Determination of Trace Metals in Estuarine Sediment Pore Waters Containing High Concentrations of Iron

J.A.J Thompson
D.W. Paton

Department of Fisheries and Oceans
Institute of Ocean Sciences
Sidney, B.C.

1991

Canadian Technical Report of Hydrography and Ocean Sciences No. 133

Fisheries and Oceans Pêches et Océans

Canada

Canadian Technical Report of Hydrography and Ocean Sciences

These reports contain scientific and technical information of a type that represents a contribution to existing knowledge but which is not normally found in the primary literature. The subject matter is generally related to programs and interests of the Ocean Science and Surveys (OSS) sector of the Department of Fisheries and Oceans.

Technical Reports may be cited as full publications. The correct citation appears above the abstract of each report. Each report will be abstracted in Aquatic Sciences and Fisheries Abstracts. Reports are also listed in the Department's annual index to scientific and technical publications.

Technical Reports are produced regionally but are numbered and indexed nationally. Requests for individual reports will be fulfilled by the issuing establishment listed on the front cover and title page. Out of stock reports will be supplied for a fee by commercial agents.

Regional and headquarters establishments of Ocean Science and Surveys ceased publication of their various report series as of December 1981. A complete listing of these publications and the last number issued under each title are published in the *Canadian Journal of Fisheries and Aquatic Sciences*, Volume 38: Index to Publications 1981. The current series began with Report Number 1 in January 1982.

Rapport technique canadien sur l'hydrographie et les sciences océaniques

Ces rapports contiennent des renseignements scientifiques et techniques qui constituent une contribution aux connaissances actuelles mais que l'on ne trouve pas normalement dans les revues scientifiques. Le sujet est généralement rattaché aux programmes et intérêts du service des Sciences et Levés océaniques (SLO) du ministère des Pêches et des Océans.

Les rapports techniques peuvent être considérés comme des publications à part entière. Le titre exact figure au-dessus du résumé du chaque rapport. Les résumés des rapports seront publiés dans la revue Résumés des sciences aquatiques et halieutiques et les titres figureront dans l'index annuel des publications scientifiques et techniques du Ministère.

Les rapports techniques sont produits à l'échelon régional mais sont numérotés et placés dans l'index à l'échelon national. Les demandes de rapports seront satisfaites par l'établissement auteur dont le nom figure sur la couverture et la page de titre. Les rapports épuisés seront fournis contre rétribution par des agents commerciaux.

Les établissements des Sciences et Levés océaniques dans les régions et à l'administration centrale ont cessé de publier leurs diverses séries de rapports depuis décembre 1981. Vous trouverez dans l'index des publications du volume 38 du *Journal canadien des sciences halieutiques et aquatiques*, la liste de ces publications ainsi que le dernier numéro paru dans chaque catégorie. La nouvelle série a commencé avec la publication du Rapport n° 1 en janvier 1982.

Canadian Technical Report of
Hydrography and Ocean Sciences 133

1991

DETERMINATION OF TRACE METALS IN ESTUARINE SEDIMENT PORE WATERS CONTAINING HIGH CONCENTRATIONS OF IRON

by

J.A.J. Thompson* and D.W. Paton

Department of Fisheries and Oceans
Institute of Ocean Sciences
Sidney, BC

*Author to whom correspondence should be addressed

(c) Minister of Supply and Services Canada 1991
Cat. No. Fs 97-18/133E ISSN 0711-6764

Correct citation for this publication:

Thompson, J.A.J., and D.W. Paton. 1991. Determination of trace metals in estuarine pore waters containing high concentrations of iron. Can. Tech. Rep. Hydrogr. Ocean Sci. 133: 13p.

ABSTRACT

Thompson, J.A.J., and D.W. Paton. 1991. Determination of trace metals in estuarine pore waters containing high concentrations of iron. Can. Tech. Rep. Hydrogr. Ocean Sci. 133: 13p.

A double extraction schema for the preconcentration of trace metals in estuarine sediment pore waters containing high concentrations of iron has been developed using Freon TF and the ligand mixture of ammonium pyrrolidine carbodithioate ("APDC") and diethylammonium carbodithioate ("DDDC"). This method differs from similar procedures for sea water in three important ways: 1. The ratio of ligand to sample volume; 2. The composition of the extractant solvent; and, 3. The buffer. Ligand volume ratio was increased to accommodate high Fe concentrations that would interfere with quantitative recovery of other analytes. The solvent was modified by the addition of 10% $CHCl_3$ to permit dissolution of an Fe-carbodithioate complex which was identified qualitatively by SEM/EDX and synthesis in the laboratory. Citrate buffer replaced acetate due to its superior iron complexing property. The analysis of the final aqueous acid extract for cadmium, cobalt, copper, lead and zinc, and examples of field data are presented.

