material can be found from ongoing DMRP research projects. A number of these sediments can be brought under a semicontrolled greenhouse environment and marsh plants grown. Plant uptake of heavy metals could then be correlated with DTPA extractable heavy metals to expand and improve the prediction equations developed in this study.

96. Prediction of plant leaf Cd appears to be complex and influenced by interaction with Zn. Additional research is recommended to determine the interaction of Zn on plant Cd uptake. Experiments in which marsh plants are grown at a fixed level of Cd and varying levels of Zn should be conducted to determine and model Zn-Cd interactions in plant uptake mechanisms. Results of these experiments should greatly substantiate the potential of predicting marsh plant uptake of Cd from DTPA extractable Zn and Cd.

97. Additional research is required to apply the results of this study to the prediction of heavy metal uptake by freshwater marsh plants from dredged material placed in a freshwater marsh environment.

98. Prediction of plant uptake of heavy metals needs to be expanded from flooded to upland environments. The present study did not delineate possible differences in plant-available heavy metals under flooded and upland environments due to funding and time constraints. In order for CE District personnel to predict the impact of dredged material placement (under either flooded or upland environments) on plant availability of heavy metals, additional research is required. This research could be incorporated into the experiments described in paragraph 95.

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Table 1

List of Dredged Material Disposal Sites Sampled

<u>Location</u>	<u>Site</u>	<u>Species Sampled</u>
1. Connecticut	1. Branford Harbor	<u>Spartina alterniflora</u>
2. New Jersey	1. Black Point-Site 60	<u>S. alterniflora</u>
	2. Peck Bay-Site 83	<u>S. alterniflora</u>
	3. Ludlam Bay-Site 90	<u>S. alterniflora</u>
3. Chesapeake Bay, Md.	1. Kent Narrows	<u>Spartina patens</u>
	2. Knapp's Narrows	<u>S. alterniflora</u>
	3. Tred Avon	<u>S. alterniflora</u>
	4. Slaughter Creek	<u>S. alterniflora</u>
	5. Honga River	<u>S. alterniflora</u>
	6. Bivalve	<u>S. alterniflora</u>
4. North Carolina	1. Southport	<u>S. alterniflora</u> , <u>Distichlis spicata</u>
	2. Little River Inlet	<u>S. alterniflora</u> , <u>D. spicata</u> , <u>S. patens</u>
5. Georgia	1. Savannah-Site 13A	<u>S. alterniflora</u>
	2. Hell's Gate	<u>S. alterniflora</u>
	3. Raccoon Key	<u>S. alterniflora</u> , <u>D. spicata</u>
	4. Andrew's Island	<u>S. alterniflora</u> , <u>D. spicata</u>
6. Florida	1. Blount Island	<u>S. alterniflora</u> , <u>D. spicata</u> , <u>S. patens</u>
	2. Mayport	<u>S. alterniflora</u>
	3. Fernandine	<u>S. alterniflora</u>

(Continued)

Table 1 (concluded)

Location	Site	Species Sampled
7. Mississippi	1. Pascagoula	<u>S. patens</u>
8. Louisiana	1. Medicant Island	<u>S. alterniflora</u> , <u>D. spicata</u>
	2. Houma Navigation Canal	<u>S. alterniflora</u> , <u>D. spicata</u>
9. Louisiana	1. Sabine-Neches Disposal Area II	<u>S. alterniflora</u> , <u>D. spicata</u> , <u>S. patens</u>
10. Texas	1. Pelican Island	<u>S. alterniflora</u> , <u>D. spicata</u>
	2. Snake Island	<u>S. alterniflora</u> , <u>D. spicata</u> , <u>S. patens</u>
	3. Atkinson Island	<u>S. alterniflora</u> , <u>D. spicata</u> , <u>S. patens</u>
11. Texas	1. Point Comfort Turning Basin	<u>S. alterniflora</u> , <u>S. patens</u>
	2. Lavaca Bay	<u>S. alterniflora</u> , <u>D. spicata</u>
	3. Corpus Christi-Nueces Bay	<u>S. alterniflora</u> , <u>D. spicata</u>

Table 2

Comparison of Two Concentrated Acid Digestions
Of Plant Leaves for Heavy Metal Determinations

<u>Heavy Metal</u>	Plant Leaf		<u>Level of Significance</u>
	<u>Heavy Metal Content, ppm</u>		
	<u>Red Fuming</u>	<u>Perchloric</u>	
	<u>Nitric Acid</u>	<u>Acid</u>	
	<u>Digestion</u>	<u>Digestion</u>	
Zn	24.870	25.100	NS
Pb	2.554	1.471	NS
Hg	0.039	0.041	NS
Cu	3.648	3.658	NS
Cd	0.202	0.164	0.01
Ni	0.684	0.282	0.01
Cr	1.042	7.333	0.01

Table 3

Heavy Metal Concentrations Found in Red and WhiteRoots of S. Alterniflora

<u>Heavy Metal</u>	<u>Heavy Metal Concentration, ppm</u>		<u>Level of Significance</u>
	<u>Red Roots*</u>	<u>White Roots**</u>	
Fe	23,867.000	5,856.000	0.01
Pb	14.590	4.920	0.01
Cr	12,600	4.980	0.05
Cu	44.400	17.220	0.05
Hg	0.553	0.183	0.01
Zn	77.510	48.290	NS
Cd	0.807	1.810	NS
Ni	4.188	11.272	NS

* Six samples of red roots were analyzed

** Twelve samples of white roots were analyzed

Table 4

Concentration Ranges (ppm) of Extractable Heavy Metals from
Dredged Material for Three Marsh Plant Species
Using Four Extraction Procedures

<u>Extraction Procedure</u>	<u>Heavy Metal</u>	<u>Heavy Metal Concentration, ppm</u>		
		<u>S. alterniflora</u>	<u>S. patens</u>	<u>D. spicata</u>
Water soluble	Zn	0.0- 54.7	0.0- 5.5	0.0- 0.7
	Cu	0.0- 12.2	0.0- 0.10	0.0- 0.29
	Cd	0.0- 0.35	0.0- 0.0	0.0- 0.0
	Ni	0.0- 8.0	0.0- 3.1	0.0- 4.1
	Pb	0.0- 0.5	0.0- 0.0	0.0- 0.0
	Cr	0.0- 0.63	0.0- 0.17	0.0- 0.56
	Hg	0.0- 0.0068	0.0- 0.0092	0.0- 0.0002
Exchangeable NH ₄ Ac	Zn	0.0- 59.0	0.0-10.4	0.0- 3.6
	Cu	0.0- 10.4	0.0- 0.3	0.0- 2.2
	Cd	0.0- 1.5	0.0- 3.1	0.0- 1.3
	Ni	0.2- 6.8	0.4- 3.4	1.7- 8.0
	Pb	0.0- 10.3	0.0- 3.8	0.0- 0.0
	Cr	0.0- 1.76	0.0- 0.83	0.0- 0.62
	Hg	0.0- 0.024	0.0- 0.030	0.0- 0.039
Dilute acid extractable	Zn	0.1- 64.8	0.2-16.2	0.2- 9.8
	Cu	0.0- 13.1	0.0- 1.8	0.0- 2.4
	Cd	0.0- 0.41	0.0- 0.15	0.0- 0.20
	Ni	0.9- 6.9	0.2- 6.4	0.5- 6.2
	Pb	0.0- 8.8	0.0- 4.7	0.0- 4.1
	Cr	0.0- 2.74	0.0- 0.74	0.0- 0.94
	Hg	0.0- 0.089	0.0- 0.039	0.0- 0.078
DTPA	Zn	0.0-182.7	0.2-20.9	1.4-204.7
	Cu	0.0- 31.9	0.2-18.0	0.0- 49.9
	Cd	0.0- 3.8	0.1- 0.2	0.1- 5.0
	Ni	0.0- 9.9	0.0- 5.0	0.0- 11.5
	Pb	0.0- 32.4	0.0-12.4	0.0- 32.9
	Cr	0.0- 0.74	0.0- 0.23	0.0- 0.72
	Hg	0.0- 0.059	0.0- 0.063	0.0- 0.004

Note: All values are based on oven-dry weight of dredged material.

Table 5
Concentrations (ppm) of Heavy Metals Extracted by
DTPA From Wet and Air-Dried Dredged
Material Samples

<u>Heavy Metal</u>	<u>Heavy Metal Concentration, ppm</u>		<u>Level of Significance</u>
	<u>Wet</u>	<u>Air-Dried</u>	
Zn	35.93*	58.97	0.01
Cd	0.55	1.39	0.05
Cu	6.00	8.60	0.01
Pb	8.96	15.86	0.01
Ni	2.75	5.11	0.01
Cr	0.008	0.30	0.01
Hg	0.004	0.002	NS

* Average value of twenty randomly selected dredged material samples.

Table 6
Ranges in Salinity and pH Found Under Field Conditions

<u>Marsh Plant</u>	<u>No. of Samples</u>	<u>Salinity, ppt</u>	<u>pH</u>
All species	127	0 - 125	2.6 - 8.5
<u>S. alterniflora</u>	79	0 - 125 (26)*	2.6 - 8.5
<u>S. patens</u>	23	0 - 25 (13)	4.8 - 8.5
<u>D. spicata</u>	25	10 - 110 (28)	7.0 - 8.3

* Average value of salinity.

Table 7

Linear and Multiple Correlation Coefficients for Water Soluble Heavy
Metals from Dredged Material and Marsh Plant Leaf Heavy Metals Content

Leaf Heavy Metal	Correlation Coefficients							
	All Species (127)*		<u>S. alterniflora</u> (79)		<u>S. patens</u> (23)		<u>D. spicata</u> (25)	
	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>
Zn	0.10	NS**	0.08	NS	0.06	NS	-0.01	NS
Cu	0.02	NS	0.04	NS	0.26	NS	<u>0.49</u>	NS
Cd	-0.06	NS	-0.06	NS	0.00	NS	0.00	NS
Ni	0.15	NS	0.15	NS	<u>0.55</u>	NS	-0.34	NS
Pb	-0.04	NS	-0.06	NS	0.00	NS	0.00	NS
Cr	-0.08	NS	-0.09	NS	0.01	NS	-0.14	NS
Hg	0.15	<u>0.31</u>	0.15	<u>0.57</u>	0.08	NS	0.26	NS

* Number in parentheses indicates number of samples used in correlation analysis.

** NS indicates no significant improvement over linear relationship.

 Underlined correlation coefficients are significant at P = 0.05.

Table 8

Linear and Multiple Correlation Coefficients for Exchangeable NH₄Ac
Heavy Metals from Dredged Material and Marsh Plant Leaf Heavy Metals Content

Leaf Heavy Metal	Correlation Coefficients							
	All Species (127)*		<u>S. alterniflora</u> (79)		<u>S. patens</u> (23)		<u>D. spicata</u> (25)	
	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>
Zn	0.10	0.22	0.06	NS	0.18	NS	<u>0.51</u>	<u>0.88</u>
Cu	0.05	NS**	0.07	NS	0.09	NS	0.03	<u>0.54</u>
Cd	0.00	NS	-0.12	NS	-0.27	NS	<u>0.70</u>	<u>0.90</u>
Ni	-0.03	NS	0.01	NS	0.10	NS	-0.39	NS
Pb	0.05	NS	0.00	NS	<u>0.41</u>	NS	0.00	NS
Cr	0.08	NS	0.20	<u>0.36</u>	-0.13	NS	-0.26	NS
Hg	-0.08	NS	-0.08	NS	-0.13	NS	-0.12	NS

* Number in parentheses indicates number of samples used in correlation analysis.

** NS indicates no significant improvement over linear relationship.

— Underlined correlation coefficients are significant at P = 0.05.

Table 9

Linear and Multiple Correlation Coefficients for Dilute Acid Extractable
Heavy Metals from Dredged Material and Marsh Plant Leaf Heavy Metals Content

<u>Leaf Heavy Metal</u>	<u>Correlation Coefficients</u>							
	<u>All Species (127)*</u>		<u>S. alterniflora (79)</u>		<u>S. patens (23)</u>		<u>D. spicata (25)</u>	
	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>
Zn	0.05	NS**	0.03	NS	0.28	NS	-0.18	NS
Cu	0.49	<u>0.65</u>	<u>0.57</u>	<u>0.75</u>	<u>0.62</u>	NS	0.11	NS
Cd	-0.11	NS	-0.10	NS	0.00	NS	-0.18	NS
Ni	-0.08	NS	-0.13	NS	0.14	NS	0.02	NS
Pb	0.19	<u>0.36</u>	0.13	<u>0.42</u>	<u>0.63</u>	NS	-0.15	NS
Cr	0.10	NS	0.15	NS	-0.06	NS	-0.04	NS
Hg	0.49	NS	-0.13	NS	0.21	NS	0.08	NS

* Number in parentheses indicates number of samples used in correlation analysis.

** NS indicates no significant improvement over linear relationship.

— Underlined correlation coefficients are significant at $P = 0.05$.

