METALLIC CONTAMINANTS IN THE SEDIMENTS OF COASTAL EMBAYMENTS OF NOVA SCOTIA

D.H. Loring, R.T.T. Rantala, and T.G. Milligan

Science Branch
Maritimes Region
Fisheries and Oceans Canada
Bedford Institute of Oceanography
P.O. Box 1006
Dartmouth, Nova Scotia B2Y 4A2
Canada

1996

Fisheries   Pêches
and Oceans   et Océans

Canada

Canadian Technical Report of

Fisheries and Aquatic Sciences 2111

1996

METALLIC CONTAMINANTS IN THE SEDIMENTS OF COASTAL EMBAYMENTS OF NOVA SCOTIA

by

D.H. Loring, R.T.T. Rantala, and T.G. Milligan

Science Branch
Maritimes Region
Fisheries and Oceans Canada
Bedford Institute of Oceanography
P.O. Box 1006
Dartmouth, Nova Scotia B2Y 4A2
Canada

Printed on recycled paper

Correct citation for this publication:

Loring, D.H., R.T.T. Rantala, and T.G. Milligan. 1996. Metallic contaminants in the sediments of coastal embayments of Nova Scotia. Can. Tech. Rep. Fish. Aquat. Sci. 2111: viii + 268 p.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

ABSTRACT

Loring, D.T., R.T.T. Rantala, and T.G. Milligan. 1996. Metallic contaminants in the sediments of coastal embayments of Nova Scotia. Can. Tech. Rep. Fish. Aquat. Sci. 2111: viii + 268 p.

This report provides an assessment of the baseline levels of metallic constituents of bottom sediments in Annapolis Basin, Country Harbour, LaHave estuary, Petpeswick Inlet, St. Mary's estuary, and Liverpool, Lunenburg, Pubnico, Shelburne, and Ship Harbours. It focusses on the abundance and distribution of the following metals: Arsenic (As), Cadmium (Cd), Chromium (Cr), Cooper (Cu), Lead (Pb), Mercury (Hg), Tin (Sn), and Zinc (Zn). These metals are potentially injurious to biota and humans if present in the marine environment in sufficient concentrations. The first part of this report summarizes the abundance of trace metals in the sediments of the several harbours, estuaries, and inlets. It provides a comparative overview of the relative concentrations within each sampling site in each of the coastal embayments. The second part of the report provides more detailed information on the characteristics of each embayment and the factors that control the levels and distribution of the metals.

The results of total and fine-grained sediment analyses indicate that Lunenburg Harbour and the LaHave estuary are the most contaminated of all the embayments studied. These two embayments contain the highest concentrations of As, Cd, Cr, Cu, Hg, Pb, Sn, and Zn. Overall, cadmium is the most ubiquitous contaminant; and background levels for this metal are exceeded in a portion of the sediments in all embayments studied.

RÉSUMÉ

Loring, D.T., R.T.T. Rantala, and T.G. Milligan. 1996. Metallic contaminants in the sediments of coastal embayments of Nova Scotia. Can. Tech. Rep. Fish. Aquat. Sci. 2111: viii + 268 p.

Le présent rapport fournit une évaluation des niveaux de référence des métaux contenus dans les sédiments du fond du bassin d'Annapolis, de Country Harbour, de l'estuaire de la rivière LaHave, de l'anse Petpeswick, de l'estuaire de la St. Mary's et des ports de Liverpool, Lunenburg, Pubnico, Shelburne et Ship Harbour. Il traite essentiellement de l'abondance et de la distribution des métaux suivants: arsenic (As), cadmium (Cd), chrome (Cr), cuivre (Cu), plomb (Pb), mercure (Hg), étain (Sn) et zinc (Zn). Ces métaux sont susceptibles de nuire à la biote et aux humains s'ils sont présents dans le milieu marin en concentrations suffisantes. La première partie du rapport fait état de l'abondance des métaux-traces dans les sédiments de plusieurs ports, estuaires et anses. Il brosse un tableau comparatif des concentrations relatives à chaque site d'échantillonnage dans chacune des baies côtières considérées. La seconde partie fournit des renseignements plus détaillés sur les caractéristiques de chaque baie et sur les facteurs qui régissent les concentrations et la distribution des métaux.

Il ressort des analyses des sédiments totaux et des sédiments à grains fins que le port de Lunenburg et l'estuaire de la rivière LaHave sont les plus contaminés des lieux étudiés. Ce sont eux qui présentent la plus forte concentration d'As, de Cd, de Cr, de Cu, d'Hg, de Pb, de Sn et de Zn. Dans l'ensemble, le contaminant le plus répandu est le cadmium, les niveaux naturels de ce métal étant dépassés dans une partie des sédiments de toutes les baies étudiées.

INTRODUCTION

The objectives of Fisheries and Oceans Canada's Science Branch Toxic Chemicals Green Plan Project 2.2.1. are to: determine the sources and distribution of sedimentary materials and associated metals, assess the nature and extent of anthropogenic metal contributions, and estimate the potential bioavailability of metallic contaminants in coastal embayments of Nova Scotia.

In many coastal regions adjacent to industrial urban areas, sediments are the largest repository for, and potential source of, metallic contaminants in the marine environment. Relatively little is known about the levels and distribution of contaminants in Nova Scotian coastal sediments, especially those receiving urban and industrial wastes. The metallic constituents of sediments are of particular interest in respect to the protection and rehabilitation of estuaries and harbours and as indicators of the presence of other contaminants.

Natural sediments in harbours and inlets may be regarded as a mixture of inorganic and organic material of a wide range of particle sizes and composition that has reached its depositional site either in the form of solid particles (i.e., detrital material) or in solution (i.e., non-detrital material). Contributions of material and contaminants can also be made by anthropogenic activities, including the discharge of effleunts and other wastes directly, or indirectly, to the marine environment. Water and wind erosion of refuse dumps and mine wastes are important sources of metal-rich solid particles that can be carried in the aquatic system by surface runoff. Precipitation products and adsorbed substances are often formed from dissolved constituents as a result of physico-chemical conditions in the receiving water. Thus, metals in sediments can originate from four sources: 1) geological weathering, 2) environmental releases from industrial processing activities, 3) leaching of metals from garbage and other solid wastes, and 4) discharges of animal and human sewage.

This report provides an assessment of the baseline levels of metallic constituents of bottom sediments in Annapolis Basin, Country Harbour, LaHave estuary, Petpeswick Inlet, St. Mary's estuary, and Liverpool, Lunenburg, Pubnico, Shelburne, and Ship Harbours (Fig. 1). It focuses on the abundance and distribution of the following metals: Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Tin (Sn), and Zinc (Zn). These metals are potentially injurious to biota and humans if present in the marine environment in sufficient concentrations.

The first part of this report summarizes the abundance of trace metals in the sediments of the several harbours, estuaries, and inlets. It provides a comparative overview of the relative concentrations within each sampling site in each of the coastal embayments. The second part of the report provides more detailed information on the characteristics of each embayment and the factors that control the levels and distribution of the metals.

In addition to the metal analyses discussed in the body of this report, some measurements of other trace elements have been made using Inductively-Coupled Plasma Mass-Spectrometry (ICP-MS). These measurements have merely been tabulated in Appendix I to this report.

In addition to the metal analyses discussed in the body of this report, some measurements of other trace elements have been made using Inductively-Coupled Plasma Mass-Spectrometry (ICP-MS). These measurements have merely been tabulated in Appendix I to this report.

MATERIALS AND METHODS

SAMPLING

Sediment samples were collected in the Annapolis Basin (21 surface samples in the outer reaches) in 1988, Country Harbour (28 surface samples) in 1992, LaHave estuary (16 surface samples and 3 cores) in 1992, Liverpool Bay and Harbour (16 surface samples) in 1992, Lunenburg Harbour (16 surface samples and 3 cores) in 1992, Petpeswick Inlet (12 surface samples) in 1994, Pubnico Harbour (12 surface samples) in 1993, Shelburne Harbour (35 surface samples) in 1993, Ship Harbour (16 surface samples) in 1991, and St. Mary's estuary (14 surface samples) during 1992. These samples were collected from sites having water depths of 1 to 30 m with a hand-held modified Eckman grab using a motorized Boston Whaler, except in Annapolis Basin where the samples were collected with a Van Veen bottom grab from the research vessel C.S.S. *Dawson* in 1988. A 5-g portion at the top surface of the grabs was removed using a 50-mL syringe or a plastic spoon and placed in a numbered plastic bag, frozen or cooled, and returned to the laboratory for chemical and sedimentological analyses. Sediment cores were obtained at selected intervals along longitudinal sections in the LaHave estuary and Lunenburg Harbour. Cores 14 to 20 cm in length were obtained by divers inserting 30-cm plastic core liners (7 cm in diameter) into the sea floor. The core tubes were capped immediately following coring. Samples were kept cool, transported in a vertical position to the laboratory, and frozen immediately. In the laboratory, the cores were thawed and split. One-half of the core was sampled and the other half was archived.

GRANULOMETRIC ANALYSES

The amount of material of size <63 μm was determined gravimetrically after wet sieving of the sample in all cases except for the samples obtained from Ship Harbour. The sediment textural classification used is that defined by Nota and Loring (1964) and is based on the proportions of sand (particles >63 μm) and mud (particles <63 μm) in each sample. Sediments containing >95% weight of material having grain-size >63 μm are referred as **sands**. Those containing >95% weight of material <63 μm are referred as **muds**. Sediments containing 5-30% by weight of sands or muds are designated **sandy** or **muddy** respectively. If the two components both represent more than 30% by weight, the finer-grained component is indicated by a noun, the other by an adjective with the adverb **very**, e.g. **very sandy mud.** For the purposes of this study, sediments containing >70% by weight of material <63 μm has been used to determine the metal concentrations in the **fine-grained sediments** from each area.

COULTER COUNTER ANALYSES

Disaggregated inorganic grain-size spectral analyses were determined by electro-resistance particle sizing using the techniques described by Milligan and Kranck (1992). Sample analyses were carried out using a Coulter Multisizer IIE for all embayments except for those from Annapolis Basin which were analyzed with a model TAII Coulter Counter. Subsamples were digested in an excess of 35% H_2O_2 and suspended in 1% NaCl before disaggregation with a sapphire-tipped sonic probe. As part of the digestion process, weight loss of organic material was calculated and is reported as % organic material in the tables. Results were plotted as frequency distributions, or frequency spectra, of $\log_{10}$ equivalent weight % of sediment, determined from the volume in logarithmically equal size classes using a specific gravity of 2.65 kg·m^{-3}. The size distribution data have been normalized to the total mass over the size range analyzed. Size classes were 1/5 φ diameter doubling every five channels for the Multisizer analyses and 1/3 φ for the Annapolis samples. Modal diameters were determined from the channel in which the greatest volume occurred, and the <63-μm value has been determined by summing the values in the size classes below the 64-μm channel.

CHEMICAL ANALYSES

The samples for chemical analyses were initially stored in plastic vials, homogenized, and oven dried at 60°C. A portion of the dried sample was removed for Hg analysis and the remainder redried at 110°C for chemical and sedimentological analyses. One portion of the oven-dried material was used for total metal analysis. Total Al, Cd, Cr, Cu, Fe, Li, Mn, Ni, Pb, V, and Zn concentrations were determined on a dried sample (0.2 g) by atomic absorption spectrophotometry (AAS) techniques described by Loring and Rantala (1992) after digestion with a combination of hydrofluoric acid and aqua regia in a microwave oven (Rantala and Loring 1989).

Mercury (Hg) was determined using a cold-vapour atomic absorption technique (Hatch and Ott 1968) described in detail by Loring and Rantala (1992). The relative accuracies for the determinations of elements were within the standard deviations of the certified values for the NRCC sediment reference materials MESS-1, BCSS-1, PACS-1, and BEST-1 (Hg only).

Determinations of As and Sn are not readily amenable to AAS measurements. These elements were determined using Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS). In addition, a selected number of samples were analyzed for other metals by ICP-MS for comparative purposes. ICP-MS metal determinations were carried out following HF/HNO$_3$/perchloric acid digestion of a 0.5 g sample by Fenwick Laboratories (Halifax, N.S.) under contract. NRCC-certified reference materials were submitted and analyzed for quality assurance purposes along with the samples.

Readily oxidizable organic matter (OM) was determined for a number of samples on a separate portion of the sediment by the wet oxidation method using cold H_2SO_4 as described by Walkey (1974).

CHEMICAL PARTITIONING

Partitioning of the total metal concentrations into their acetic acid (HOAc) soluble and insoluble contributions allows some deductions to be made regarding the site of their structural position in the sediments as well as the sources and the pathways by which they have entered the marine environment. For selected core and surface sediment samples, acetic acid (25% v/v HOAc) soluble and insoluble fractions of Ca, Mg, Fe, Mn, Cd, Cr, Cu, Pb, and Zn were determined using the extraction procedures described by Loring and Rantala (1992). As reference materials do not exist for metals in the operationally defined acetic acid soluble fraction, the accuracy of these results is not determinable.

The weak acid insoluble contribution, referred to here as the detrital fraction, represents that portion of the total metal concentration held in the lattices of silicate minerals, discrete oxides, sulphide minerals, and authigenic acetic acid insoluble minerals and compounds (Hirst 1962; Loring 1978; 1979). The weak acid soluble fraction, referred to here as the non-detrital fraction, is considered to represent that proportion of the metal held in carbonates, easily soluble amorphous compounds of Fe and Mn, adsorbed form and ion-exchange positions, and/or weakly attached to organic matter. Accordingly, this fraction is assumed to be potentially available to biota.

GEOCHEMICAL DATA ANALYSES

Grain Size Parameters

Sediments can be characterized by the manner in which the sedimentary material was deposited. Sediment particle size distribution is a function of physical transport processes. A record of those processes will be preserved in the sediments and can be deciphered based on an understanding of the particle size distribution. Kranck and Milligan (1985) and Kranck (1986; 1993) have described a model which parameterizes the disaggregated inorganic grain-size distributions of bottom sediments using three variables to describe the source material, transport energy, and reworking history.

The model equation is of the form:

$$C = Qw^m e^{-Kw}$$

where C is the concentration of sediment in a class interval, Q is the intercept with the Y axis at a settling velocity of 0.01 m.s^{-1}, w is the settling velocity for the class interval calculated using the

equation derived by Gibbs et al. (1971) for quartz spheres, **m** is the slope of the distribution and is related to the size distribution of the source material, and **K** defines the fall off at the coarse end of the distribution and has units of inverse settling velocity. Using this model, bottom sediments can be examined in terms of their formation from a flocculated suspension and subsequent reworking. Size spectra can be broken down into three basic divisions: material which was deposited as aggregates or flocs; material deposited as single grains from suspension; and material moved as higher-energy bottom load (Fig. 2). The floc portion of the sediment occurs as a flat tail of fine particles, normally extending below the detection limit of analysis. Sediment deposition from a flocculated suspension preserves the shape of the size distribution of the material in suspension and is derived from the source material (Kranck 1980; Kranck and Milligan 1985). The broad peak, slope=1, usually found between 10 μm and 100 μm, represents the material deposited from suspension as single grains. The third component of the sediment is material which has undergone further sorting after deposition from suspension or material that has been introduced as bed load. The steepness of the curve in this region, expressed as an integer value, termed sediment "round," indicates the degree of sorting which the single grain portion has undergone.

The erosion of terrestrial material tends to create "straight" size distributions with the amounts of material in each size class varying regularly. After being delivered to a bay or estuary by runoff or shore erosion, these straight size distributions are modified to reflect the transport energy in the water. In high-energy environments, such as rivers, the distributions can extend into coarse sand and, in extreme cases, gravels. As the turbulent energy decreases, either as a result of slowing of the river flow or transport into less dynamic deeper water offshore, the size of the material being carried in suspension will decrease. In Ship Harbour this change in transport energy can be see by comparing the size distribution of a glacial till taken from an eroding bank at the head of the Harbour and that of the bottom sediment just offshore (Fig. 3). The fine particulate material in suspension is unable to settle through the water column unless it flocculates with other particles to form large, fast-settling aggregates or marine snow. Flocculation involves all the suspended particles in proportions equal to that in which they are found in the suspension, and hence the deposits constitute an exact replica of the size distribution of that suspension on the bottom (Kranck 1980).

Statistical Analyses

The means, standard deviations, and ranges of the concentration were determined for each element in each embayment. Correlation matrices (Bonferroni corrected) and factor analyses were used to clarify the relationships between the trace metals and textural and geochemical characteristics represented, in some cases, by proxy normalizing elements. For the factor analyses, the variables are grouped on the basis of their correlation into factors that are associations of highly correlated variables. These factors are statistically the most dominant features of the data variability and are derived from correlation matrices. For this study, the principal factors (correlation matrices) are rotated to produce normal varimax orthogonal solutions. Student "t" tests were performed to compare population means among the data sets.

Normalization Procedures

Normalization procedures, using grain-size, Al, and Li (Loring 1991; 1990), are also used to clarify the inter-relationships among the trace metals and with the textural and major element chemistry of the sediment. Elevated trace metal concentrations and their geographic location can be of natural origin or partially the result of anthropogenic activities. As metals from anthropogenic sources normally accumulate together, predominantly in the fine-grained sediment fractions, examination of enrichment usually requires compensation for grain-size and mineralogical variability through the use of normalization techniques. Normalization provides a basis for discriminating, both qualitatively and quantitatively, among contributions of metals from natural and anthropogenic sources. The content of the material having grain-size <63 μm is often used for normalization because natural metal carriers are usually fine-grained (DeGroot and Zschuppe 1981; Ackermann 1980). Aluminum and lithium are also effective geochemical normalizers because they are conservative lattice constituents of fine-grained aluminosilicate minerals with which most of the metals are associated (Windom et al. 1989; Loring 1990; 1991).

SUMMARY RESULTS

ABUNDANCE AND REGIONAL DISTRIBUTIONS

Table 1 summarizes the mean concentrations of Al, As, Cd, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sn, V, and Zn in Annapolis Basin (AB), Country Harbour (CH), LaHave estuary (LA), Liverpool Harbour (LV), Lunenburg Harbour (LU), Petpeswick Inlet (PI), Pubnico Harbour (PU), Shelburne Harbour (SB), Ship Harbour (SH), and St. Mary's estuary (SM). Table 2 shows the frequency with which As, Cd, Cu, Hg, Pb, Sn, and Zn exceed normal background levels in each of the embayments based on the results of analyses of all samples taken from each of them. Figures 4 to 11 illustrate the total concentrations of As, Cd, Cr, Cu, Hg, Pb, Sn, and Zn in the total samples. The solid horizontal line in each of these figures indicates the background, or threshold for contamination, for each element in the sediments. These background levels, which are based on the variation of natural metal concentrations in marine sediments from pristine environments, are: As 20 $mg \cdot kg^{-1}$; Cd 0.3 $mg \cdot kg^{-1}$; Cu 40 $mg \cdot kg^{-1}$; Hg 0.1 $mg \cdot kg^{-1}$; Pb 40 $mg \cdot kg^{-1}$; Sn 5 $mg \cdot kg^{-1}$; and Zn 150 $mg \cdot kg^{-1}$. See Appendix II for the derivation of background levels.

REGIONAL COMPARISONS

Trace metal concentrations usually increase with decreasing grain size because most of the natural host minerals for the metals are fine-grained. Accordingly, comparisons among sediments should be made among texturally equivalent sediments. Table 3 summarizes the abundance of the trace metals in the fine-grained sediments (containing >70% material <63 μm) from each sampling site. Figures 12 to 19 illustrate the mean concentrations of As, Cd, Cr, Cu, Hg, Pb, Sn, and Zn in fine-grained sediments from each of the embayments studied, with the exceptions of Liverpool

Harbour and Annapolis Basin that do not contain sufficient fine-grained sedimentary material to provide estimates. Again, in these figures the solid horizontal line indicates the background level for each of the elements. The results of total and fine-grained sediment analyses indicate that Lunenburg Harbour and the LaHave estuary are the most contaminated of all the embayments studied. These two embayments contain the highest concentrations of As, Cd, Cr, Cu, Hg, Pb, Sn, and Zn. Overall, Cadmium is the most ubiquitous contaminant; and background levels for this metal are exceeded in a portion of the sediments in all embayments studied. The sequence of relative contamination by the metals based on a Student "t" test at the $p \leq 0.05$ level of significance is as follows:

Arsenic:	LA>CH=LU=SB=SH=SM=PI>PU=AB>LV
Cadmium:	LU>SH>SB=CH=PI=LV=LA=SM=PU>AB
Chromium:	LU=AB=LA>SH=CH=PI=PU>SM=LV=SB
Copper:	LU>LA>SH>CH=PI=SB=AB=SM=PU=LV
Mercury:	LU>LA>SB=SH=CH=LV=SM=PI=PU=AB
Lead:	LH=LU=SH=SB=CH>PU=PI=AB=LV=SM
Tin:	LU=LA=SB>PI=CH=SH=PU=SM=AB=LV
Zinc:	LU>LA>SH=CH=PI=SM=SB=PU=AB=LV

Key:
AB = Annapolis Basin
CH = Country Harbour
LA = LaHave estuary
LV = Liverpool Harbour
LU = Lunenburg Harbour
PI = Petpeswick inlet
PU = Pubnico Harbour
SB = Shelburne Harbour
SH = Ship Harbour
SM = St. Mary's estuary

DISPERSAL FACTORS

In general, the trace metals are introduced into the sediments as constituents or in association with solid inorganic and organic particles supplied from natural and anthropogenic sources or derived from solution. The mineralogy and grain size of natural sedimentary detrital minerals depend on the composition of their source rocks and the nature of weathering processes. These factors determine most of the natural abundances and distribution of heavy metals in crystalline sediments. Most of the natural concentrations of heavy metals are associated, or structurally combined, with a limited number of detrital aluminosilicate minerals such as micas, pyroxenes, amphiboles, and secondary clay minerals (Table 4). They are also found in varying amounts in discrete particles of detrital metal oxides, sulphides, and detrital carbonates. Detrital organic material in sewage and wood-processing wastes is also an important carrier of trace metals such as Cd and Hg. In most cases, as already stated, metal concentrations increase with

decreasing grain size. This factor has to be compensated (normalized) for in the comparison of sedimentary heavy metal concentrations among different areas. The general effects of high proportions of quartz, feldspar, and detrital carbonates are to dilute natural trace metal concentrations in sediments. The detrital portion of the sediment constitutes the largest reservoir and, potentially, the long-term source of supply of metals to the environment.

A small, but biologically significant, part of each total metal concentration is associated with the non-detrital fraction. Because this fraction contains weakly bound constituents, it is assumed to correspond to the proportion of the metal that is potentially readily bioavailable. This fraction contains metals that were either initially leached from source rocks or released in dissolved form from anthropogenic sources and incorporated with fine-grained inorganic and organic material during weathering, transportation, and deposition. The behaviour of non-detrital metals is determined by the salinity, pH, redox values, porosity, microbial activity, and hydrodynamics conditions in the aqueous transporting medium, the properties of the metals, the Fe, S, carbonate, and organic matter concentrations in sediments, and the nature of the particulates available for reactions.

A number of physical, chemical, hydrological, and sedimentological factors control the abundance and distribution of the trace metals in sediments found in embayments of the Nova Scotian coastline. Table 5 summarizes the role played by the inorganic and organic sedimentological components as metal carriers at the different sites. Regionally, inputs of metals from natural and anthropogenic sources and physical and chemical exchanges between particulate and dissolved phases in the water column and sediments control the abundance and distribution of the metals. Physically, fine-particle size is the dominant controlling factor at most sites. The deposition of fine-grained, metal-bearing, organic-rich particles occurs mostly at the head (landward end) of the embayments where tidal action is minimal, i.e., accumulation of fine-grained particles is directly related to the intensity of hydrodynamic activity in the embayment. Factor analyses indicate that the fine-grained sedimentation factor accounts for 50-80% of the total variance. This is because the dominant inorganic and organic metal carriers are fine-grained and small particles provide the largest surface-to-volume ratio for adsorption from solution. The metals largely remain adsorbed in the non-detrital fraction during subsequent transport and deposition as long as the physical chemical conditions remain fairly invariant. The main anthropogenic sources for metals are the disposal of metallic inorganic and organic waste products in the embayments. In some embayments, smaller amounts are contributed by wastes deposited during previous gold-mining activities. The chemical composition of glacial tills and potential source rocks for the sediments are outlined in Appendix III.

The remaining sections of this report present and discuss the results of the sediment surveys of each of the embayments.

Table 1

Summary of Geochemical Data for Nova Scotian inlets and harbours

Concentrations in mg kg^{-1} except percent by weight (%) for Al and Fe

		n	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Ni	Pb	Sn	V	Zn
AB	AVG	21	4.26	5	0.04	76	12	2.10	0.02	24	544	17	16	1.7	55	39
	SD		0.31	1	0.01	39	2	0.37	0.01	2	112	1	1	0.4	10	5
CH	AVG	28	5.52	15	0.41	59	18	2.55	0.05	49	486	21	25	2.4	67	70
	SD		0.71	5	0.18	16	6	0.56	0.02	11	86	5	7	0.6	19	17
LA	AVG	35	6.25	21	0.27	75	31	3.46	0.12	56	661	22	45	4.8	86	96
	SD		0.44	9	0.11	15	15	0.95	0.09	9	223	6	22	2.1	22	38
LV	AVG	12	4.35	4	0.30	30	7	1.22	0.05	22	732	12	15	1.6	27	32
	SD		0.43	1	0.28	6	4	0.25	0.03	4	320	3	3	0.6	7	15
LU	AVG	14	6.24	14	1.31	83	58	3.45	0.22	55	612	27	42	5.4	81	59
	SD		0.52	5	0.50	13	27	0.79	0.12	8	40	6	17	2.2	15	70
PI	AVG	15	4.29	8	0.41	52	16	2.25	0.03	33	495	20	19	2.7	59	57
	SD		0.83	3	0.35	16	6	0.68	0.02	11	217	8	9	0.5	21	28
PU	AVG	12	5.04	6	0.19	43	9	2.14	0.02	29	600	18	20	2.0	47	42
	SD		0.36	1	0.09	10	1	0.28	0.01	4	196	3	3	0.7	7	7
SB	AVG	32	4.66	14	0.48	28	16	1.80	0.06	33	625	16	29	3.9	43	44
	SD		0.65	6	0.39	19	11	0.53	0.05	12	547	7	16	2.5	21	25
SH	AVG	24	4.49	11	0.81	64	23	2.68	0.06	39	436	27	32	2.3	61	71
	SD		0.68	4	0.44	13	5	0.54	0.03	7	56	6	9	0.6	18	19
SM	AVG	14	4.34	9	0.20	32	10	1.74	0.04	31	431	13	15	1.9	38	49
	SD		0.38	8	0.16	11	4	0.59	0.03	8	122	5	7	0.2	14	23

n = number of samples; AVG = average; SD = standard deviation
AB = Annapolis Basin; CH = Country Harbour; LA = LaHave Estuary; LV = Liverpool Harbour;
LU = Lunenburg Harbour; PI = Petpeswick Inlet; PU = Pubnico Harbour;
SB = Shelburne Harbour; SH = Ship Harbour, SM = St.Marys Estuary

Table 2

Frequency Data (% of samples) for metals exceeding background levels in Nova Scotian Harbours and Inlets

	n	As	Cd	Cu	Hg	Pb	Sn	Zn
AB	21	0	0	0	0	0	0	0
CH	28	14	71	0	0	0	0	0
LA	35	51	34	31	48	49	48	0
LV	12	0	42	0	8	0	0	0
LU	14	0	86	71	71	64	57	57
PI	15	0	60	0	0	0	0	0
PU	12	0	17	0	0	0	0	0
SB	32	5	59	3	25	19	14	0
SH	24	0	92	0	17	17	0	0
SM	14	8	29	0	7	0	0	0
Contaminant Levels:	20		0.3	40	0.1	40	5	150 mg kg^{-1}

n = number of samples.

AB = Annapolis Basin; CH = Country Harbour; LA = LaHave Estuary; LV = Liverpool Harbour; LU = Lunenburg Harbour; PI = Petpeswick Inlet; PU = Pubnico; SB = Shelburne Harbour; SH = Ship Harbour; SM = St.Marys Estuary
CH = Cd 3 samples>0.6mg kg^{-1}; LV = Cd 2 samples >0.6 mg kg^{-1}
LU = Cd 12 samples >0.6; 11>1.0 mg kg^{-1} ;PI = Cd 3 samples >0.6,1>1.0 mg kg^{-1};
SH = Cd 15 samples>0.6; 5>1.0mg kg^{-1}; SB = Cd 10 samples >0.6; 2>1.0 mg kg^{-1}

Table 3

Contaminant metal concentrations in Fine grained[a] Sediments

Concentrations in mg kg^{-1}

		n	As	Cd	Cr	Cu	Hg	Pb	Sn	Zn
CH	AVG	22	16	0.47	63	20	0.06	27	2.6	72
	SD		4	0.15	15	5	0.02	6	1.0	17
LA	AVG	20	27	0.33	84	39	0.16	58	6.0	118
	SD		6	0.10	12	11	0.09	18	1.6	25
LU	AVG	9	17	1.57	90	70	0.28	48	6.0	189
	SD		2	0.13	3	16	0.07	8	1.0	48
PI	AVG	7	11	0.68	65	21	0.04	26	2.7	81
	SD		2	0.32	6	2	0.02	6	0.5	18
PU	AVG	9	6	0.20	44	9	0.02	21	2.2	44
	SD		1	0.09	7	1	0.01	3	0.7	6
SB	AVG	18	16	0.74	43	23	0.09	38	3.4	61
	SD		5	0.25	9	8	0.04	14	1.3	11
SH	AVG	24	11	0.81	64	23	0.06	32	2.3	71
	SD		4	0.44	13	5	0.03	9	0.6	19
SM	AVG	5	19	0.38	44	14	0.08	21	1.9	72
	SD		7	0.13	4	3	0.02	5	0.2	17

[a]For sediments containing >70% material <63μm in diameter
n = number of samples; AVG = average; SD = standard deviation
CH = Country Harbour; LA = LaHave Estuary; LU = Lunenburg Harbour;
PI = Petpeswick Inlet; PU = Pubnico Harbour; SB = Shelburne Harbour;
SH = Ship Harbour; SM = St.Marys Estuary

Table 4

Relative Amounts of Selected Major and Trace elements in Common Constituents of Sediments

Mineral	Metal	Abundance			Grain Size
	X%	0.X%	0.0X%	0.00X% or less	
Quartz	Si				sand/silt
Alumino silicates	Al Si				
Feldspars					
Plagioclase*	Na Ca Al Si	K	Ba Rb Ti Mn	Zn Ni Pb Cu	sand /silt /clay
Potash Feldspar*	K Si Al	Ca Ba Sr	Rb, Ti	Pb V Zn Ni	sand /silt /clay
Micas					sand /silt /clay
Muscovite	K Al Si	Fe Li Na	Cr Mn V	Zn Sn Cu	sand /silt /clay
Biotite	K Mg Fe Ti	Ca Na Mn	Zn V Cr Li Ni		sand /silt /clay
Ferromagnesium Minerals	Fe Mg Al				sand /silt /clay
Amphiboles*	Ca Mg Fe	Ti K Mn	Zn Cr V Ni	Cu Co Pb Li	sand /silt /clay
Pyroxene*	Mg Fe Al	Ti Na Mn	Cr V Ni	Cu Co Zn Li	sand /silt /clay
Olivine	Mg Fe Al	Ni Mn	Al Cr Ti Co	Zn V Cu	sand /silt /clay
Clay Minerals					Clay (<2µm)
Illite	K Al Si	Na Fe Mg	Zn Cu Pb Li Cr V	Co Ni	Clay
Chlorite	Si Al Fe Mg	Mn	Zn V Cr Li Ni	Cu Pb Co	silt/clay
Fe Oxides**	Fe	Mn	Zn Cu Pb	Cr V	sand/ silt/ clay
Magnetite	Fe Ti Cr Al	Mn V	Zn Cu Sn Ni	Co Pb Mo	silt/ clay
Ilmenite	Fe Ti Mn	Mg Ca	Cr V Ni Co		silt/ clay
Chromite	Cr Fe Mg	Mn Zn	Cr V Ni		silt/ clay
Sulphides***	Fe Zn Cu Pb	Co Ni			Clay
Pyrite (FeS$_2$)	Fe As Cu Zn	Pb Sn			silt/ clay
Arsenopyrite	Fe As	Co Ni			silt/ clay
Chalcopyrite	Fe Cu	Sn Ni Co			silt/ clay
Galena	Pb S	As Cu Sn	Ni		silt/ clay
Sphalerite	Zn Cd As Cu	Hg Sn	Ni		silt/ clay

* Abundantly present in the clay size fraction of sediments derived from the glacial erosion of igneous rocks

** Fe oxides occur as grain coating and are soluble in HOAc

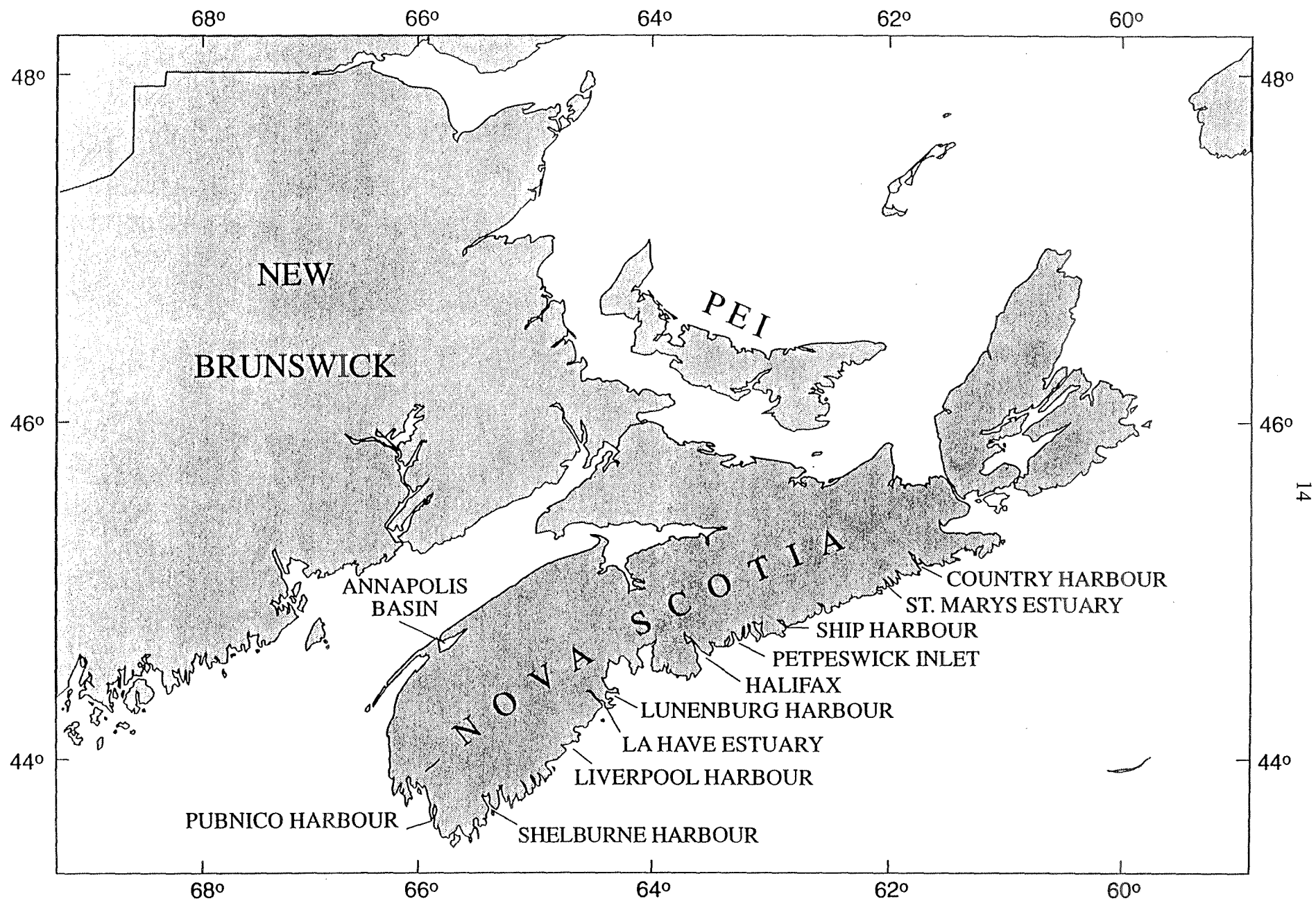*** Sulphides as inclusions in Al silicates or detrital/authigenic particles.