Keywords: sediments, interstitial water, analysis, trace metals, estuarine

RESUME

Thompson, J.A.J., and D.W. Paton. 1991. Determination of trace metals in estuarine pore waters containing high concentrations of iron. Can. Tech. Rep. Hydrogr. Ocean Sci. 133: 13p.

Une nouvelle méthode de double extraction pour la préconcentration des méteaux-tracesdans les eaux interstitielles des sédiments estuariens contenant des concentrations élevées de fer a été mis au point. Cette méthode utilise le Fréon TF et un mélange de pyrrolidine carbodithioate d'ammonium et de diethylammonium carbodithioate lié par coordination. Cette méthode se distingue à trois niveaux importants des procédures utilisées pour l'eau de mer: 1. Le rapport du coordinat par rapport au volume de l'échantillon; 2. La composition du solvant d'extraction; et 3. La solution tampon. Le rapport du volume du coordinat a été augmenté pour tenir compte des concentrations élevées de fer qui auront une incidence sur la récupération quantitative des autres sustances à analyser. Le solvant a été modifié en y ajoutant une concentration de 10% de $CHCl_3$ afin de faciliter la dissolution d'un complexe Fe-carbodithioate qui a été identifié qualitativement par microscope électronique à balayage/rayons X à dispersion d'energie et par synthèse en laboratoire. La solution tampon de citrate a remplacé l'acétate en raison de la propriété complexante supérieure du fer qu'elle contient. On présente ici l'analyse de l'extrait acide aqueux pou le cadmium, le cobalt, le cuivre, le plomb, et le zinc ainsi que des exemples de données recueillies sur le terrain.

Mots-Clés: sédiments, eaux interstitielles, dosage, métaux traces, estuarien

1 INTRODUCTION

The analysis of marine sediment interstitial water exemplifies a specific matrix condition not normally encountered in seawater investigations. In particular, there can be higher burdens of dissolved solids, including trace metals, wide ranges of redox conditions, higher organic carbon, and often free sulfide ion. Interstitial waters thus present unique matrices which dictate essentially custom-designed analyses.

Recent methodologies reported for the determination of trace metals or metalloids in interstitial water include, *inter alia,* coprecipitation *[Boyle and Edmond, 1977; Lyons et al., 1980; Sawlan and Murray, 1983]*, extraction *[Thompson and Paton, 1978; Westerlund et al., 1986]*, hydride generation *[Reimer and Thompson, 1988]* and Chelex-100 (cation exchange resin) adsorption *[Murray et al., 1978]*, all combined with atomic absorption spectrometry and occasionally, anodic stripping voltammetry *[Pedersen, 1985; Gobeil et al., 1987]*. Manganese and iron can be determined in estuarine pore waters by direct aspiration into flame atomisers after appropriate dilution while other metals such as copper and molybdenum have been assayed by direct injection into a carbon furnace *[Pedersen, 1985]*. The availability of Zeeman background correction has permitted the determination of other elements by direct injection after suitable matrix modifications for Cu, Cd or Co *[Heggie and Lewis, 1984; Heggie et al., 1986]*. However, detection limits may be limited by the need for a preconcentration step in the case of these and other analytes.

In most cases, it is desirable to separate trace metals from the saline matrix for two reasons. Sea salts present serious matrix interferences which can reduce atomic absorption spectrometric responses severely. Secondly, and more importantly, separation usually permits a concomitant preconcentration which is necessary to provide acceptable levels of detection of many of the analytes. Although concentrations of metals in pore waters are generally one or two orders of magnitude greater than in overlying waters, some, notably lead, cadmium and copper, benefit from preconcentration.

In our work with estuarine sediments, we have found that dissolved iron in pore waters can attain concentrations which, upon addition of carbodithioate ligands, can result in the formation of insoluble precipitates of iron complexes. In turn, other trace metals may coprecipitate with the iron complex. Also, because of the additional iron loading, there has been a need to alter the amounts of ligand used. We describe here the adaptation of the Freon extraction procedures reported by Westerlund and coworkers *[Danielsson et al., 1978, 1982]*, which have been used successfully for seawater analysis in this laboratory for some years. In our work, estuarine sediments, which in some cases have been impacted by mine-mill tailings, were examined. Close attention was given to quality control through the use of clean-room conditions throughout the separation and concentration steps. The metals copper, cadmium, lead, cobalt and zinc can be quantitatively recovered utilising this procedure.

2 METHODS AND MATERIALS

A.Sample Bottle Preparation

All plastic containers utilised for sample collection and/or storage were prepared by exhaustive cleaning in hot 6M HNO_3 and repeated rinsing with doubly deionised water. Bottles were stored with 0.1M HNO_3 which was discarded just prior to use.