Table 10

Linear and Multiple Correlation Coefficients for DTPA Extractable Heavy
Metals from Dredged Material and Marsh Plant Leaf Heavy Metals Content

Leaf Heavy Metal	Correlation Coefficients							
	All Species (127)*		<u>S. alterniflora</u> (79)		<u>S. patens</u> (23)		<u>D. spicata</u> (25)	
	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>	<u>Linear</u>	<u>Multiple</u>
Zn	<u>0.76</u>	<u>0.81</u>	<u>0.82</u>	<u>0.91</u>	0.18	NS	<u>0.83</u>	<u>0.90</u>
Cu	<u>0.51</u>	NS	<u>0.55</u>	NS	0.15	NS	<u>0.57</u>	NS
Cd	<u>0.82</u>	<u>0.91</u>	<u>0.90</u>	<u>0.97</u>	0.34	NS	<u>0.91</u>	NS
Ni	-0.01	NS**	-0.01	NS	0.18	NS	0.01	NS
Pb	-0.05	<u>0.36</u>	-0.05	<u>0.38</u>	-0.30	NS	<u>0.50</u>	<u>0.87</u>
Cr	0.03	<u>0.31</u>	0.00	<u>0.40</u>	0.31	NS	-0.06	NS
Hg	-0.11	NS	-0.11	NS	-0.23	NS	-0.21	NS

* Number in parentheses indicates number of samples used in correlation analysis.

** NS indicates no significant improvement over linear relationship.

— Underlined correlation coefficients are significant at $P = 0.05$.

Table 11

Comparison of Correlation Coefficients Between Plant Leaf Heavy
Metals Content and DTPA Extractable Heavy Metals from
Field Moist and Air-Dried Dredged Material

<u>Extraction</u> <u>Procedure</u>	Leaf Heavy Metal	<u>Correlation Coefficients*</u>	
		<u>Wet</u>	<u>Air-Dried</u>
DTPA	Zn	0.94	0.95
	Cu	0.84	0.84
	Cd	0.94	0.91
	Ni	-0.13	0.10
	Pb	0.17	0.07
	Cr	-0.50	0.00
	Hg	-0.21	-0.40

* Twenty samples of dredged material were selected randomly and tested both in the field moist and air-dried condition.

Table 12
Concentration Ranges of Heavy Metals
Extracted by DTPA from Verification Samples

Location	Heavy Metals	Concentration Range, ppm	
		<u>S. alterniflora</u>	<u>D. spicata</u>
Greenhouse Study*	Zn	0.4 - 24.4	
	Cu	0.0 - 0.35	
	Cd	0.0 - 0.34	
	Ni	0.8 - 1.88	
	Pb	0.0 - 17.0	
	Cr	0.04 - 0.09	
Corpus Christi**	Zn	41.7 - 426.5	109.3 - 322.8
	Cu	2.17 - 14.49	3.37 - 14.74
	Cd	1.11 - 7.49	1.29 - 4.04
	Ni	0.45 - 2.86	0.56 - 2.24
	Pb	5.0 - 68.49	12.0 - 32.0
	Cr	0.0 - 0.031	0.01 - 0.055

* Greenhouse study had 16 samples.

** Corpus Christi study had 22 and 20 samples for S. alterniflora and D. spicata, respectively.

Table 13
Variation Observed in DTPA Extraction
of Heavy Metals from Dredged Material from Corpus Christi

<u>Heavy Metal</u>	<u>Mean Concentration ppm</u>	<u>Standard Deviation of Concentration, ppm</u>		<u>Lab Coefficient of Variation, %</u>
		<u>Within Site</u>	<u>Within Lab</u>	
Zn	322.6	172.9	40.7	12.6
Cu	7.251	3.001	0.699	9.6
Cd	5.210	3.357	0.901	17.3
Ni	1.218	0.519	0.248	20.4
Pb	30.305	12.652	2.326	7.7
Cr	0.0087	0.00544	0.00548	63.0

Note: Estimation of variability in data was obtained from triplicate determinations on 10 randomly selected samples of dredged material.

Table 14

Concentration Ranges of Heavy Metals in MarshPlant Leaves for Verification Samples

Location	Heavy Metals	Concentration Range, ppm	
		<u>S. alterniflora</u>	<u>D. spicata</u>
Greenhouse Study	Zn	0.4 - 37.75	
	Cu	2.32 - 3.9	
	Cd	0.002 - 0.0575	
	Ni	0.075 - 2.38	
	Pb	0.0 - 0.275	
	Cr	0.0 - 1.55	
Corpus Christi	Zn	40.6 - 250.6	33.1 - 213.1
	Cu	2.72 - 8.88	2.35 - 5.62
	Cd	0.058 - 0.43	0.045 - 0.705
	Ni	0.15 - 4.075	0.3 - 10.2
	Pb	1.02 - 19.4	2.8 - 18.3
	Cr	0.02 - 2.55	0.0 - 1.85

Table 15

The Influence of Washing Plant Leaves on the Concentrations (ppm)
of Selected Heavy Metals Found in Leaves of *Spartina Alterniflora*

<u>Heavy Metal</u>	<u>Heavy Metal</u> <u>Concentration, ppm</u>		<u>Level of</u> <u>Significance</u>
	<u>Washed*</u>	<u>Unwashed**</u>	
<u>Phase I</u>			
Zn	20.355	17.453	NS
Cd	0.169	0.069	NS
Cu	3.664	4.547	NS
Pb	2.635	3.453	NS
Ni	1.191	2.002	0.01
Cr	0.958	2.878	0.01
<u>Phase II</u>			
Zn	116.6	130.9	0.01
Cd	0.198	0.067	0.05
Cu	4.85	4.23	NS
Pb	5.32	5.5	NS
Ni	1.076	1.921	0.1
Cr	-	-	-

* Leaves rubbed with methanol, water, hydrochloric acid, and water.

** Leaves rinsed with water.

Phase I - 10 plant leaves were randomly sampled from 127 samples.

Phase II - 22 *S. alterniflora* leaf samples were evaluated.

Table 16

Variation Observed in Acid Digestion and Analysis
of Heavy Metals in Marsh Plant Leaves from Corpus Christi

<u>Heavy Metal</u>	<u>Mean Concentration ppm</u>	<u>Standard Deviation of Concentration, ppm</u>		<u>Lab Coefficient of Variation, %</u>
		<u>Within Site</u>	<u>Within Lab</u>	
Zn	111.8	58.6	6.2	5.5
Cu	4.566	1.361	0.346	7.6
Cd	0.197	0.084	0.061	30.9
Ni	1.062	0.855	0.806	75.9
Pb	4.769	3.734	0.945	19.8
Cr	1.053	0.475	0.322	30.6

Note: Estimation of variability in data was obtained from triplicate determinations on 10 randomly selected samples of marsh plant leaves.

Table 17
Accuracy of the Phase I Equations in Predicting
Marsh Plant Heavy Metal Contents from DTPA
Extractable Heavy Metals from Dredged Material

<u>Marsh Plant Species</u>	<u>Heavy Metal</u>	<u>Plant Leaf Heavy Metal Content, ppm</u>		<u>% Deviation</u>	<u>No. of Samples</u>	<u>No. of Samples Within a Given % Deviation**</u>	
		<u>Predicted*</u>	<u>Observed*</u>			<u>No.</u>	<u>% Range</u>
<u>S. alterniflora</u>	Zn	132.5	148.0	- 10.5	5	3	± 39
	Cu	3.97	4.85	- 18.1	22	16	± 36
	Cd	1.312	0.20	+556.0	11	4	±180
	Pb	7.195	5.506	+ 30.7	13	7	-40 to 80
	Cr	0.94	1.081	- 13.0	20	12	± 24
<u>D. spicata</u>	Zn	59.6	45.3	+ 31.6	7	5	± 49
	Cu	4.256	3.698	+ 15.1	20	14	± 36
	Cd	0.942	0.175	+438.0	20	15	0 to 850
	Pb	0.743	11.055	- 93.3	19	15	-80 to -104
	Cr	-	-	-	-	-	-

* Average values for predicted and observed values.

** Comparison of individual predicted and observed values of heavy metals.

Table 18
Correlation Coefficients and Predictive Equations* for Marsh Plant Leaf
Heavy Metal Content Using DTPA Extraction of Dredged Material

Marsh Plant Species	Leaf Heavy Metal	Range of DTPA Heavy Metal, ppm	Number of Observations	Correlation Coefficient r or R	S_Y^2/X	Prediction Equation
All species	Zn	0.16-427	168	0.751	32.0	$Y = 16.56 - 0.364X + 0.021X^2 - 1.55 \times 10^{-4}X^3 + 4.30 \times 10^{-7}X^4 - 4.13 \times 10^{-10}X^5$
				0.779	30.3	$Y = 12.4 + 0.152 \text{ DTPA Zn} + 39.5 \text{ DTPA Cd} - 0.096 \text{ DTPA Zn} \times \text{DTPA Cd}$
	Cu	0.0-49.9	169	0.470	1.63	$Y = 3.12 + 0.126X$
	Cd	0.0-7.5	168	0.361	0.36	$Y = 0.077 + 0.205X - 0.027X^2$
				0.479	0.34	$Y = 0.063 + 0.336 \text{ DTPA Cd} - 8.9 \times 10^{-4} \text{ DTPA Zn} \times \text{DTPA Cd}$
	Pb	0.0-68.5	169	0.398	7.0	$Y = 6.22 - 2.34X + 0.293X^2 - 0.012X^3 + 1.99 \times 10^{-4}X^4 - 1.15 \times 10^{-6}X^5$
<u>S. alterniflora</u>	Cr	0.0-0.74	169	0.377	0.69	$Y = 1.03 - 21.6X + 199X^2 - 497X^3 + 362X^4$
	Zn	0.23-427	100	0.835	29.9	$Y = 19.3 - 0.813X + 0.033X^2 - 2.23 \times 10^{-4}X^3 + 5.74 \times 10^{-7}X^4 - 5.19 \times 10^{-10}X^5$
				0.846	28.8	$Y = 12.9 + 0.190 \text{ DTPA Zn} + 53.3 \text{ DTPA Cd} - 0.138 \text{ DTPA Zn} \times \text{DTPA Cd}$
	Cu	0.0-31.9	101	0.511	1.81	$Y = 2.96 + 0.165X$
	Cd	0.0-7.5	100	0.465	0.39	$Y = 0.044 + 0.382X - 0.055X^2$
				0.502	0.38	$Y = 0.052 + 0.387 \text{ DTPA Cd} - 1.0 \times 10^{-3} \text{ DTPA Zn} \times \text{DTPA Cd}$
<u>D. spicata</u>	Pb	0.0-68.5	101	0.385	5.7	$Y = 6.37 - 2.13X + 0.253X^2 - 0.010X^3 + 1.68 \times 10^{-4}X^4 - 9.74 \times 10^{-7}X^5$
	Cr	0.0-0.74	101	0.352	0.64	$Y = 1.07 - 12.9X + 63.8X^2 - 62.5X^3$
	Zn	1.35-323	45	0.687	31.9	$Y = 13.6 + 0.267X$
				0.524	1.20	$Y = 3.292 + 0.087X$
	Cd	0.0-5.0	45	0.869	0.17	$Y = 0.135 - 0.458X + 0.612X^2 - 0.242X^3 + 0.030X^4$
				0.805	0.20	$Y = 0.095 + 2.17 \times 10^{-5} \text{ DTPA Zn}^2 + 0.189 \text{ DTPA Cd}^2 - 0.0040 \text{ DTPA Zn} \times \text{DTPA Cd}$
	Pb	0.0-51.0	45	0.338	10.7	$Y = 0.310 + 0.317X$
	Cr	0.0-0.72	45	0.565	0.80	$Y = 1.20 - 33.6X + 321X^2 - 840X^3 + 635X^4$

* Using all data combined for Phases I and II.

Y = Marsh plant leaf heavy metal content (ppm).

X = DTPA extractable heavy metal (ppm).

S_Y^2/X = Standard error of estimate of Y.

APPENDICES

CONTENTS OF HEAVY METALS IN PLANT AND DREDGED MATERIAL SAMPLES

Data collected and used to make statistical
comparisons and develop prediction equations

Key to data format:

Spec

1. Spartina alterniflora
2. Spartina patens
3. Distichlis spicata

Location, site, and species sampled are shown in Table 1 and Figure 1
of main text.