Table 5

Geochemical Role played by various textural, inorganic and organic components in sediments

Textural	Size Fraction (μm)	Role or Site	Metals
Sand	> 63μm	Diluent	All except Cr, Ni and Fe in AB
Mud	< 63μm	Concentrator	All except Cr, Ni and Fe in AB
Mineralogical/Chemical			
Quartz (Si)	> 63μm	Diluent	All metals
Aluminosilicates (Al)	< 63μm	Normalizer	All except Cd, Hg and Sn
Feldspars (K, Na, Ca)	> 63μm	Diluent	All metals except Al
Mica (K, Fe, Mg)	< 63μm	Li Normalizer /Carrier	Cu, Cr, V, Zn
Ferromagnesian Minerals	><63μm	>63μm Carrier	Cr, Ni, V. and Fe in Ab
(Fe, Mg, Al, Si)		<63μm Carrier	all metals except Cd, Hg, and Sn
Chlorite (Fe, Mg, Al, Si)	< 63μm	Li Normalizer /Carrier	Cu, Cr, V, Zn
Clay Minerals			
Illite (K, Al, Si)	< 63μm	Li Normalizer /Carrier	Cu, Cr, V, Zn
Fe Oxides (Fe, Mn)	Grain Coatings	HOAc soluble Carrier	Cu, Pb, Zn
Fe Sulfides (Fe, S$_2$)	< 63μm	Detrital /nondetrital Carrier	Cd, Cu, Pb, Hg, Zn
Chromite (Cr)	> 63μm	Carrier:	Cr, Ni, V. and Fe in AB
	< 63μm	Carrier	Cr, Ni, V
Magnetite (Fe)	><63μm	>63μm Carrier	Cr, Ni, V. and Fe in AB
		<63μm Carrier	Cr, Ni, and V
Organic Matter (C, H, N, O$_2$)	< 63μm	Carrier	Cd, Hg, Cu, Pb, Zn

[a] AB = Annapolis Basin

Figure 1. Location Map

NEW BRUNSWICK

PEI

NOVA SCOTIA

ANNAPOLIS BASIN

COUNTRY HARBOUR
ST. MARYS ESTUARY
SHIP HARBOUR
PETPESWICK INLET
HALIFAX
LUNENBURG HARBOUR
LA HAVE ESTUARY
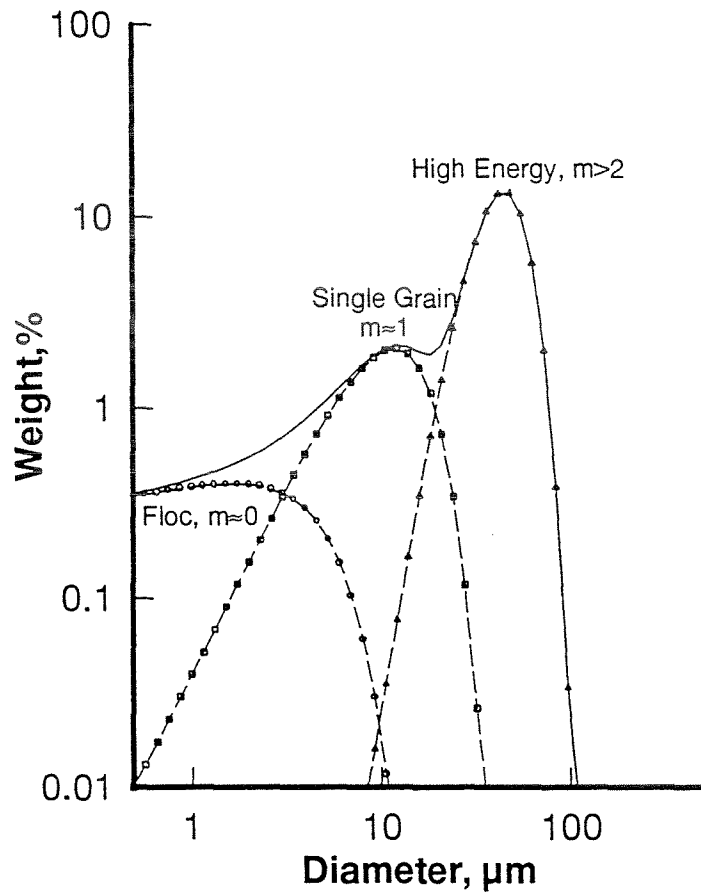LIVERPOOL HARBOUR
PUBNICO HARBOUR
SHELBURNE HARBOUR

Figure 2. Hypothetical inorganic grain size distribution (solid line) showing relative shapes of the three settling components floc tail (circles), single grain from suspension (squares) and bed load (triangles).
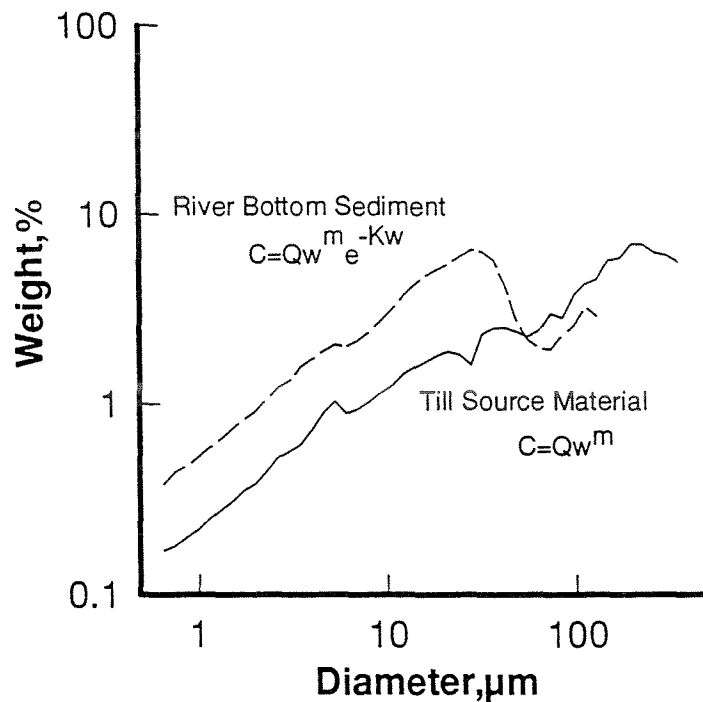

Figure 3. Disaggregated inorganic grain size distributions of till source material (solid line) and river bottom sediment (dashed line) from Ship Harbour N.S. showing fall off at coarse end. See text for explanation of equations.
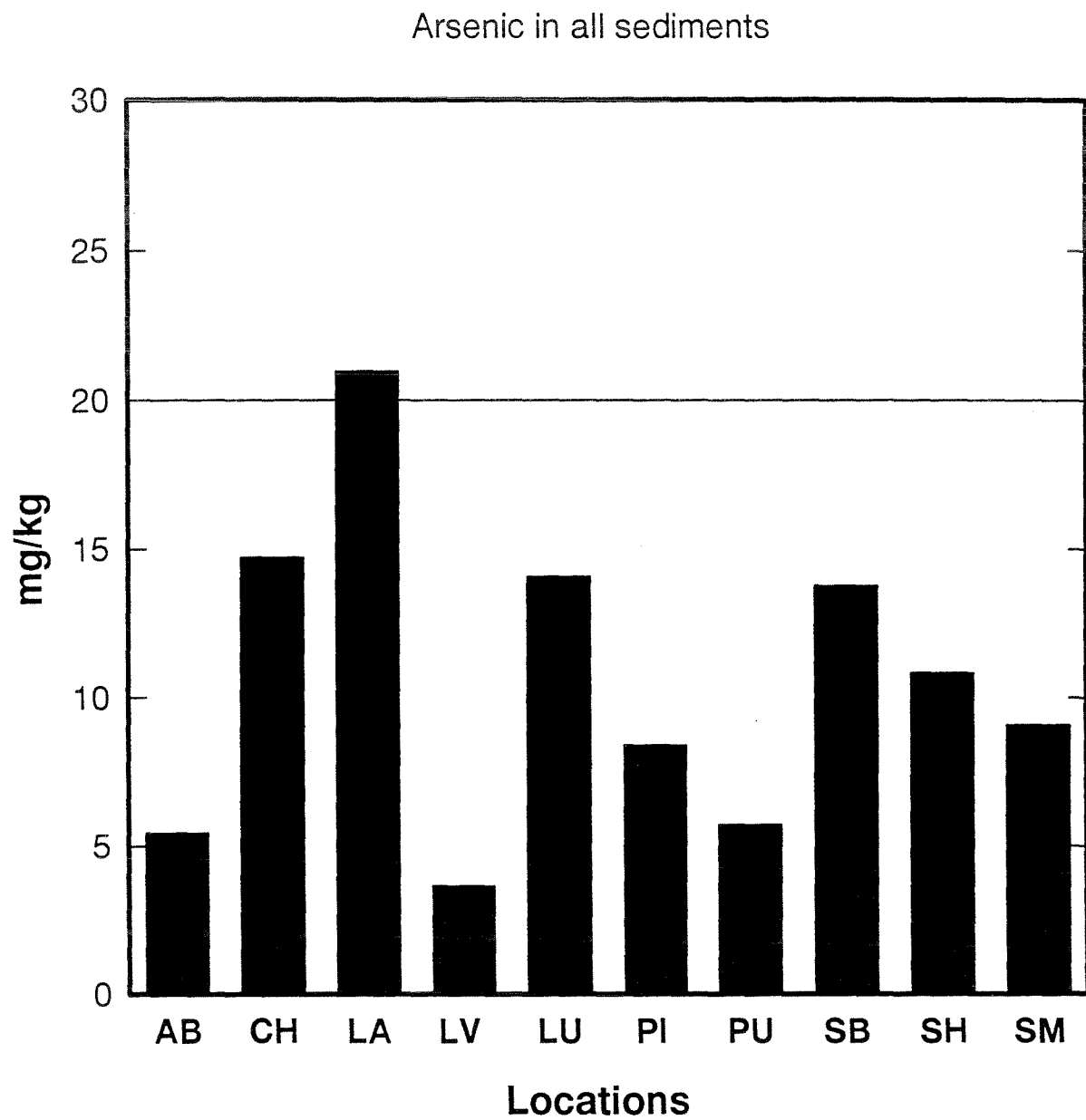
Arsenic in all sediments

Figure 4. Average arsenic concentrations in all sediment samples. The horizontal line indicates background value.
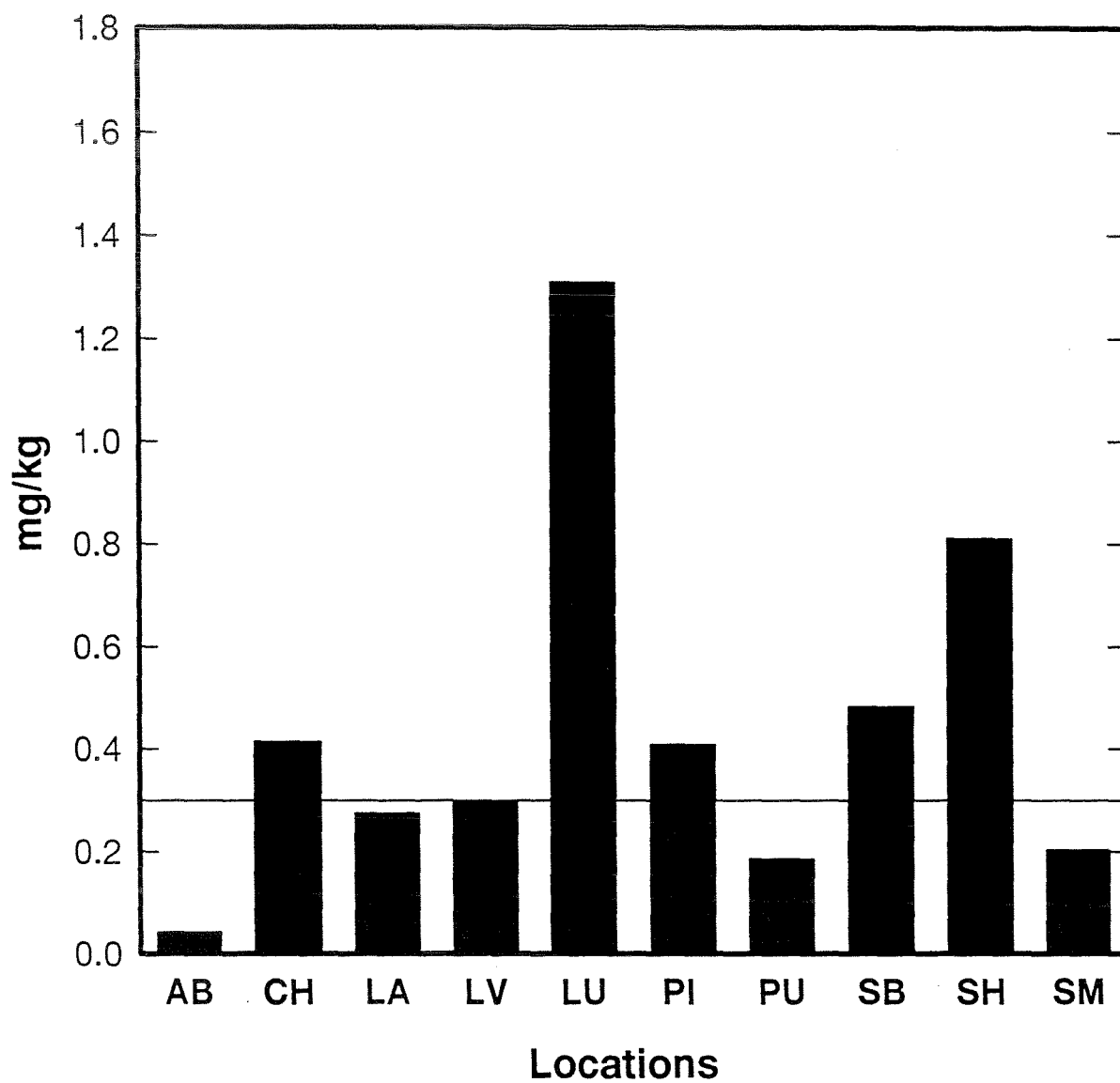
Cadmium in all sediments

Figure 5. Average cadmium concentrations in all sediment samples. The horizontal line indicates background value.
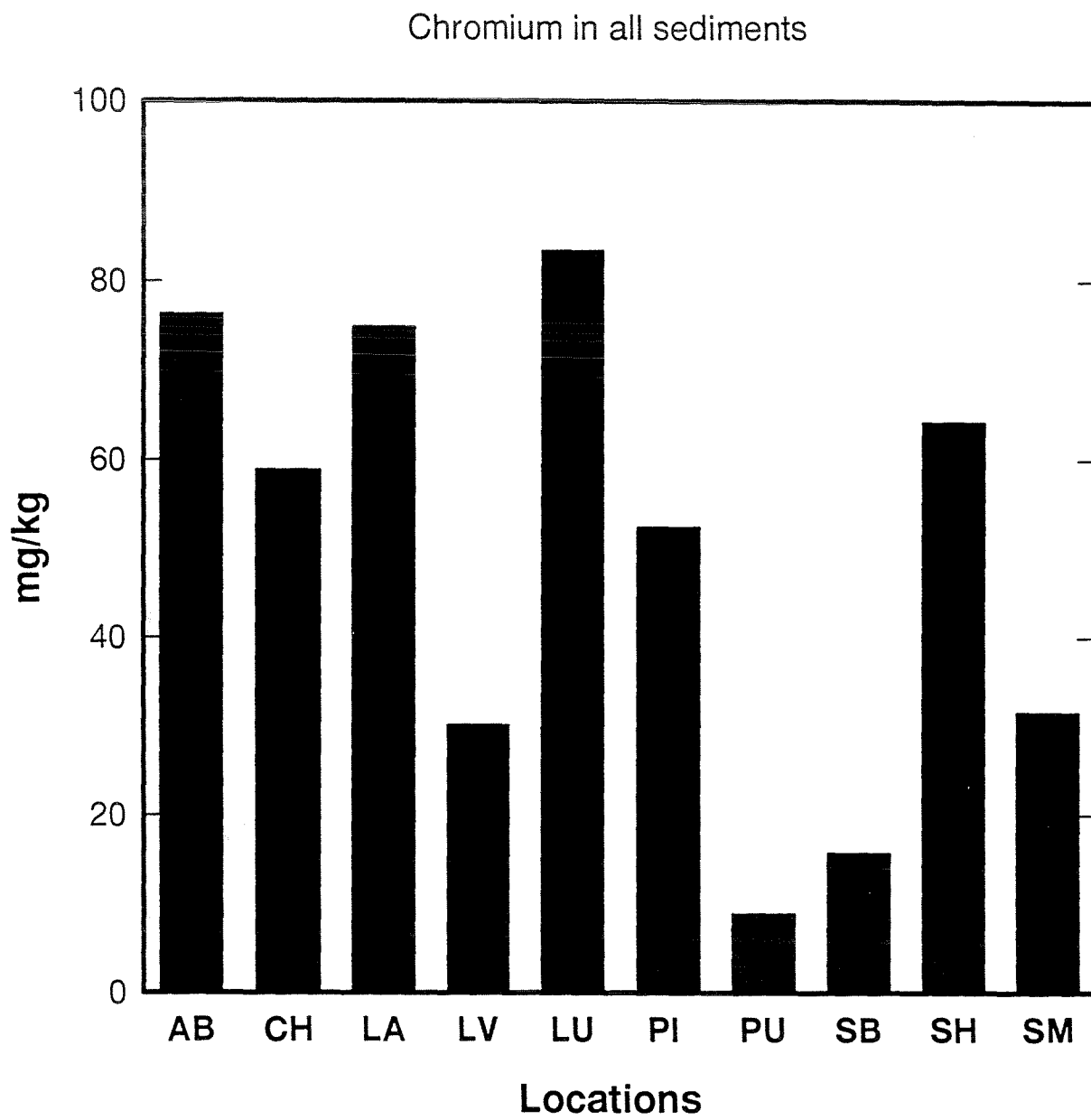
Chromium in all sediments

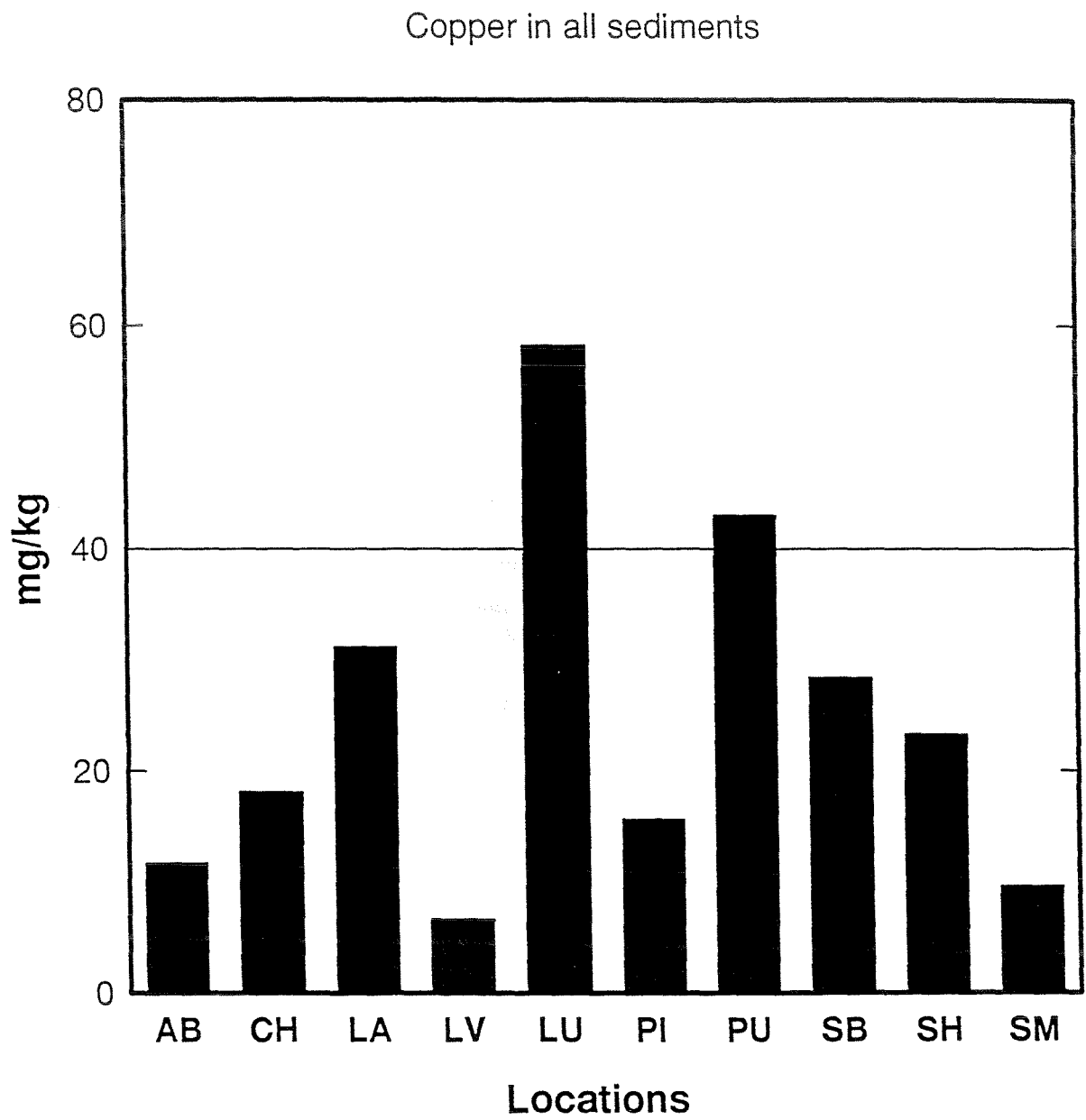**Figure 6.** Average chromium concentrations in all sediment samples.

Copper in all sediments

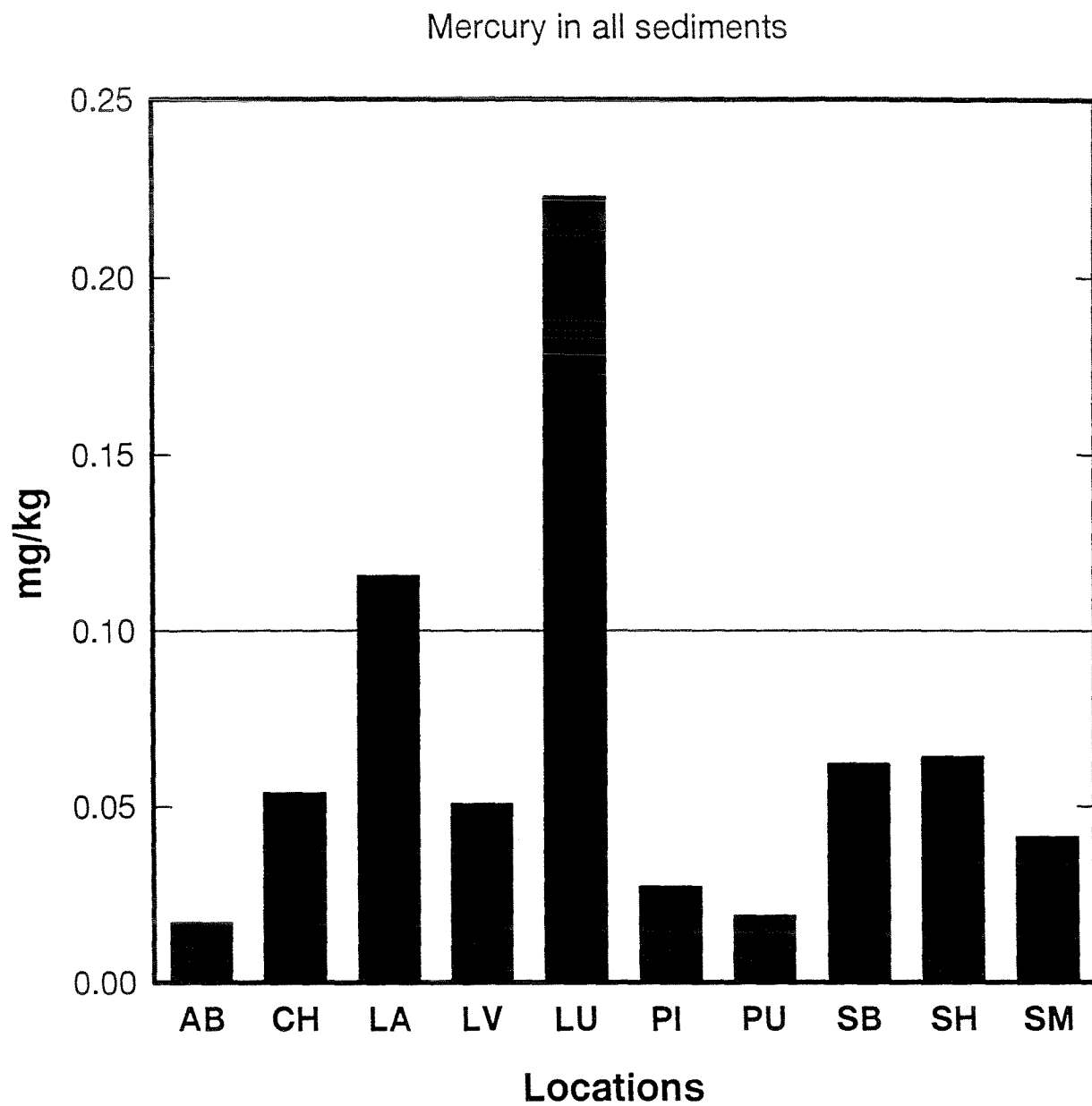**Figure 7.** Average copper concentrations in all sediment samples. The horizontal line indicates background value.

Mercury in all sediments

Figure 8. Average mercury concentrations in all sediment samples. The horizontal line indicates background value.

Lead in all sediments

Figure 9. Average lead concentrations in all sediment samples. The horizontal line indicates background value.

Tin in all sediments

Figure 10. Average tin concentrations in all sediment samples. The horizontal line indicates background value.