B. Collection Procedures

Sediments were collected using a box corer (Model #216WA102; Kahlsico, San Diego) which had been modified with a longer box (60 cm) and a removable face plate through which rows of holes were drilled to accept plastic, 50 cc syringes. For corer deployment, the face plate was lined with polyethylene film. Upon retrieval of the corer, the film was cut away and the precleaned syringes with the tapered end cut off were inserted horizontally into the sediment at each depth and withdrawn. Samples were either placed directly into a nitrogen-filled glove box (Model 50004; Labconco) or into a refrigerator at 4° C with the exposed sediment

covered with plastic film to minimize exposure to air. In the glove box, samples were expressed from the syringe into acid-washed Oak Ridge style plastic centrifuge bottles. The bottles were capped tightly, removed from the glove-box and placed into a refrigerated centrifuge (Sorvall Model RC-5; Model HS-4 swing-bucket rotor at 5° C) and spun at 6900 xg (6 000 rpm) for 30 min. After being returned to the glove-box, supernatant water was removed by suction and passed directly through an acid-washed 0.45 μm membrane filter (Millipore, 149 mm) into a tared, acid-cleaned polypropylene bottle enclosed in a vacuum intercept chamber (V. Stukas, Sidney, BC, unpublished design). Samples were sealed tightly under N_2, placed in plastic bags and frozen for return to the laboratory. In our experience, the necessity to add acid for sample preservation has not been demonstrated.

C. Sampling

The unacidified samples were thawed under a nitrogen atmosphere and were transferred to a Class 100 clean room where the weight of water was determined by difference. Samples were acidified with 0.5 M HNO_3 (12.5 mg.g^{-1} of pore water) to a pH of≈4 and split into three aliquots.

D. Analysis

i. Reagents

Freon TF (Freon 113; bp 47.6° C; Dupont; 600 mL) was cleaned by the addition of one mL quartz-distilled (QD) nitric acid (Seastar Ltd., Sidney, BC) followed by 20 mL QD water. Glass-distilled chloroform (Caledon, Georgetown, Ontario) was cleaned by extraction (4x) with aqueous acid. 1-Pyrrolidine carbodithioic acid, ammonium salt ("APDC"), was prepared and purified by the method of Mallissa and Schoeffmann *[1955]*. Diethylcarbodithioic acid, diethylammonium salt ("DDDC") was provided by ICN Pharmaceuticals (Plainsview, NY). Mixed solutions of APDC and DDDC (each 1%, w/v) were prepared in QD water and extracted 4x with Freon TF. Diammonium citrate buffer (Fisher; 0.5 M) was prepared in QD water from ACS grade chemical and cleaned (4x) by APDC/DDDC chelation and extraction with Freon TF. Aqueous ammonia was prepared by passing ammonia gas (Matheson) through QD water.

ii. Extraction

Interstitial water (approximately 20 g) was weighed accurately into each of two, 125 mL Teflon separatory funnels. Citrate buffer (5 mg g^{-1} of sample or about 100 μL)was added to adjust pH to 4.0 $\pm$ 0.3. After the addition of the mixed ligand solution (0.5 mL or 25 mg g^{-1} of sample), 10 mL of the Freon-chloroform mixture (9:1) was added and the contents shaken for a minimum of 2 min. After phase separation, the organic layer was drained. The chelation and extraction steps were repeated and the two organic layers were combined. An additional 5 mL solvent mixture was added to the aqueous layer and shaken for 30 sec. This extract was combined with the first two. (This step must be repeated until all color in the aqueous layer has been removed). The combined organic layer was washed with approx. 5 mL aqueous ammonia, pH 8, to remove residual salts and drained into a clean 125 mL Teflon separatory funnel. Concentrated, quartz distilled nitric acid (approx. 30 μg)was weighed accurately into the funnel and shaken with the extract for 30 sec. QD water (1.5 mL, accurately weighed) was added and shaken for one min and allowed to separate. The organic layer was drained and a portion of the aqueous concentrate was transferred to a one mL vial which was capped and sealed with Teflon tape until analysis.

iii. Analysis

The metals cadmium, cobalt, copper, lead and zinc were determined in the aqueous acid concentrates using a Perkin-Elmer Model 503 atomic absorption spectrometer fitted with a Model 400 carbon furnace and Model AS-1 autosampler. Absorbances were registered on a strip-chart recorder. Instrument settings, conditions and precision for each element are shown in Table 1. Calibration curves were established using absorbance data from multi-element standards in an aqueous nitric acid matrix.