APPENDIX A

PHASE I: PREDICTION EQUATION DEVELOPMENT DATA

				WATER EXTRACTION								
SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM	SAL	pH
1	01	1	1	.12500	.0	1.49	.0	.0	.0	.0	30.00	6.95
1	01	1	2	.0	.0	1.24	.0	.0	.0	.0	50.00	7.29
1	01	1	3	.0	.0	.62500	.0	.04750	.0	.0	30.00	7.49
1	02	1	1	5.67	.0	1.46	.0	.08750	.0	.00250	25.00	4.55
1	02	1	2	3.67	.0	1.85	.0	.0	.0	.0	25.00	4.99
1	02	1	3	1.32	.0	.99000	.0	.0	.0	.00750	22.50	4.21
1	02	2	1	.02500	.0	.98000	.0	.01750	.0	.0	30.00	6.00
1	02	2	2	1.07	.0	.64500	.0	.14750	.0	.00250	30.00	4.16
1	02	2	3	1.42	.0	.69000	.0	.0	.00075	.00250	32.50	4.93
1	02	2	4	.47500	.0	1.26	.0	.0	.0	.0	30.00	6.10
1	02	3	1	.0	.0	.65000	.0	.0	.0	.0	30.00	7.91
1	02	3	2	.0	.0	.77500	.0	.0	.0	.0	30.00	8.06
1	02	3	3	.55500	.0	.49500	.0	.0	.0	.12750	30.00	7.47
1	02	3	4	.0	.0	1.14	.0	.0	.00025	.0	57.50	7.23
2	03	1	1	.0	.0	.0	.0	.0	.0	.0	.0	5.23
2	03	1	2	.0	.0	.0	.0	.0	.0	.0	.0	4.83
2	03	1	3	.0	.0	.08500	.0	.16750	.0	.04750	.0	6.15
1	03	2	1	40.67	.20350	5.75	.0	.0	.0	8.29	20.00	3.07
1	03	2	2	49.67	.35350	7.50	.0	.22250	.0	9.64	20.00	2.83
1	03	2	3	54.67	.35350	7.40	.0	.63250	.0	12.19	30.00	2.56
1	03	3	1	20.67	.20350	4.69	.50000	.0	.0	.24750	20.00	3.53
1	03	3	2	33.67	.20350	5.65	.0	.24250	.0	1.89	25.00	2.74
1	03	3	3	39.17	.30350	5.20	.50000	.06250	.0	.58750	20.00	3.29
1	03	4	1	.57500	.0	.85500	.0	.0	.0	.0	.0	4.22
1	03	4	2	.0	.0	.08000	.0	.0	.0	.0	10.00	7.38
1	03	5	1	.0	.0	.0	.0	.0	.0	.0	.0	5.26
1	03	5	2	.0	.0	.0	.0	.0	.0	.0	.0	5.59
1	03	6	1	3.32	.0	2.54	.0	.11750	.0	.20750	20.00	2.60
1	03	6	2	5.17	.0	2.79	.0	.02250	.0	.41750	20.00	2.67
3	04	1	1	.0	.0	3.04	.0	.0	.0	.0	32.50	7.05
1	04	1	1	.0	.0	1.88	.0	.08750	.0	.0	35.00	7.12
3	04	1	2	.0	.0	.44500	.0	.0	.0	.0	20.00	7.48
1	04	1	2	.0	.0	3.32	.0	.0	.0	.0	45.00	7.08
1	04	1	3	.0	.0	1.60	.0	.0	.0	.0	45.00	7.26
2	04	2	1	.0	.0	2.48	.0	.09250	.0	.0	20.00	7.16
2	04	2	2	.0	.0	3.13	.0	.07250	.0	.0	20.00	7.20
2	04	2	3	.0	.0	2.58	.0	.02250	.0	.0	20.00	7.27
1	04	2	1	.0	.0	.84000	.0	.13750	.0	.0	25.00	7.57
1	04	2	2	.0	.0	1.00	.0	.42250	.0	.0	30.00	7.36
1	04	2	3	.0	.0	1.54	.0	.53750	.0	.0	40.00	7.26
3	04	2	1	.0	.0	1.47	.0	.55750	.0	.0	25.00	7.42
3	04	2	2	.0	.0	1.08	.0	.42750	.0	.0	25.00	7.42
3	04	2	3	.0	.0	1.40	.0	.0	.0	.01750	30.00	7.31
1	05	1	1	.0	.0	2.89	.0	.0	.0	.0	40.00	6.75

WATER EXTRACTION

SPEC	LOCT	SITE	SAMP	WATER ZNPPM	EXTRACTION CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM	SAL	pH
1	05	1	2	.0	.0	.92000	.0	.0	.0	.0	40.00	7.15
1	05	1	3	.0	.0	2.21	.0	.0	.0	.0	30.00	6.94
1	05	2	1	.0	.0	.68500	.0	.0	.0	.0	25.00	7.60
1	05	2	2	.0	.0	1.05	.0	.0	.0	.0	40.00	7.37
1	05	2	3	.0	.0	.63500	.0	.0	.0	.0	25.00	7.60
1	05	3	1	.0	.0	1.11	.0	.0	.0	.0	22.50	7.40
1	05	3	2	.0	.0	.99000	.0	.02250	.0	.02250	22.50	7.38
1	05	3	3	.0	.0	.77000	.0	.0	.0	.0	20.00	7.29
1	05	4	2	.0	.0	4.25	.0	.25750	.0	.0	100.	6.93
1	05	4	3	3.85	.0	3.57	.0	.04250	.0	.0	125.	7.22
1	05	4	4	.0	.0	2.49	.0	.06250	.0	.0	45.00	7.15
3	05	3	1	.0	.0	2.61	.0	.0	.0	.0	60.00	7.11
3	05	4	2	.0	.0	4.09	.0	.0	.0	.0	110.	6.99
3	05	4	3	.0	.0	3.65	.0	.0	.0	.0	100.	6.98
3	05	4	4	.0	.0	.81500	.0	.0	.0	.07250	30.00	7.59
1	06	1	1	.17000	.0	.43500	.0	.0	.0	.0	15.00	7.45
1	06	1	2	.0	.0	.70500	.0	.0	.0	.0	25.00	7.36
1	06	1	3	.0	.0	.75500	.0	.0	.0	.0	17.50	7.13
3	06	1	1	.0	.0	.40000	.0	.0	.0	.0	10.00	7.62
3	06	1	2	.0	.0	.43500	.0	.0	.0	.0	10.00	7.33
2	06	1	1	.0	.0	.12500	.0	.0	.0	.0	10.00	7.36
2	06	1	2	.0	.0	.31500	.0	.0	.0	.0	10.00	7.68
1	06	2	1	.01500	.0	.43000	.0	.0	.0	.02250	20.00	7.64
1	06	2	2	.00500	.0	1.38	.0	.0	.0	.0	35.00	7.41
1	06	2	3	.0	.0	.91500	.0	.0	.0	.0	20.00	7.65
1	06	3	1	.00500	.0	.64000	.0	.0	.0	.0	5.00	6.67
1	06	3	2	.0	.0	.84500	.0	.0	.0	.0	5.00	6.24
2	07	1	1	.10000	.0	.88000	.0	.0	.0	.0	20.00	7.05
2	07	1	2	.16500	.0	.72500	.0	.0	.00675	.0	5.00	7.27
2	07	1	3	.72500	.0	1.90	.0	.0	.0	.0	25.00	5.50
2	07	1	4	5.52	.0	.60000	.0	.0	.0	.0	15.00	7.39
1	08	1	1	.C	.0	1.88	.0	.0	.0	.0	20.00	7.09
1	08	1	2	.0	.0	.94000	.0	.0	.0	.0	15.00	7.10
1	08	1	3	.0	.0	.69000	.0	.0	.0	.0	15.00	7.30
3	08	1	1	.0	.0	1.24	.0	.0	.0	.0	17.50	7.22
3	08	1	2	.C2000	.0	2.17	.0	.0	.0	.0	17.50	7.40
1	08	2	1	.0	.0	.40500	.0	.0	.0	.0	15.00	7.81
1	08	2	2	.0	.0	.37500	.0	.0	.0	.02250	15.00	7.94
1	08	2	3	.0	.0	.27000	.0	.0	.0	.0	10.00	7.96
3	08	2	1	.0	.0	.02500	.0	.0	.0	.0	10.00	8.28
3	08	2	2	.C	.0	.21000	.0	.0	.0	.00250	10.00	7.95
1	09	1	1	.0	.0	1.12	.0	.0	.0	.0	17.50	7.43
1	09	1	2	.0	.0	1.01	.0	.0	.0	.11750	17.50	7.33
1	09	1	3	.C	.0	.62000	.0	.0	.0	.0	17.50	7.28

A2

SPEC	LOCT	SITE	SAMP	WATER ZNPPM	EXTRACTION CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM	SAL	pH
3	09	1	1	.0	.0	1.31	.0	.0	.0	.00250	20.00	7.03
2	09	1	1	.0	.0	.99000	.0	.0	.0	.00250	20.00	7.35
3	09	1	2	.0	.0	.81000	.0	.0	.0	.0	10.00	8.00
2	09	1	2	.0	.0	.31500	.0	.0	.0	.0	10.00	8.11
2	09	1	3	.0	.0	.78000	.0	.0	.00225	.10250	15.00	7.55
1	10	1	1	.0	.0	.50500	.0	.0	.0	.00250	22.50	7.86
1	10	1	2	.11500	.0	.35500	.0	.0	.0	.00250	20.00	8.03
1	10	1	3	.0	.0	.23000	.0	.0	.0	.12750	20.00	8.12
3	10	1	1	.0	.0	.49000	.0	.0	.0	.0	27.50	8.32
1	10	2	1	.23000	.0	.40500	.0	.0	.00025	.0	20.00	7.78
1	10	2	2	.0	.0	.54000	.0	.0	.00075	.06750	15.00	8.15
1	10	2	3	.0	.0	1.15	.0	.0	.00425	.12750	25.00	7.67
2	10	2	1	.0	.0	.48500	.0	.0	.00725	.00250	15.00	8.04
2	10	2	2	.0	.0	.22000	.0	.0	.00925	.15250	15.00	8.14
3	10	2	1	.0	.0	.58000	.0	.0	.00025	.23250	17.50	7.72
3	10	2	2	.0	.0	.75500	.0	.0	.0	.29250	20.00	7.69
2	10	3	1	.0	.0	1.08	.0	.0	.0	.0	10.00	7.56
2	10	3	2	.0	.0	1.45	.0	.0	.00175	.0	10.00	7.56
1	10	3	1	.0	.0	.44500	.0	.0	.00625	.00750	10.00	7.63
1	10	3	2	.05000	.0	.39000	.0	.0	.00675	.0	10.00	7.75
1	10	3	3	.0	.0	.64500	.0	.0	.00275	.0	10.00	7.57
3	10	3	1	.0	.0	.42000	.0	.0	.00225	.0	15.00	7.42
3	10	3	2	.72500	.0	.56000	.0	.0	.0	.0	10.00	7.55
2	10	3	3	.0	.0	.32000	.0	.0	.00475	.00250	20.00	8.21
1	11	1	1	.0	.0	.64000	.0	.0	.00075	.0	25.00	7.90
1	11	1	2	.0	.0	.82500	.0	.0	.00175	.0	32.50	7.89
1	11	1	3	.0	.0	.60500	.0	.0	.00225	.0	30.00	7.93
2	11	1	1	.0	.0	.29500	.0	.0	.0	.0	15.00	8.49
2	11	1	2	.0	.0	.33500	.0	.0	.0	.0	10.00	7.99
2	11	1	3	.0	.0	.34500	.0	.0	.0	.0	20.00	8.12
1	11	2	1	.0	.0	.66500	.0	.0	.0	.0	10.00	7.54
1	11	2	2	.0	.0	.39500	.0	.0	.0	.0	20.00	8.08
1	11	2	3	.0	.0	.55500	.0	.0	.02025	.0	30.00	8.46
3	11	2	1	.0	.0	.62000	.0	.0	.0	.0	30.00	7.91
1	11	3	1	.38500	.0	.71500	.0	.0	.0	.0	30.00	8.17
1	11	3	2	.0	.0	.69500	.0	.0	.0	.0	27.50	8.05
1	11	3	3	.34000	.0	.60000	.0	.0	.0	.0	27.50	8.18
3	11	3	1	.37500	.0	.58000	.0	.0	.0	.0	30.00	8.12
3	11	3	2	.0	.0	.65000	.0	.06750	.0	.0	22.50	8.19