Figure 11. Average zinc concentrations in all sediment samples. The horizontal line indicates background value.
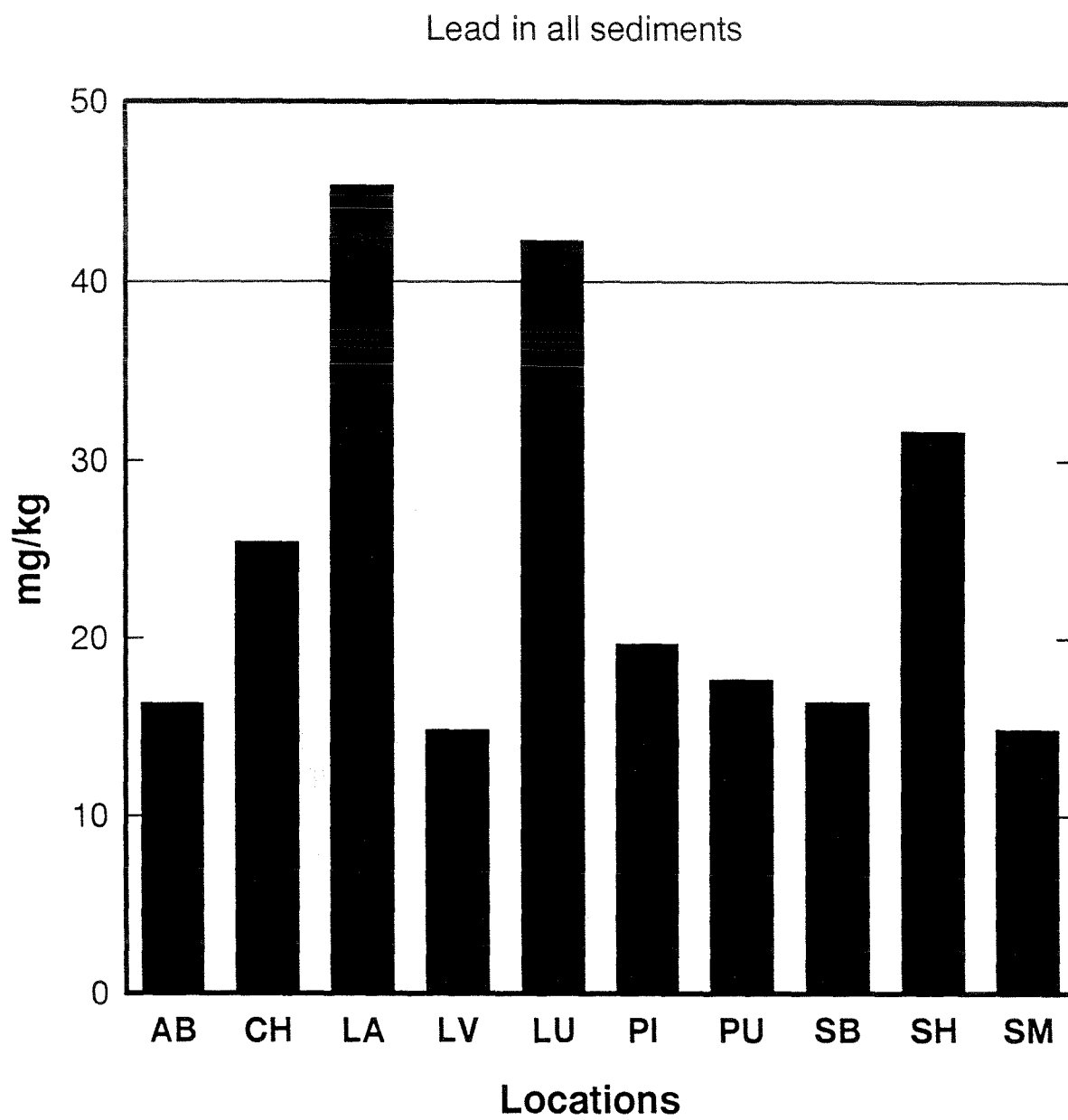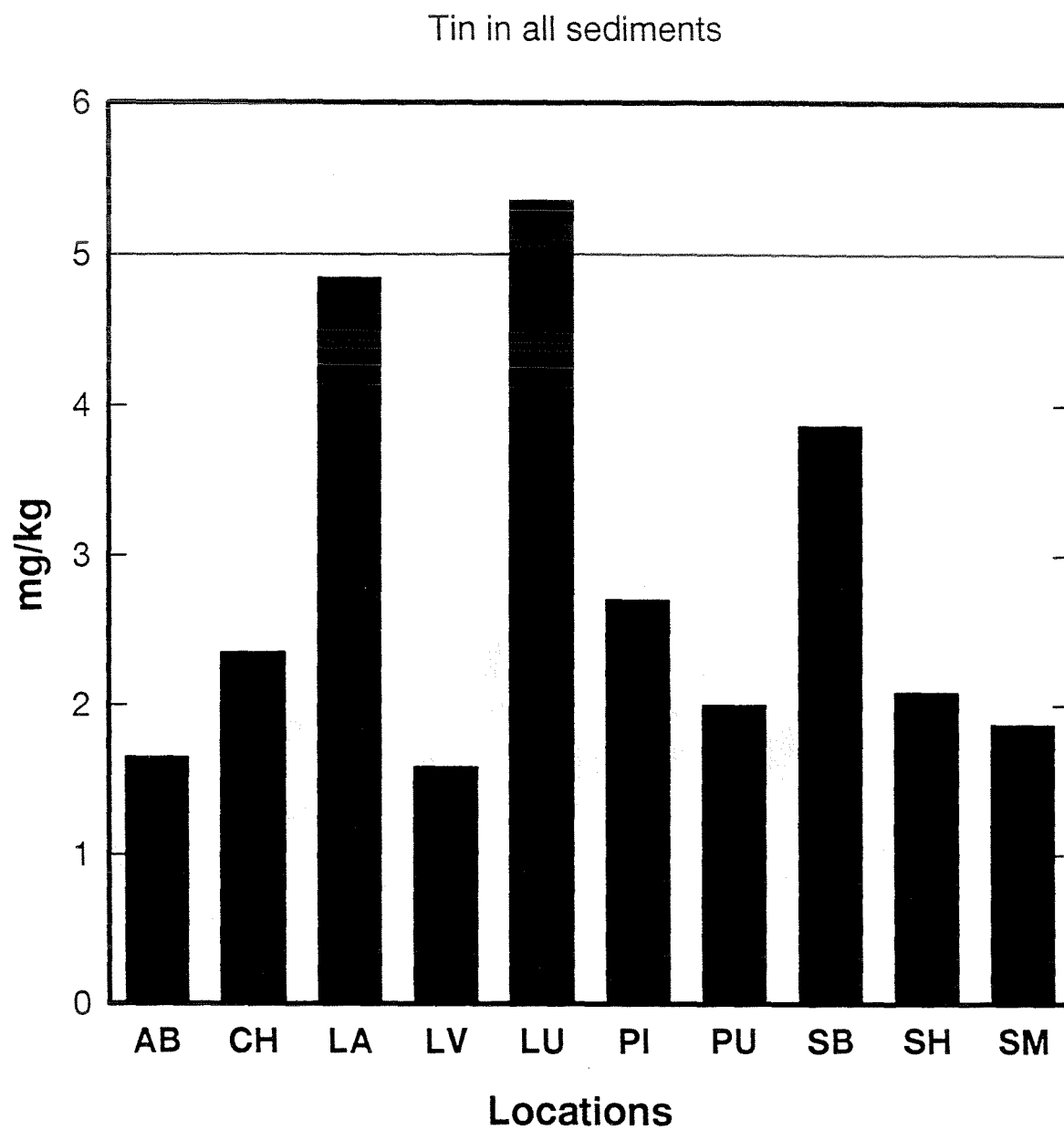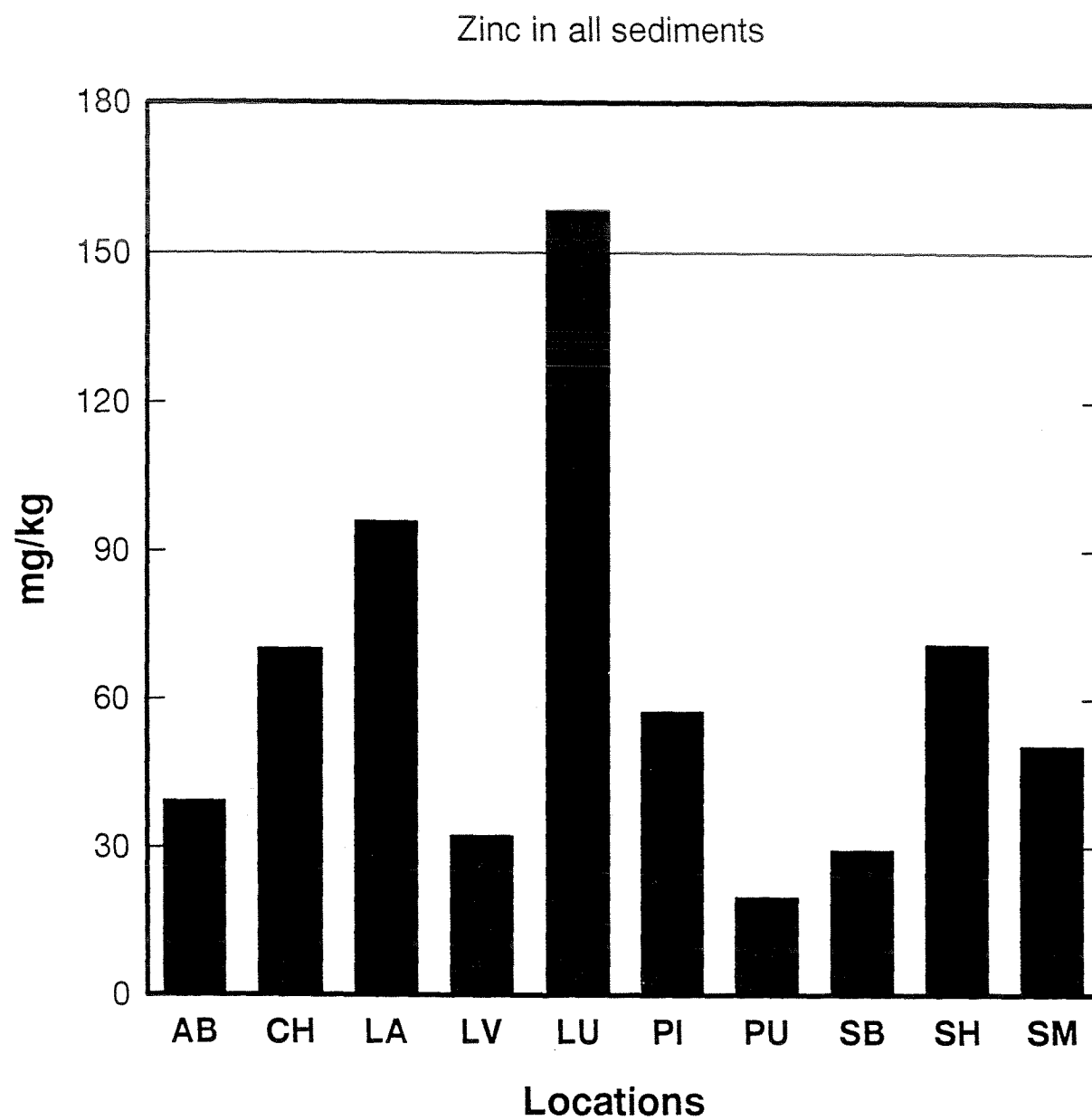
Figure 12. Average arsenic concentrations in fine-grained sediment samples. The horizontal line indicates background value.

Cadmium in fine-grained sediments

Figure 13. Average cadmium concentrations in fine-grained sediment samples. The horizontal line indicates background value.

Figure 14. Average chromium concentrations in fine-grained sediment samples.

Copper in fine-grained sediments

Figure 15. Average copper concentrations in fine-grained sediment samples. The horizontal line indicates background value.
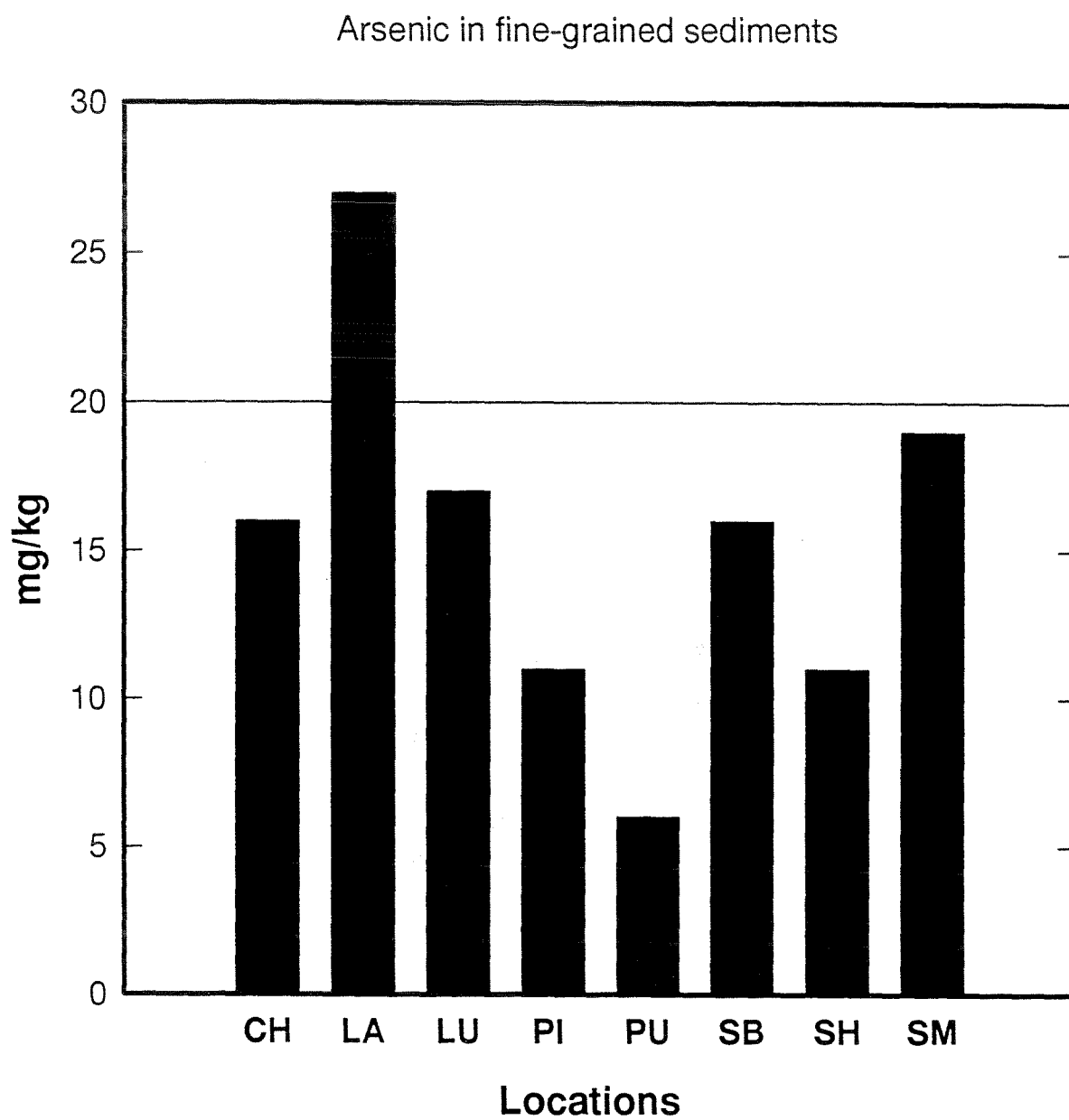
Mercury in fine-grained sediments

Figure 16. Average mercury concentrations in fine-grained sediment samples. The horizontal line indicates background value.

Figure 17. Average lead concentrations in fine-grained sediment samples. The horizontal line indicates background value.
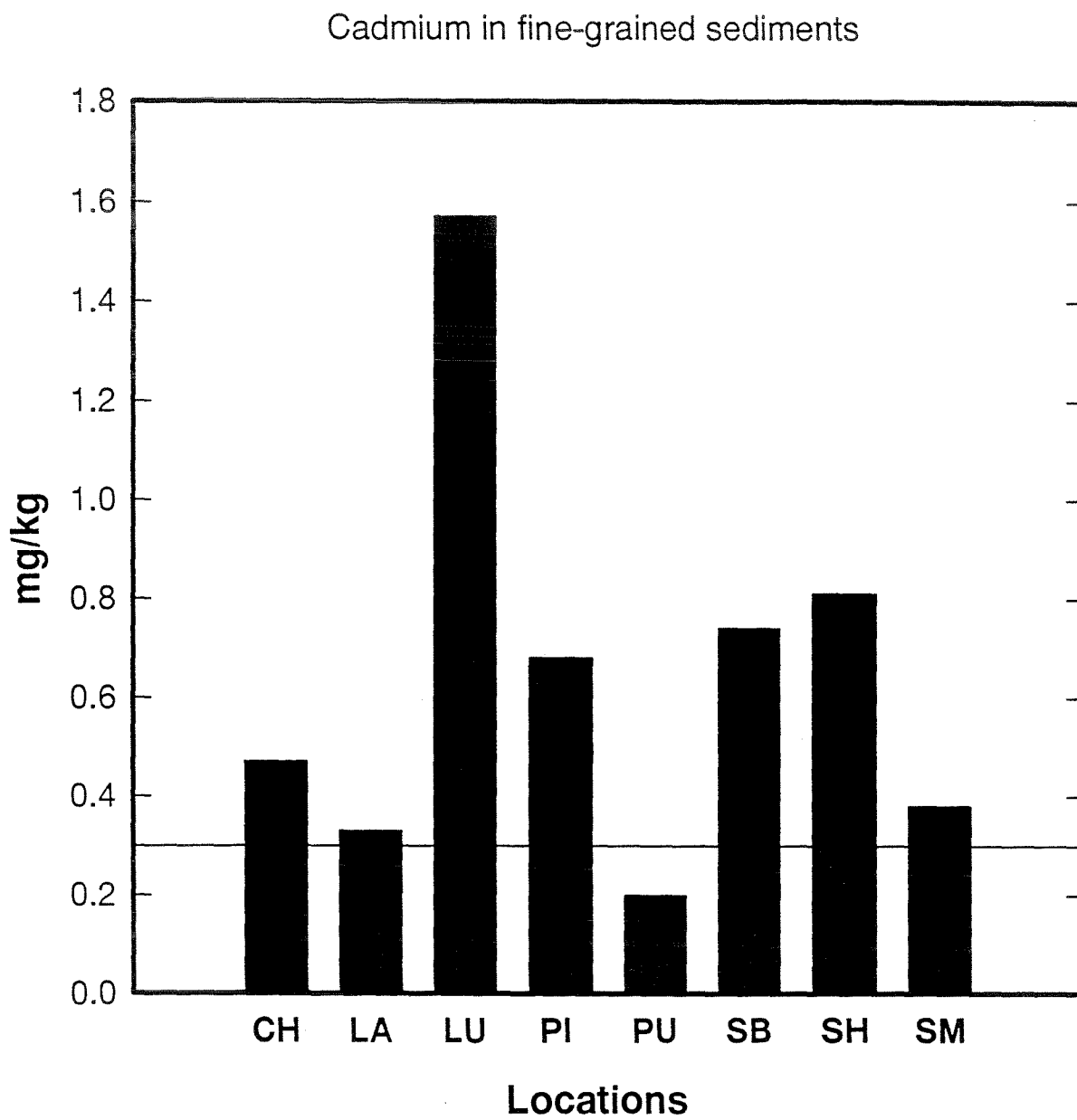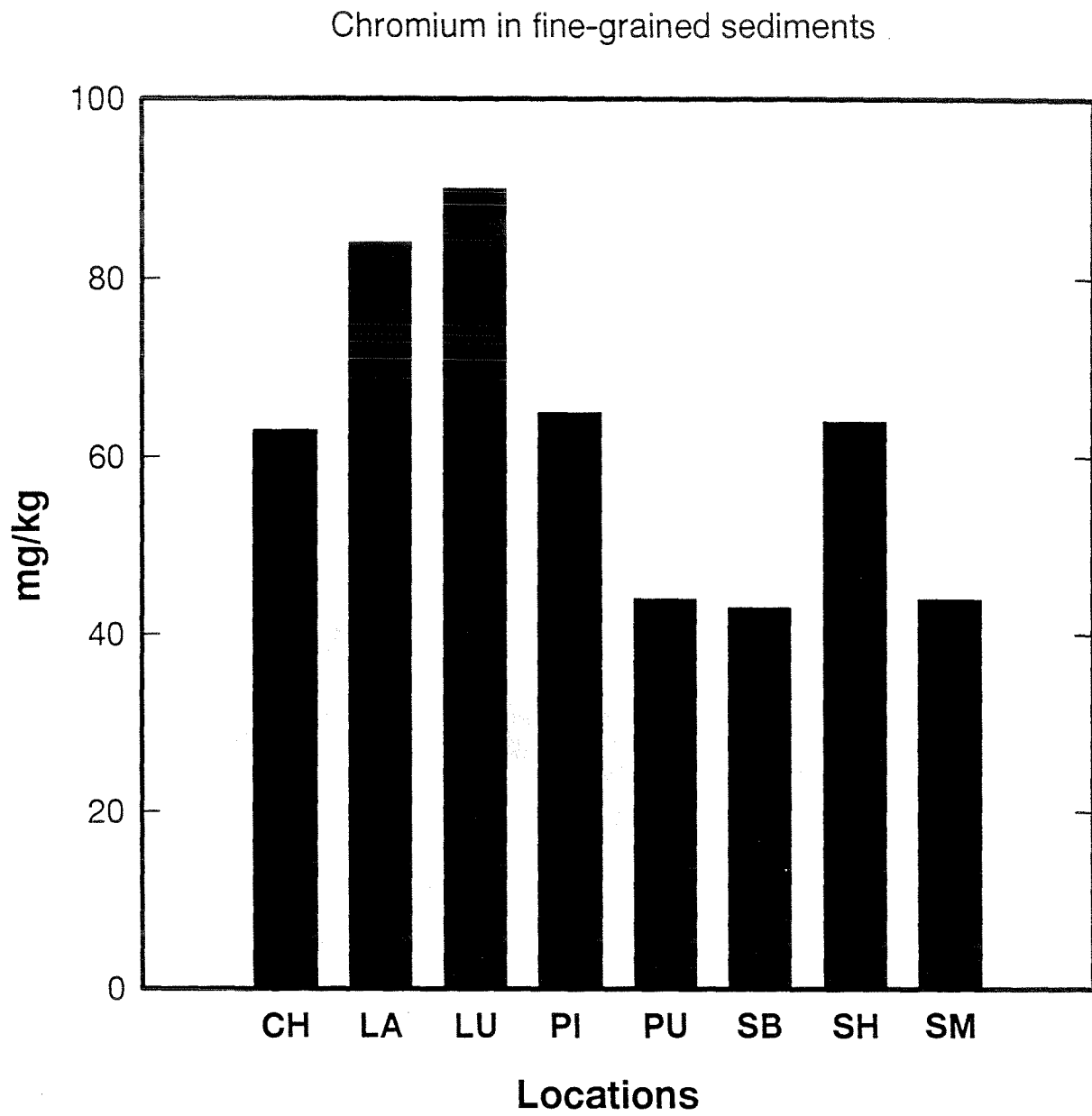
Tin in fine-grained sediments

Figure 18. Average tin concentrations in fine-grained sediment samples. The horizontal line indicates background value.

Zinc in fine-grained sediments

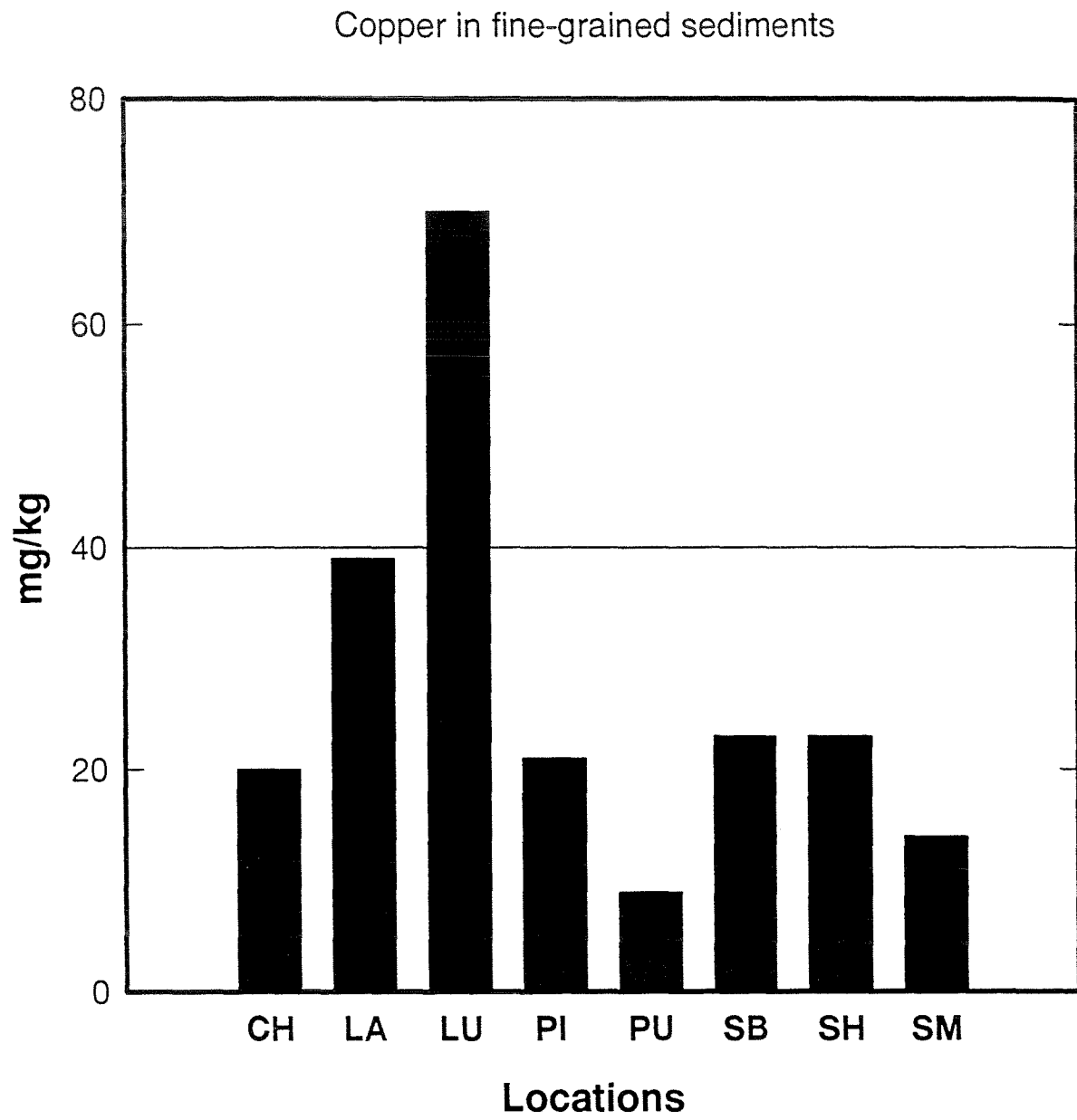**Figure 19.** Average zinc concentrations in fine-grained sediment samples. The horizontal line indicates background value.

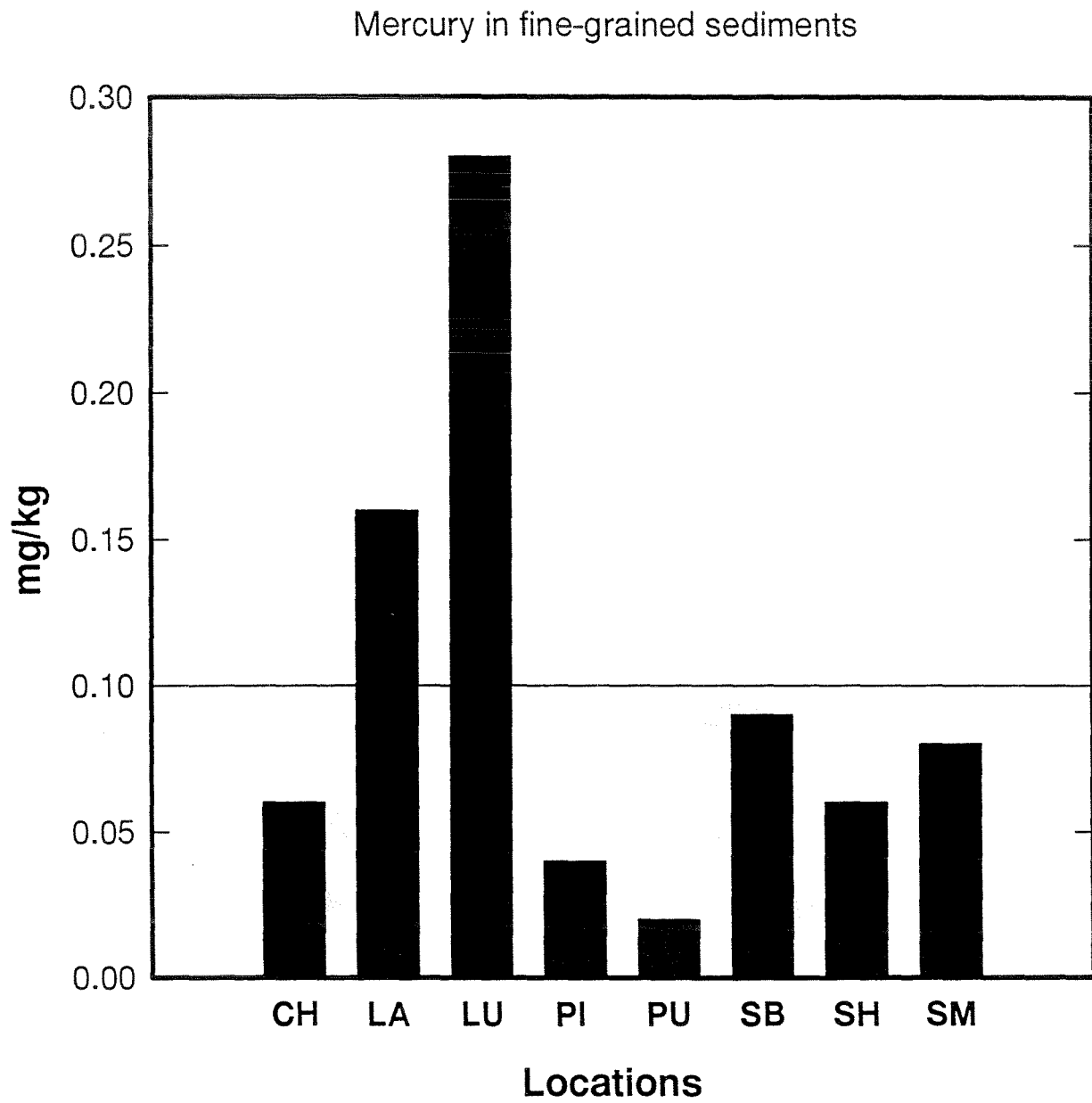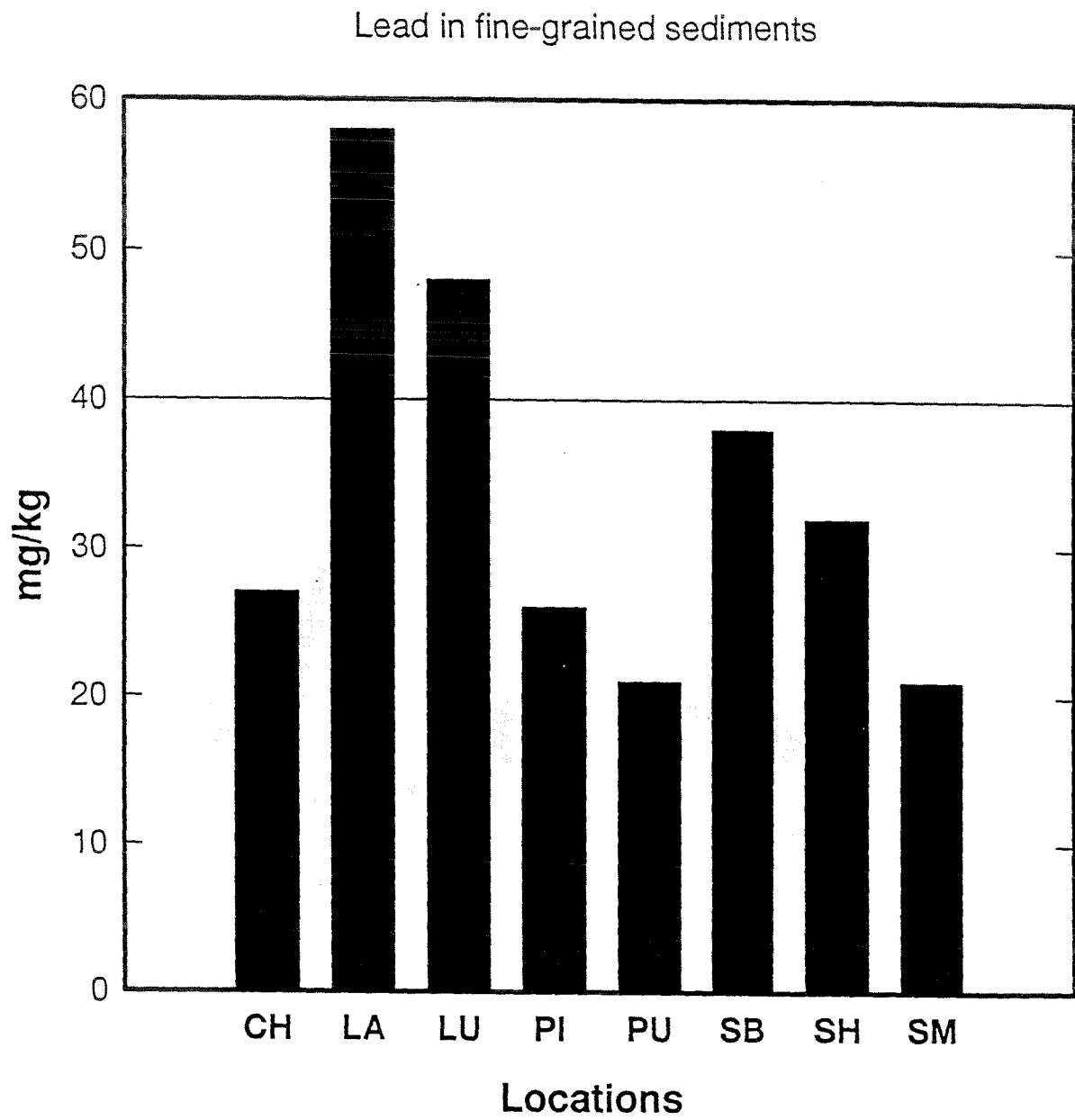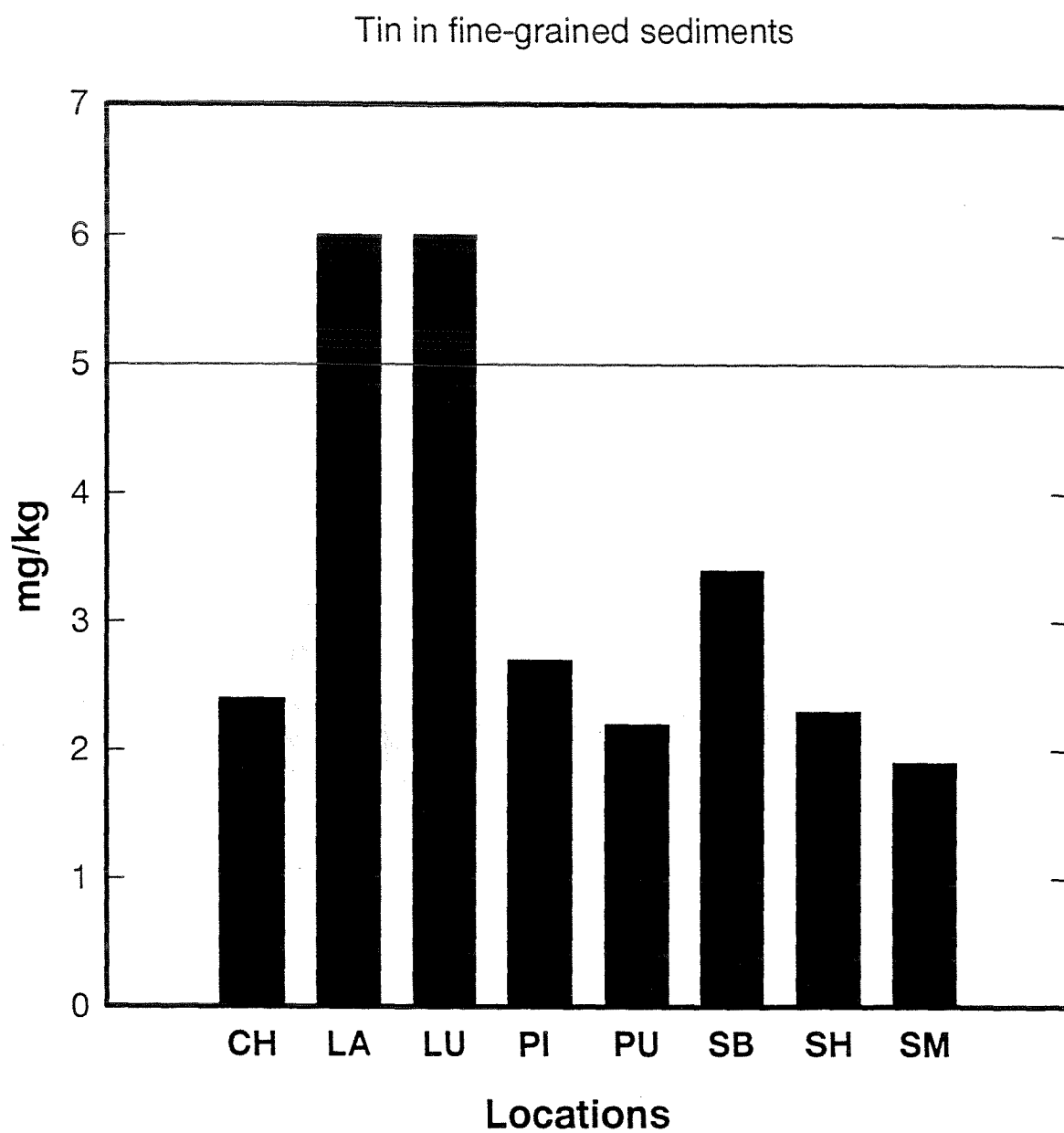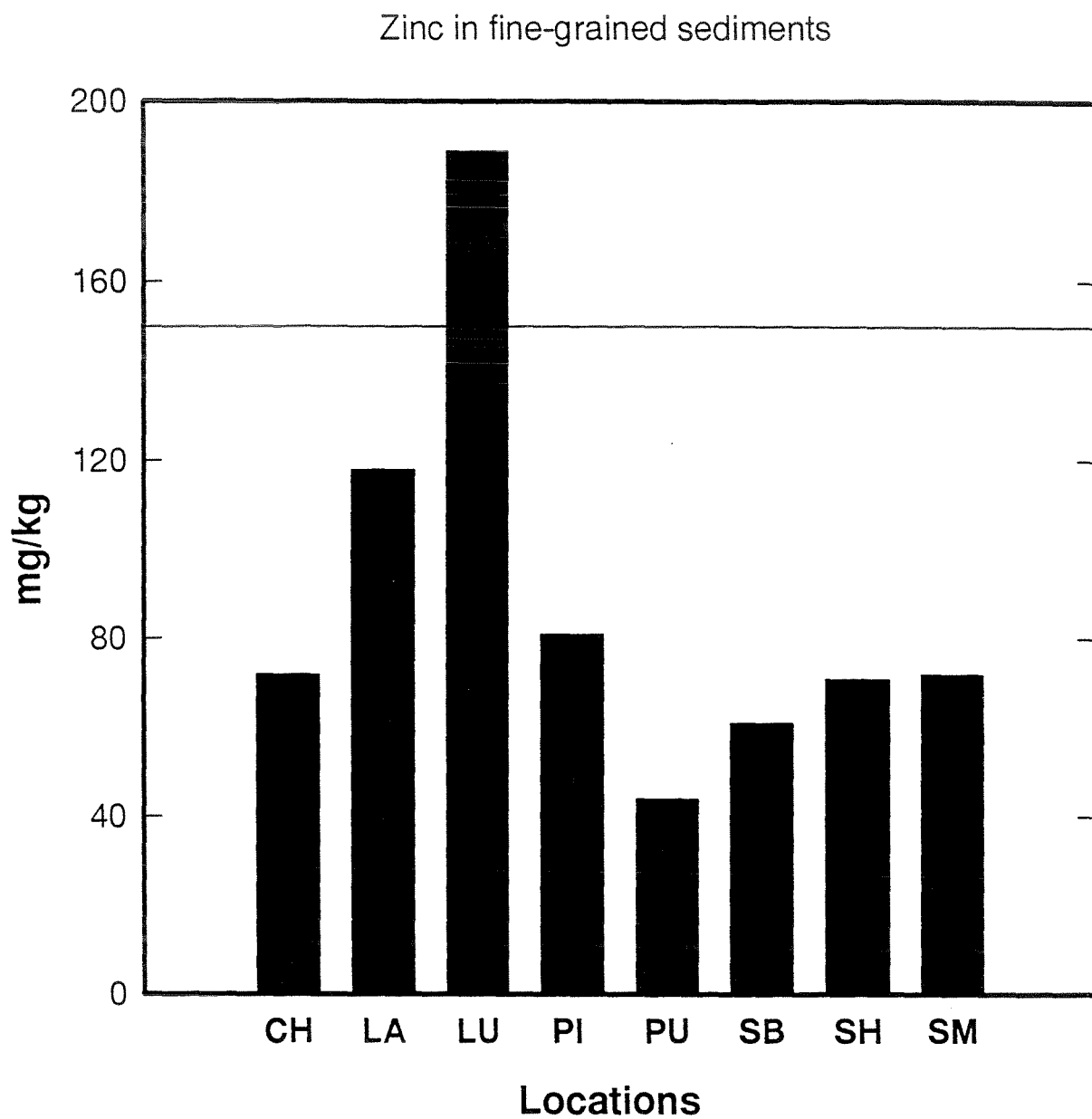## ANNAPOLIS BASIN