Table 1: Instrumental Settings and Analytical Conditions [a]

ELEMENT	VOL. INJECTED (μL)	ARGON FLOW	AAS LINE (nm)	PRECISION CV (%)
Cadmium	20	40 Mini	228.8	4.85; N=5
Cobalt	50	40 Stop	240.7	11.5; N=9
Copper	20	40 Mini	324.7	4.3; N=5
Lead [b]	50	Stop	217.0	10.7; N=8
Zinc	10	Full	213.8	13.9; N=14

[a] Perkin-Elmer Model 503 with Model HGA 400 graphite atomiser.
[b] L'vov platform; deuterium background correction.

Since blank values were generally below instrument detection capabilities, method limits of detection (LOD) were calculated using data from field samples having concentrations at the lower end of the detectable range. Standard deviations were calculated for replicate (9X) analysis of a typical water sample. Values of LOD reported are based on three times the standard deviation.

An energy-dispersive X-ray (EDX) spectrum of the Fe-carbodithioate complex (see discussion) was obtained using a JEOL JEM 1200 EX scanning electron microscope located in the Biological Sciences Department of the University of Victoria, Victoria, BC.

3 RESULTS AND DISCUSSION

The extraction schema that we have developed for estuarine sediment interstitial waters differs from methods previously published for seawater analysis *[Danielsson, et al., 1978, 1982]* in three areas: 1. Buffer; 2. Quantity of the carbodithioate ligand combination; and 3. Extracting solvent. All of these factors relate to the need to accommodate the high and variable iron loadings found in pore waters. Danielsson et al. *[1982]* addressed the complexation of iron in low salinity estuarine waters where concentrations of this element ranged up to 3.6 μM kg^{-1}. Their procedure was reported to give 100 percent recoveries at Fe concentrations an order of magnitude greater than this value. Problems of recovery of iron from river water experienced by Danielsson et al. *[1982]* using their earlier procedure *[1978]* were attributed to localized areas of high pH during neutralization. Low solubility of the Fe-carbodithioate complexes in Freon-TF was ruled out in this instance.

A. Buffer

We chose to use citrate as the buffer for this extraction procedure because of its superior Fe-complexing capacity, relative to acetate, which is necessary to keep iron in solution at higher pH values. Kinrade and Van Loon *[1974]* suggested that acetate may not be desirable because of stable complexes this ion can form with lead and silver. We were able to produce solutions which were acceptably free of trace metals by a four-fold Freon TF extraction after addition of mixed chelator solution.

B. Carbodithioates

While the concentrations of the mixed ligands remained at one percent w/v *[Danielsson et al.,1978, 1982]* we found it necessary to increase the ratio of ligand to sample volume by an order of magnitude. This increase proved to be sufficient to accommodate the greater quantities of trace metals, in particular iron, characteristically found in pore waters. Because Fe can reach concentrations of 500 μM or more in fjord pore waters of coastal British Columbia *[Pedersen, 1985]* it was necessary to supply sufficient ligand to complex all of the iron which will otherwise compete with the elements of interest (Fe itself is determined, after dilution, by flame AA). Because of high Fe concentrations encountered, addition of the carbamate solutions generally resulted in generation of a strong blue-green color in the extraction medium. At higher Fe concentrations one or two repetitions of the Freon step would be required to ensure quantitative transfer into the organic layer.

The need for photo-oxidation of the sample to eliminate organic material prior to the extraction was also discounted. Samples of estuarine pore water were split and one portion was exposed to UV radiation for 24 h. Recovery of metals with or without irradiation was essentially identical. The ligand strength of the carbodithioates is probably sufficient to displace analyte metals from most complexes with naturally occurring organics.

C. Extraction Solvent

Early in the development of this method we utilised a bulk sample of pore water isolated from sediments of Saanich Inlet, BC. Iron concentrations were low, and consequently no precipitate formation during the complexation step was observed. Later, during the analysis of samples from a fjord on the British Columbia mainland, addition of the carbodithioates to some samples resulted in the formation of a dark precipitate which was sparingly soluble in Freon TF. It was also determined that the micro-crystalline precipitate was soluble in chloroform, ruling out the remote possibility that the material was an authigenic mineral such as a sulfide of iron. Examination of this material using SEM-EDX revealed only peaks for iron and sulfur. Synthesis of an identical material using Fe(II) and the ligand mixture in the laboratory led us to conclude that the unknown was an iron-carbodithioate complex (Fig. 1). As we felt this material might provide a medium for coprecipitative losses of trace-metal analytes we undertook experiments to determine the quantity of chloroform which could be added to the Freon to maintain solubility of the iron complex. It was found that a 9:1 solution of $CHCl_3$ provided sufficient solubility for the highest concentrations encountered in the estuarine pore waters. This quantity of the more polar solvent was insufficient to elevate reagent blanks and did not reduce the efficacy of the extraction. Pore waters containing up to 800 μM (44.8 mg kg^{-1}) Fe were extracted successfully for the determination of five trace elements.