AMMONIUM ACETATE EXTRACT PH 2.6-8.5

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
1	01	1	1	6.09	1.47	2.32	.0	.13678	.0	.06480
1	01	1	2	1.09	.0	2.03	.0	.0	.0	.0
1	01	1	3	.96028	.0	1.92	.0	.0	.0	.0
1	02	1	1	.26785	.0	.79425	.0	.48905	.0	.12880
1	02	1	2	6.63	.21373	2.81	3.78	1.05	.00178	.13500
1	02	1	3	2.80	.0	1.58	.0	.82798	.0	.48060
1	02	2	1	1.34	.0	1.13	.0	.24478	.0	.17280
1	02	2	2	1.12	.03553	1.17	.0	.72538	.0	.17820
1	02	2	3	1.28	.11113	1.35	.0	.96838	.00178	.18360
1	02	2	4	1.18	.32173	1.64	.0	.44998	.0	.08640
1	02	3	1	.46989	.27060	1.82	.0	.27462	.03868	.09095
1	02	3	2	.0	.34550	1.54	.0	.15157	.00284	.02140
1	02	3	3	.0	.05713	1.40	.0	.15838	.00556	.07020
1	02	3	4	.0	1.40	1.77	.0	.08278	.0	.06480
2	03	1	1	.04228	.0	.38248	.0	.60658	.0	.15120
2	03	1	2	.15028	.0	.39868	.0	.57418	.0	.15660
2	03	1	3	.31228	3.09	.41488	.54000	.0	.0	.26460
2	03	2	1	42.81	.06253	3.64	.0	1.03	.0	3.05
2	03	2	2	48.21	.0	6.21	.0	1.04	.0	7.30
2	03	2	3	53.61	.22993	6.38	.0	1.76	.0	10.38
2	03	3	1	17.43	.08953	2.49	9.18	.65518	.0	.07560
2	03	3	2	41.73	.37573	4.33	3.78	1.25	.0	1.45
2	03	3	3	59.01	.52153	3.41	10.26	1.01	.0	.68580
2	03	4	1	.58228	.0	1.06	.0	.77938	.0	.12960
2	03	4	2	.0	.64573	.54988	.0	.0	.0	.0
2	03	5	1	5.55	.13813	2.25	1.08	.85498	.00016	.14580
2	03	5	2	.52828	.0	.21508	.0	.0	.0	.00540
2	03	6	1	5.01	.09493	3.36	.0	1.44	.0	.34020
2	03	6	2	59.01	.46753	3.59	.0	1.16	.0	.49680
3	04	1	1	.0	.0	3.28	.0	.15581	.0	.08250
3	04	1	2	.0	.03619	2.93	.0	.10631	.0	.0
3	04	1	3	.0	.03013	2.13	.0	.04498	.0	.0
3	04	1	4	.0	.36619	2.98	.0	.24381	.0	.0
3	04	2	1	.0	.0	2.36	.0	.13931	.0	.0
3	04	2	2	.0	.0	2.38	.0	.10081	.0	.00550
3	04	2	3	.0	.0	2.73	.0	.38131	.0	.08250
3	04	2	4	.0	.0	2.53	.0	.34281	.0	.07700
3	04	2	5	.0	.22453	2.45	.0	.29878	.0	.11340
3	04	2	6	.0	.18673	6.27	.0	1.18	.0	.13500
3	04	2	7	.0	.31093	5.19	.0	.41218	.0	.09180
3	04	2	8	.0	.0	4.89	.0	.40678	.0	.07020
3	04	2	9	.0	.03553	4.85	.0	.44998	.0	.0
3	04	2	10	.0	.44593	3.28	.0	.31498	.0	.0
1	05	1	1	.42257	.57519	3.57	.0	.37031	.0	.01100

SPEC	LOCT	SITE	SAMP	AMMONIUM ZNPPM	ACETATE CDPPM	EXTRACT NIPPM	PH 2.6-8.5 PBPPM	CRPPM	HGPPM	CUPPM
1	05	1	2	.0	.54769	3.20	.0	.52981	.0	.0
1	05	1	3	.0	.45673	3.52	.0	.32038	.0	.0
1	05	2	1	.0	.55415	1.89	.0	.25857	.0	.06420
1	05	2	2	.0	.59173	3.29	.0	.31498	.0	.0
1	05	2	3	.0	.30805	1.78	.0	.17297	.0	.0
1	05	3	1	.0	.55393	2.89	.0	.27718	.0	.0
1	05	3	2	.0	.45133	4.45	.0	.42838	.0	.08100
1	05	3	3	.58228	.62953	3.26	.0	.44998	.0	.0
1	05	4	1	.0	.36069	6.82	.0	.87081	.0	.12100
1	05	4	2	.0	.59169	6.38	.0	.57381	.0	.09350
1	05	4	3	.0	.12969	6.05	.0	.43631	.00896	.07700
3	05	3	1	.0	.18673	6.00	.0	.43378	.0	.06480
3	05	4	1	.0	.33869	7.98	.0	.61781	.0	.10450
3	05	4	2	.0	.19019	7.48	.0	.54631	.0	.08800
3	05	4	3	.0	.24405	3.20	.0	.25945	.0	.07280
1	06	1	1	.0	.0	2.54	.0	.0	.0	.0
1	06	1	2	.0	.77869	3.62	.0	.29881	.0	.11550
1	06	1	3	.0	.35953	2.34	.0	.05578	.0	.07020
3	06	1	1	.0	.29445	1.70	.0	.23145	.00129	.0
3	06	1	2	.0	.19213	2.45	.0	.18538	.0	.0
2	06	1	1	.02608	.20293	1.42	.0	.06658	.0	.0
2	06	1	2	.37985	.0	.97905	.0	.0	.03041	.0
1	06	2	1	.0	.37285	1.81	.0	.07465	.0	.06720
1	06	2	2	.0	.40813	3.51	.0	.27178	.0	.08100
1	06	2	3	.0	.03125	2.13	.0	.15865	.0	.0
1	06	3	1	.0	.0	.81665	.0	.0	.0	.0
1	06	3	2	.0	.0	.97648	.0	.01258	.01852	.0
2	07	1	1	2.69	.29473	2.76	.0	.27178	.0	.0
2	07	1	2	.69028	.09493	2.45	.0	.14218	.0	.0
2	07	1	3	10.41	.08953	3.45	.0	.82798	.0	.09180
2	07	1	4	2.47	.52153	2.25	.0	.18538	.0	.0
1	08	1	1	.20428	.68353	2.72	.0	.24478	.0	.07560
1	08	1	2	.0	.52153	2.46	.0	.24478	.0	.0
1	08	1	3	.0	.56473	2.32	.0	.17458	.0	.0
3	08	1	1	1.99	.27313	2.76	.0	.19078	.0	.0
3	08	1	2	.0	.25693	2.69	.0	.18538	.0	.0
1	08	2	1	.26785	.0	2.05	.0	.33785	.0	.12320
1	08	2	2	.71585	.00325	2.04	.0	.22585	.0	.03360
1	08	2	3	2.73	.0	2.21	.0	.10265	.0	.10640
3	08	2	1	.0	.0	2.09	.0	.09145	.0	.07840
3	08	2	2	2.34	.24405	2.45	.0	.13065	.02705	.03360
1	09	1	1	.09628	.04093	2.06	.0	.10438	.0	.00540
1	09	1	2	.04228	.0	2.19	.0	.11518	.0	.0
1	09	1	3	.0	.0	2.10	.0	.10978	.0	.0

				AMMONIUM ACETATE EXTRACT PH 2.6-8.5						
SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
3	09	1	1	.20428	.12733	2.55	.0	.21238	.0	.08100
2	09	1	1	.04228	.10033	2.26	.0	.17458	.0	.08100
3	09	1	2	1.22	.0	1.54	.0	.05225	.0	.02800
2	09	1	2	.42028	.24613	2.39	.0	.18538	.0	.02700
2	09	1	3							
1	10	1	1	.0	.40813	2.06	.0	.19078	.0	.06480
1	10	1	2	5.17	.46213	1.94	.0	.32578	.0	.14580
1	10	1	3	10.95	.0	.76588	.0	.03958	.0	.05940
3	10	1	1	.0	.49993	1.78	.0	.28798	.0	2.17
1	10	2	1	.54785	.0	1.05	.0	.0	.02481	.04480
1	10	2	2	3.01	.0	.69905	.0	.24825	.0	3.59
1	10	2	3	1.56	.0	1.14	.0	.04665	.0	.11760
2	10	2	1	.15585	.0	.47505	.0	.0	.0	.17920
2	10	2	2	.60385	.0	1.41	.0	.02425	.00073	.52080
3	10	2	1	2.23	.0	1.26	.0	.04105	.0	.42000
3	10	2	2	3.01	.0	1.61	.0	.0	.0	1.12
2	10	3	1	1.01	.0	.89548	.0	.01258	.0	.00540
2	10	3	2	.0	.0	.98728	.0	.0	.0	.0
1	10	3	1	.0	.0	2.13	.0	.11518	.0	.0
1	10	3	2	.0	1.42	2.12	.0	.03958	.0	.04860
1	10	3	3	.0	.38113	2.42	.0	.84958	.0	.02160
3	10	3	1							
3	10	3	2	.0	1.23	2.38	.0	.00178	.0	.0
2	10	3	3	.0	.32173	3.94	.0	.02338	.00016	.11880
1	11	1	1	.0	.73213	3.92	.0	.02878	.0	.0
1	11	1	2	.0	.49453	3.79	.0	.01258	.0	.0
1	11	1	3	.14488	.0	3.47	.0	.16378	.0	.06480
2	11	1	1	.0	0.99	3.27	.0	.07738	.0	.24840
2	11	1	2	.0	2.32	1.67	.0	.16378	.0	.0
2	11	1	3	.0	1.49	2.75	.0	.14758	.0	.10800
1	11	2	1	.0	.0	1.96	.0	.06118	.0	.0
1	11	2	2	.0	.0	1.31	.0	.0	.0	.0
1	11	2	3	9.87	.26773	1.46	.0	.13138	.0	.0
3	11	2	1	.0	.0	1.73	.0	.01258	.0	.0
1	11	3	1	.63628	.0	1.90	.0	.02338	.0	.0
1	11	3	2	2.69	.0	1.65	.0	.07198	.0	.0
1	11	3	3	1.77	1.02	2.52	.0	.07198	.0	.09720
3	11	3	1	.58228	1.07	2.42	.0	.05578	.0	.07560
3	11	3	2	3.55	1.32	2.41	.0	.08278	.0	.07020

				DILUTE ACID EXTRACT						
SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
1	01	1	1	64.80	.15366	4.21	5.70	2.74	.0	13.12
1	01	1	2	1.99	.0	2.95	.01747	.79768	.01019	.09360
1	01	1	3	2.07	.0	2.91	.0	1.44	.00395	.12480
1	02	1	1	13.63	.12038	2.91	1.02	1.09	.00395	1.65
1	02	1	2	38.17	.36166	4.48	3.10	.94848	.00135	6.88
1	02	1	3	4.83	.01222	2.09	.0	.78728	.00395	3.83
1	02	2	1	4.79	.01014	2.26	.0	.65208	.0	2.46
1	02	2	2	3.17	.00442	1.26	.0	.67808	.00603	2.47
1	02	2	3	4.07	.03302	1.48	.0	.77168	.00135	3.08
1	02	2	4	7.34	.00858	2.51	.0	1.56	.00239	.78520
1	02	3	1	8.95	.01482	3.35	.12147	.89648	.00811	.24440
1	02	3	2	14.25	.03874	3.95	1.02	1.01	.0	.80080
1	02	3	3	29.59	.25766	5.15	4.14	1.05	.00239	3.54
1	02	3	4	5.52	.0	3.65	.0	.71968	.00083	.20280
2	03	1	1	.89596	.00858	.15548	.10587	.05928	.01539	.26000
2	03	1	2	.55796	.00962	.05668	.08507	.09568	.01123	.30680
2	03	1	3	1.70	.01430	1.03	.55827	.04888	.00499	.90480
1	03	2	1	42.80	.20566	3.77	.00707	.41808	.00967	7.19
1	03	2	2	51.07	.36166	6.04	.00707	.66248	.00239	8.96
1	03	2	3	49.56	.30966	5.67	.0	1.15	.00187	12.18
1	03	3	1	24.13	.20566	3.16	8.82	.47528	.00083	2.92
1	03	3	2	31.36	.20566	3.57	1.02	.63128	.00759	3.93
1	03	3	3	29.65	.20566	3.23	7.78	.43368	.01071	4.15
1	03	4	1	.82836	.00702	.71708	.08507	.06968	.00759	.17160
1	03	4	2	2.19	.02626	1.36	2.06	.21008	.00239	2.55
1	03	5	1	1.07	.02314	.75348	.50107	.07488	.00707	.38480
1	03	5	2	1.13	.01534	.40508	.42827	.14768	.00343	.24440
1	03	6	1	4.29	.02158	2.93	.11107	.60528	.00343	.73840
1	03	6	2	5.26	.07722	2.79	.08507	.41288	.00083	1.00
3	04	1	1	.59956	.0	5.78	.07467	.68328	.00239	.10920
1	04	1	1	.49556	.0	5.88	.07987	.61048	.0	.08840
3	04	1	2	2.09	.0	4.72	.05907	.45968	.0	.0
1	04	1	2	.86476	.0	6.04	.06427	.65208	.0	.09360
1	04	1	3	.62556	.0	5.72	.03307	.56368	.00031	.08320
2	04	2	1	1.18	.01430	5.15	.02787	.45448	.00135	.02080
2	04	2	2	4.08	.06994	4.41	.50107	.57408	.01279	.03120
2	04	2	3	.39156	.00598	3.93	.02267	.50648	.00447	.00520
1	04	2	1	.47996	.0	4.42	.03307	.64168	.00135	.0
1	04	2	2	.62556	.0	4.40	.0	.73008	.00551	.01040
1	04	2	3	.48516	.00286	4.50	.0	.69368	.00239	.01040
3	04	2	1	.64116	.00130	4.03	.0	.57928	.00447	.01560
3	04	2	2	.48516	.00546	4.14	.0	.64688	.00447	.06760
3	04	2	3	.61516	.00234	4.23	.0	.69368	.00863	.01040
1	05	1	1	7.96	.41366	5.62	.01227	1.24	.00343	.17160