The Annapolis Basin, with an axial length of 25.8 km and a maximum depth of 94.2 m, is located on Bay of Fundy about 230 km west of Halifax. It is bounded to the north by the basaltic lavas of North Mountain and to the south by the lowlands of the Annapolis Valley. It is connected to the Bay of Fundy by a narrow (0.7 km long), deep channel known as Digby Gut. On each tide, this westerly trending oval-shaped Basin receives over 21×10^3 m^3 of salt water though this channel. The Basin has an area of 66.5 km^2 at low tide and 96.2 km^2 at high tide. The Annapolis River has a drainage basin of area 2408 km^2 containing the farms and habitations of the Annapolis Valley.

POTENTIAL SOURCES OF CONTAMINATION

The main sources of metal contamination are wastes from the town of Digby (population approx. 2,300), located on the western side of the Basin, and the small towns and villages in the drainage basin of the Annapolis River. Farming activities constitute a large proportion of the anthropogenic activity within the drainage basin.

RESULTS

Sediment Samples and Composition

The locations of the sampling stations (n=21) are shown in Figure 20. Sampling data indicate that medium- to fine-grained brown muddy sands and very sandy muds, containing varying amounts of organic matter (Fig. 21), occupy the area sampled.

Annapolis Basin sediments were collected from within the shipping channel at depths in excess of 6 m. In this current-dominated region, the size distributions have high concentrations of well-sorted fine sands, modal diameter 100 to 300 μm, and minor floc tail portions with a constant source slope of mean -0.04 (Fig. 22). A general coarsening trend can be seen in the modal diameters as the very high current region of Digby Gut is approached. The concentration of material being deposited in a flocculated form is extremely low, ranging from less than 2% to 9%. The samples collected have been deposited from the same source material and have been subjected to frequent resuspension and deposition which gives the spectra characteristic well-sorted, steeply sloped modal peaks.

Abundance and Distribution of Metals

The abundance and distribution of the metals in the Annapolis Basin are shown in Figures 23 to 36. The range of total metal concentrations in Annapolis Basin sediments (n=21) are: As, 4-8 mg·kg^{-1}; Cd, 0.03-0.08 mg·kg^{-1}; Cr, 50-226 mg·kg^{-1}; Cu, 9-20 mg·kg^{-1}; Hg, 0.01-

0.03 mg·kg^{-1}; Pb 14-19 mg·kg^{-1}, and Zn 33-49 mg·kg^{-1} (Table 6). All the trace metals are at natural levels except for a few anomalous concentrations of Cr that are related to the local geology.

Potential Bioavailability of Metals

No data are available for chemical partitioning in Annapolis Basin sediments.

Metal Carriers and Sources

Significant correlations ($p \leq 0.001$) of Pb and Zn with Al and Li suggest that these metals are held in the lattices of the aluminosilicate minerals (Table 7). A significant correlation of Sn with the <63 μm fraction and organic matter indicates an association of Sn with small amounts of organic matter in the fine-grained components of the sediments. In contrast, significant correlations of As and Cr, as well as Ni and V (not shown in Table 7), with Fe and Mn indicate that these metals are held in ferromagnesium silicate minerals and in discrete oxide minerals such as illmenite, magnetite, and chromite. In addition, the strong correlations of these metals with mode size indicate that the heavy minerals with which they are associated increase in concentration with increasing mode (grain size) of the sediments. The small amounts of Cd, Cu, and Hg have no significant correlations with either Al or Li and are most likely held in various lattice positions in aluminosilicates and discrete oxide minerals. Factor analyses show that the association of the small amounts of Cd, Cu, Hg, Pb, Sn, and Zn with the fine-grained aluminosilicate/organic matter fraction of the sediments accounts for 38% of their variance. These analyses also show the association of As, Cr, Ni, and V with Fe- and Mn-bearing minerals. This accounts for 38% of the variance of these metals in sandy sediments. Such associations reflect the presence of detrital heavy minerals, such as pyroxenes and amphiboles, as well as discrete oxide minerals, such as illmenite and chromite, in the coarser sediments. Such minerals derive from the erosion products of the adjacent basaltic rocks (Loring 1982).

There is no evidence in the sediments of anthropogenic influence, and most of the metals are at natural levels. The relatively high Cr values (Fig. 27) merely reflect the presence of the erosion products of the adjacent basaltic rocks (Loring 1982).

Table 6

Textural and metal statistics[a] for the Annapolis Basin sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	18	24.9	±12.3	9-51	OM%	21	0.58	± 0.20	0.27-0.93
Metal					**Metal**				
Al%	21	4.26	± 0.31	3.90-5.00	Fe%	21	2.10	± 0.37	1.0-3.50
As	21	5.4	± 0.87	4-8	Li	21	23.5	± 2.2	20-28
Cd	21	0.04	± 0.01	0.03-0.08	Ni	21	17.1	± 4.8	13-36
Cr	21	76.4	±39.3	50-226	Pb	21	16.3	± 1.2	14-19
Cu	21	11.8	± 2.2	9-20	V	21	55.3	±10.2	42-91
Hg	21	0.02	± 0.01	0.01-0.03	Zn	21	39.3	± 4.6	33-49
Mn%	21	0.054	± 0.011	0.042-0.080	Sn	6	1.7	± 0.4	1-2

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM), Al, Fe, and Mn

Table 7

Correlation Matrix Annapolis Basin

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	x	x	1									
Cr	x	0.81	x	1								
Cu	x	x	x	x	1							
Fe	x	0.85	x	0.95	x	1						
Hg	x	x	x	x	x	x	1					
Li	0.78	x	x	x	x	x	x	1				
Mn	x	0.78	x	0.82	x	0.76	x	x	1			
Pb	0.76	x	x	x	x	x	x	0.63	x	1		
Sn	0.95	x	x	x	x	x	x	x	x	x	1	
Zn	0.74	x	x	x	x	x	x	0.82	x	0.73	x	1
mud	0.94	x	x	x	x	x	x	x	x	x	0.96	x
OM	0.89	x	x	x	x	x	x	0.66	-.68	x	0.95	x
mode	x	0.81	x	0.92	x	0.82	x	x	0.86	x	x	x

n = 21 Sn:n = 6
For p ≤ 0.001 x = not significant
mud = >70% by weight material<63μm
mode = Coulter Counter equivalent grain size
OM = % by weight organic matter

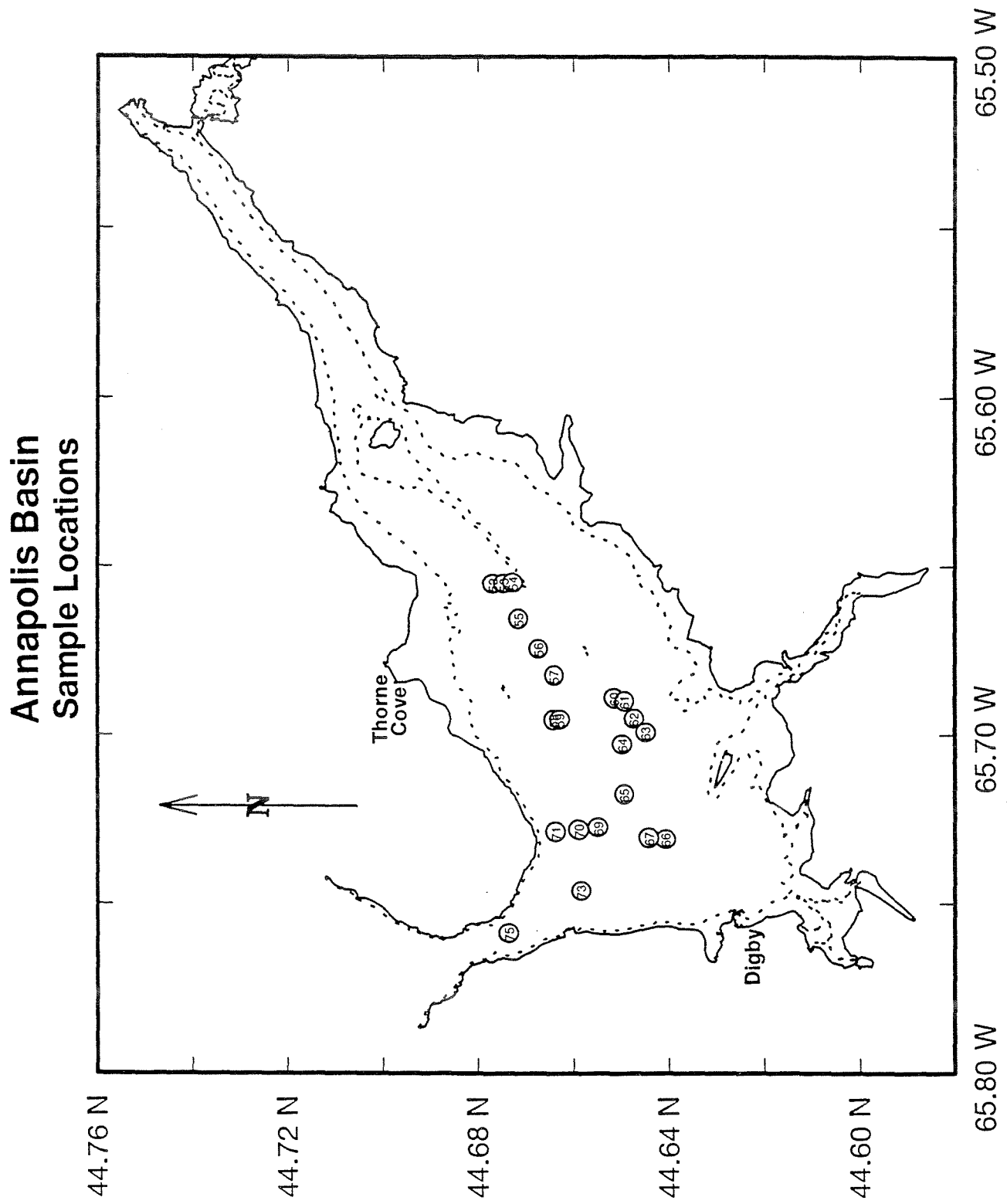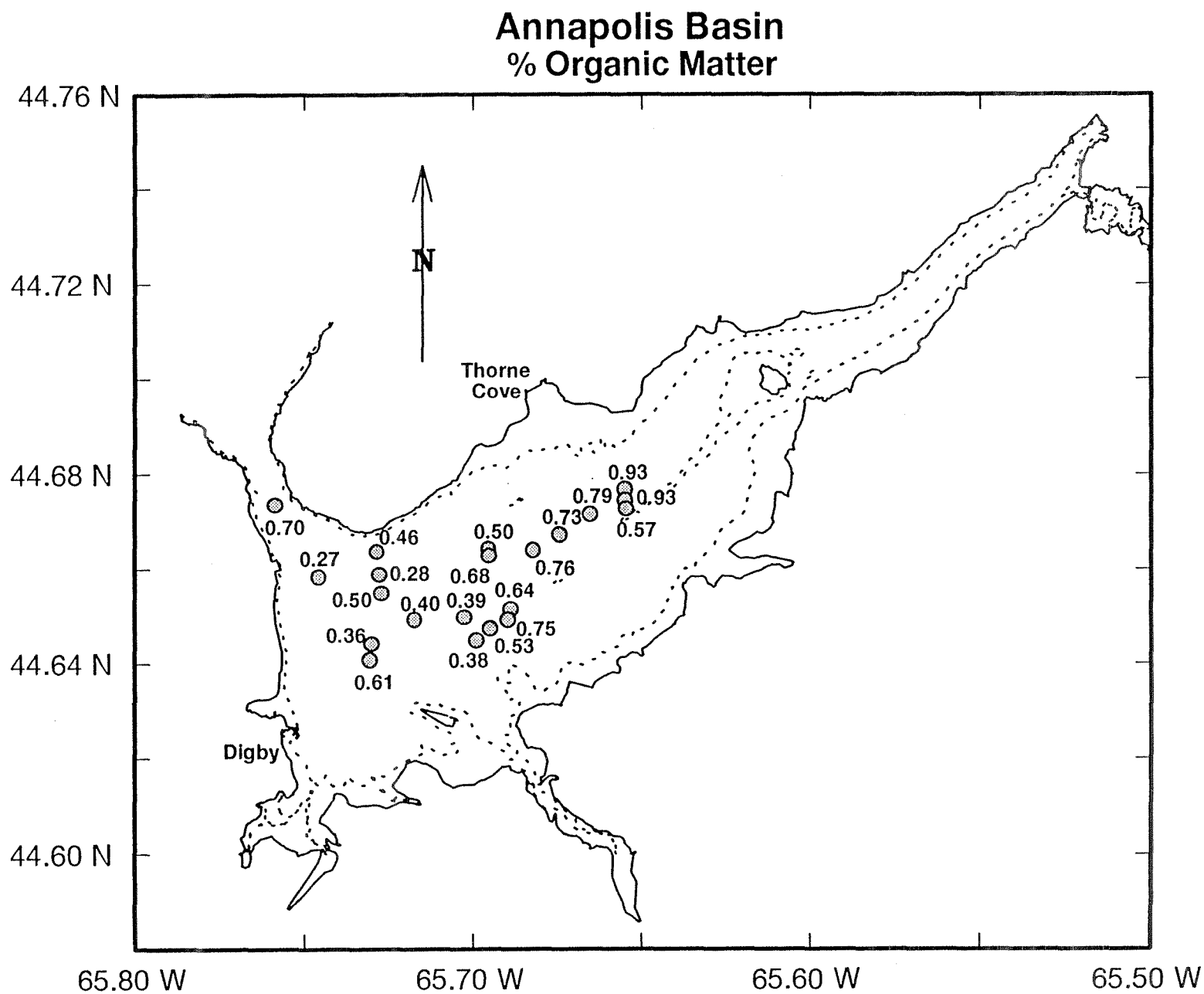**Figure 20.** Sample locations for Annapolis Basin

Annapolis Basin
% Organic Matter

Figure 21. Organic matter concentrations in surficial sediments

37

Annapolis Basin 1988
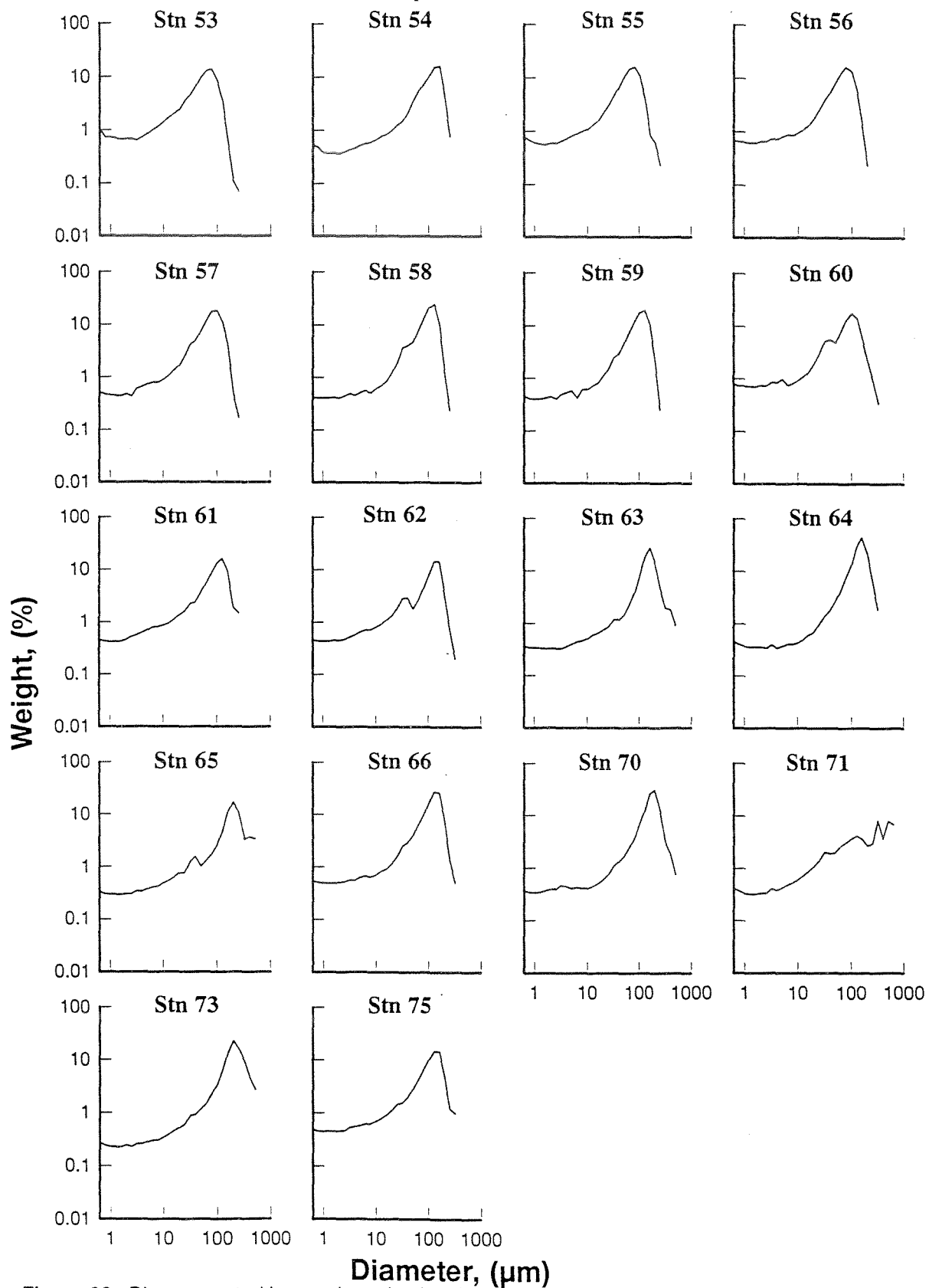
Figure 22. Disaggregated inorganic grain size distributions

Annapolis Basin
Al %

Figure 23. Aluminium concentrations in surficial sediments

39

Annapolis Basin
Fe %
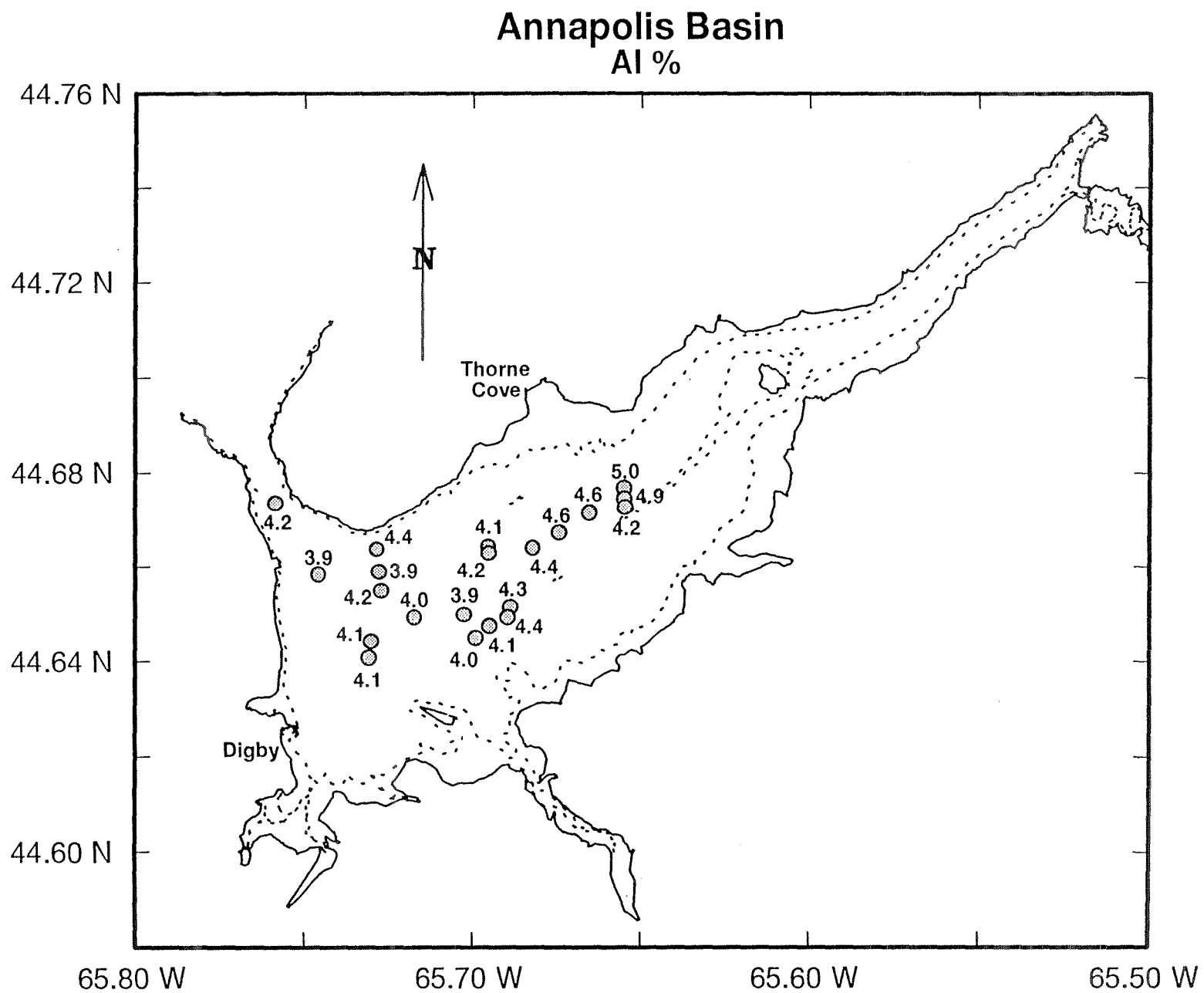
Figure 24. Iron concentrations in surficial sediments

41
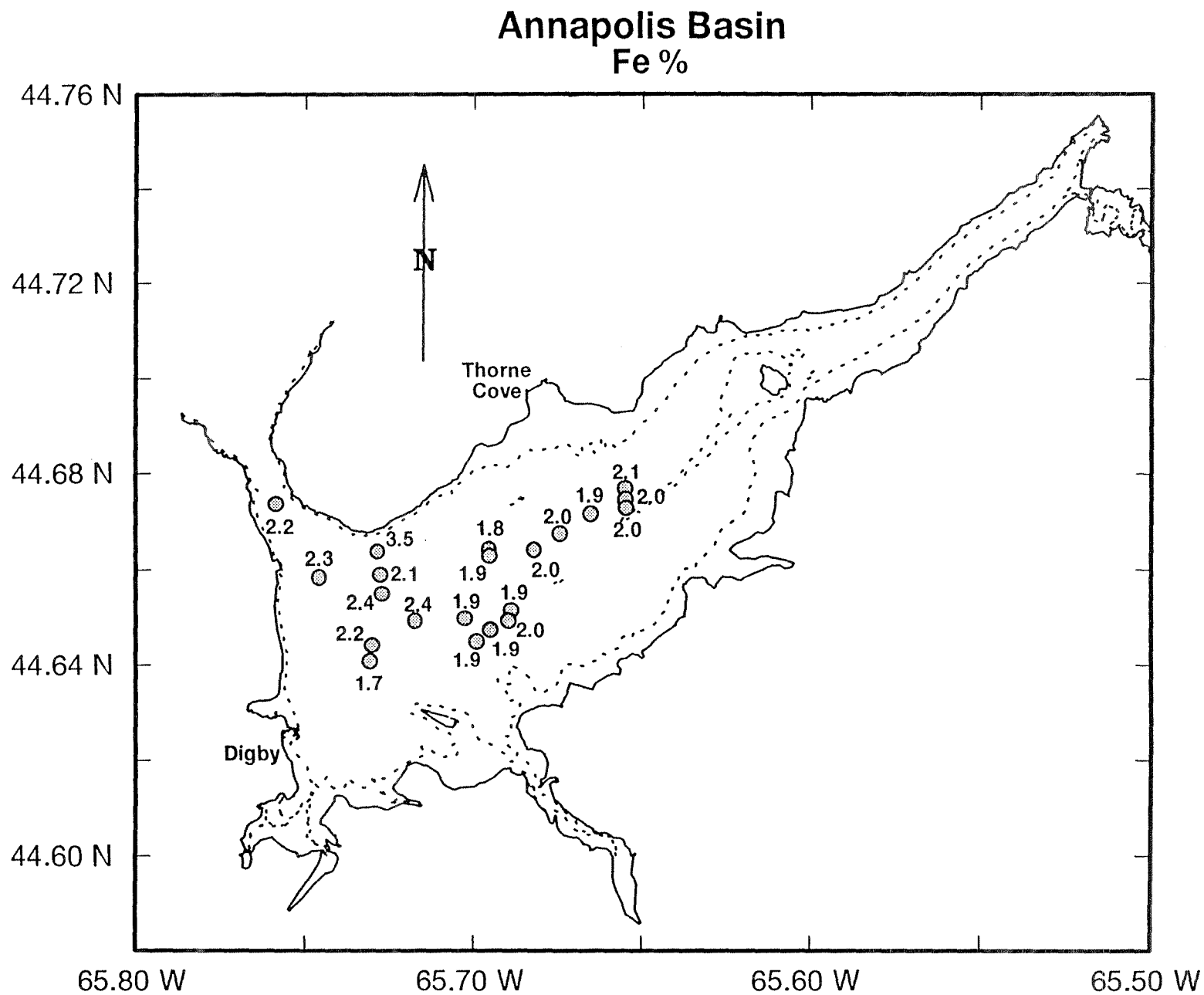
Figure 25. Arsenic concentrations in surficial sediments

Annapolis Basin
Cd mg/kg

44.76 N
44.72 N
44.68 N
44.64 N
44.60 N

Thorne
Cove

0.06
0.04 0.05
0.06 0.03
0.08 0.04
0.04 0.04
0.04 0.03 0.03 0.06
0.04 0.04 0.03 0.04
0.04 0.04 0.04
0.03 0.04
0.04