D. Analytical Results and Discussion

While there have been numerous reports regarding the analysis of pore waters for trace metals in the past two decades, only a few have described quantitative recoveries of cobalt, lead and zinc. In the case of lead and zinc the primary obstacle to accurate data was high blanks due to contamination from plastics and/or the sampling process itself. Cobalt has received little attention as a trace constituent of interstitial waters until recently *[Heggie and Lewis, 1984; Huynh-Ngoc, et al., 1989]*. In our work it was of interest to examine this element in waters obtained from mine tailings which had been deposited on the floor of a coastal British Columbia fjord, Alice Arm. Tissues of a local species of King Crab were found to have cobalt concentrations which correlated with the presence of tailings in the crab habitat.

i. Cobalt

In this work, a 13-fold concentration factor and injections of 50 μL into the carbon furnace permitted a detection limit of 0.93 nmol Co kg^{-1}. Recent reports of the determination of cobalt in interstitial water have been given by Heggie and Lewis *[1984]* and Huynh-Ngoc et al. *[1989]*. In the former case, direct injection of a 60 μL sample into a GFAAS/Zeeman system permitted an LOD of 2.5 nmol kg^{-1}. In the latter, dimethylglyoxime complexation combined with cathodic stripping voltammetry permitted much lower detection limits of about 0.018 nmol kg^{-1}. In our field studies, cobalt concentrations ranged from $\approx$ 3 to 120 nmol kg^{-1}, indicating sufficient sensitivity for this method was attained. Rutgers van der Loeff and Waijers *[1986]* reported the use of the Danielsson et al. *[1982]* procedure for the analysis of NE Atlantic pore waters but did not present values for the detection limit.

ii. Lead and Zinc

Historically, these elements have presented particular difficulties in the attainment of low analytical blanks, especially in geochemical analysis. Zinc is an ubiquitous contaminant arising primarily from catalysts used in plastics formulations. Contamination by lead arises from atmospheric input, *inter alia*, and is difficult to control without use of an ultra-clean sampling and sample processing protocol. The limits of detection for lead and zinc obtained by this procedure were determined to be 0.54 and 14.7 nmol kg^{-1}, respectively. Figure 2 illustrates a sample profile of each of these elements for pore waters from Alice Arm, British Columbia. Concentrations in these coastal conditions ranged from near detection limits to 564 and 27.3 nmol kg^{-1} for Zn and Pb, respectively.

Few recent data have been reported for these elements in interstitial water, which probably reflects the aforementioned difficulties of quality control. Table 2 lists representative data from the recent literature.

TABLE 2: RECENT LEAD AND ZINC DATA FOR GLOBAL PORE WATERS

ZINC (nM kg^{-1})	LEAD (nM kg^{-1})	LOCATION	REFERENCE
255 [a]	———	Central Pacific	Schnier, et al., 1981
0.63-39.3 [b]	———	Gulf of Thailand	van den Berg and Dharmvanij, 1984
3.8 - 225 [b]	———	Gironde Estuary France	El Ghobary, 1982
———	8 -13.5 [c]	Gulf of St. Lawrence	Gobeil and Silverberg, 1989
4.6 - 11.6 [b]	0.58 - 0.97 [b]	Swedish Coast	Westerlund et al., 1986
150 - 626 [b]	LOD - 27.3 [b]	Northern British Columbia Coast	This Work

[a] Nuclear activation analysis
[b] Extraction - GFAAS
[c] Anodic stripping voltammetry

iii. Cadmium and Copper

The LOD for copper (8.34 nmol kg^{-1}), like zinc, was high relative to the values derived for Pb, Cd and Co. Reasons for this are not clear; however it may possibly be due to differences in the complex stability constants which are seven to eight orders of magnitude greater for Pb and Co *[Scharfe, et al., 1973]*. The stability constant for the Cd-1-pyrrolidinecarbodithioate complex has not been reported in this particular medium. However, Sachinidis and Grant *[1981]* report that the constants for the DDDC complexes of Cd, Ni, Cu, Zn, Pb and Hg in dimethyl sulfoxide are in the order Hg > Cu > Ni > Pb≈ Cd > Zn.

Likussar and Boltz *[1971]* have reported extraction constants for a series of metals in water-chloroform sytems. Calculated values of K_E for 1-pyrrolidinecarbodithioate complexes were 23.7, 11.5, 13.3 and 12.6 for Cu, Co, Cd and Zn respectively. The extraction for Cu was made at a pH of 7.1 whereas the latter three metals were studied at pH values of about five.