DILUTE ACID EXTRACT

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
1	05	1	2	4.11	.00234	3.20	.00187	.63648	.00239	.05200
1	05	1	3	12.59	.20566	4.65	.19427	2.23	.01175	1.96
1	05	2	1	1.81	.01742	4.28	.07467	.71968	.00343	.16120
1	05	2	2	2.45	.05226	4.49	.00707	.91208	.00239	.03120
1	05	2	3	1.98	.05954	4.12	.06947	.74568	.01175	.11440
1	05	3	1	2.89	.06682	3.50	.25147	.64688	.00551	.34840
1	05	3	2	3.89	.04966	3.85	.25147	.67808	.00343	.32760
1	05	3	3	3.53	.04966	3.28	.49067	.65208	.00031	.46280
1	05	4	1	2.02	.02002	4.90	.11107	.91728	.00239	.05720
1	05	4	2	.98436	.01950	5.00	.00187	.87568	.00447	.10400
1	05	4	3	4.79	.02678	4.58	.24107	.74568	.00343	.05720
3	05	3	1	2.76	.01014	4.54	.00187	.79768	.00343	.06760
3	05	4	1	.94276	.04706	4.98	.00707	.88608	.0	.07800
3	05	4	2	1.17	.04238	4.99	.00187	.94328	.0	.07800
3	05	4	3	3.22	.04966	4.13	.00707	.69368	.00031	.06760
1	06	1	1	1.31	.00234	3.75	.0	.36608	.00239	.02080
1	06	1	2	4.43	.01430	4.12	.00187	.46488	.00239	.03640
1	06	1	3	2.05	.02314	3.78	.0	.45448	.0	.13000
3	06	1	2	2.47	.04966	3.84	.03827	.45448	.0	.22360
3	06	1	1	3.34	.10166	3.18	.18907	.38688	.0	.29120
2	06	1	1	2.59	.04966	2.12	.33987	.36088	.0	.52520
2	06	1	2	1.55	.04966	3.20	.10067	.44408	.0	.26000
1	06	2	2	.35516	.01898	3.74	.0	.61048	.0	.01560
1	06	2	1	2.23	.04966	3.98	.0	.53248	.0	.06760
1	06	2	3	.11596	.00910	4.08	.0	.56368	.0	.02080
1	06	3	1	.30316	.01066	.94068	.01747	.28808	.02683	.00520
1	06	3	2	.54756	.01326	1.14	.03307	.40248	.01643	1.79
2	07	1	1	13.11	.10166	2.31	3.10	.74048	.01019	.69680
2	07	1	2	8.85	.04966	1.72	3.10	.54288	.02371	.50440
2	07	1	3	16.18	.15366	2.56	4.66	.62608	.01019	1.76
2	07	1	4	14.05	.10166	2.54	3.10	.70408	.01747	1.37
1	08	1	1	8.12	.20566	5.15	1.02	.23088	.01955	1.76
1	08	1	2	4.47	.10166	3.19	1.02	.26208	.02163	1.40
1	08	1	3	6.45	.10166	4.71	1.02	.49608	.02423	.14560
3	08	1	1	9.78	.20566	5.98	1.02	.54288	.01331	1.10
3	08	1	2	8.17	.20566	6.19	1.02	.54808	.02475	1.19
1	08	2	1	7.08	.10166	5.00	1.02	.55328	.02579	.78520
1	08	2	2	6.04	.15366	5.20	.05907	.51168	.03619	.55120
1	08	2	3	5.47	.15366	5.62	.00707	.50648	.08923	.43160
3	08	2	1	3.48	.15366	5.06	.0	.44928	.07883	.12480
3	08	2	2	5.00	.10166	4.14	1.02	.36088	.07259	2.36
1	09	1	1	7.18	.04966	2.69	1.54	.55848	.03515	1.82
1	09	1	2	8.53	.04966	3.40	3.62	.61568	.01643	2.16
1	09	1	3	8.74	.04966	3.00	2.58	.63128	.04503	2.12

				DILUTE ACID EXTRACT						
SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
3	09	1	1	9.16	.04966	3.36	3.10	.64168	.03723	2.01
2	09	1	1	7.44	.05902	2.76	3.10	.51688	.02631	1.82
3	09	1	2	3.67	.01846	2.57	4.14	.30368	.02839	1.05
2	09	1	2	5.15	.05694	3.50	2.06	.36088	.03931	1.48
2	09	1	3	6.56	.14170	2.85	3.62	.61568	.03203	1.50
1	10	1	1	5.47	.04966	4.17	2.58	.53248	.01955	1.50
1	10	1	2	4.66	.03770	4.28	2.06	.54808	.01799	1.29
1	10	1	3	3.66	.01014	3.93	2.06	.46488	.01539	.69680
3	10	1	1	5.15	.03094	5.14	2.06	.65728	.00863	1.22
1	10	2	1	3.80	.00130	5.57	.0	.52728	.00707	.00520
1	10	2	2	2.63	.02158	6.92	.0	.49608	.01019	.00520
1	10	2	3	2.78	.01118	6.66	.0	.49038	.02787	.00520
2	10	2	1	.58396	.01170	6.45	.0	.46488	.01175	.0
2	10	2	2	3.75	.04966	6.19	.50107	.51168		.01560
3	10	2	1	2.81	.01950	5.83	.0	.48048	.00759	.0
3	10	2	2	3.55	.04966	6.09	.0	.53248	.03411	.13520
2	10	3	1	2.51	.00182	5.67	.00707	.55328	.01435	.01560
2	10	3	2	1.12	.00078	5.93	.0	.46488	.00551	.00520
1	10	3	1	2.35	.00494	3.60	1.02	.32448	.00395	.0
1	10	3	2	1.96	.00494	5.36	.16307	.53248	.00447	.01040
1	10	3	3	.72436	.00234	5.67	.0	.45448	.00759	.02600
3	10	3	1	.53196	.00130	5.72	.0	.39728	.00135	.02600
3	10	3	2	.88036	.0	.50388	.0	.03328	.0	.0
2	10	3	3	.27196	.00598	5.31	.0	.52208	.00291	.08320
1	11	1	1	.46436	.00442	5.93	.0	.62088	.01279	.06240
1	11	1	2	.63076	.00182	5.52	.00187	.73008	.00603	.0
1	11	1	3	.27196	.00078	5.20	.0	.53248	.00447	.0
2	11	1	1	.36036	.00494	5.52	.0	.49608	.00603	.01040
2	11	1	2	.21476	.0	5.26	.0	.45448	.00811	.0
2	11	1	3	.37076	.00442	5.57	.0	.49088	.00395	.0
1	11	2	1	4.31	.01430	4.42	2.06	.36088	.00395	.07800
1	11	2	2	.15756	.00442	5.62	.01539	.44928	.00239	.0
1	11	2	3	.44356	.00598	5.20	.0	.43888	.00551	.06760
3	11	2	1	.22516	.00546	5.62	.0	.47008	.0	.0
1	11	3	1	.47996	.00130	5.31	.0	.43368	.00239	.0
1	11	3	2	.42796	.00234	5.36	.0	.42848	.01539	.0
1	11	3	3	.85956	.00806	5.41	.0	.41808	.00343	.0
3	11	3	1	.48516	.00286	5.46	.0	.44408	.00863	.0
3	11	3	2	1.77	.00754	5.46	.02631	.41808	.00343	.0

ALO

				DTPA EXTRACT PH 7.3							
SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NI	PPM	PBPPM	CRPPM	HGPPM	CUPPM
1	01	1	1	88.68	.20924	3.43	11.60	.0	.0	.01198	31.68
1	01	1	2	6.06	.02003	2.69	.0	.0	.0	.00191	.09434
1	01	1	3	2.52	.0	1.29	.01325	.0	.0	.0	.03604
1	02	1	1	11.46	.10324	1.76	.23585	.0	.0	.0	4.09
1	02	1	2	18.88	.26224	2.79	2.06	.0	.0	.0	5.97
1	02	1	3	4.18	.00943	.44679	.11395	.0	.0	.0	5.34
1	02	2	1	3.41	.01685	.64289	.08215	.0	.0	.0	4.12
1	02	2	2	2.07	.00784	.27189	.15105	.0	.0	.0	3.09
1	02	2	3	2.33	.01473	.56339	.01325	.0	.0	.0	2.21
1	02	2	4	3.07	.01314	1.07	.0	.0	.0	.0	1.58
1	02	3	1	3.84	.01844	1.73	1.00	.0	.0	.0	.04664
1	02	3	2	6.22	.02215	1.82	.09275	.0	.0	.0	.04664
1	02	3	3	5.95	.05024	1.95	2.06	.0	.0	.0	.03604
1	02	3	4	4.46	.00413	2.79	.0	.0	.0	.00191	.04134
2	03	1	1	.27560	.00784	.0	.10865	.0	.0	.0	.25334
2	03	1	2	.49820	.00890	.0	.11925	.0	.0	.0	.37524
2	03	1	3	0.99	.00784	.0	2.06	.0	.0	.0	.74094
1	03	2	1	47.34	.26224	2.53	1.00	.0	.0	.0	9.21
1	03	2	2	54.23	.31524	4.76	.0	.0	.0	.0	5.97
1	03	2	3	64.83	.42124	5.66	.0	.12561	.0	.0	8.30
1	03	3	1	28.21	.26224	1.95	8.42	.0	.0	.0	3.29
1	03	3	2	29.38	.31524	2.11	.0	.0	.0	.0	.82574
1	03	3	3	34.09	.31524	2.21	11.07	.0	.0	.0	7.19
1	03	4	1	1.14	.01314	.0	1.00	.0	.0	.0	.26394
1	03	4	2	1.59	.01540	.10650	3.94	.0	.0	.0	3.48
1	03	5	1	.91000	.00590	.0	.94250	.0	.0	.0	.35400
1	03	5	2	1.15	.00840	.0	1.44	.0	.0	.0	.34900
1	03	6	1	3.72	.01740	1.27	.0	.0	.0	.0	.09900
1	03	6	2	6.36	.03890	1.99	.0	.0	.0	.0	.19900
3	04	1	1	12.16	.09740	3.64	1.94	.0	.0	.0	.31900
1	04	1	1	12.56	.09740	2.94	4.44	.0	.0	.0	3.85
3	04	1	2	1.35	.00740	.49650	.0	.0	.0	.0	.0
1	04	1	2	11.21	.04740	3.59	5.94	.0	.0	.0	2.92
1	04	1	3	2.72	.01390	1.26	.0	.0	.0	.0	.03900
2	04	2	1	10.96	.09740	3.54	4.94	.0	.0	.0	4.50
2	04	2	2	11.26	.09740	2.94	4.44	.04850	.0	.0	3.87
2	04	2	3	10.41	.09740	2.29	5.44	.0	.0	.0	6.28
1	04	2	3	2.94	.03240	.40650	3.94	.0	.0	.0	.0
1	04	2	2	2.41	.03390	.50150	2.44	.0	.0	.0	.0
1	04	2	3	2.85	.04240	.91650	1.94	.00350	.0	.0	.0
3	04	2	2	3.12	.03240	.29150	3.94	.0	.0	.0	.0
3	04	2	2	2.75	.02740	.16150	3.44	.0	.0	.0	.0
3	04	2	3	3.38	.03740	.88150	3.44	.0	.00030	.0	.0
1	05	1	1	14.06	.64740	3.34	.94250	.0	.0	.0	4.35