Digby

65.80 W   65.70 W   65.60 W   65.50 W

Figure 26. Cadmium concentrations in surficial sediments

Annapolis Basin
Cr mg/kg
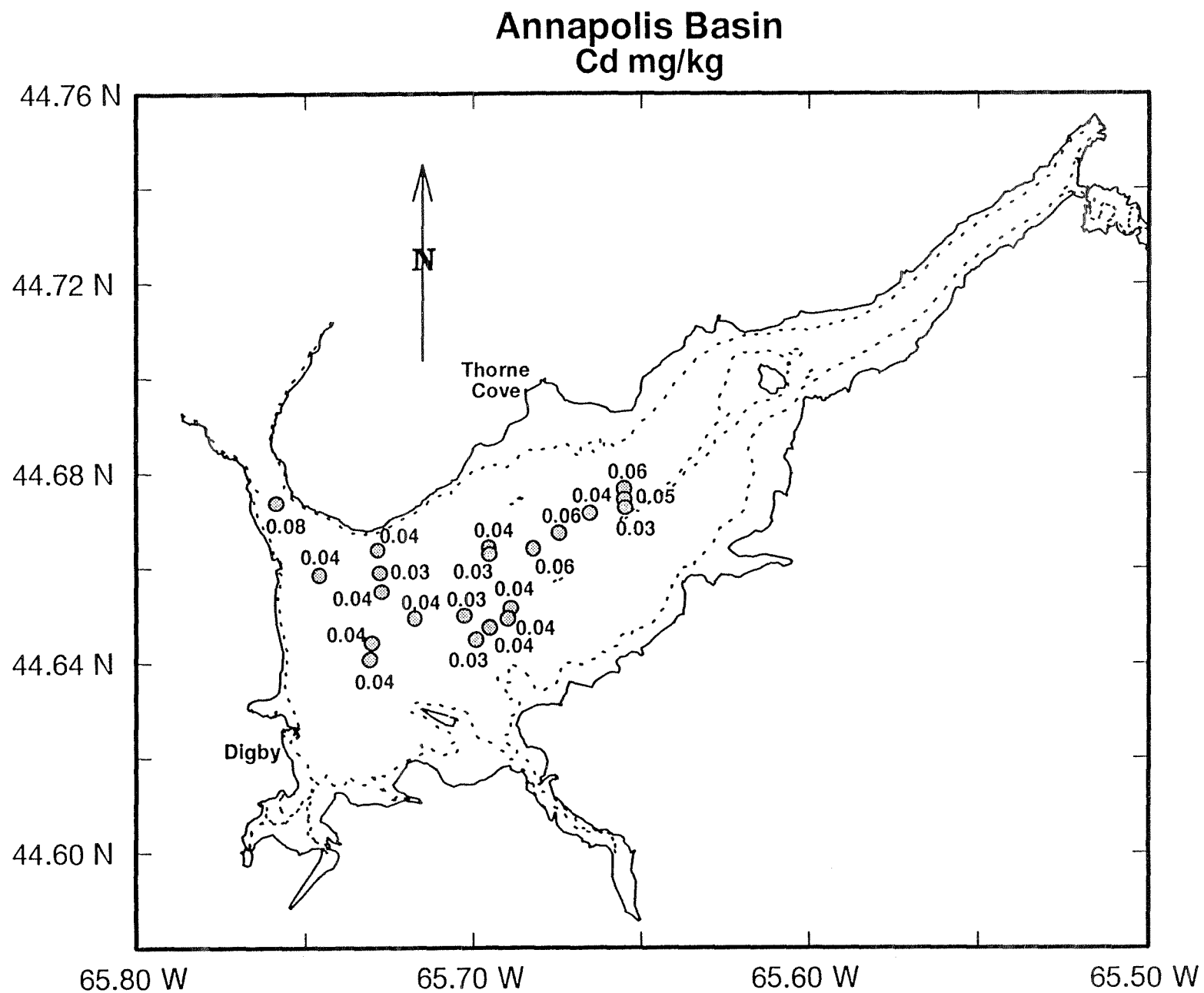
Figure 27. Chromium concentrations in surficial sediments

Annapolis Basin
Cu mg/kg

44.76 N

N

Thorne
Cove

44.72 N

44.68 N

11
11
11
13
10
11
20
13
11
10
14
12
13
12
12
12
11
9
12
11
11
11
12
10

44.64 N

Digby

44.60 N

65.80 W   65.70 W   65.60 W   65.50 W
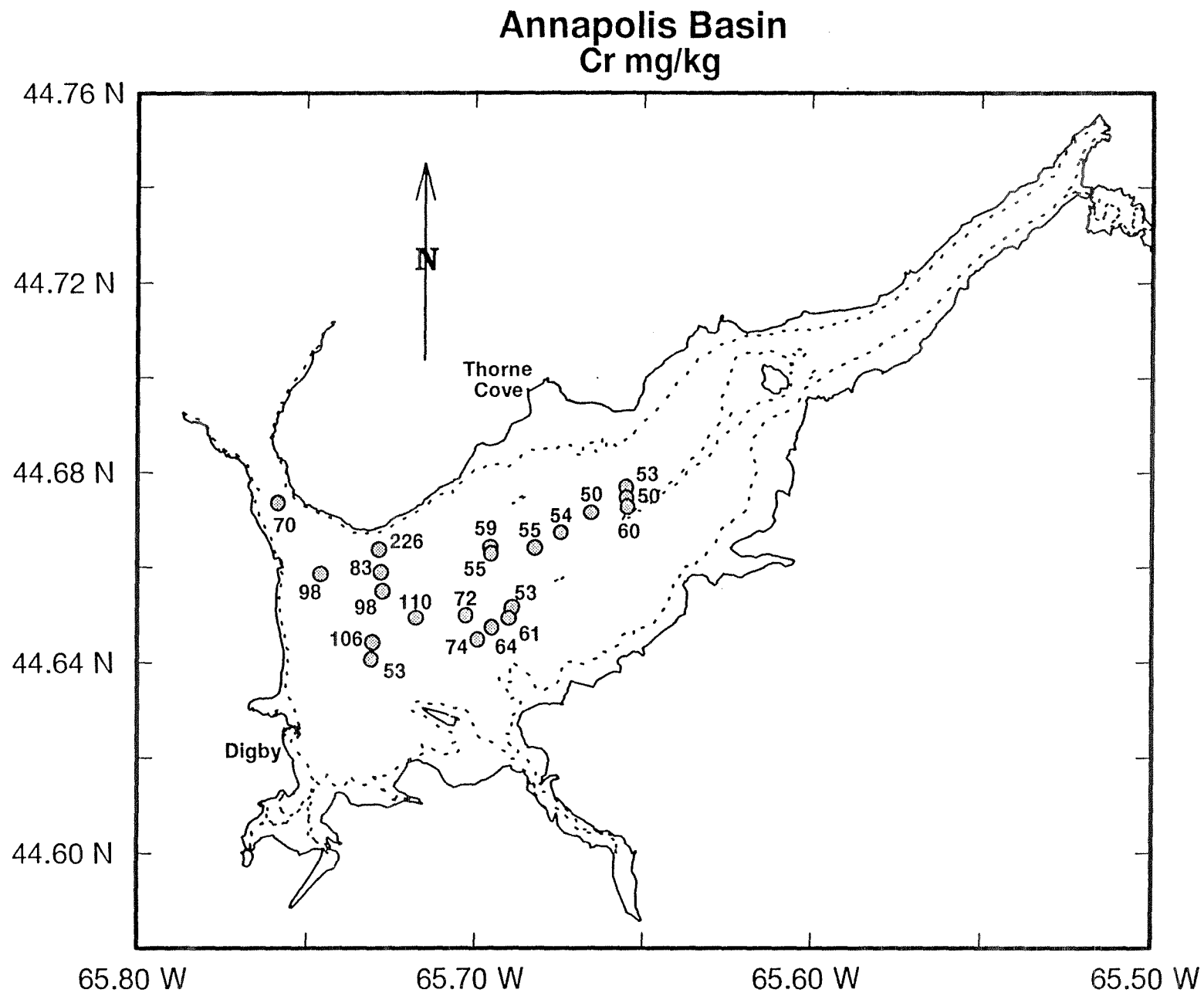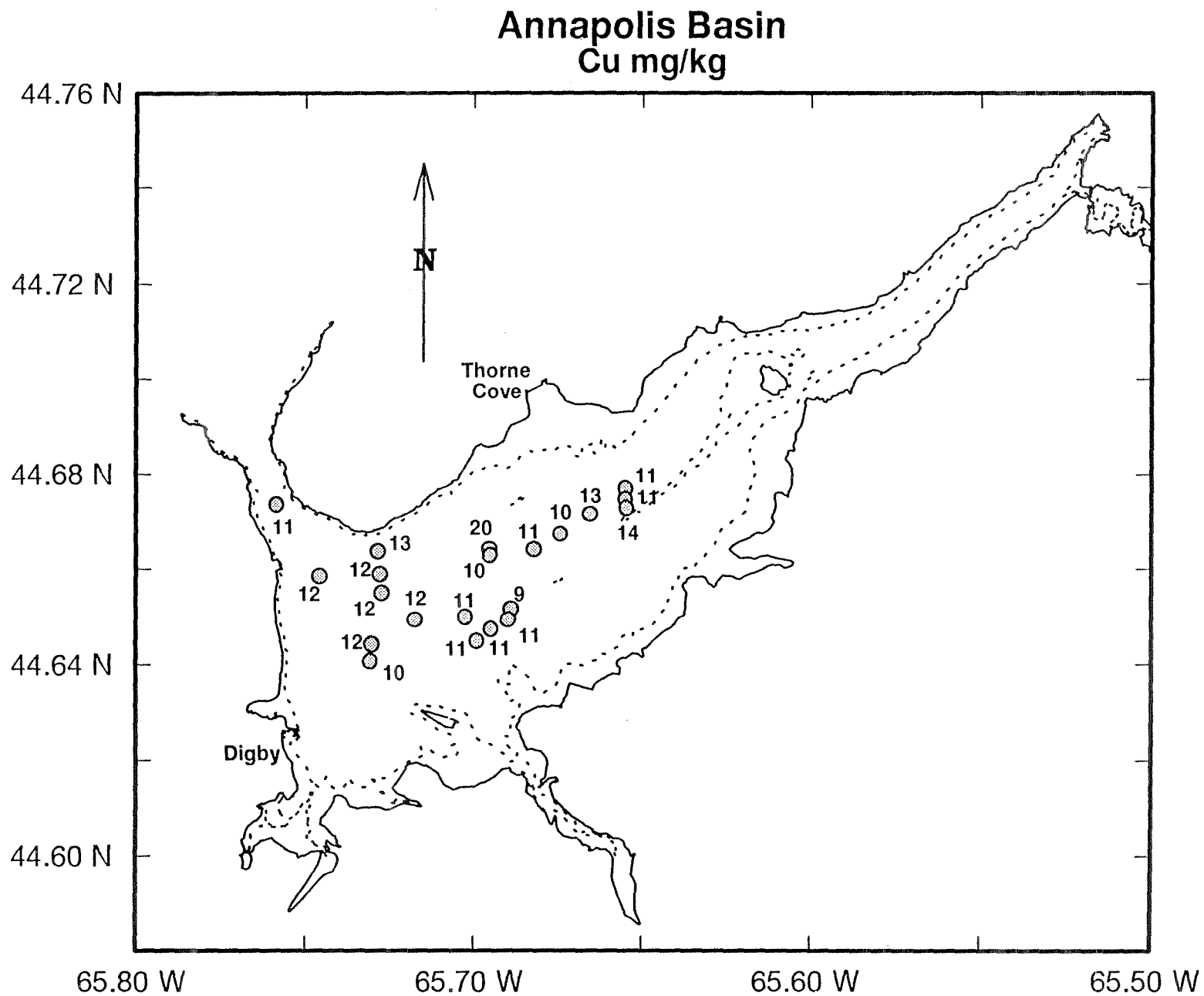
Figure 29. Mercury concentrations in surficial sediments

Annapolis Basin
Li mg/kg

44.76 N

44.72 N

N

Thorne
Cove

44.68 N

28
24 26
27 24
22 23 27 24
26
27
21
20 22
23 24 22 22
22 25
22 21
22
23

44.64 N

Digby

44.60 N

65.80 W   65.70 W   65.60 W   65.50 W
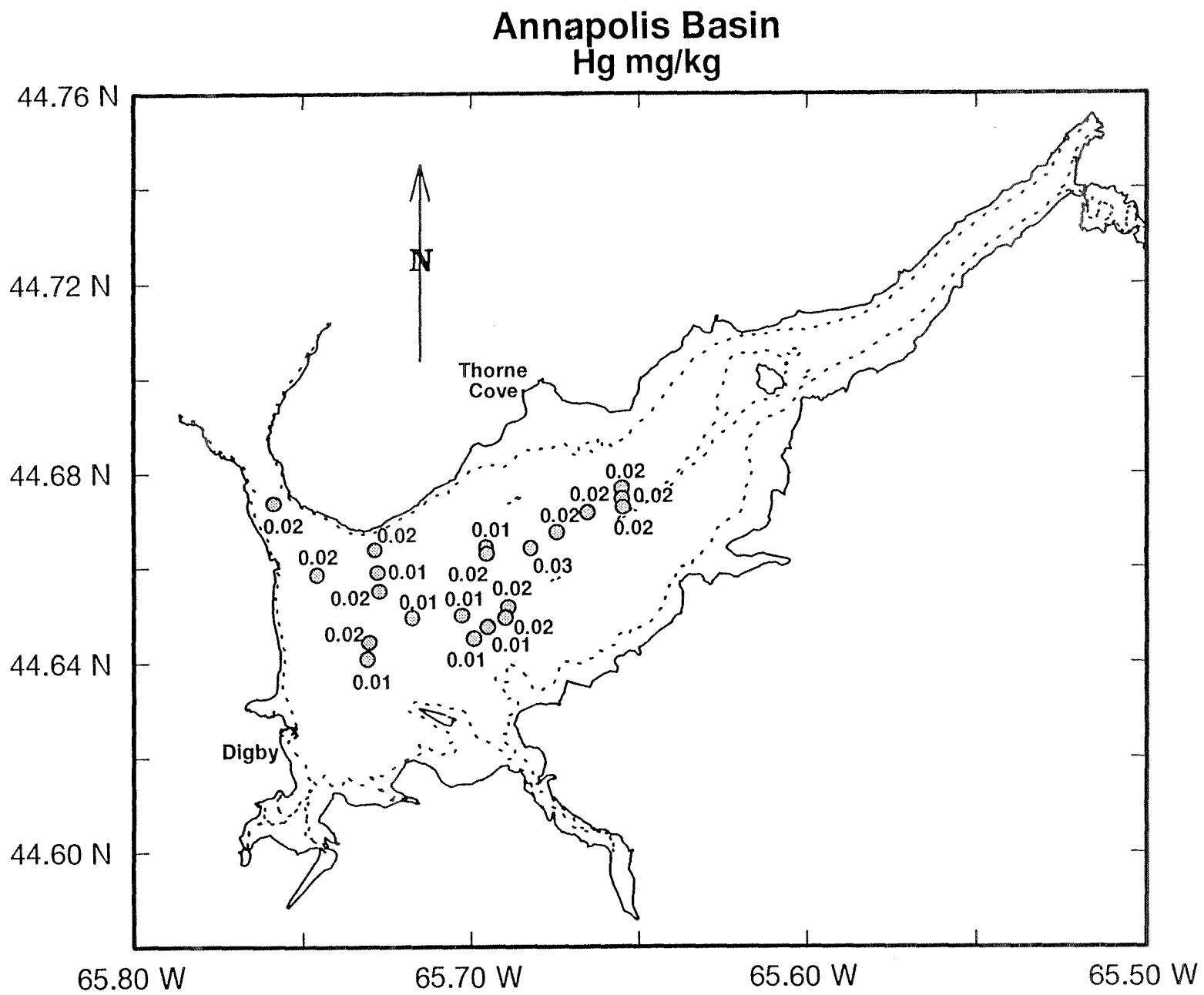
Figure 30. Lithium concentrations in surficial sediments

46

Annapolis Basin
Mn mg/kg

44.76 N

44.72 N

N

Thorne
Cove

44.68 N

439
451 416
458
627 480
803 522
714
636 576 492
638 418
713 520
604 422
573 476
439

44.64 N

Digby

44.60 N

65.80 W   65.70 W   65.60 W   65.50 W
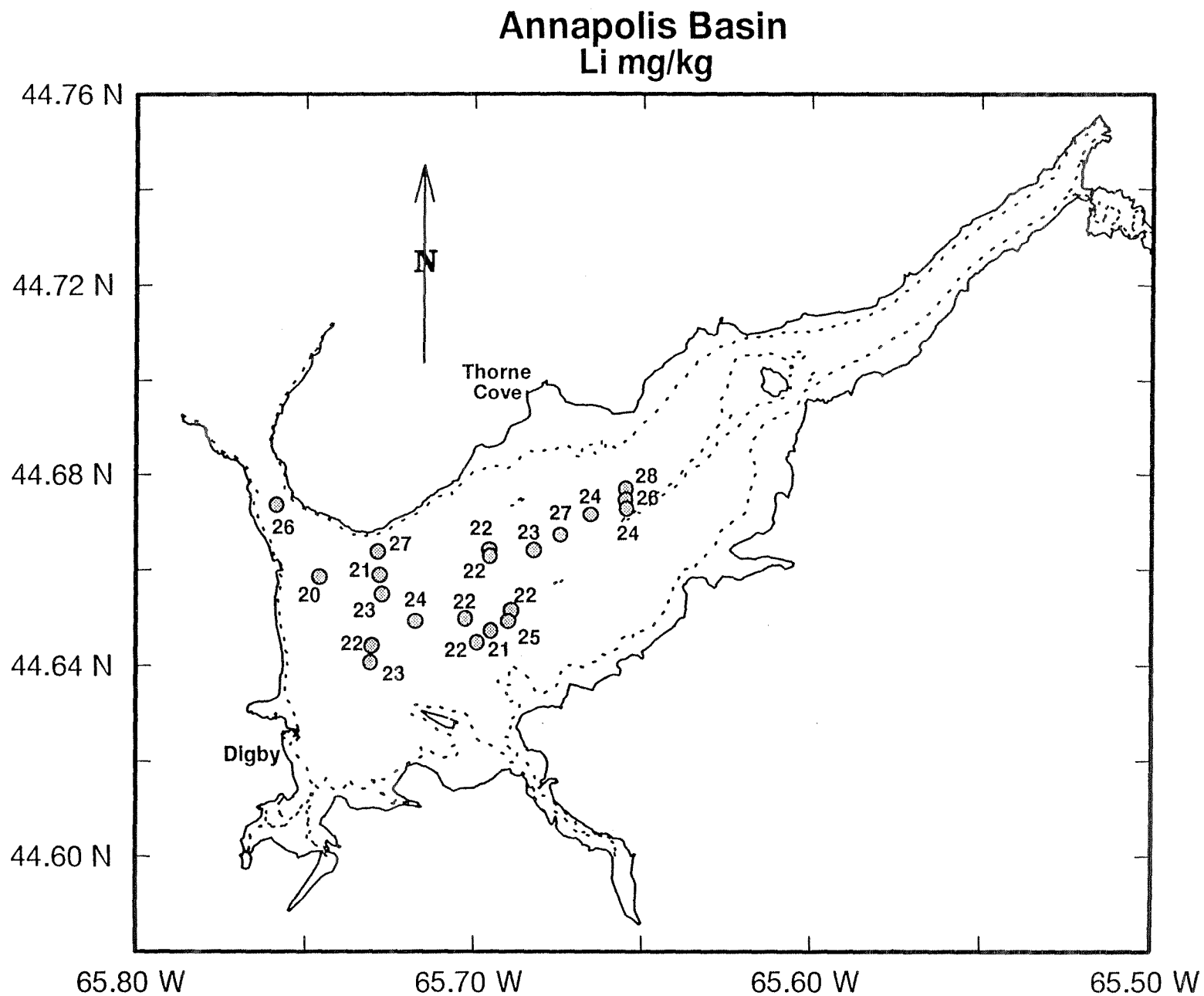
Figure 31. Manganese concentrations in surficial sediments

Annapolis Basin
Ni mg/kg

Thorne Cove

Digby
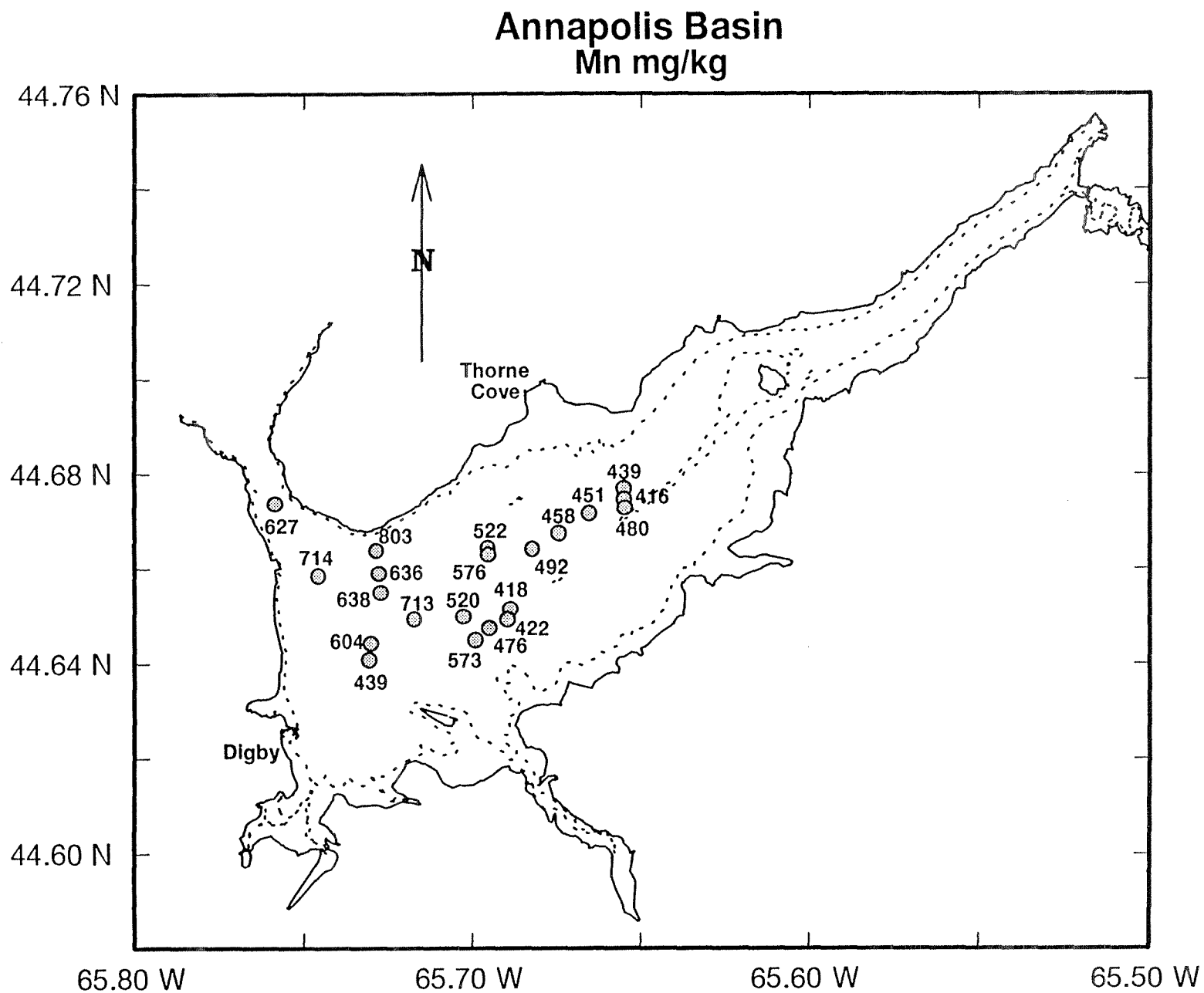
Figure 32. Nickel concentrations in surficial sediments

Annapolis Basin
Pb mg/kg
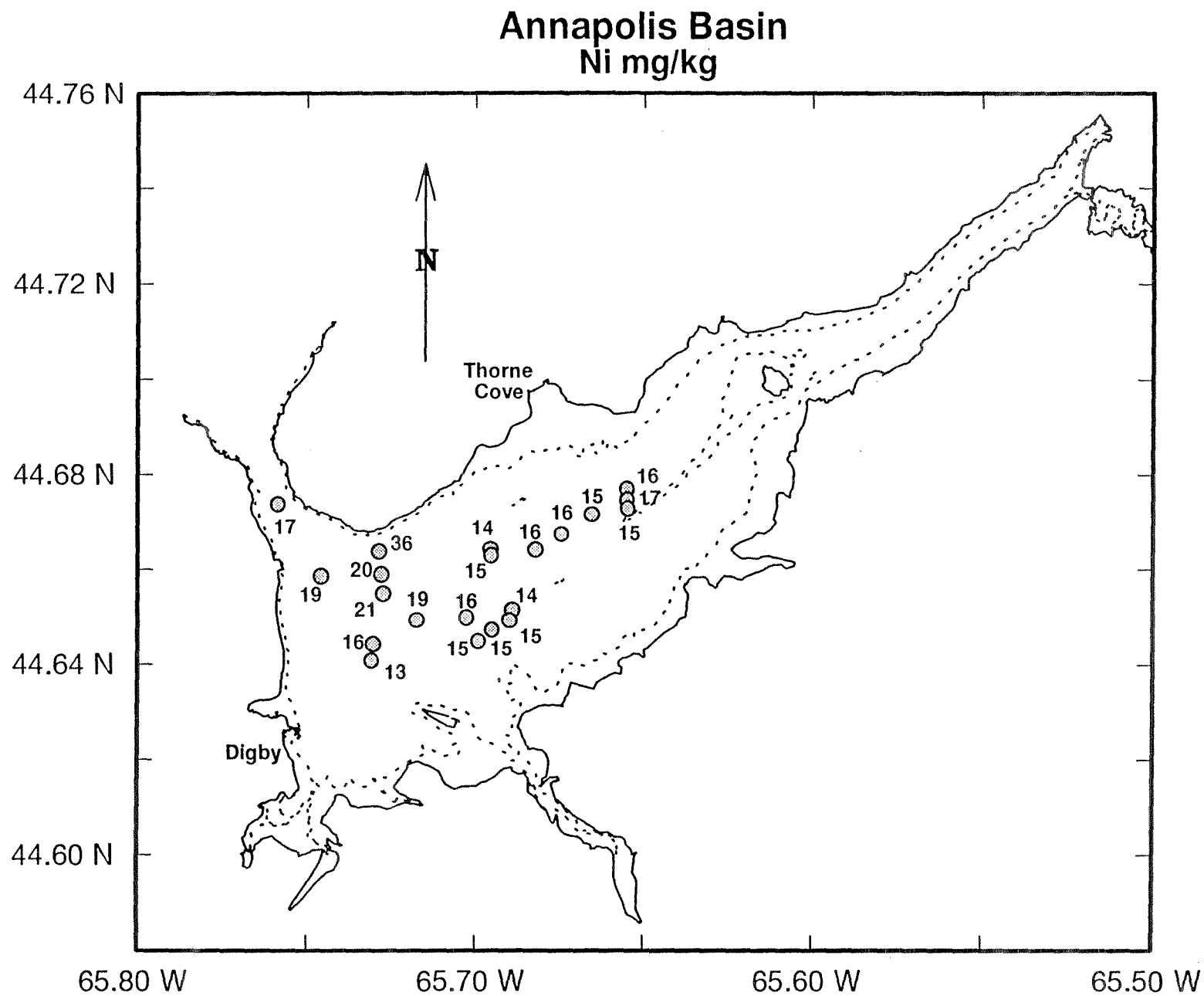
Figure 33. Lead concentrations in surficial sediments

Annapolis Basin
Sn mg/kg
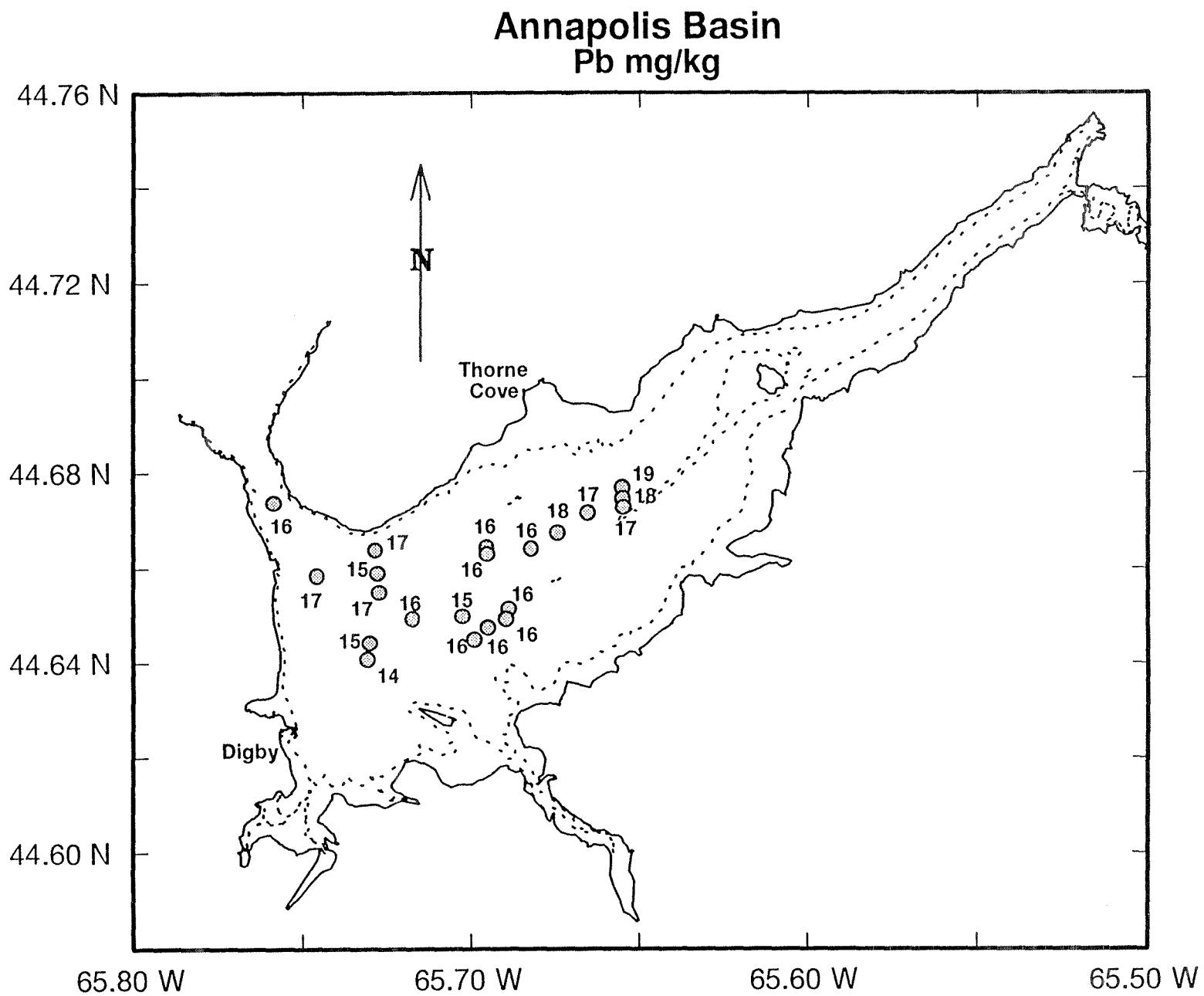
Figure 34. Tin concentrations in surficial sediments

Annapolis Basin
V mg/kg
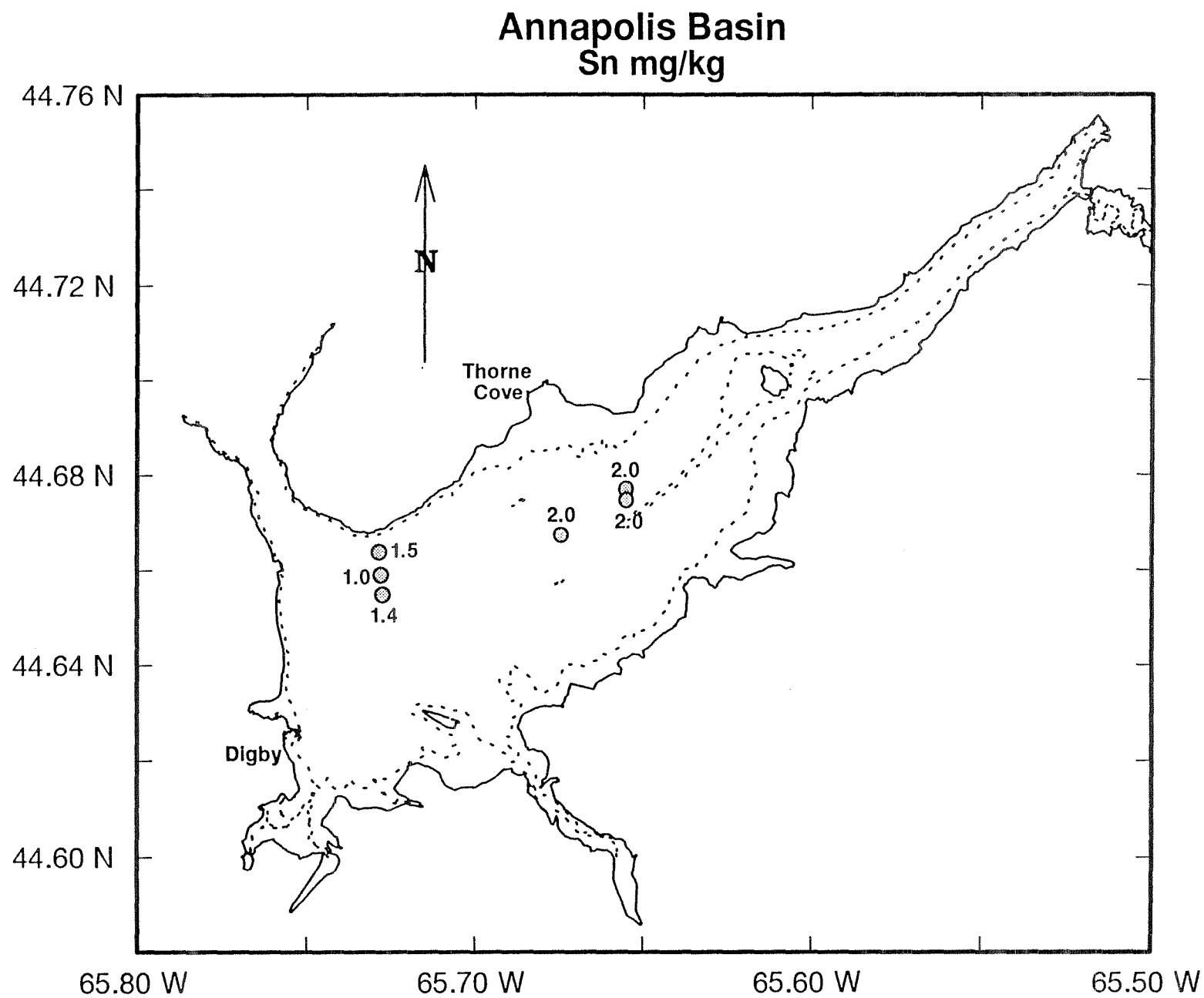
Figure 35. Vanadium concentrations in surficial sediments