At 0.13 nmol kg^{-1} cadmium was the most sensitive to detection of the five elements examined. It should be noted that the constant value reported *[Scharfe, et al., 1973]* for Fe^{2+} is greater than those for Cu and Zn. This would place greater emphasis upon the importance of assuring that a sufficient quantity of ligand is available to remove the relatively high quantities of the former element.

CONCLUSIONS

A Freon TF - carbodithioate extraction procedure has been developed for application to estuarine and fjord sediment interstitial waters which are characterised *(inter alia)* by higher iron concentrations, compared to open ocean water. Quantities of ligand utilised to accommodate these higher concentrations resulted in the formation of a Freon-insoluble iron complex. To forestall potential occlusion of other analytes in this precipitate the solvent properties of the Freon were optimized by the addition of chloroform. With the employment of clean sampling and separation techniques this method permits satisfactory recoveries of cadmium, cobalt, copper, lead and zinc all of which are determined by flameless AAS.

ACKNOWLEDGEMENT

We thank Dawna Brand (Biology Department, University of Victoria) for assistance in obtaining the SEM/EDX data.

REFERENCES

Boyle, E.A. and J.M. Edmond. 1977. Determination of copper, nickel and cadmium in sea water by APDC chelate coprecipitation and flameless atomic absorption spectrometry. Anal. Chim. Acta, **91**:189-197.

Danielsson, L-G., B. Magnusson, and S. Westerlund. 1978. An improved metal extraction procedure for the determination of trace metals in sea water by atomic absorption spectrometry with electrothermal atomisation. Anal. Chim. Acta, **98**:47-57.

Danielsson, L-G., B. Magnusson, S. Westerlund, and K. Zhang. 1982. Trace metal determination in estuarine waters by electrothermal atomic absorption spectrometry after extraction dithiocarbamate complexes into Freon. Anal. Chim. Acta, **144**:183-188.

El Ghobary, H. 1982. Fe, Mn, Cu and Zn in interstitial water of near-shore sediments. Mar. Geol., **47**:M11-M20.

Gobeil, C., N. Silverberg, B. Sundby, and D. Cossa. 1987. Cadmium diagenesis in Laurentian Trough sediments. Geochim. Cosmochim. Acta, **51**:589-596.

Gobeil, C. and N. Silverberg. 1989. Early diagenesis of lead in Laurentian Trough sediments. Geochim. Cosmochim. Acta, **53**:1889-1895.

Heggie, D. and T. Lewis. 1984. Cobalt in pore waters of marine sediments. Nature, **311**:453-455.

Heggie, D., D. Kahn, and K. Fischer. 1986. Trace metals in metalliferous sediments, MANOP Site M: interfacial pore water profiles. Earth Planet. Sci. Lett., **80**:106-116.

Huynh-Ngoc, L., N.E. Whitehead, and M. Boussemart. 1989. Dissolved nickel and cobalt in the aquatic environment around Monaco. Mar. Chem. **26**:119-132.

Kinrade, J.D. and J.C. Van Loon. 1974. Solvent extraction for use with flame atomic absorption spectrometry. Anal. Chem., **46**:1894-1898.

Likussar, W. and F. Boltz. 1971. Spectrophotometric determination of extraction constants for certain metal 1-pyrrolidine carbodithioates. Anal. Chem., **43**:1273-1277.

Lyons, W.B., K.M. Wilson, P.B. Armstrong, G.M. Smith, and H.E. Gaudette. 1980. Trace metal pore water geochemistry of nearshore Bermuda carbonate sediments. Oceanologica Acta, **3**:363-367.

Murray, J.W., V. Grundmanis, and W.M. Smethie Jr. 1978. Interstitial water chemistry in the sediments of Saanich Inlet. Geochim. Cosmochim. Acta, **42**:1011-1026.

Mallissa, H. and E. Schoeffmann. 1955. Über die Verwendung von substitutierten Dithiocarbamaten in der Mikroanalyse. III. Mikrochim. Acta, **1**:187-202.

Pedersen, T.F. 1985. Early diagenesis of copper and molybdenum in mine tailings and natural sediments in Rupert and Holberg Inlets, British Columbia. Can. J. Earth Sci., **22**:1474-1484.

Reimer, K.J. and J.A.J. Thompson. 1988. Arsenic speciation in marine interstitial water. The occurrence of organoarsenicals. Biogeochem., **6**:211-237.

Rutgers van der Loeff, M.M. and D.A. Waijers. 1986. In: Application of Distribution Coefficients to Radiological Assessment Models, T.H. Sibley and C. Myttenaere, Eds., Elsevier, Amsterdam, 181-191.

Sachinidis, J. and M.W. Grant. 1981. Metal exchange reactions between divalent metal ions and their dithiocarbamate complexes in dimethyl sulfoxide: a kinetic and mechanistic study. Aust. J. Chem., **34**:2195-2215.