ALL

				DTPA EXTRACT PH 7.3							
SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM	
1	05	1	2	15.61	.14740	1.51	.01250	.0	.0	1.13	
1	05	1	3	11.86	.14740	2.19	.00250	.0	.0	.0	
1	05	2	1	1.75	.01740	.44650	2.94	.0	.0	1.10	
1	05	2	2	3.17	.04740	0.99	4.94	.0	.00130	2.13	
1	05	2	3	1.89	.01490	.27650	3.44	.0	.0	1.18	
1	05	3	1	2.38	.04740	.74650	3.44	.01850	.0	1.12	
1	05	3	2	2.95	.04740	.82650	3.94	.02350	.0	1.20	
1	05	3	3	2.80	.04740	.75650	4.44	.15850	.0	1.46	
1	05	4	1	13.51	.09662	3.91	1.93	.74251	.0	2.89	
1	05	4	2	1.89	.03740	4.59	.94250	.17350	.0	.0	
1	05	4	3	5.56	.03040	4.24	3.94	.03350	.0	.0	
3	05	3	1	11.01	.04740	4.49	2.94	.44350	.0	2.05	
3	05	4	1	14.00	.09662	6.53	1.43	.72267	.0	2.75	
3	05	4	2	5.71	.04890	4.99	.94250	.26350	.0	.08400	
3	05	4	3	3.93	.04740	1.65	1.44	.0	.0	1.27	
1	06	1	1	2.03	.02890	.0	1.44	.0	.0	.0	
1	06	1	2	8.26	.09740	2.64	.94250	.0	.0	.14900	
1	06	1	3	2.95	.02390	.68650	2.44	.0	.0	.92400	
3	06	1	1	2.28	.01740	.62650	1.94	.0	.0	.64900	
3	06	1	2	4.08	.04390	1.21	2.44	.0	.0	1.20	
2	06	1	1	2.22	.03740	.14650	2.94	.0	.0	1.23	
2	06	1	2	1.31	.05090	.25650	1.44	.0	.0	.45900	
1	06	2	1	5.26	.09740	.86150	6.94	.0	.0	3.74	
1	06	2	2	58.46	.14740	2.99	5.44	.0	.0	5.38	
1	06	2	3	6.71	.14740	1.05	9.44	.0	.0	5.38	
1	06	3	1	.23000	.00590	.0	.09750	.0	.0	.07400	
1	06	3	2	.31000	.00840	.0	.13250	.0	.0	.13400	
2	07	1	1	18.31	.19740	3.04	2.94	.0	.06330	4.31	
2	07	1	2	15.01	.09740	1.68	2.94	.0	.0	1.39	
2	07	1	3	20.91	.24740	3.69	1.44	.0	.0	4.23	
2	07	1	4	18.66	.14740	2.84	2.44	.0	.00230	3.14	
1	08	1	1	11.61	.29740	6.69	3.94	.0	.00880	8.48	
1	08	1	2	5.91	.14740	4.04	5.44	.0	.0	6.63	
1	08	1	3	3.61	.09740	3.19	5.94	.0	.0	.03900	
3	08	1	1	13.71	.24740	11.49	7.44	.0	.00030	15.93	
3	08	1	2	11.16	.24740	7.24	3.44	.0	.00080	6.48	
1	08	2	1	6.66	.14740	9.94	10.44	.0	.0	17.88	
1	08	2	2	12.06	.29740	8.74	4.94	.0	.0	8.88	
1	08	2	3	7.26	.19740	7.84	3.94	.0	.0	7.43	
3	08	2	1	6.41	.19740	7.09	3.44	.0	.0	6.83	
3	08	2	2	11.96	.29740	9.44	5.94	.0	.00280	16.98	
1	09	1	1	13.91	.09740	7.14	7.44	.0	.05430	6.48	
1	09	1	2	11.11	.04740	4.99	9.94	.0	.0	7.53	
1	09	1	3	15.51	.09740	5.04	9.44	.0	.00130	10.28	

				DTPA EXTRACT PH 7.3						
SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
3	09	1	1	14.21	.09740	5.79	8.94	.00850	.0	10.23
2	09	1	1	13.36	.09740	4.99	9.94	.0	.00330	10.18
3	09	1	2	3.27	.00940	.36650	13.94	.0	.0	1.27
2	09	1	2	4.91	.05940	1.53	5.44	.00350	.0	2.50
2	09	1	3	15.26	.09740	4.19	7.44	.04850	.00130	9.28
1	10	1	1	6.36	.04740	2.69	6.94	.07850	.0	6.33
1	10	1	2	5.61	.04740	2.24	5.44	.07350	.00130	5.48
1	10	1	3	3.15	.01090	1.38	4.94	.0	.0	3.77
1	10	1	1	4.81	.04740	2.69	4.94	.19350	.0	3.27
3	10	2	1	45.01	.19740	1.89	15.44	.16350	.0	31.88
1	10	2	2	23.51	.09740	.94150	10.94	.41850	.0	31.73
1	10	2	3	54.16	.24740	2.14	16.44	.28350	.0	29.93
2	10	2	1	7.56	.09740	.74650	8.44	.23350	.00380	10.38
2	10	2	2	14.31	.14740	1.07	12.44	.07850	.0	17.98
3	10	2	1	29.46	.19740	.96150	15.94	.03350	.00430	26.63
3	10	2	2	49.21	.34740	2.09	20.94	.26350	.0	49.93
2	10	3	1	2.40	.02640	1.25	4.44	.0	.0	1.78
2	10	3	2	2.50	.03740	1.60	4.44	.12350	.0	1.62
1	10	3	1	.73500	.00590	.56150	2.44	.01850	.05930	.64900
1	10	3	2	.66500	.03740	.58650	3.44	.0	.0	1.47
1	10	3	3	2.13	.02390	.92650	5.94	.0	.0	1.95
3	10	3	1	1.84	.01940	1.37	5.94	.0	.0	.08400
3	10	3	2	2.18	.02840	0.99	4.44	.0	.0	1.82
2	10	3	3	1.99	.01740	1.40	4.44	.07350	.00280	2.55
1	11	1	1	2.20	.02390	1.54	8.94	.06850	.0	3.90
1	11	1	2	2.99	.03290	1.74	10.94	.08350	.0	4.65
1	11	1	3	2.01	.01940	1.62	9.94	.0	.0	4.42
2	11	1	1	.30500	.01190	1.46	3.44	.0	.0	.82400
2	11	1	2	.16500	.00840	.78150	2.44	.0	.0	.24900
2	11	1	3	.51000	.01390	2.04	3.44	.0	.0	1.38
1	11	2	1	2.72	.02390	1.84	5.44	.0	.0	2.37
1	11	2	2	1.75	.01740	1.94	6.94	.0	.0	3.21
1	11	2	3	2.11	.03540	1.94	10.94	.0	.0	4.98
3	11	2	1	2.21	.02190	2.24	8.44	.0	.0	4.36
1	11	3	1	182.66	3.75	2.64	29.44	.0	.0	7.63
1	11	3	2	143.66	3.25	2.89	32.44	.03850	.0	7.53
1	11	3	3	129.66	1.70	2.24	30.44	.09350	.00030	8.08
3	11	3	1	148.16	2.30	2.74	27.44	.11850	.0	1.93
3	11	3	2	204.66	5.05	2.89	32.94	.10350	.0	10.08

				WASHED LEAVES NITRIC ACID						
SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
1	01	1	1	27.82	.05425	7.17	29.86	2.34	.0	16.71
1	01	1	2	15.82	.01675	2.92	17.36	2.11	.02175	6.46
1	01	1	3	22.82	.02925	5.92	4.86	.73925	.01425	5.21
1	02	1	1	16.32	.15425	1.30	9.86	2.44	.0	4.46
1	02	1	2	32.82	.05425	.67500	9.86	1.24	.00675	5.21
1	02	1	3	32.82	.08425	1.02	7.36	2.29	.34925	6.21
1	02	2	1	45.32	.16425	1.12	4.86	1.59	.19425	5.21
1	02	2	2	27.82	.04925	.67500	7.36	1.21	.08175	4.21
1	02	2	3	25.32	.02675	1.15	4.86	1.19	.25425	3.46
1	02	2	4	13.32	.04675	.50000	4.86	.88925	.08425	3.21
1	02	3	1	7.32	.04925	.65000	.78225	1.14	.08175	1.96
1	02	3	2	10.82	.01175	4.92	29.86	1.36	.04675	3.46
1	02	3	3	12.57	.01675	.80000	.65725	1.39	.10675	3.71
1	02	3	4	11.82	.01175	.07500	.70725	.78925	.06675	2.71
2	03	1	1	17.82	.05925	.90000	4.86	.73925	.08925	4.21
2	03	1	2	14.35	.01239	1.70	.01330	.43899	.06743	4.51
2	03	1	3	40.19	.04643	1.67	.56706	1.29	.09405	5.49
1	03	2	1	19.57	.16175	2.20	7.36	2.51	.08675	2.21
1	03	2	2	16.07	.05175	1.65	9.86	1.14	.05425	5.96
1	03	2	3	11.32	.04925	3.22	7.36	.16425	.06175	3.21
1	03	3	1	82.82	.06675	1.72	.70725	.38925	.07425	5.96
1	03	3	2	35.32	.05925	2.92	9.86	1.26	.09675	4.71
1	03	3	3	55.32	.05175	.12500	.98225	1.46	.04175	6.21
1	03	4	1	9.82	.03175	.87500	.78225	1.24	.05925	1.96
1	03	4	2	18.77	.05245	5.74	.30833	2.77	.17010	5.80
1	03	5	1	19.07	.13425	.57500	.55725	1.01	.06925	2.71
1	03	5	2	14.82	.02925	1.12	.30725	.61425	.10425	4.71
1	03	6	1	7.07	.03175	.75000	1.08	.0	.05175	1.96
1	03	6	2	8.32	.00925	8.17	29.86	1.24	.06925	2.21
3	04	1	1	20.32	.02175	1.02	.80725	.73925	.12175	7.21
1	04	1	1	32.82	.06425	.75000	.70725	.98925	.09175	2.96
3	04	1	2	35.32	.00925	.65000	.0	.36425	.05675	4.96
1	04	1	2	22.57	.03925	.92500	.33225	.56425	.02425	2.96
1	04	1	3	19.32	.02925	.07500	.48225	.68925	.02675	2.96
2	04	2	1	9.32	.48425	4.42	.30725	.0	.01175	2.96
2	04	2	2	10.07	.12425	2.67	.05725	.21425	.07925	3.96
2	04	2	3	13.07	.48425	1.10	.05725	.51425	.05425	3.46
1	04	2	1	11.32	.04675	.52500	.15725	1.61	.04175	1.21
1	04	2	2	16.57	.02425	2.42	.15725	1.06	.05425	.95725
1	04	2	3	10.82	.01925	.65000	.08225	.16425	.09175	.95725
3	04	2	1	8.57	.06425	.57500	.35725	.28925	.00175	2.21
3	04	2	2	11.07	.01175	1.10	2.31	1.34	.17175	2.46
3	04	2	3	11.32	.01925	1.12	.00725	1.19	.09175	2.71
1	05	1	1	12.32	.12675	.60000	.30725	1.34	.08925	2.96

SPEC	LOCT	SITE	SAMP	WASHED LEAVES NITRIC ACID							
				ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM	
1	05	1	2	17.82	.04425	.60000	.08225	1.09	.09175	3.96	
1	05	1	3	15.32	.05175	.07500	.38225	.63925	.17175	3.46	
1	05	2	1	9.07	.08175	.45000	.40725	1.21	.05425	1.96	
1	05	2	2	9.57	.10925	.90000	.08225	1.24	.46175	.95725	
1	05	2	3	9.82	.01425	.50000	.00725	.66425	.04675	1.46	
1	05	3	1	10.57	.08925	.42500	.70725	.0	.0	4.46	
1	05	3	2	10.32	.02175	.75000	.05725	1.34	.0	1.71	
1	05	3	3	9.07	.0	.60000	.03225	.66425	.0	2.21	
1	05	4	1	19.57	.12425	.35000	.18225	1.09	.0	3.21	
1	05	4	2	15.07	.02175	.07500	.08225	1.11	.0	2.71	
1	05	4	3	15.07	.01925	.97500	4.86	.48925	.0	1.46	
3	05	3	1	17.82	.08425	.25000	.90725	.53925	.0	2.21	
3	05	4	1	21.07	.09425	.47500	.33225	.53925	.0	2.71	
3	05	4	2	25.32	.05425	.75000	.05725	1.29	.0	3.71	
3	05	4	3	15.57	.02675	.90000	.28225	1.39	.0	5.21	
1	06	1	1	13.07	.04425	.17500	.28225	.98925	.0	1.21	
1	06	1	2	14.07	.04925	.05000	.65725	1.11	.0	2.96	
1	06	1	3	10.82	.02425	.45000	.15725	.58925	.0	.95725	
3	06	1	1	23.32	.48425	.62500	1.21	.98925	.0	3.46	
3	06	1	2	18.57	.03175	.42500	.03225	.16425	.0	2.21	
2	06	1	1	8.07	.48425	.40000	.53225	1.26	.0	2.96	
2	06	1	2	11.32	.12175	.62500	.33225	.96425	.03425	3.46	
1	06	2	1	10.07	.09175	1.35	.65725	1.24	.00425	1.46	
1	06	2	2	9.07	.06425	.57500	.20725	1.19	.02675	2.71	
1	06	2	3	16.32	.03175	.97500	.38225	.71425	.0	2.21	
1	06	3	1	11.07	.05425	.97500	.93225	.53925	.0	.95725	
1	06	3	2	9.57	.04675	.57500	.45725	.33925	.0	1.96	
2	07	1	1	23.07	.19925	.85000	9.86	1.01	.0	6.21	
2	07	1	2	14.07	.05425	.60000	12.36	.33925	.0	3.46	
2	07	1	3	15.57	.09175	.77500	9.86	1.01	.03925	5.46	
2	07	1	4	14.07	.08425	.80000	7.36	1.06	.01675	5.21	
1	08	1	1	15.32	.25925	3.52	.78225	.83925	.02925	3.96	
1	08	1	2	12.82	.05675	.07500	.15725	1.19	.02675	4.71	
1	08	1	3	16.32	.05925	.55000	.20725	1.16	.08175	3.46	
3	08	1	1	14.07	.06925	1.27	.63225	2.21	.06175	4.46	
3	08	1	2	13.07	.02925	.17500	.80725	2.31	.0	4.46	
1	08	2	1	16.07	.14675	.82500	1.38	.78925	.0	4.21	
1	08	2	2	15.57	.07675	.70000	.53225	1.41	.06925	3.96	
1	08	2	3	13.57	.04175	.07500	.20725	1.49	.0	3.71	
3	08	2	1	14.82	.10175	2.07	1.56	2.54	.0	7.21	
3	08	2	2	13.57	.01425	.77500	.50725	3.29	.00925	6.46	
1	09	1	1	19.82	.07925	.72500	1.66	.58925	.01175	5.71	
1	09	1	2	16.82	.03675	.57500	.68225	.0	.0	3.71	
1	09	1	3	21.07	.03425	.97500	.40725	.51425	.01175	6.71	