Annapolis Basin
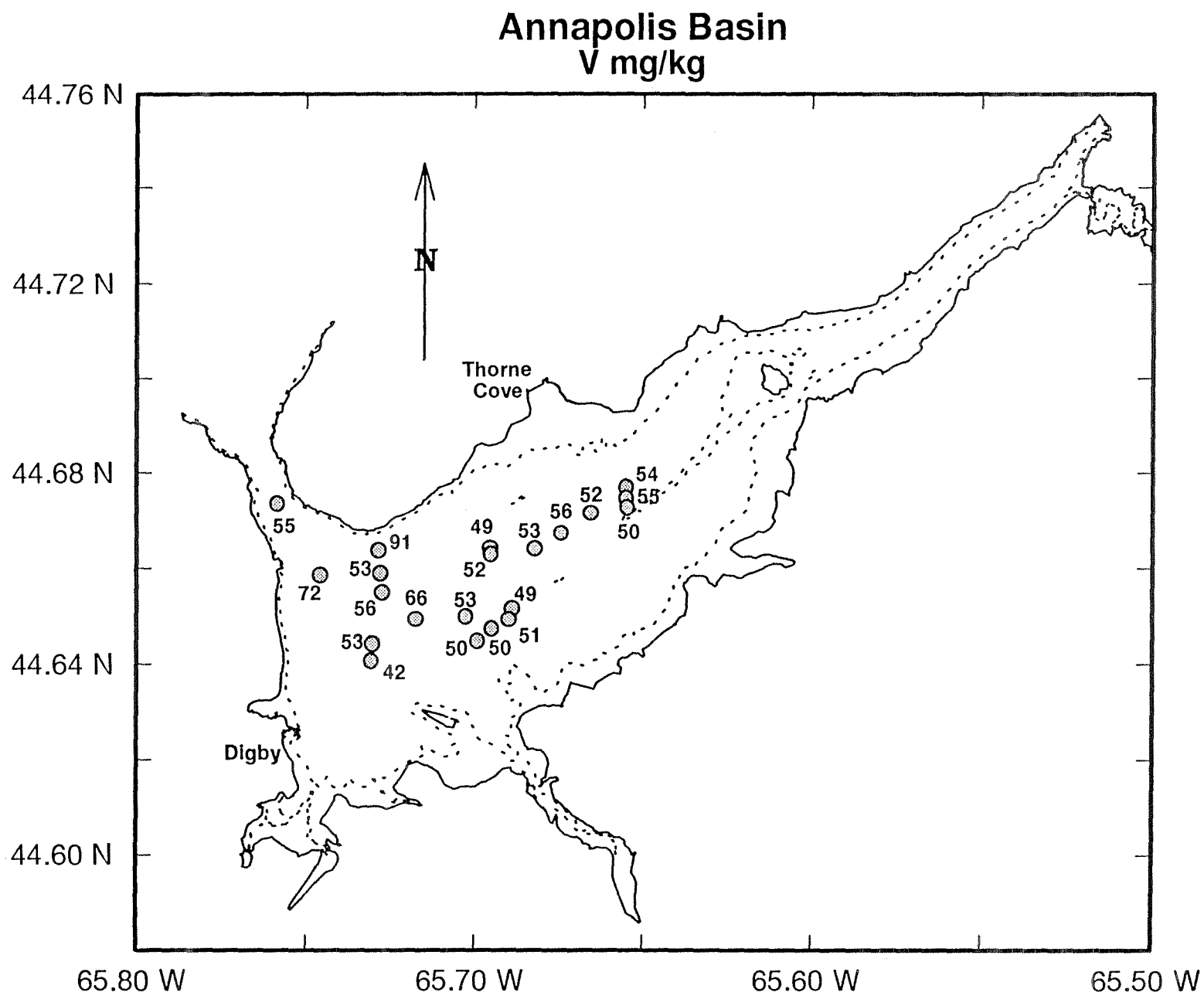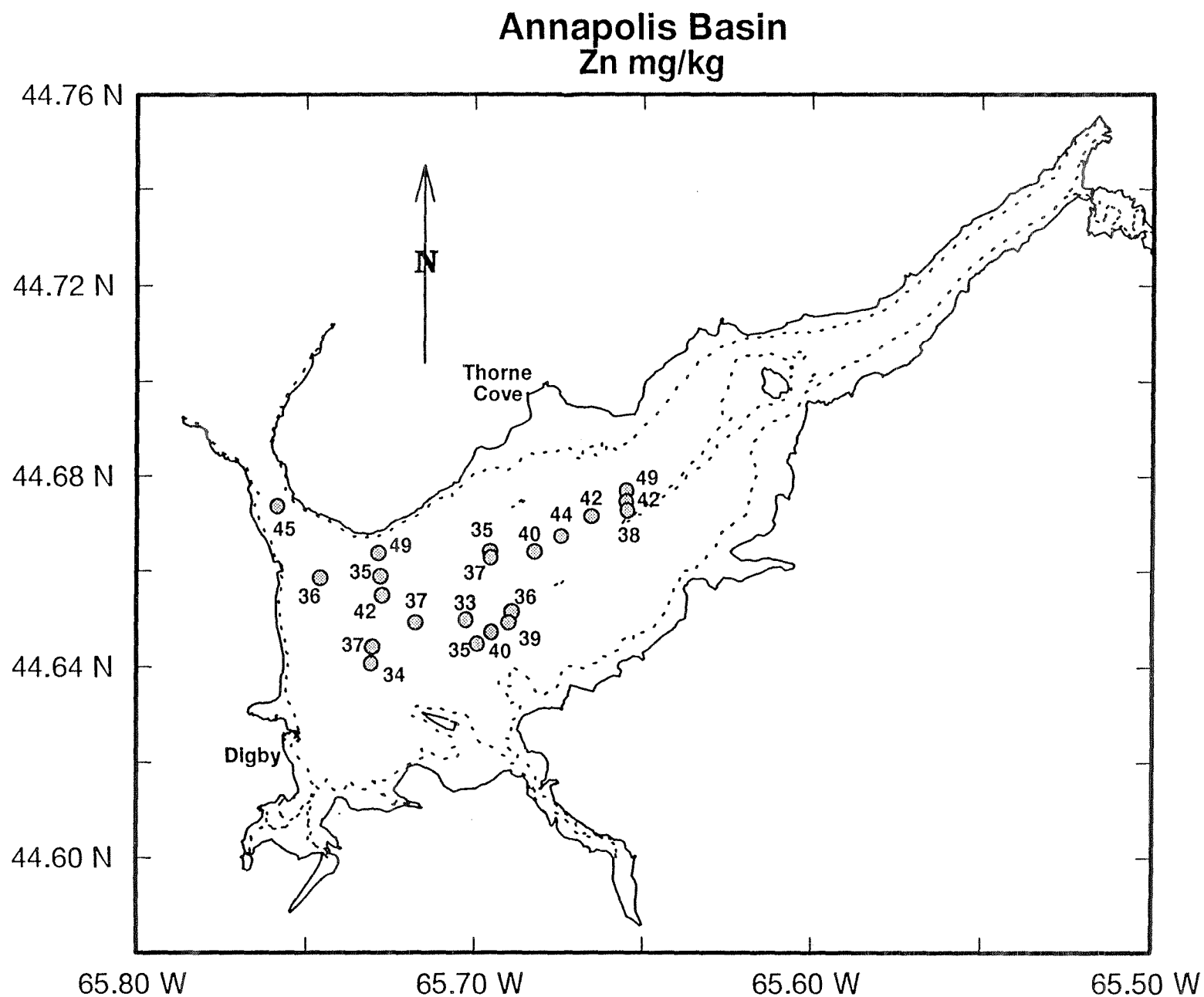Zn mg/kg

Figure 36. Zinc concentrations in surficial sediments

COUNTRY HARBOUR

Country Harbour occupies a long (19.1 km), narrow (0.5-1.4 km), deep (water depths up to 30 m) inlet running into the eastern shore of Nova Scotia, approximately 20 km northeast of the town of Sherbrooke, Guysborough County. At its head, the Harbour receives drainage via Country Harbour River which drains an area of 313 km^2. The drainage basin is mainly wooded, with vegetation developed on a thin mantle of glacial till underlain primarily by Precambrian quartzites and slates.

POTENTIAL SOURCES OF CONTAMINATION

Aside from contaminant contributions from local inhabitants, the only potential source of industrial contamination is the leaching of mine wastes and tailings derived from gold-mining activity that occurred in the area between 1891 and 1909 (Malcom 1912).

RESULTS

Sediment Samples and Composition

The locations of the sediment samples are shown in Figure 37. Grain-size analyses show that fine-grained grey-black muds occupy most of the Harbour with sandy muds, containing varying amounts of organic matter (Figure 38), occurring at the head and mouth. Modal diameters in Country Harbour slowly decrease landward from a mean of 40 μm to a low of 10 μm in the inner reaches (Fig. 39). At the head of the Harbour, the sediment mode is dominated by coarser sediments introduced at the river mouth with modal diameters between 100 μm and 300 μm. The source slopes for the entire region vary from 0.14 to 0.3 with a mean value of 0.23. The relatively constant source slope value indicates that Country Harbour receives material from a single dominant source and that there is little or no deposition of material derived from offshore within the area sampled. The small modal diameter and lack of a coarse peak in the outermost samples shows that high-energy resuspension does not occur frequently at these stations. This also suggests that there is little offshore influence. Samples throughout the area have well-defined floc tails and single grain peaks with higher-energy coarse sediment being present only above Stormont. The poorly defined modes and broad distributions of the sediments at the head of the Harbour are typical of river-dominated sedimentation and are likely to primarily result from conditions occurring during spring runoff. The floc settled component in the sediments increases significantly inland of Station 6 and remains high until it is effectively diluted by the coarse riverine material. The fine-grained nature and prominent floc tail inshore of Station 6 indicate that little resuspension occurs in this region and that the sediments consist almost entirely of material deposited from suspension.

Abundance and Distribution of Metals

Concentrations of the metals at each sampling station are shown in Figures 40 to 53. The means, standard deviations, and ranges of the metals in Country Harbour sediments are shown in Table 8. The range of total metal concentrations measured are: As, 2-21 mg·kg^{-1}; Cd, 0.02-0.78 mg·kg^{-1}; Cr, 31-82 mg·kg^{-1}; Cu, 8-28 mg·kg^{-1}; Hg, 0.01-0.09 mg·kg^{-1}; Ni, 12-30 mg·kg^{-1}; Pb, 13-40 mg·kg^{-1}; Sn, 2-4 mg·kg^{-1}; V, 36-100 mg·kg^{-1}; and Zn, 32-111 mg·kg^{-1}.

These concentrations, except for As and Cd, are at or near natural levels in the sediments. Arsenic concentrations slightly exceed background levels (20 mg·kg^{-1}) in 14% of the samples (Table 2). However, anomalous Cd concentrations (>0.3 mg·kg^{-1}) occur in 71% of the sediments sampled throughout the Harbour, and 11% exceed the guideline for ocean dumping under Part VI of the Canadian Environmental Protection Act (CEPA) of 0.6 mg·kg^{-1} Cd.

Potential Bioavailability of Metals

Partitioning of six selected samples indicate that 80 to >90% of total Cd, 8-13% of total Cu, 23-37% of total Pb, and 19-26% of total Zn are potentially bioavailable. Thus, most of the Cd and minor normal amounts of Cu, Pb, and Zn are potentially bioavailable.

Metal Carriers and Sources

The strong positive correlations of the metals with organic matter and weaker, but nevertheless significant, correlations with increasing mud (material of grain-size <63 µm) content suggest that the metal carriers are associated primarily with organic matter and only incidentally with fine-grained material (Table 9). The positive correlations of all the metals, excepting Mn, Sn, and Zn, with increasing Al and Fe, but not Li, indicate that these metals are associated with, but not necessarily structurally combined with, fine-grained aluminosilicate material such as the ferromagnesium minerals, illite, chlorite, and kaolinite (Table 9). The positive covariances (p<0.01) of As (r=0.64), Cd (r=0.64), Cr (r=0.85), Cu (r=0.81), Hg (r=0.67), Pb (r=0.89), and Zn (r=0.59) with Al (Table 9) demonstrate that Al normalizes for varying amounts of the granular and mineralogical variability of these metals in the surface sediments.

The proportion of the metal variability explained by aluminosilicates decreases in the order: Pb (78%) > Cr (71%) > Cu (64%) >> Hg (42%) > Cd (40%) = As (40%) > Zn (32%) >> Sn (1%). Inspection of the correlation matrix indicates strong correlations between Cd, Pb, Zn, Hg, and organic matter (OM) and weaker correlations with Fe, Cu, and Cr. Within the fine-grained sediments there are also significant relationships between Cd, Hg, Pb, Zn, and Li that represent the amounts of these metals naturally associated with the phyllosilicates. The strong association of As, Cd, Cr, Cu, Hg, Pb, and Zn with Fe also suggests the presence of ferriferous metal-bearing particles. These would have been derived from the deposition of detrital minerals associated with natural gold-bearing veins, detrital material transported into the Harbour from

mine wastes, leaching of tailings from gold mining activity in the area between 1891 and 1909, or *in situ* formation of metal-bearing iron monosulphides and/or pyrite. A concurrent association of Cd, Hg, Pb, Fe, and, to lesser extent, As and Zn, with the organic component in all sediments (Table 9) suggests that all these metals excepting Cd are held in metal-bearing iron monosulphides and/or pyrite. The strong positive correlation of Cd, which is mainly acid soluble, with organic matter indicates that it is weakly held by the organic component and also present in the sulphides which form *in situ* in the organic fraction below the sediment-water interface. The highest concentrations of Cd occur in the region of greatest floccuation and most likely reflect the association of this metal with organic waste deposited in the Harbour.

Table 8

Textural and metal statistics[a] for the Country Harbour sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	26	81.6	±22.5	21-100	OM%	15	4.67	± 2.45	1.25-9.67
Metal					Metal				
Al%	28	5.52	± 0.71	4.00-6.50	Fe%	28	2.55	± 0.56	1.50-3.30
As	28	14.7	± 5.0	2-21	Li	28	49.0	±10.6	24-75
Cd	28	0.41	± 0.18	0.02-0.78	Ni	28	21.3	± 5.2	12-30
Cr	28	58.9	±16.3	31-82	Pb	28	25.4	± 7.1	13-40
Cu	28	18.1	± 5.7	8-28	Sn	23	2.4	± 0.6	2-4
Hg	28	0.05	± 0.02	0.01-0.09	V	27	67.3	±19.2	36-100
Mn%	28	0.049	± 0.009	0.033-0.075	Zn	28	70.2	±16.6	32-111

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM), Al, Fe, and Mn

Table 9

Correlation Matrix Country Harbour

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	0.64	1										
Cd	0.64	0.81	1									
Cr	0.85	0.82	0.76	1								
Cu	0.81	0.78	0.76	0.94	1							
Fe	0.82	0.78	0.78	0.94	0.93	1						
Hg	0.66	0.81	0.85	0.71	0.69	0.68	1					
Li	x	x	x	x	x	x	x	1				
Mn	x	x	x	x	x	x	x	x	1			
Pb	0.89	0.77	0.87	0.91	0.87	0.85	0.83	x	x	1		
Sn	x	x	x	x	x	x	x	x	x	x	1	
Zn	0.59	0.69	0.84	0.72	0.69	0.77	0.86	x	x	0.78	x	1
Mud	0.74	0.70	x	0.65	0.71	0.63	x	x	x	0.69	x	x
OM	0.85	0.78	0.95	0.90	0.91	0.96	0.91	x	x	0.95	x	0.81

n = 28
For $p \leq 0.001$ x = not significant
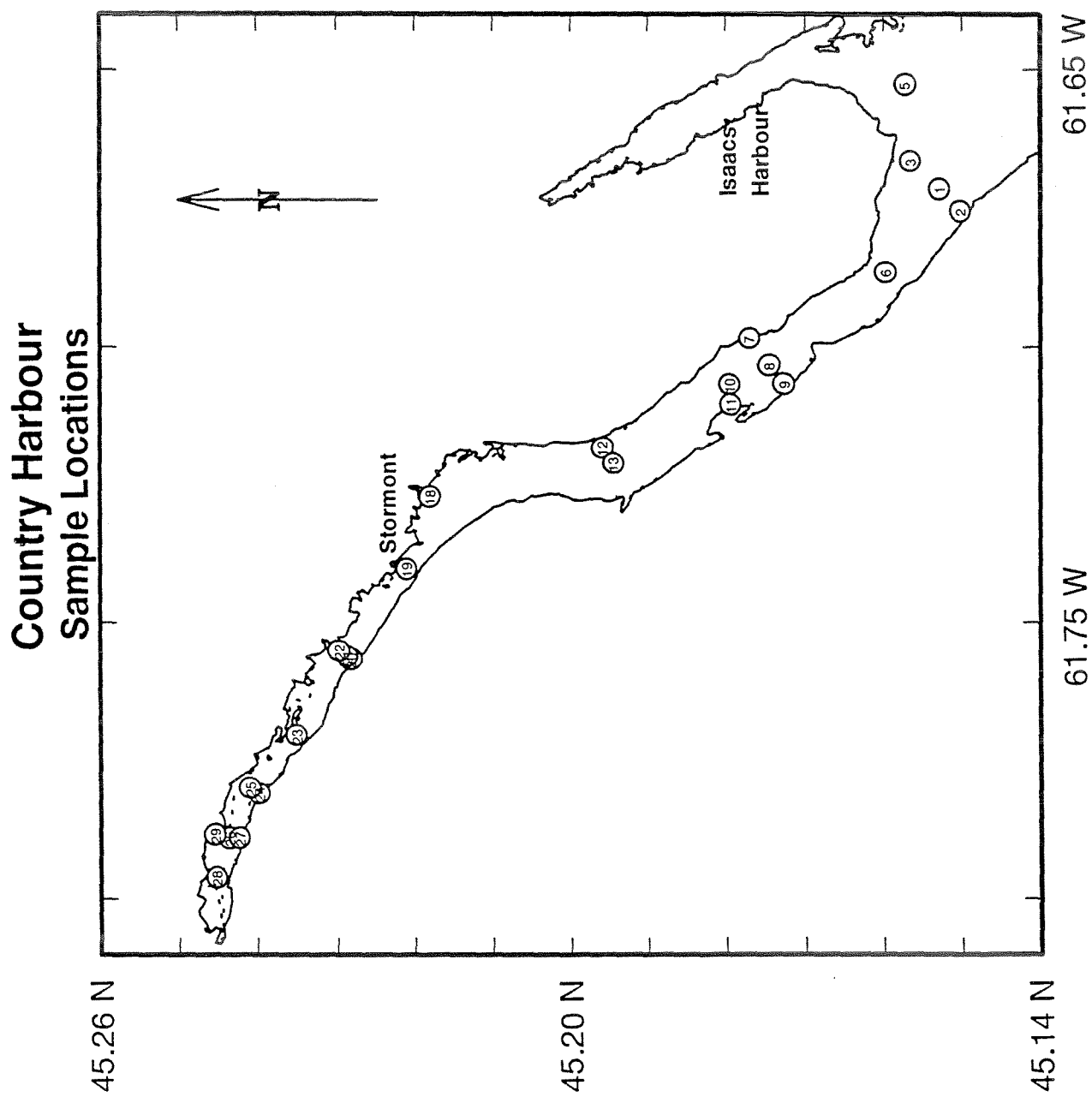mud = >70% by weight material<63μm
OM = % by weight organic matter

Figure 37. Sample locations for Country Harbour

Country Harbour
% Organic Matter

45.26 N

2.62
6.67
1.25 5.87
2.48
9.67
3.50
4.32 Stormont

N

45.20 N

7.13
7.03

6.44

Isaacs
Harbour

5.26
2.38
1.38

4.09

45.14 N

61.75 W   61.65 W

Figure 38. Organic matter concentrations in surficial sediments
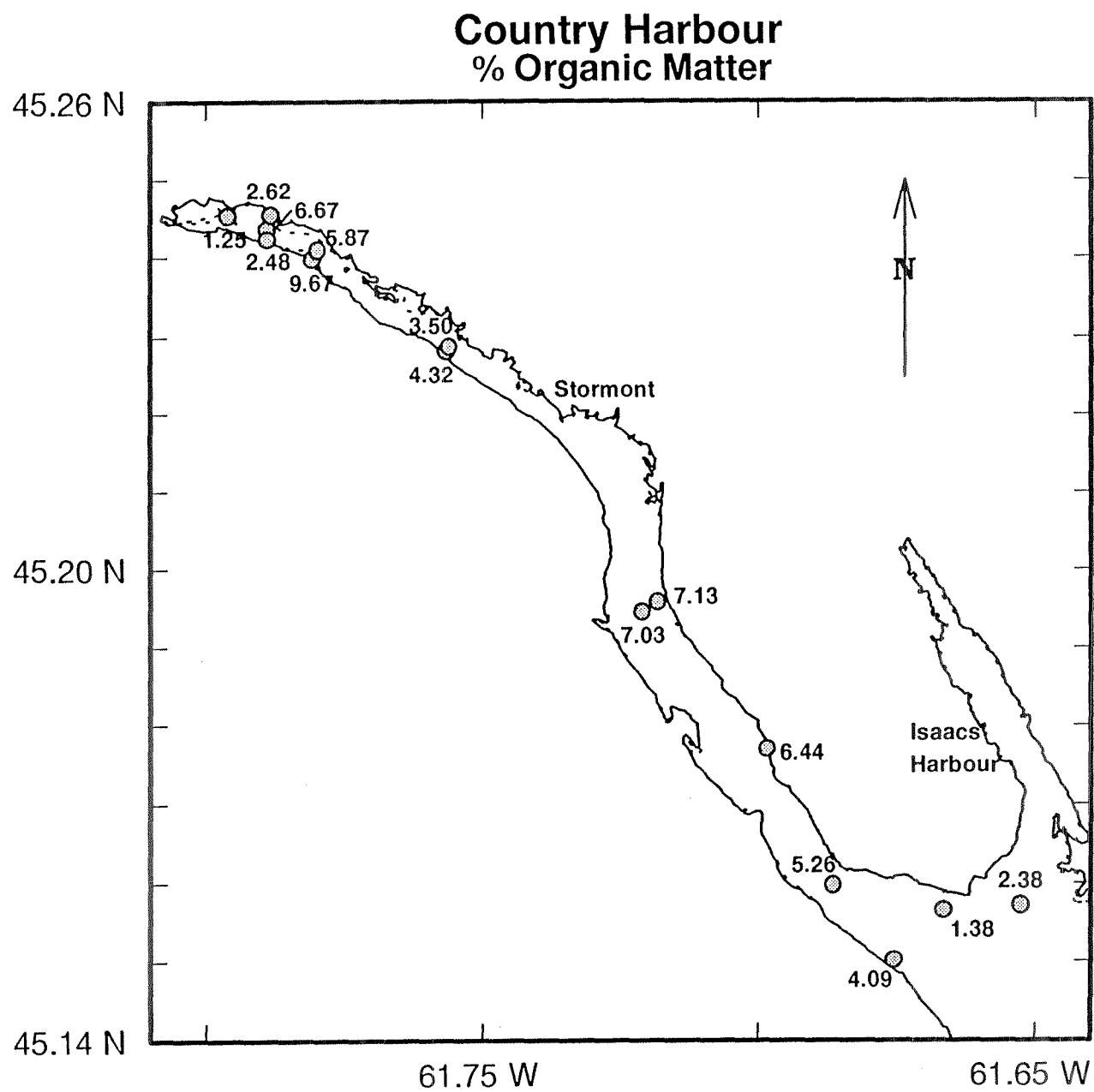
59

Figure 39. Disaggregated inorganic grain size distributions

Country Harbour

Stn 28   Stn 29

Weight, (%)

Diameter, (μm)

Figure 39. Disaggregated inorganic grain size distributions
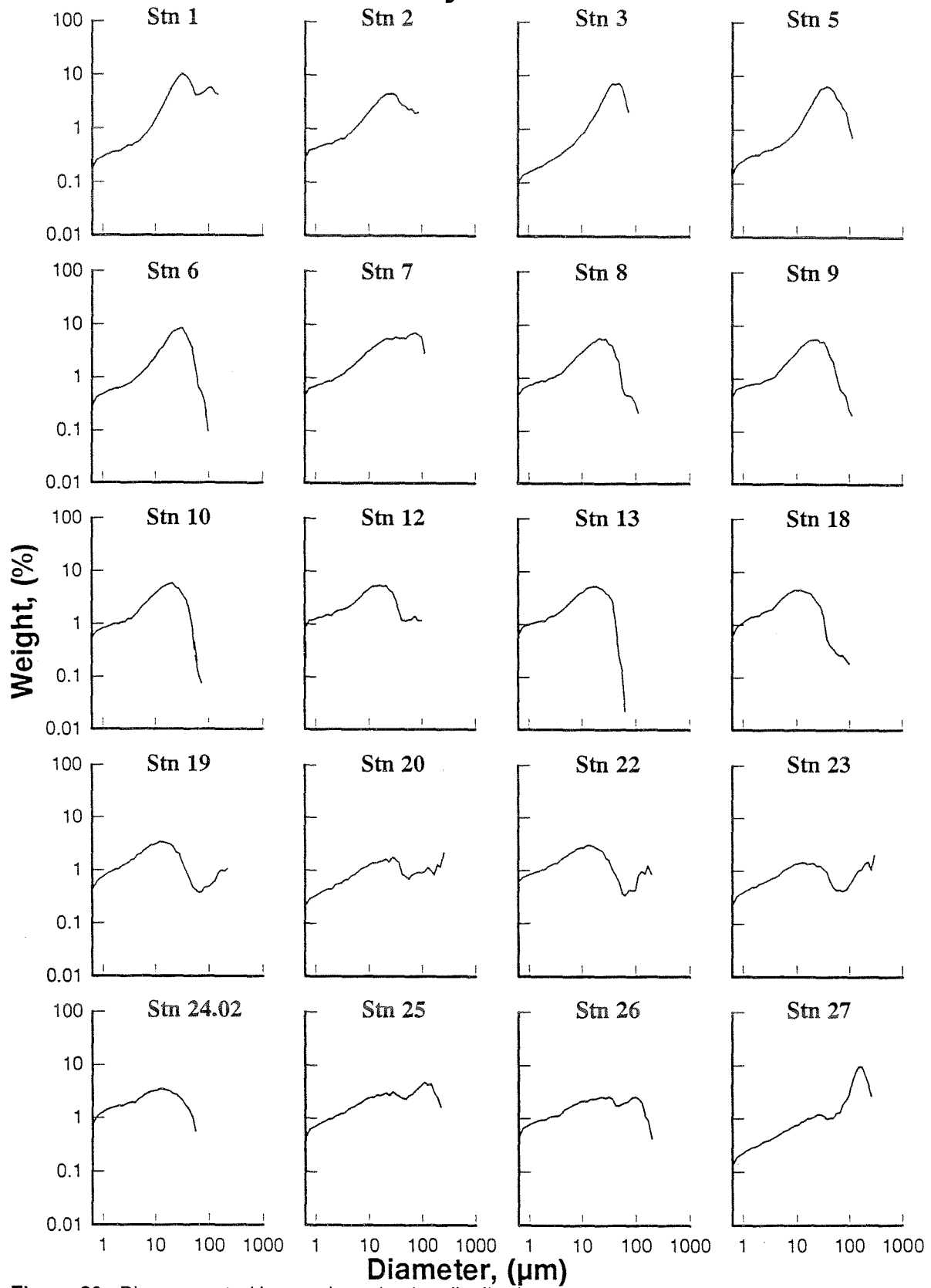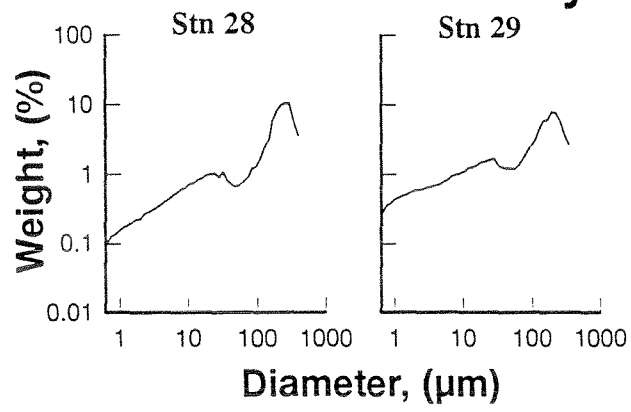
Country Harbour
Al %