Sawlan, J.J. and J.W. Murray. 1983. Trace metal remobilization in interstitial waters of red clay and hemipelagic marine sediments. Earth Planet. Sci. Lett., **64**:213-230.

Scharfe, R.R., V.S. Sastri, and C.L. Chakrabarti. 1973. Stability of metal dithiocarbamate complexes. Anal. Chem., **54**:413-415.

Schnier, C., V. Marchig, and H. Gundlach. 1981. The chemical composition of sea water and pore water in the manganese nodule area of the central Pacific. Geologische Rundschau, **70**:1152-1163.

Thompson, J.A.J. and D.W. Paton. 1978. Copper in sediment interstitial waters and overlying waters of Howe Sound, B.C. Fish. Mar. Ser. Tech. Rept. (Canada), No. 775, 29p.

van den Berg, C.M.G. and S. Dharmvanij. 1984. Organic complexation of zinc in estuarine interstitial and surface water samples. Limnol. Oceanogr., **29**:1025-1036.

Westerlund, S.F.G., L.G. Anderson, P.O.J. Hall, Å. Iverfeldt, M.M. Rutgers van der Loeff, and B. Sundby. 1986. Benthic fluxes of cadmium, copper, nickel, zinc and lead in the coastal environment. Geochim. Cosmochim. Acta, **50**:1289-1296.