SPEC	LOCT	SITE	SAMP	WASHED LEAVES NITRIC ACID						
				ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
3	09	1	1	10.32	.05675	1.32	.20725	1.36	.0	3.46
2	09	1	1	12.07	.18675	.67500	.35725	.41425	.24425	2.96
3	09	1	2	9.57	.03925	1.42	.08225	.98925	.03925	3.96
2	09	1	2	11.07	.07425	.70000	.40725	.43925	.12925	4.71
2	09	1	3	15.82	.03925	.65000	.10725	.13925	.07675	5.71
1	10	1	1	42.82	.48425	1.15	.48225	.13925	.02675	2.71
1	10	1	2	16.57	.14175	.55000	.58225	.0	.0	3.71
1	10	1	3	15.07	.04675	.97500	.83225	.0	.46675	2.46
3	10	1	1	7.82	.03175	.87500	1.18	.0	.0	2.46
1	10	2	1	18.32	.03175	.70000	.73225	1.01	.0	4.21
1	10	2	2	50.32	.98425	.70000	.55725	2.06	.0	4.46
1	10	2	3	21.82	.16675	.57500	.35725	.98925	.0	6.21
2	10	2	1	7.82	.31175	.67500	.83225	1.24	.06925	3.21
2	10	2	2	13.57	.98425	1.12	1.46	1.89	.22925	3.71
3	10	2	1	20.57	.23175	1.00	.25725	1.64	.0	6.46
3	10	2	2	18.57	.48425	2.45	.25725	4.16	.0	6.96
2	10	3	1	6.32	.01925	1.00	1.33	.0	.03425	1.46
2	10	3	2	5.57	.00675	1.07	1.08	.31425	.03425	1.71
1	10	3	1	9.07	.03675	1.27	7.36	.66425	.0	2.21
1	10	3	2	8.17	.11587	2.13	1.42	.55599	.49910	1.75
1	10	3	3	9.84	.02652	2.16	1.93	3.43	.16677	1.47
3	10	3	1	9.57	.03175	.92500	.58225	.0	.11425	2.96
3	10	3	2	12.57	.48425	1.17	.38225	.66425	.06175	2.96
2	10	3	3	6.07	.01425	1.52	4.86	1.84	.05925	1.21
1	11	1	1	13.32	.06925	.85000	.33225	.0	.06675	2.96
1	11	1	2	13.57	.05175	.92500	.40725	.03925	.85675	4.71
1	11	1	3	11.07	.02175	1.12	.43225	.0	.17175	1.71
2	11	1	1	5.32	.06675	.95000	.48225	.38925	.22675	2.21
2	11	1	2	10.82	.04675	.65000	.53225	.03925	.23425	2.21
2	11	1	3	5.82	.05925	.90000	.28225	.0	.13925	2.21
1	11	2	1	23.07	.14675	1.80	1.68	1.11	.21925	3.96
1	11	2	2	22.07	.05925	.90000	.58225	.26425	.13925	4.71
1	11	2	3	9.32	.01675	.05000	.75725	.33925	.10925	2.96
3	11	2	1	10.57	.04425	.95000	.43225	.28925	.10675	2.96
1	11	3	1	152.82	2.48	.85000	7.36	.38925	.07925	4.71
1	11	3	2	137.82	3.48	.60000	4.86	.0	.09425	2.96
1	11	3	3	125.32	.48425	.92500	6.11	.0	.11425	5.21
3	11	3	1	30.32	.48425	.95000	.93225	1.01	.14925	3.71
3	11	3	2	90.32	1.98	.62500	4.86	.66425	.03175	5.21

UNWASHED LEAVES NITRIC ACID

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
1	01	1	2	15.57	.02925	3.25	9.86	1.69	.0	4.96
1	02	1	1	17.82	.08175	2.80	9.86	1.56	.0	4.96
1	02	3	4	14.32	.03425	2.75	4.86	3.09	.03675	3.96
1	03	3	3	51.61	.03375	4.50	1.29	3.07	.04625	7.29
1	04	1	2	21.07	.03425	1.30	.53225	.96425	.0	3.21
2	04	2	3	12.07	.07425	1.37	.20725	1.34	.0	3.46
1	04	2	1	11.07	.06175	1.45	1.33	1.99	.0	1.46
1	05	1	3	13.57	.04675	1.85	.10725	1.16	.01675	3.46
1	05	3	1	13.57	.03175	1.30	.05725	1.94	.02925	2.71
1	05	4	2	9.82	.02675	1.35	.38225	2.49	.03175	1.96
3	05	4	2	25.07	.09175	.65000	.05725	1.54	.04425	3.71
1	06	1	2	11.82	.04925	1.45	.33225	2.39	.00675	4.71
3	06	1	2	16.07	.02675	1.27	.50725	2.16	.0	4.96
2	06	1	2	9.82	.13925	1.47	1.11	1.31	.00675	3.21
2	07	1	1	25.07	.11925	3.40	17.53	4.36	.04675	9.21
2	07	1	4	20.07	.09675	2.62	19.86	5.29	.02925	7.21
1	08	2	3	16.57	.07425	2.12	.38225	2.34	.04425	3.96
1	09	1	1	19.57	.04925	2.17	.88225	3.06	.03675	6.46
3	09	1	2	9.57	.03175	1.60	.58225	3.51	.04675	3.21
2	10	2	1	11.07	.17925	1.72	1.51	5.94	.03175	3.21
3	10	2	2	21.32	.12925	1.65	1.28	9.24	.00425	8.21

WHITE ROOTS NITRIC ACID

SPEC	LOCT	SITE	SAMP	FEPPM	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
1	02	1	1	14189.	49.52	.63311	3.18	6.37	5.17	.37635	52.59
1	02	3	4	9890.	24.33	.51483	2.58	5.18	3.82	.11374	8.70
1	04	1	2	7250.	62.82	1.73	4.92	4.86	9.16	.14675	9.46
2	04	2	1	1750.	15.57	.23425	2.67	2.36	3.36	.0	3.96
1	05	1	3	9500.	45.32	3.23	4.42	2.36	10.94	.68925	10.71
1	05	3	1	2500.	30.32	1.73	1.17	2.36	3.49	.05425	6.21
3	05	4	1	13636.	47.11	.97828	6.41	4.76	6.04	.30151	5.97
3	06	1	2	11000.	25.32	.48425	3.92	4.86	7.46	.28175	8.46
2	07	1	1	2750.	20.57	.23425	3.67	2.36	2.66	.07925	8.46
2	07	1	4	9000.	20.07	.48425	3.17	4.86	2.06	.02925	7.71
1	08	1	2	2500.	57.82	5.23	11.92	2.36	1.66	.02175	8.96
1	08	2	3	2538.	43.47	4.04	12.11	2.39	1.66	.0	18.48
1	09	1	1	2000.	67.82	1.48	5.42	2.36	2.21	.0	12.21
2	09	1	1	2119.	24.70	.82076	27.84	4.00	1.72	.01144	15.18
1	10	1	1	3147.	140.	6.62	25.07	10.29	3.90	.12133	56.23
2	10	2	1	3000.	30.32	1.23	4.42	7.36	16.79	.07675	21.96
3	10	2	2	2885.	102.	5.74	78.70	9.34	18.49	.28221	91.26
2	10	3	2	11250.	23.57	.48425	10.92	7.36	2.96	.17925	6.96
1	10	3	1	9000.	21.57	.23425	16.42	4.86	1.56	.14925	7.46
2	11	1	2	3779.	8.51	.27238	1.37	2.74	.19099	.24041	4.89
1	11	2	2	3608.	46.72	.75696	6.37	5.01	1.48	.45541	8.20
1	11	3	1	1544.	155.	2.66	11.31	9.88	2.84	.40839	4.98

RED ROOTS NITRIC ACID

SPEC	LOCT	SITE	SAMP	FEPPM	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	HGPPM	CUPPM
1	02	1	1	42500.	47.82	.23425	2.92	27.36	13.16	.72675	61.21
1	02	3	4	27083.	64.09	1.35	3.26	13.49	3.72	.38681	34.60
1	05	4	2	11000.	45.32	.98425	2.92	4.86	3.69	.32175	3.46
1	06	1	2	25000.	40.32	.48425	6.17	12.36	7.91	.40425	7.71
1	10	2	1	13750.	190.	.98425	5.67	14.86	34.54	.92675	115.

Washed Leaves - Cold Digestion for Mercury

<u>Species</u>	<u>Location</u>	<u>Site</u>	<u>Sample</u>	<u>Hg PPM</u>
1	01	1	2	0.080
1	01	1	3	0.220
1	02	1	1	0.300
1	08	2	2	0.460
1	02	1	3	0.320
1	02	2	3	0.200
1	02	2	4	0.080
1	11	1	2	0.100
1	05	2	1	0.260
1	02	3	4	0.220
1	06	1	2	0.020
1	03	2	3	0.160
1	03	3	1	0.080
1	03	4	1	0.120
1	04	1	2	0.370
1	04	2	1	0.350
1	05	2	2	0.670
1	05	3	1	0.170
1	06	1	1	0.150
1	06	2	1	0.290
1	10	1	3	0.310
1	10	2	2	0.430
1	08	2	1	0.490
1	08	2	3	0.630
1	09	1	1	0.250
1	09	1	3	0.730
3	10	2	2	0.630
2	10	3	1	0.330
2	10	3	2	0.750

APPENDIX B

PHASE II: VERIFICATION DATA

CORPUS CHRISTI DTPA EXTRACT

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	CUPPM	LAB DETERMINATION
1	12	1	01	155.	.78055	.58350	20.99	.00600	6.39	1
1	12	1	02	860.	15.90	1.16	53.49	.01100	4.69	1
1	12	1	02	870.	16.00	1.12	54.99	.01100	5.14	2
1	12	1	02	865.	13.40	1.20	55.99	.01600	5.09	3
1	12	1	03	408.	6.05	.91850	34.49	.00600	5.99	1
1	12	1	04	164.	2.49	1.04	14.99	.00100	4.03	1
1	12	1	04	216.	3.15	1.05	16.99	.00600	3.17	2
1	12	1	04	161.	2.60	1.36	15.99	.00600	4.86	3
1	12	1	05	422.	.06455	.44850	4.99	.00600	1.23	1
1	12	1	06	131.	1.12	.88350	14.99	.00600	4.98	1
1	12	1	07	290.	6.15	.85350	18.49	.0	4.62	1
1	12	1	07	310.	5.60	.85350	19.49	.0	4.45	2
1	12	1	07	358.	6.30	.95350	21.49	.0	4.60	3
1	12	1	08	406.	5.85	1.29	25.49	.01100	5.69	1
1	12	1	08	245.	4.00	1.64	19.49	.00600	5.69	2
1	12	1	08	227.	3.39	1.71	18.99	.01100	4.74	3
1	12	1	09	345.	6.30	.85850	34.99	.00600	9.64	1
1	12	1	10	282.	4.95	1.16	31.49	.00100	10.09	1
1	12	1	10	316.	5.85	1.17	32.49	.00100	10.49	2
1	12	1	10	278.	6.45	.97350	33.49	.00600	10.79	3
1	12	1	11	399.	6.10	1.05	33.99	.01100	7.34	1
1	12	1	11	399.	6.80	1.05	33.99	.00600	6.84	2
1	12	1	11	411.	6.75	1.08	34.99	.00600	7.84	3
1	12	1	12	222.	3.44	1.24	27.99	.01100	8.49	1
1	12	1	13	332.	5.90	.87850	33.99	.00600	11.34	1
1	12	1	13	393.	7.45	.92350	34.99	.01100	9.74	2
1	12	1	13	321.	7.65	.85350	32.49	.00600	10.34	3
1	12	1	14	190.	4.85	1.17	29.49	.01100	9.74	1
1	12	1	14	179.	2.19	1.15	28.49	.04100	7.39	2
1	12	1	14	194.	2.75	1.24	26.99	.01600	6.99	3
1	12	1	15	325	6.40	2.05	36.49	.00600	7.54	1
1	12	1	16	221.	5.45	.89350	25.99	.00600	11.74	1
1	12	1	17	244.	1.81	.78850	35.99	.03100	9.14	1
1	12	1	18	264.	3.79	1.52	37.49	.01100	11.99	
1	12	1	18	310.	3.06	1.54	36.99	.01600	10.99	2
1	12	1	18	357.	4.35	1.29	43.99	.01100	11.69	3
1	12	1	19	427.	7.50	1.18	68.49	.01100	14.49	1
1	12	1	20	119.	3.44	.70850	8.99	.0	2.17	1
1	12	1	21	271.	5.80	.79350	21.49	.0	3.80	1
1	12	1	22	213.	2.26	3.64	27.49	.01100	6.49	1
1	12	1	22	209.	2.27	2.58	32.49	.01100	5.59	2
1	12	1	22	247.	2.55	2.31	35.49	.01100	6.59	3