Figure 40. Aluminium concentrations in surficial sediments

Country Harbour
Fe %

Stormont

Isaacs Harbour

45.26 N

2.0 2.8
1.8 2.5
1.9 3.2
1.9 1.8 2.6
2.1
2.3 3.2

45.20 N

3.1 3.0

3.0
2.4 2.7
2.9 2.9

2.6 1.8
1.5
2.1
2.3

45.14 N

61.75 W 61.65 W
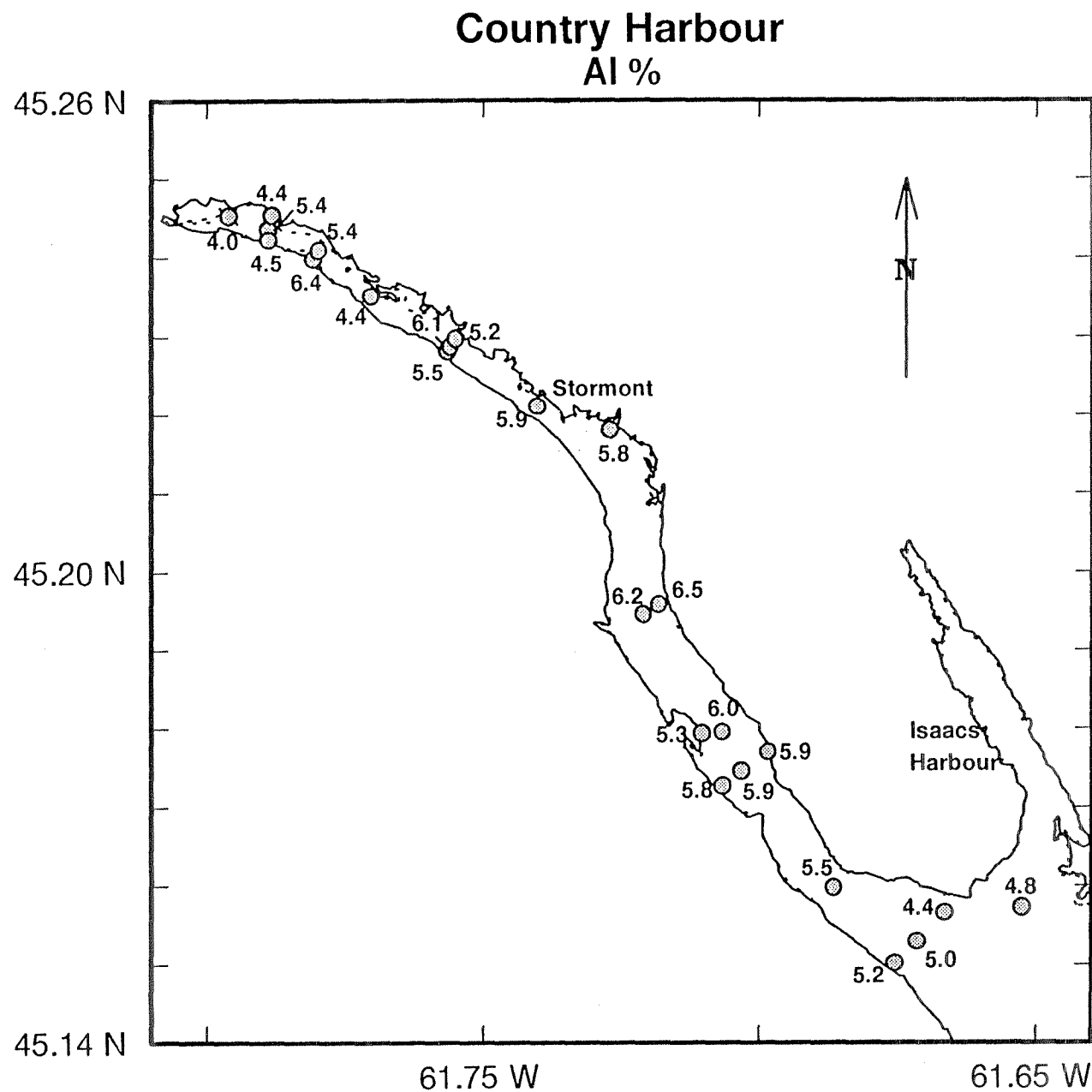
Figure 41. Iron concentrations in surficial sediments

63

Country Harbour
As mg/kg

45.26 N

8
18
8 18
11 18
11
9 17
9
17 Stormont
21

45.20 N
19 17

18
2 13
18 16

16
14 10
11 11

45.14 N

61.75 W   61.65 W

Isaacs
Harbour

N
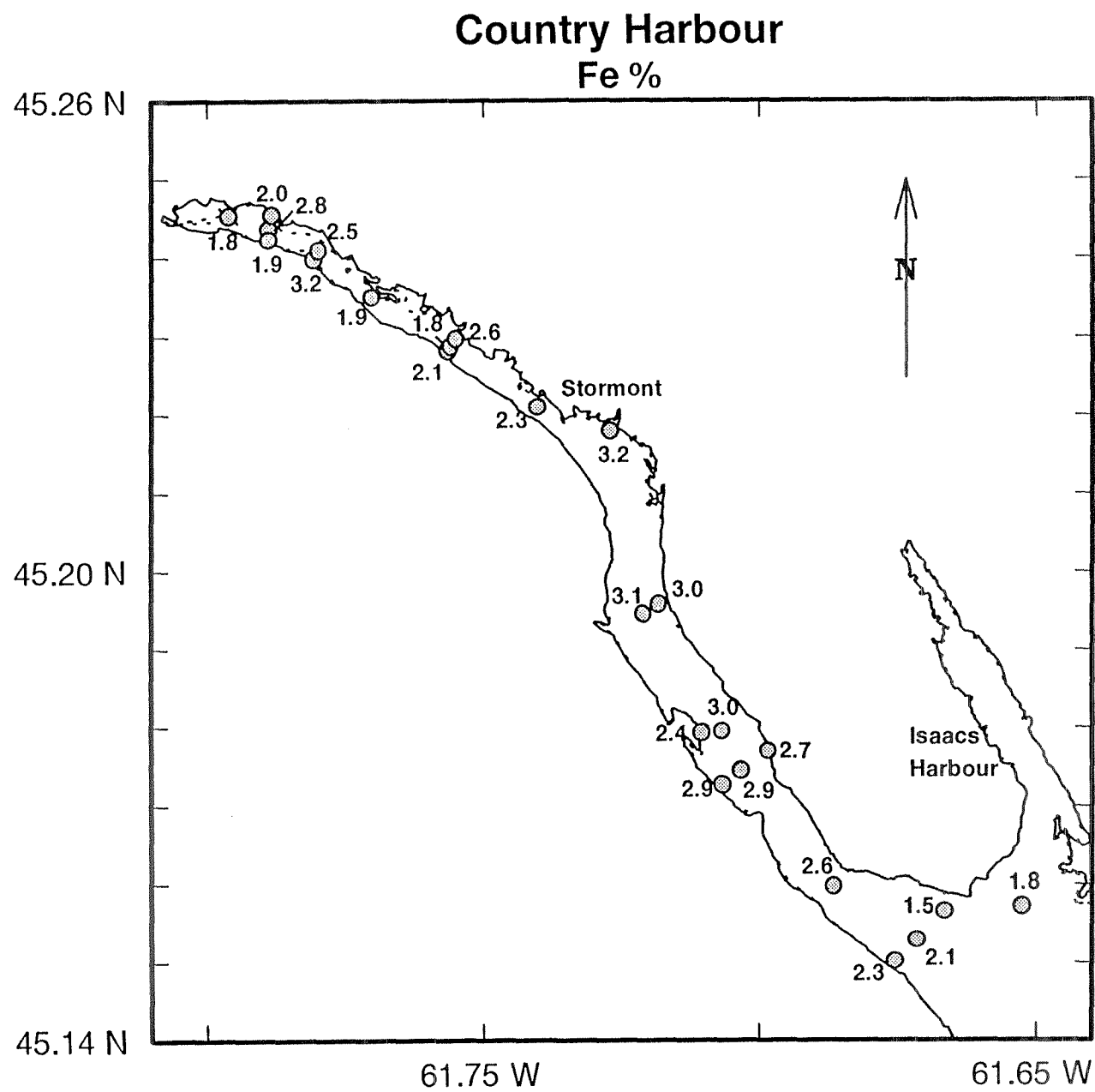
Figure 42. Arsenic concentrations in surficial sediments

Country Harbour
Cd mg/kg

45.26 N

0.25
0.58
0.12 0.47
0.22
0.78
0.39 0.29 0.62
0.43
Stormont
0.45
0.74

N

45.20 N

0.41
0.48

0.45
0.02
0.42
0.52
0.49

Isaacs
Harbour

0.39
0.22
0.30 0.12
0.31

45.14 N

61.75 W   61.65 W
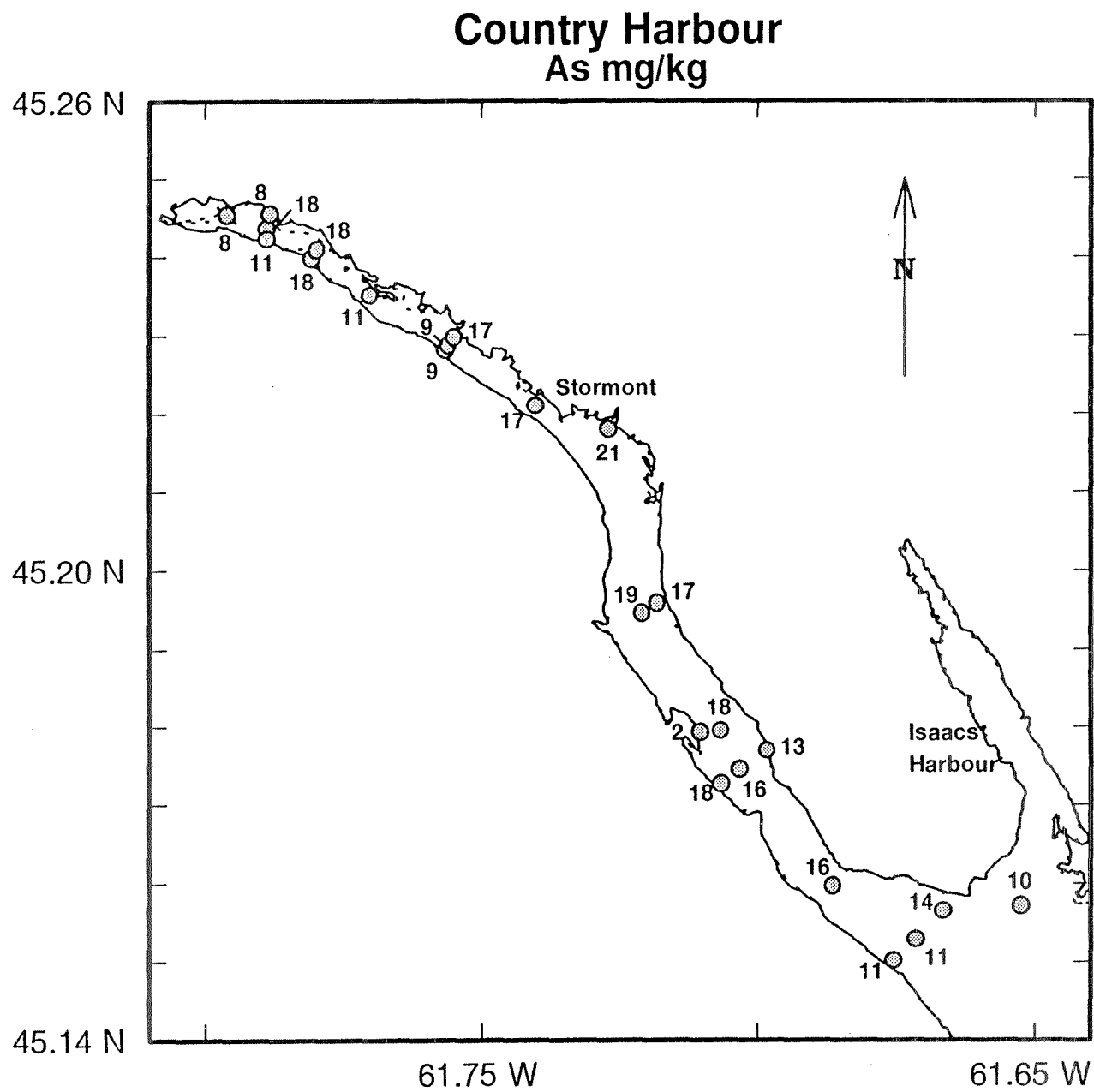
Figure 43. Cadmium concentrations in surficial sediments

Country Harbour
Cr mg/kg

45.26 N

41 53
38 57
41 73
43 43 57
46

Stormont

57 73

45.20 N

75 82

75
37 70
70 70

60 36
31
53 51

Isaacs
Harbour

N

45.14 N

61.75 W   61.65 W
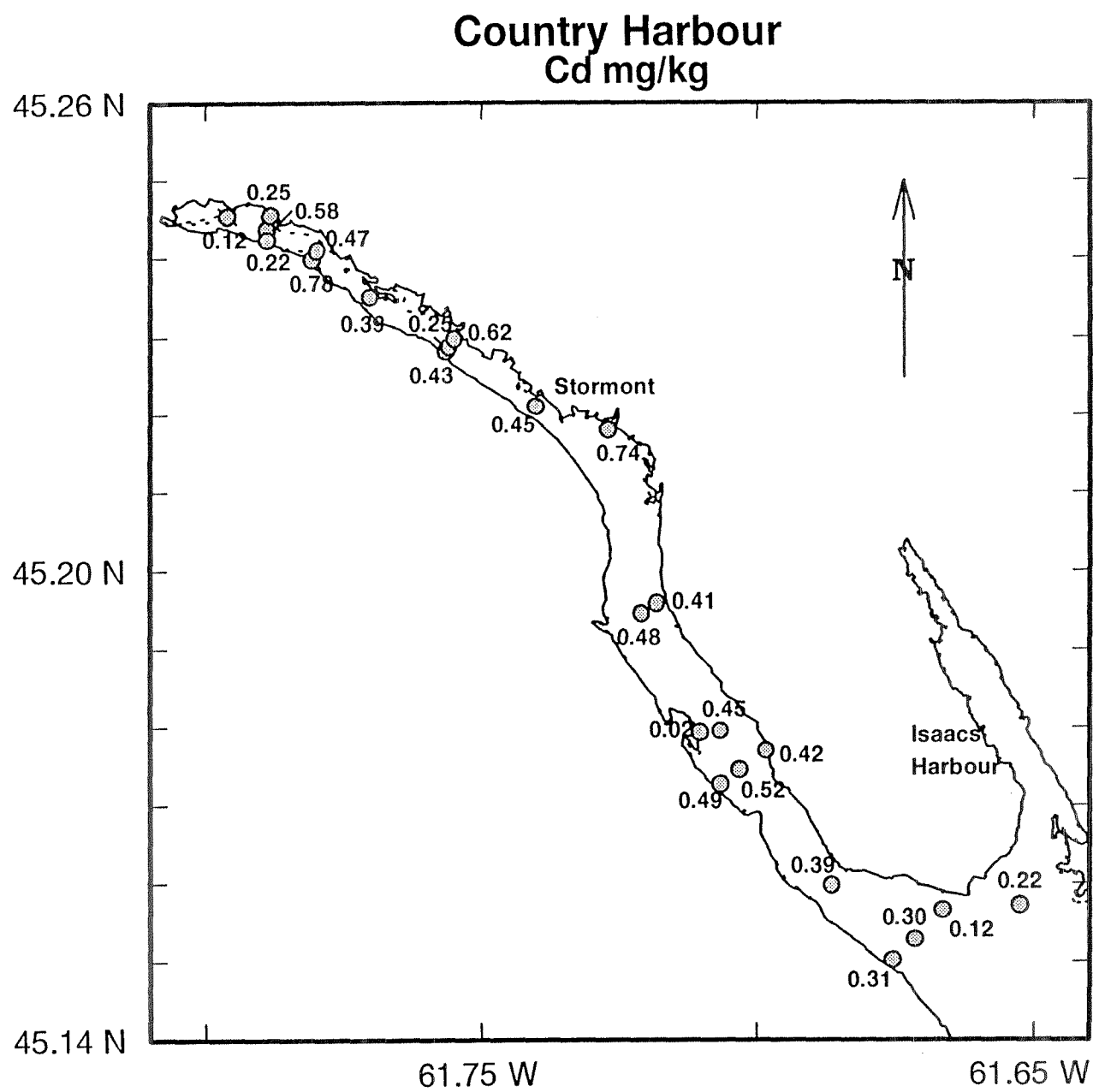
Figure 44. Chromium concentrations in surficial sediments

Country Harbour
Cu mg/kg

45.26 N

10
17
8
17
12
25
17
11 21
11
17 Stormont
24

45.20 N

23 28

24
15
20
21 22

18
9
11
16 15

N

Isaacs
Harbour

45.14 N

61.75 W
61.65 W
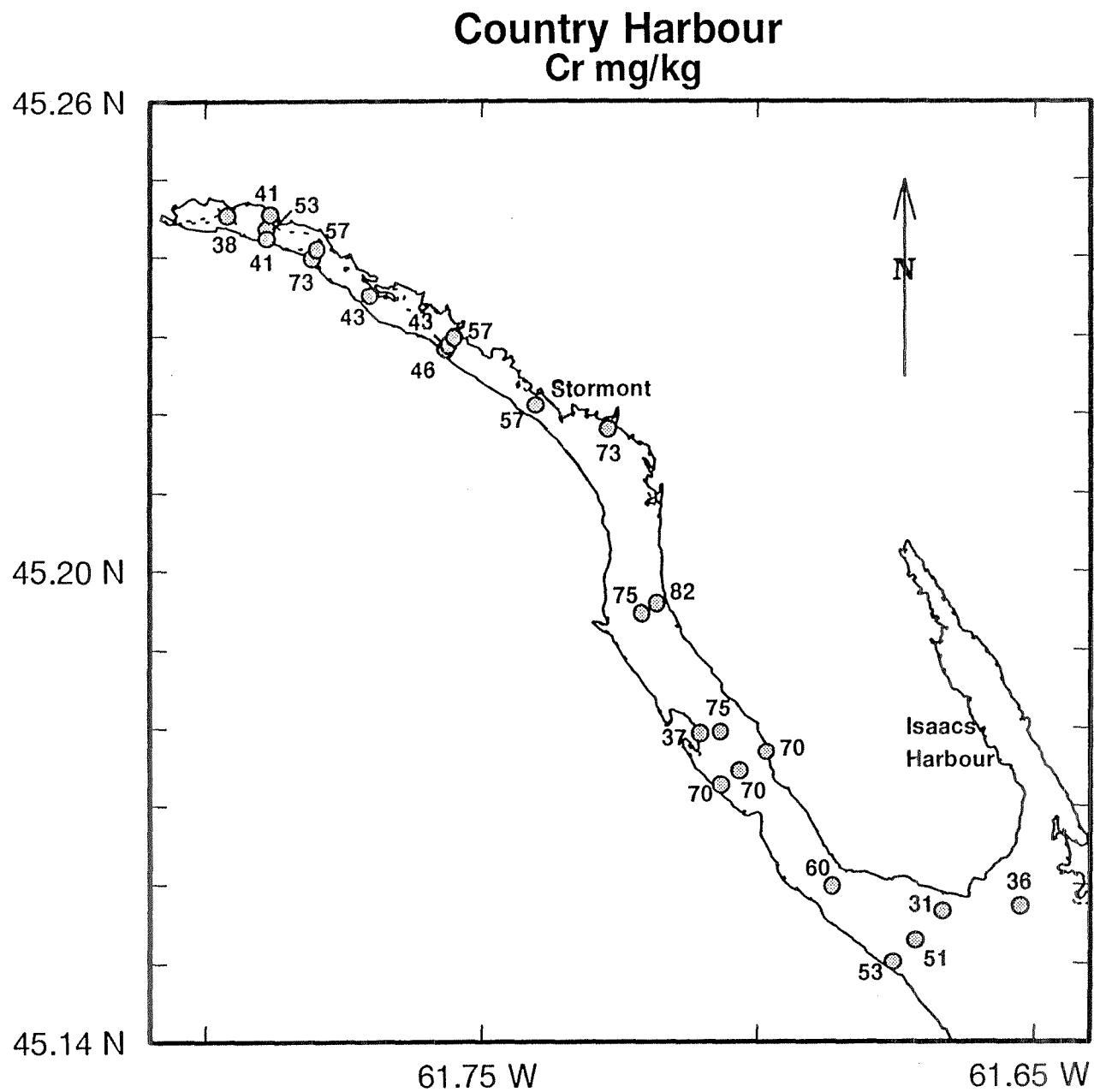
Figure 45. Copper concentrations in surficial sediments

Country Harbour
Hg mg/kg

45.26 N

0.04
0.08
0.03
0.07
0.04
0.09
0.05
0.05 0.06
0.05

Stormont
0.07
0.07

N

45.20 N

0.07
0.07

0.06
0.01 0.05
0.05

Isaacs
Harbour

0.05 0.05

0.04
0.03
0.04 0.03
0.04

45.14 N

61.75 W   61.65 W
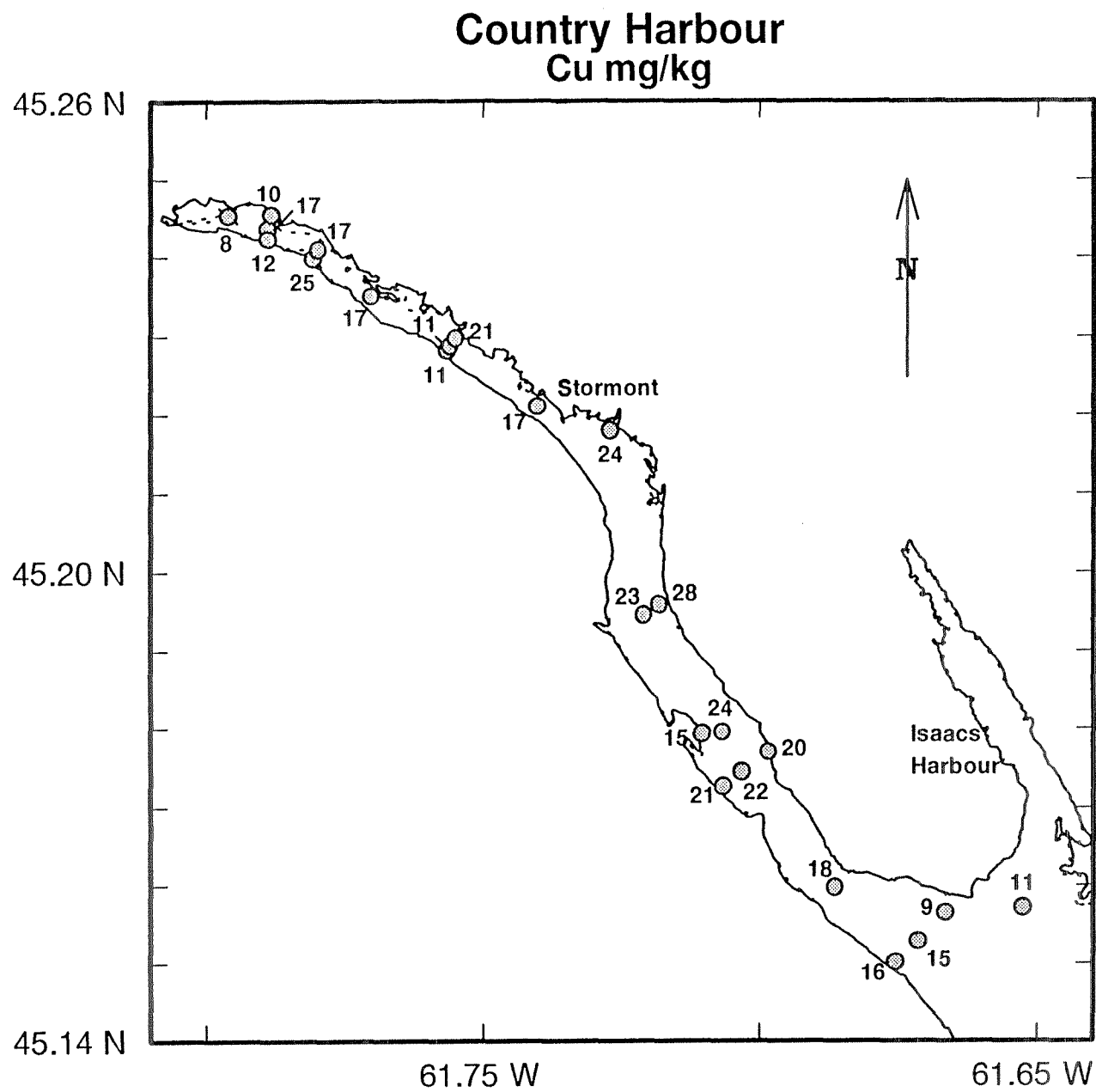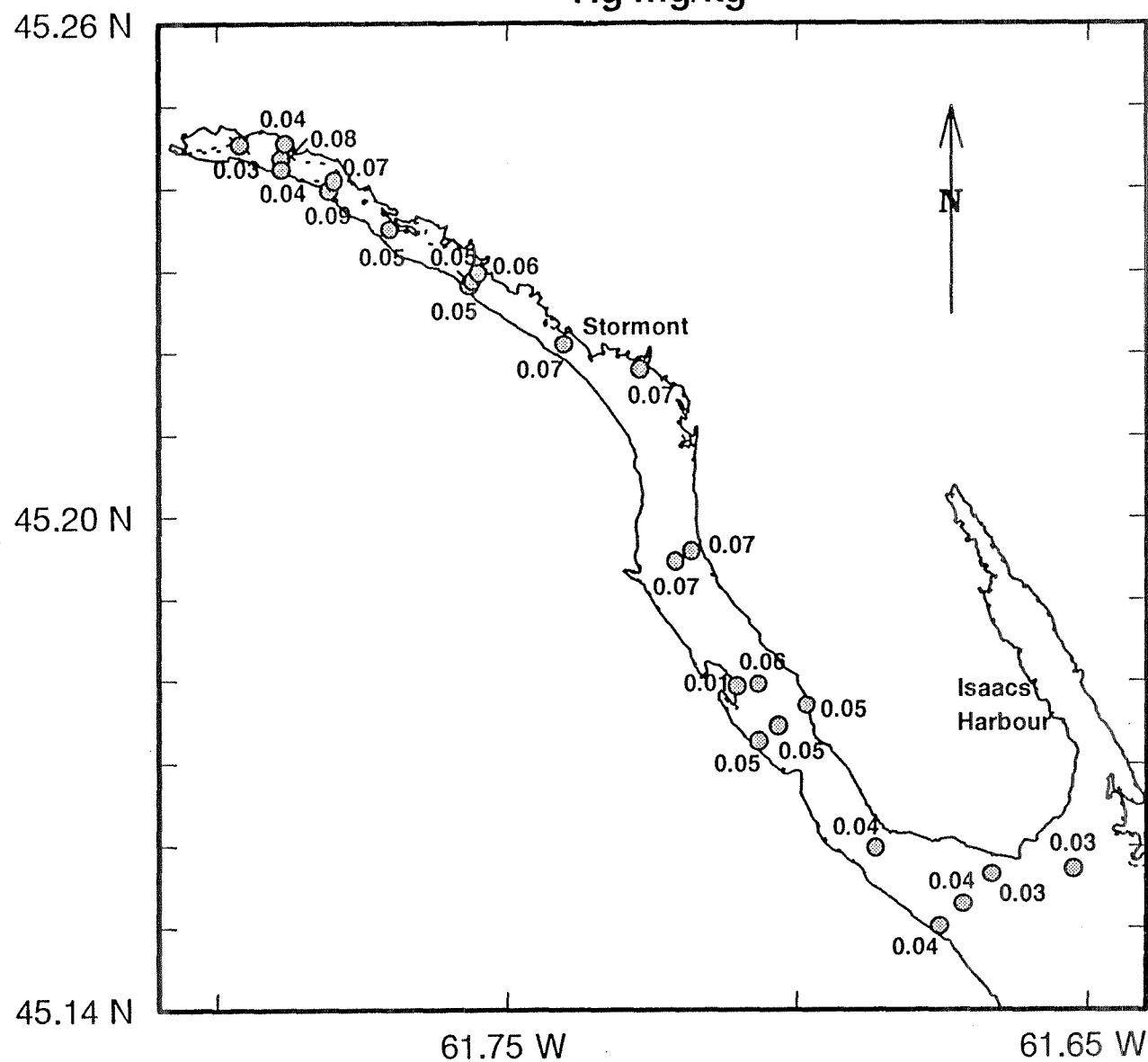
Figure 46. Mercury concentrations in surficial sediments

Country Harbour
Li mg/kg

Figure 47. Lithium concentrations in surficial sediments

Country Harbour
Mn mg/kg
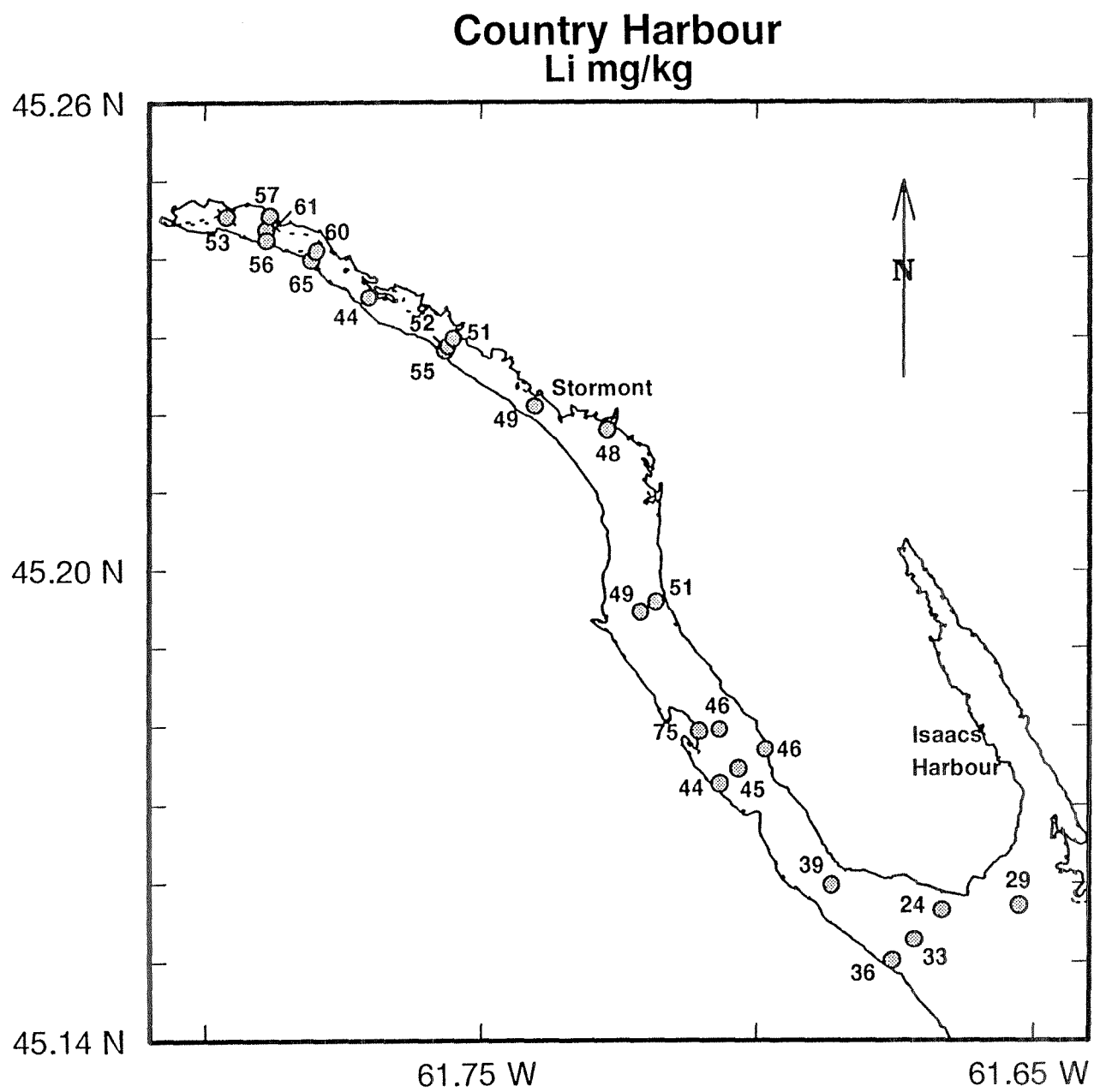
Figure 48. Manganese concentrations in surficial sediments

Country Harbour
Ni mg/kg
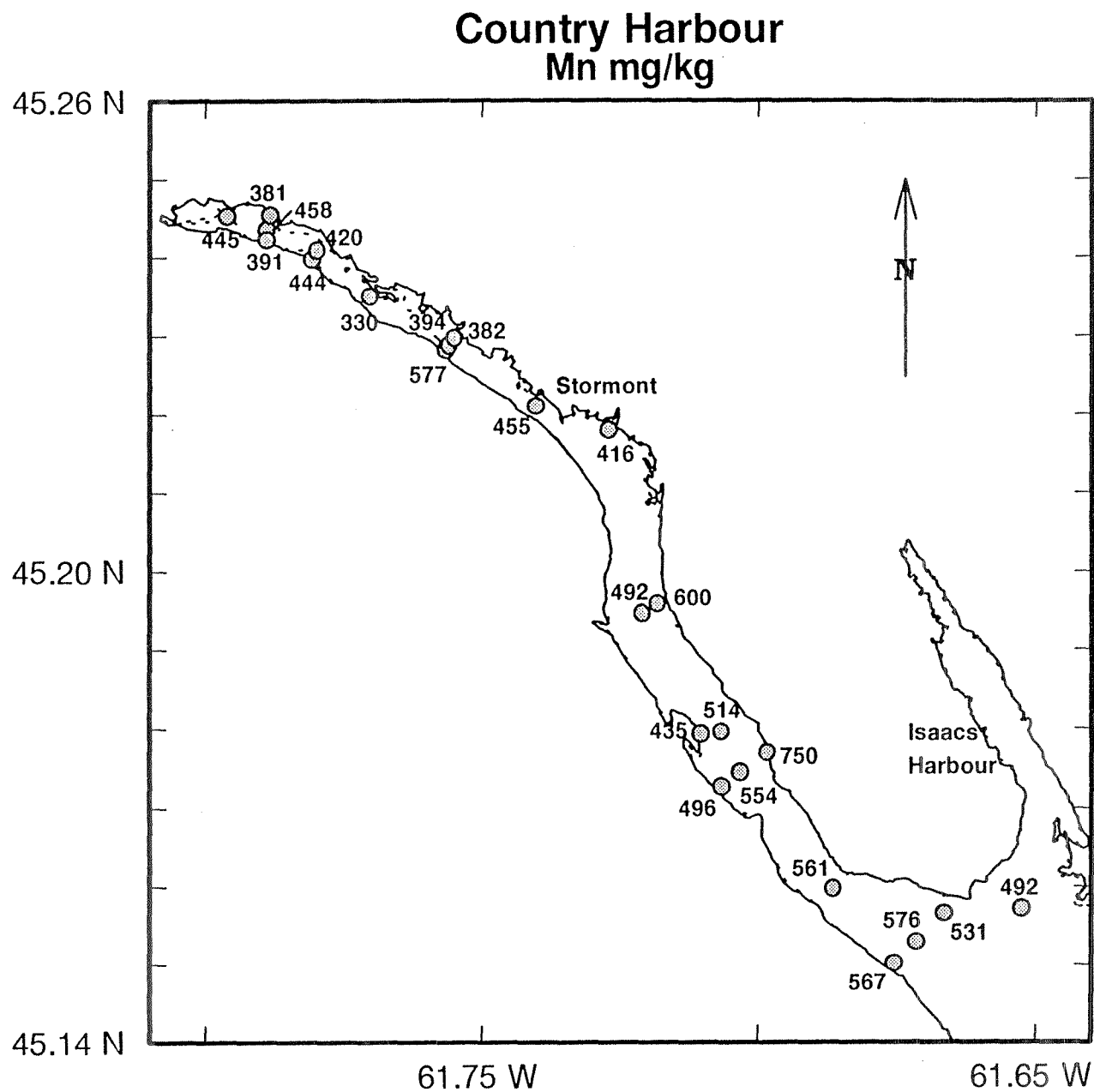
Figure 49. Nickel concentrations in surficial sediments