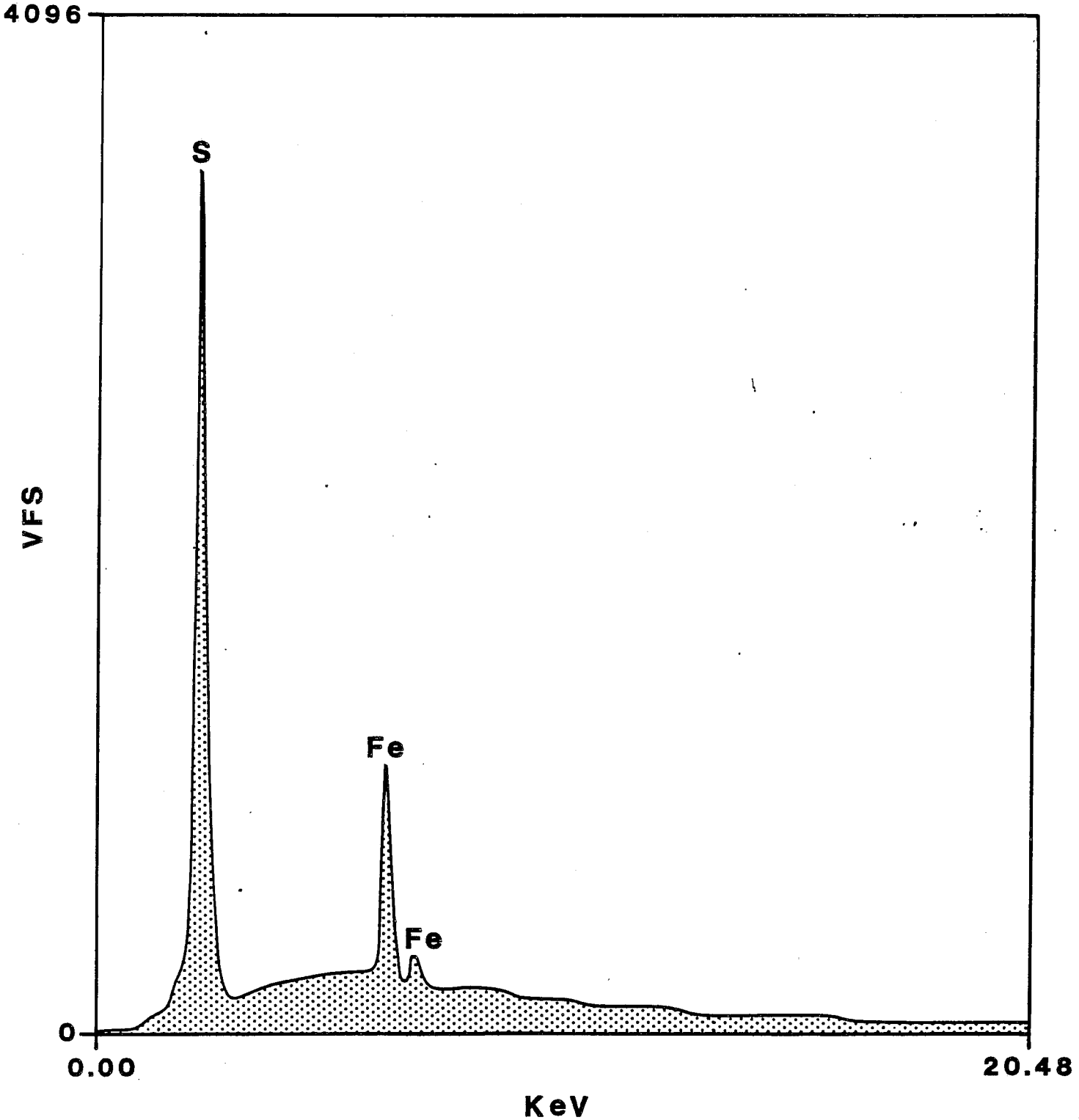

FIGURE 1:
Energy dispersive X-ray spectrum of Fe-carbodithioate complex precipitated from fjord sediment interstitial water.

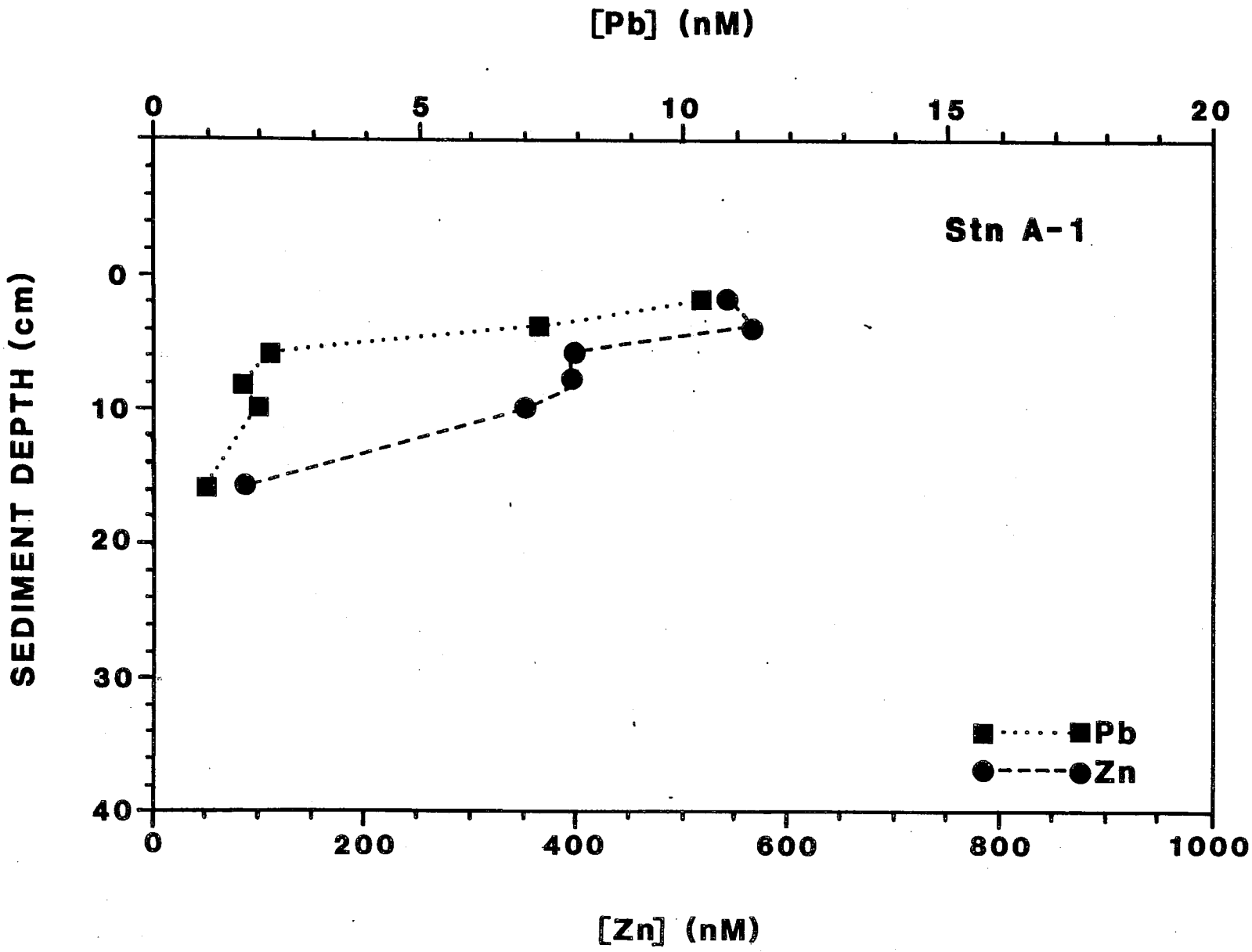

FIGURE 2:
Profiles of lead and zinc in interstitial water from surficial sediment in Alice Arm, British Columbia.