CORPUS CHRISTI DTPA EXTRACT

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	CUPPM
3	12	1	01	189.	3.74	1.16	22.49	.01600	14.74
3	12	1	02	254.	4.04	1.05	21.99	.03600	10.19
3	12	1	03	283.	3.03	1.49	24.99	.04100	8.14
3	12	1	04	185.	2.04	1.60	17.99	.04100	8.29
3	12	1	05	240.	2.71	1.31	23.49	.02100	7.34
3	12	1	06	323.	3.42	1.00	25.99	.01100	8.29
3	12	1	07	176.	2.95	1.96	24.49	.03100	8.59
3	12	1	08	240.	3.52	1.73	31.99	.03100	10.24
3	12	1	09	235.	3.49	2.24	26.99	.02600	7.79
3	12	1	10	204.	1.45	1.10	24.99	.04100	6.84
3	12	1	11	257.	2.57	1.19	28.49	.02600	9.49
3	12	1	12	211.	1.29	.86350	50.99	.04100	8.29
3	12	1	13	196.	1.51	1.29	22.99	.04600	6.64
3	12	1	14	210.	1.91	1.74	23.99	.05600	7.84
3	12	1	15	230.	2.43	1.92	26.49	.03600	7.74
3	12	1	16	238.	3.24	1.41	24.49	.06100	.94
3	12	1	17	250.	1.86	.55350	29.49	.03100	8.44
3	12	1	18	237.	2.53	.88350	24.49	.03600	9.04
3	12	1	19	130.	1.60	1.03	14.99	.04600	4.28
3	12	1	20	109.	1.36	.57350	11.99	.07600	3.37

CORPUS CHRISTI WASHED LEAVES

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	CUPPM	LAB DETERMINATION
1	12	1	01	122.	.43125	1.59	19.41	2.15	8.89	1
1	12	1	02	79.55	.20125	2.165	3.58	1.67	5.94	1
1	12	1	02	84.55	.38125	1.940	3.98	1.25	6.09	2
1	12	1	02	74.55	.20125	2.940	3.23	1.52	5.76	3
1	12	1	03	92.05	.25625	2.89	18.28	1.45	8.19	1
1	12	1	04	89.55	.21625	1.740	4.18	1.55	3.81	1
1	12	1	04	105.	.2313	1.665	4.31	1.17	3.79	2
1	12	1	04	92.05	.19375	3.44	3.83	1.17	3.46	3
1	12	1	05	57.05	.11125	.24000	2.21	.22500	4.44	1
1	12	1	06	82.05	.05875	.59000	4.38	1.23	5.21	1
1	12	1	07	67.05	.08125	.31500	3.38	1.57	3.71	1
1	12	1	07	59.55	.08875	.19000	5.36	1.50	3.41	2
1	12	1	07	59.55	.06375	.14000	3.28	.87500	4.56	3
1	12	1	08	39.55	.08875	1.240	2.18	.0	2.64	1
1	12	1	08	34.55	.06875	1.250	2.11	.0	3.04	2
1	12	1	08	44.55	.06875	4.065	2.38	.0	2.51	3
1	12	1	09	127.	.15125	.34000	5.16	1.00	5.19	1
1	12	1	10	175.	.21375	.24000	8.81	1.075	5.84	1
1	12	1	10	172.	.38125	.46500	9.41	0.425	5.16	2
1	12	1	10	175.	.23125	.24000	5.41	0.925	5.99	3
1	12	1	11	170.	.25625	.24000	5.48	1.000	5.36	1
1	12	1	11	167.	.25625	.19000	5.08	1.200	4.84	2
1	12	1	11	150.	.21125	.14000	4.28	1.050	4.49	3
1	12	1	12	57.05	.09875	.09000	1.03	1.42	5.04	1
1	12	1	13	52.05	.20625	3.69	1.13	1.50	4.89	1
1	12	1	13	47.05	.18625	1.515	1.03	1.13	4.81	2
1	12	1	13	47.05	.19375	0.740	1.83	1.07	5.16	3
1	12	1	14	182.	.30625	.01500	5.08	2.37	5.39	1
1	12	1	14	202.	.21875	.0	7.51	1.32	4.76	2
1	12	1	14	187.	.20375	.24000	7.61	1.32	4.39	3
1	12	1	15	180.	.21375	1.39	2.03	.92500	4.79	1
1	12	1	16	162.	.20625	3.86	4.68	1.25	4.26	1
1	12	1	17	200.	.22375	.39000	6.61	1.77	5.24	1
1	12	1	18	59.55	.07875	.26500	2.21	0.725	3.01	1
1	12	1	18	59.55	.07125	.61500	1.96	1.15	2.96	2
1	12	1	18	62.05	.06125	1.09	2.08	1.10	2.99	3
1	12	1	19	42.05	.06375	.51500	1.36	.0	2.96	1
1	12	1	20	250.	.35625	.91500	6.78	1.20	5.21	1
1	12	1	21	127.	.21625	.41500	3.38	.92500	4.74	1
1	12	1	22	152.	.20125	.21500	4.88	.20000	2.81	1
1	12	1	22	152.	.30625	.14000	4.51	.0	2.94	2
1	12	1	22	155.	.43125	.24000	4.88	.85000	3.11	3

CORPUS CHRISTI WASHED LEAVES

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	CUPPM
3	12	1	01	47.05	.20625	1.74	4.41	.15000	5.64
3	12	1	02	100.	.35625	.61500	7.36	.52500	3.76
3	12	1	03	32.05	.12625	.31500	2.81	.0	2.99
3	12	1	04	62.05	.11625	.29000	5.61	.0	3.76
3	12	1	05	72.05	.11125	4.51	6.46	.50000	4.54
3	12	1	06	77.05	.25625	.46500	6.36	1.67	4.19
3	12	1	07	32.05	.04875	.36500	18.33	.0	3.94
3	12	1	08	49.55	.10625		4.31	1.07	3.31
3	12	1	09	37.05	.08125	.64000	3.56	.0	3.14
3	12	1	10	37.05	.05875	1.51	4.26	.0	3.86
3	12	1	11	42.05	.07375	.41500	3.51	.0	3.76
3	12	1	12	54.55	.11375	1.29	4.21	.32500	5.34
3	12	1	13	64.55	.10625	1.39	6.13	.0	2.84
3	12	1	14	155.	.07375	.94000	16.33	.0	3.09
3	12	1	15	212.	.70625	.96500	22.48	.0	2.94
3	12	1	16	137.	.40625	.54000	13.91	.0	2.94
3	12	1	17	57.05	.13625	3.24	6.01	.52500	3.31
3	12	1	18	107.	.30625	4.54	70.81	.55000	5.54
3	12	1	19	34.55	.04625	.84000	4.51	.50000	2.71
3	12	1	20	39.55	.06125	1.19	2.88	.50000	2.36

CORPUS CHRISTI UNWASHED LEAVES

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	CUPPM
1	12	1	01	132.	.10500	6.13	6.94	.69675	4.14
1	12	1	02	110.	.02750	3.53	3.94	.62175	5.04
1	12	1	03	105.	.03500	2.13	3.87	.64675	5.49
1	12	1	04	107.	.03000	2.30	4.02	.62175	2.56
1	12	1	05	49.75	.02000	.02800	1.32	.84675	2.91
1	12	1	06	105.	.09250	3.18	3.74	.94675	3.81
1	12	1	07	72.25	.01000	.00300	2.74	.09675	3.91
1	12	1	08	47.25	.0	9.30	14.39	.12175	2.86
1	12	1	09	135.	.09500	.0	4.84	.0	4.14
1	12	1	10	165.	.12250	7.40	5.54	.0	4.61
1	12	1	11	127.	.02750	.0	4.47	.0	3.34
1	12	1	12	84.75	.22000	.52800	3.77	.0	5.51
1	12	1	13	44.75	.03250	.0	1.57	.0	5.21
1	12	1	14	275.	.09000	.05300	10.64	.89675	5.01
1	12	1	15	227.	.10250	.0	5.44	.0	5.16
1	12	1	16	170.	.04500	.0	5.79	.0	4.11
1	12	1	17	215.	.10500	.0	7.04	.02175	5.41
1	12	1	18	67.25	.01000	3.50	4.42	.0	2.96
1	12	1	19	77.25	.0	1.95	3.34	.0	2.89
1	12	1	20	272.	.14500	2.23	11.72	.14675	5.84
1	12	1	21	152.	.09000	.0	6.04	.02175	4.86
1	12	1	22	140.	.06250	.0	5.49	.0	3.36

CORPUS CHRISTI UNWASHED LEAVES

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	CUPPM
3	12	1	01	57.25	.07000	1.53	3.02	1.07	5.06
3	12	1	02	130.	.16500	.87800	10.92	.42175	4.74
3	12	1	03	67.25	.07250	.32800	4.42	.49675	4.14
3	12	1	04	62.25	.08250	2.08	4.57	.47175	4.01
3	12	1	05	59.75	.29500	.67800	5.02	.32175	3.89
3	12	1	06	87.25	.14250	1.08	17.09	.72175	4.06
3	12	1	07	39.75	.22000	.67800	2.39	.69675	6.41
3	12	1	08	62.25	.08500	.57800	4.57	.72175	7.89
3	12	1	09	44.75	.09750	.72800	2.67	.69675	5.36
3	12	1	10	47.25	.07750	.82800	3.87	.72175	5.44
3	12	1	11	64.75	.09750	.87800	5.22	.47175	4.36
3	12	1	12	54.75	.08500	.0	3.14	.54675	5.19
3	12	1	13	79.75	.13500	1.43	5.02	.82175	4.96
3	12	1	14	147.	.27000	.67800	11.49	.52175	4.54
3	12	1	15	230.	.44500	.92800	19.29	.74675	5.41
3	12	1	16	157.	.21250	.67800	11.04	.44675	4.69
3	12	1	17	67.25	.08000	1.18	6.57	.59675	5.56
3	12	1	18	105.	.12750	4.45	20.79	.37175	5.19
3	12	1	19	44.75	.22000	1.13	2.59	1.00	3.09
3	12	1	20	44.75	.06250	.70300	1.64	.74675	21.49

GREENHOUSE STUDY DTPA EXTRACT

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	CUPPM
1	13	1	01	15.55	.03375	1.21	.0	.0	3.36
1	13	1	02	19.55	.00125	.91500	.23500	2.25	3.84
4	13	1	01	37.05	.06375	3.71	.43500	1.60	2.49
4	13	1	02	27.05	.50625	9.11	.76000	1.93	2.31
1	13	2	01	15.55	.05375	.94000	.0	.0	2.74
1	13	2	02	22.05	.00625	1.56	.01000	.85000	3.64
1	13	2	03	37.05	.01625	2.41	.0	.0	3.06
1	13	2	04	12.55	.00625	.29000	.03500	.97500	2.24
1	13	3	01	14.05	.02625	.44000	.03500	.92500	3.09
1	13	3	02	42.05	.01625	.51500	.13500	.0	2.99
1	13	3	03	9.30	.0	.11500	.0	.0	2.26
1	13	3	04	8.30	.00375	.11500	.0	1.00	3.09

GREENHOUSE STUDY WASHED LEAVES

SPEC	LOCT	SITE	SAMP	ZNPPM	CDPPM	NIPPM	PBPPM	CRPPM	CUPPM
1	13	1	01	1.77	.0	1.37	.0	.0	.0
1	13	1	02	3.15	.0	1.18	.0	.0	.0
4	13	1	01	15.40	.0	2.25	.0	.0	.0
4	13	1	02	11.70	.0	1.48	.0	.0	.0
1	13	2	01	23.95	.02050	1.86	16.95	.0	.27250
1	13	2	02	19.65	.02900	1.80	16.45	.0	.0
1	13	2	03	9.00	.00550	1.22	14.65	.0	.0
1	13	2	04	4.40	.0	1.04	9.45	.0	.0
1	13	3	01	.0	.0	1.57	.0	.0	.0
1	13	3	02	.01500	.0	.78560	.0	.0	.0
1	13	3	03	2.37	.0	1.24	.0	.0	.0
1	13	3	04	1.36	.0	1.07	.0	.0	.0

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Lee, Charles R

Prediction of heavy metal uptake by marsh plants based on chemical extraction of heavy metals from dredged material / by C. R. Lee, R. M. Smart, T. C. Sturgis, R. N. Gordon, Sr., and M. C. Landin. Vicksburg, Miss. : U. S. Waterways Experiment Station ; Springfield, Va. : available from National Technical Information Service, 1978.

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