Country Harbour
Pb mg/kg

45.26 N

16
25
13   25
16
40
22   26   27
25
26   Stormont
32

45.20 N

31   32

31
13   31
28   28

Isaacs
Harbour

25
13   16
20
23

45.14 N

61.75 W   61.65 W
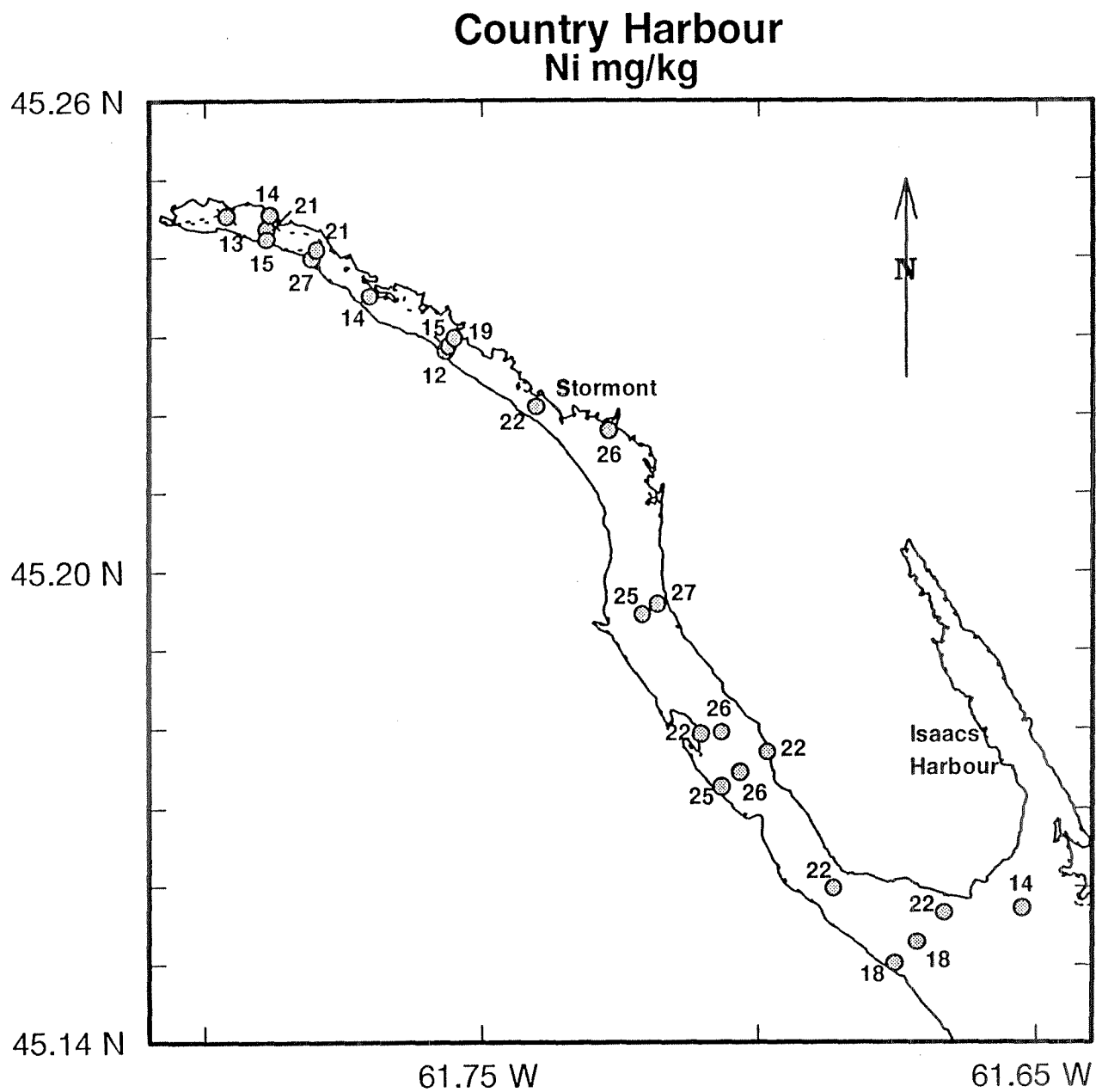
Figure 50. Lead concentrations in surficial sediments

Country Harbour
Sn mg/kg

45.26 N

2.3
2.2
3.6
2.0   2.0 2.0
2.0
Stormont
2.0
3.0

N

45.20 N

2.0 3.0

2.0
2.0
2.0 2.0

Isaacs
Harbour

2.0

2.0
2.0 4.0
2.0

45.14 N

61.75 W   61.65 W
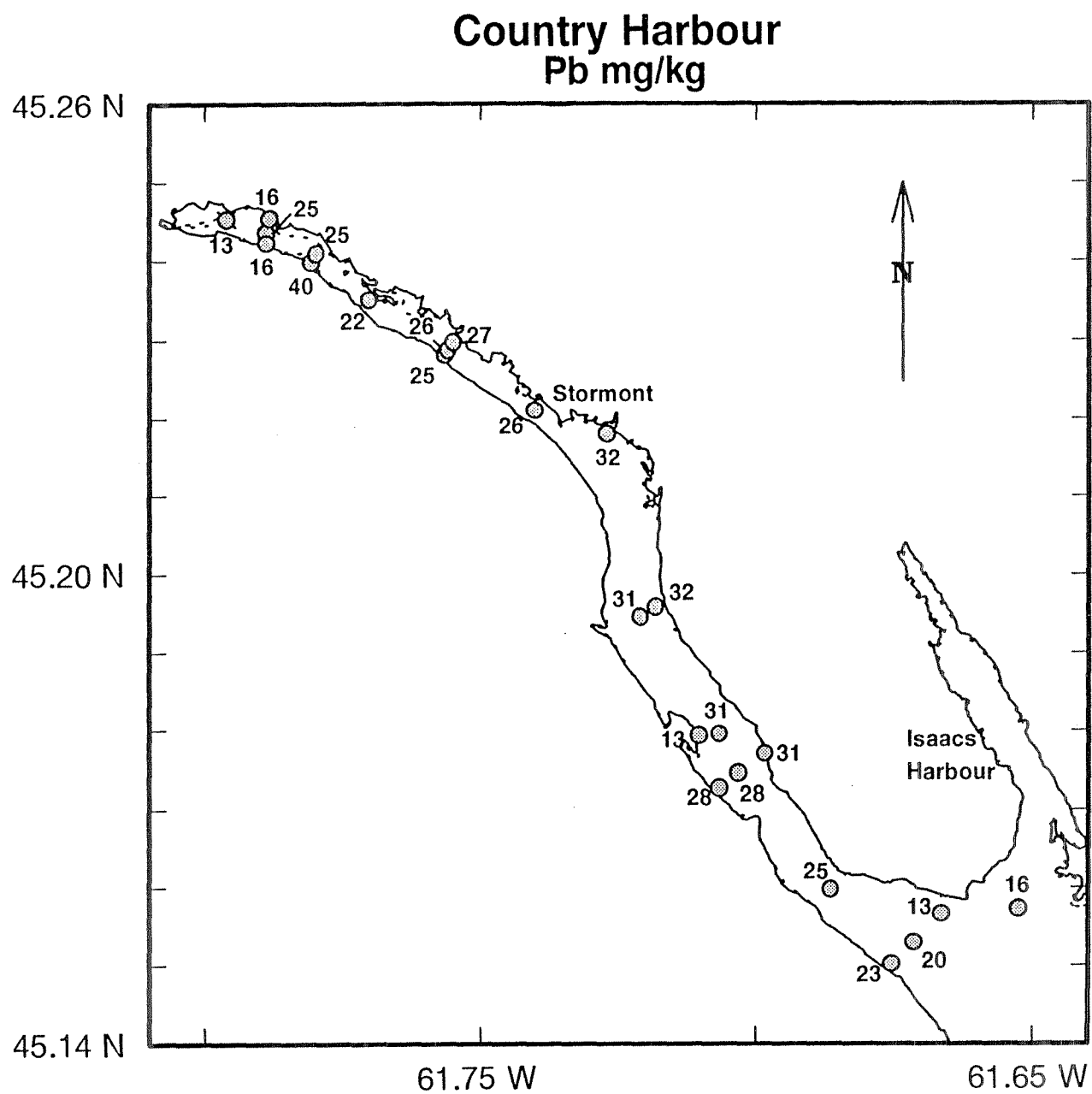
Figure 51. Tin concentrations in surficial sediments

Country Harbour
V mg/kg

45.26 N

43
57
57
36
43
79
47
50 70
43
Stormont
74
92

45.20 N

83 92

84
47
72
79 79

Isaacs
Harbour

67
41
63

54

45.14 N

61.75 W   61.65 W
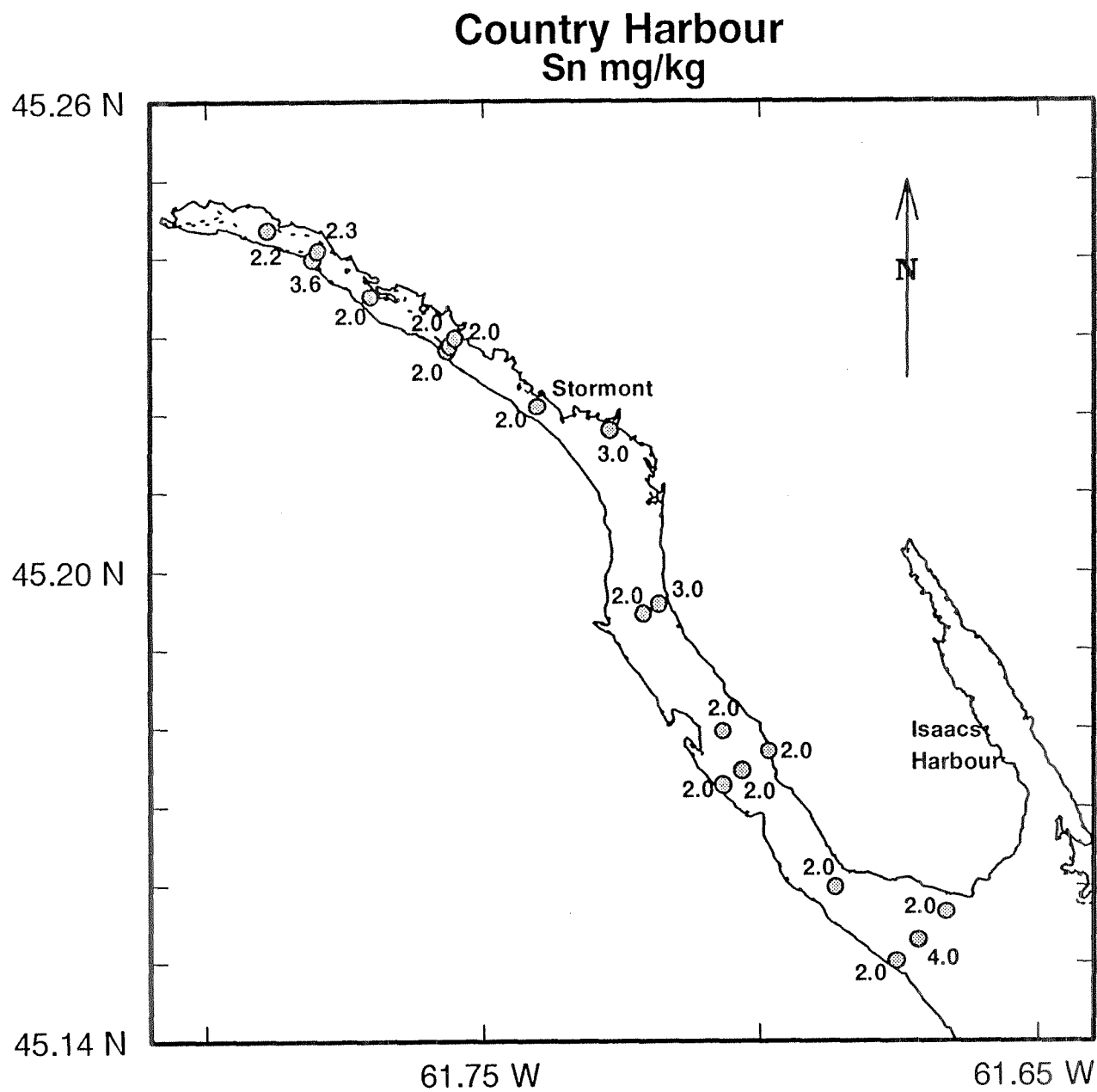
Figure 52. Vanadium concentrations in surficial sediments

Country Harbour
Zn mg/kg

Figure 53. Zinc concentrations in surficial sediments

LAHAVE ESTUARY

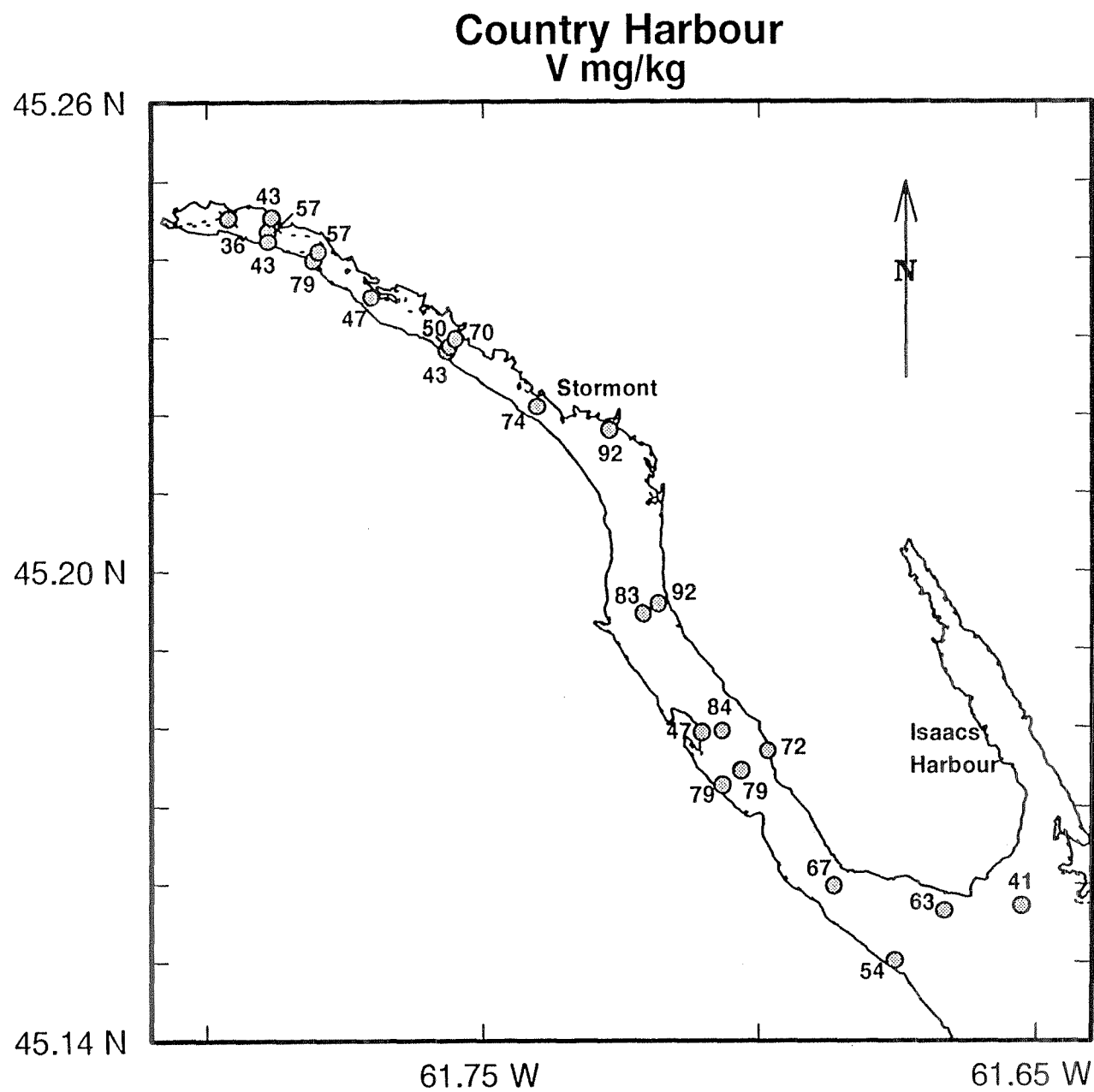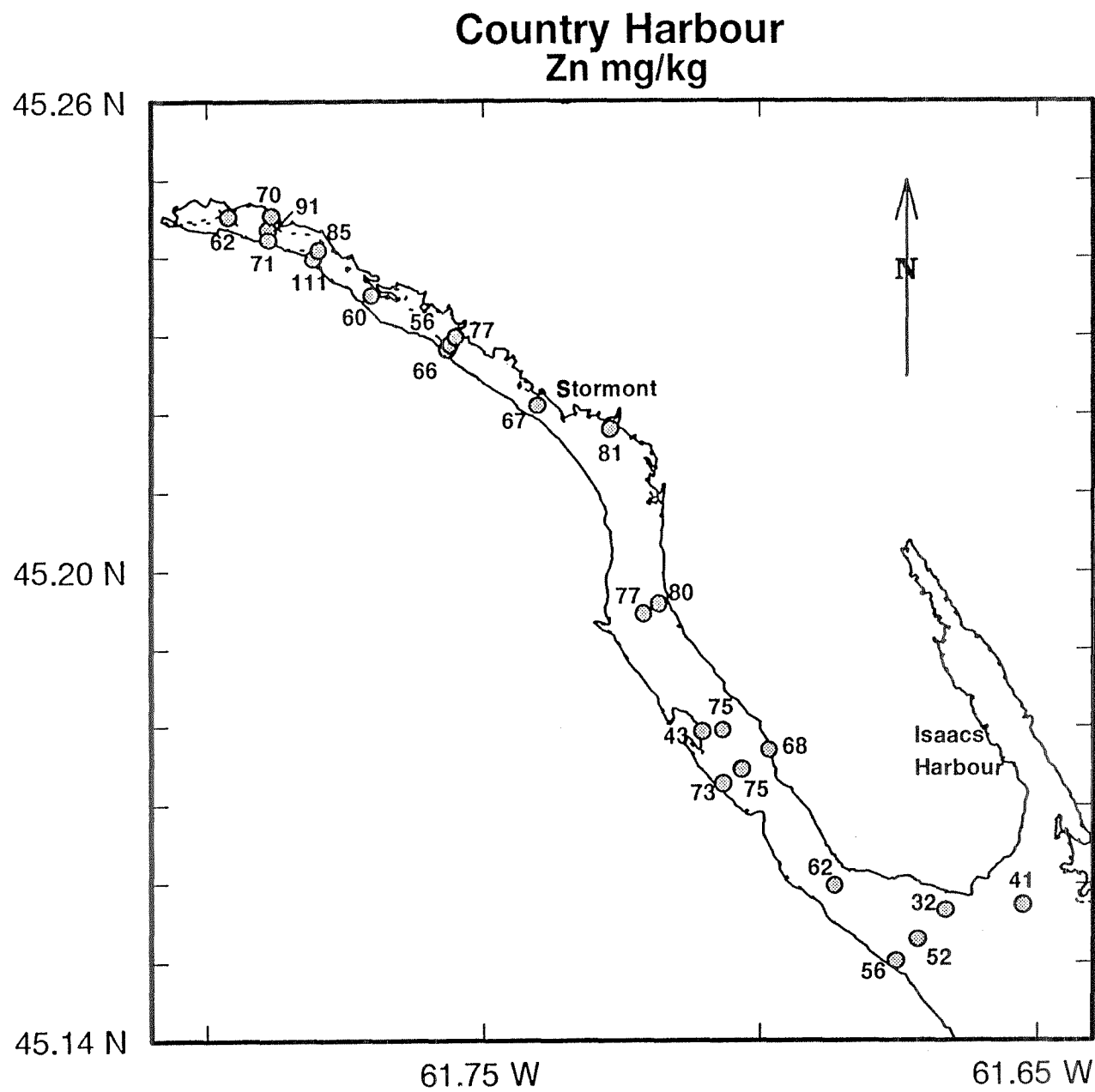The LaHave estuary occupies a long (24.3 km), narrow (0.3-3.3 km), deep (water depths up to 22 m) inlet running into the south shore of Nova Scotia, approximately 100 km southwest of Halifax. The estuary receives drainage from the LaHave River which has a comparatively large drainage area of 1741.6 km². The drainage basin is mainly wooded with vegetation developed on a thin mantle of glacial till underlain primarily by Devonian granites and Precambrian quartzites and slates. Cultivated land along the river supports mixed farming.

POTENTIAL SOURCES OF CONTAMINATION

Agricultural, urban, and industrial discharges are potentially the main sources of contaminants in the estuary. Tidal water extends inland to the commercial town of Bridgewater which has a population of approx. 7,000. Aside from the potential contamination from urban wastes, the Michelin Tire Company, the largest industrial plant in the area, is situated on the River upstream of the town. Rural dwellings and small villages are also scattered along both sides of the River and seaward to the mouth of the estuary.

RESULTS

Sediment Samples and Composition

Surface sediments: The locations of the sampling stations (n=35) are shown in Figure 54. Grain-size data indicate that fine-grained sandy muds and black organic-rich muds (Fig. 55) occupy most of the estuary with the sediments becoming increasingly sandy toward its mouth. Fine sediments in the upper part of the estuary contain relatively high amounts of wood fibers, twigs, and leaves.

The samples collected in the LaHave estuary show the transition of sediment sizes and relative proportions of floc, single grain, and sorted sediments typically found in estuaries (Fig. 56). At the River mouth, samples have undefined modes and are relatively coarse, reflecting the nature of the material by the River (source slope -0.356) and the rapid deposition that occurs as River flow decreases. Proceeding seaward from the line of Stations 4 to 6, where there is no apparent sorting of the sediment, the development of a one round, single-grain settling peak can be observed in Stations 16 to 18 and beyond. Further offshore, the one round peak and floc tail start to disappear as sorting by tidal currents increases. In distal areas, well sorted fine sands dominate the size distribution. The development of the prominent floc tail in the central region is a result of the increase in tidal influence. Floc-settled material varies from less than 20% in the river mouth to a maximum of 35% at Stations 6 and 9 and then decreases seaward to less than 1% at Station 35. The high concentration of floc-settled material and the very fine-grained nature (modal diameter ~10 µm) of the samples collected in the central part of the LaHave estuary suggests that a turbidity maximum in which fine particles are trapped is located in this region.

Core Sediments: Sediment cores ranging in length from 7 to 20 cm were obtained at three stations: Station CA at the head of the estuary, and Stations CB and CC, respectively 3 km and 14 km seaward (Fig. 54). The core from Station CA is 7 cm in length and is composed of black organic-rich (10-16% OM) muds containing many wood shavings and chips. Sediments from the core obtained at Station CB (20 cm in length) also comprise black organic-rich (7-8% OM) muds. The core from Station CC is 20 cm in length. Within it, there is a general increase in fine material (<63 µm) with depth. The top part of the core is characterized by a 4- to 5-cm layer of muddy sand underlain by 15 cm of very sandy muds and sandy muds. The stratigraphy of the core suggests recent burial of the fine-grained material by the deposition of sandy material either from local erosional processes or dredging.

Abundance and Distribution Metals in Surface and Subsurface Sediments

Surface Sediments: The abundances and distributions of the metals in the surface sediments are shown in Figures 57 to 70. The highest concentrations of As, Cd, Cu, Hg, Pb, Sn, and Zn occur in the upper part of the estuary near Bridgewater and decrease seaward. Anomalous levels of Cd, Cu, Pb, and Sn also occur near the wharf at Riverport in the lower part of the estuary. The concentrations of Cr, V, and Ni, however, show only slight seaward decreases or remain relatively constant throughout the estuary.

The range of total metal concentrations measured in the LaHave estuarine sediments (n=35) are: As, 6-42 mg·kg^{-1}; Cd, 0.02-0.49 mg·kg^{-1}; Cr, 52-128 mg·kg^{-1}, Cu, 4-55 mg·kg^{-1}; Hg, 0.01-0.34 mg·kg^{-1}; Ni, 12-46 mg·kg^{-1}; Pb, 15-78 mg·kg^{-1}; Sn, 1.6-8.4 mg·kg^{-1}; V, 33-115 mg·kg^{-1}; and Zn, 24-150 mg·kg^{-1} (Table 10). The LaHave estuarine sediments contain above-normal levels of As, Cd, Cu, Hg, Pb, and Sn (Fig. 12 to 18). The data (Table 2) indicate that 51% of the samples contain >20 mg·kg^{-1} As, 34% contain >0.3 mg·kg^{-1} Cd, 31% contain >40 mg·kg^{-1} Cu, 48% contain >0.1 mg/kg^{-1} Hg, 49% contain >40 mg·kg^{-1} Pb, and 48% contain >5 mg·kg^{-1} Sn.

Subsurface Sediments: The means, standard deviations, and range of the metals in the sediment cores are shown in Table 11. The vertical distributions of As, Cd, Cu, Hg, Pb, Sn, and Zn in each of the cores are shown in Figures 71 to 73. These data indicate that the subsurface sediments are contaminated over their entire length with As, Cd, Cu, Hg, Sn, and Zn in the core obtained at Station CA and with As, Cu, Pb, Sn, and Zn in the core obtained at Station CB. Metal concentrations, however, are lower in the sandy muds and muddy sands comprising the core obtained from Station CC, although Cd concentrations exceed background levels below 5 cm in this core.

Potential Bioavailability of Metals

Chemical partitioning of selected samples indicate that most (78-82%) of the total Cd, 9-20% of the total Cu, 21-36% of the total Pb, and 20-50% of the total Zn are weakly held in the

sediments. Thus, most of the Cd and considerable amounts of Pb and Zn are potentially bioavailable. Chemical partitioning of two samples (4 and 7 cm) from the Station CA core showed that 41-81% of the total Cd, 13-20% of the total Cu, 28-40% of the total Pb, and 50% of the total Zn are weakly held in the sediments. Partitioning of two samples (1 and 18 cm) from the Station CB core showed that 81-86% of the total Cd, 3-6% of the total Cu, 19-39% of the total Pb, and 37-40% of the total Zn are weakly held in the core sediments. Similar partitioning of two samples (1 and 8 cm) from the Station CC core showed that 60-74% of the total Cd, 10-22% of the total Cu, 17-28% of the total Pb, and 9-34% of the total Zn are weakly held in the sediments.

Metal Carriers and Sources

Significant positive correlations of the metals with increasing content of fine material (<63 μm) (excepting Hg and Mn) and organic matter (excepting Mn) indicate that the predominant metal carriers are fine-grained organic-rich material (Table 12). The significant covariances ($p<0.01$) of As, Cd , Cr, Cu, Hg , Pb, Sn, and Zn with Li show that fine-grained aluminophyllosilicate minerals normalize only partially for the granular and mineralogical variability of these metals in the surface sediments. The proportion of the metal variability explained by the granular variability of the Al-Li bearing minerals is relatively small compared to some of the other embayments. It decreases in the order of Zn (72%) > Pb (63%) > As (61%) = Sn (61%) = Cu (61%) > Cr (63%) > Hg (45%) > Cd (41%). Inspection of the correlation matrix indicates stronger correlations of Cd, Cu, Hg, Pb, Sn, and Zn, with Fe, Li, and organic matter. These relationships suggest that discrete fine-grained metallic particles are carriers of Cu, Cd, Hg, Pb, Sn, and Zn of non-detrital origin and that these are associated with the organic component of the sediments rather than the Fe-Li bearing aluminosilicates (chlorite). Anomalous levels of these metals are most likely present in metal-bearing iron monosulphides and/or pyrite formed *in situ* in these organic-rich, fine-grained sediments.

The relatively high amounts of Cd, Pb, and Zn in the HOAc soluble fraction suggest that these metals are weakly held by the monosulphides and the organic component of the sediments. The strong correlation of As with Fe suggests that As is associated with the iron-rich fraction of the fine-grained particles throughout the estuarine sediments either as primary As-Fe sulphides or in a diagenetic association in the oxidized layer at the sediment water interface. The highest As concentrations are found in mid-estuary (Stations 10 to 12) and do not appear to be related to any known point source other than a possible rural sewer outfall.

The strong positive correlations of As and Cr with Fe, Li, and grain-size suggests that these metals are most likely present in fine discrete oxide and sulfide particles in addition to proportions of Cr being naturally structurally combined in the lattices of the aluminosilicate minerals. Factor analyses indicate that the seaward decrease in the concentrations of Cd, Cu, Hg, Pb, Sn, and Zn associated with organic matter is the most important factor (accounting for 47% of the variance) controlling the distribution of these metals. Factor analyses also indicate that the distribution of the fine-grained aluminosilicates containing Al, Fe, and Li appear to control the distribution of Cr, Ni, and V (accounting for 34% of the total variance). The seaward decrease

and high proportion of HOAc-extracted Cd (>90%), Pb (34-45%), and Zn (41-53%) in sediments from the upper parts of the estuary points to industrial and urban discharges as sources of these metals, and Cu, Hg, and Sn in the LaHave estuary.

Table 10

Textural and metal statistics[a] for the LaHave estuarine sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	30	75.8	± 26.4	2-99	OM%	34	5.60	± 3.04	0.14-10.9
Metal					Metal				
Al%	35	6.25	± 0.44	5.11-6.95	Fe	35	3.46	± 0.95	1.60-4.84
As	35	21.0	± 9.0	6-42	Li	35	56.0	± 8.6	29-69
Cd	35	0.27	± 0.11	0.02-0.49	Ni	35	21.7	± 6.3	12-46
Cr	35	74.9	± 15.1	.52-128	Pb	35	45.3	±22.1	15-78
Hg	33	0.12	± 0.09	0.01-0.34	V	35	85.5	±22.4	33-115
Mn%	35	0.066	± 0.02	0.037-0.185	Zn	35	96.0	±37.8	24-150

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM), Al, Fe, and Mn

Table 11

Statistical data for trace element, Al and Fe concentrations (mg kg^{-1} except % for Al and Fe) in LaHave subsurface sediments

Core sediments:

Core CA n= 7	As	Cd	Cr	Cu	Hg	Li	Mn
Mean	21	0.55	62	60	0.20	55	638
SD	2	0.05	7	3	0.08	1	54
CV%	11	8	11	5	36	3	9

	Ni	Pb	Sn	V	Zn	Al%	Fe%
Mean	24	85	7	90	152	5.62	5.62
SD	2	5	1	8	7	0.24	0.24
CV%	7	6	17	9	5	4	3

Core CB n=13	As	Cd	Cr	Cu	Hg	Li	Mn
Mean	27	0.25	88	36	0.11	68	687
SD	6	0.02	4	2	0.02	2	21
CV%	24	11	4	6	18	3	3

	Ni	Pb	Sn	V	Zn	Al%	Fe%
Mean	30	62	5	114	126	7.10	4.50
SD	2	2	0.4	7	4	0.13	0.15
CV%	7	4	8	6	3	2	3

Core CC n=13	As	Cd	Cr	Cu	Hg	Li	Mn
Mean	11	0.38	54	18	0.03	45	630
SD	6	0.17	5	5	0.01	3	58
CV%	12	45	9	32	45	7	9

	Ni	Pb	Sn	V	Zn	Al%	Fe%
Mean	19	25	2.3	61	58	5.56	2.24
SD	7	6	0.5	10	18	0.19	0.48
CV%	35	22	21	17	30	3	21

n = number of samples:
SD = standard deviation.
CV% = coefficient of variation = standard deviation/mean X100

Table 12

Correlation Matrix LaHave Estuary

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	x	0.65	1									
Cr	0.69	0.65	x	1								
Cu	x	0.78	0.88	0.53	1							
Fe	0.61	0.90	0.69	0.75	0.86	1						
Hg	x	0.67	0.84	x	0.93	0.74	1					
Li	0.77	0.78	0.64	0.75	0.78	0.93	0.67	1				
Mn	x	x	x	x	x	x	x	x	1			
Pb	x	0.80	0.81	0.53	0.98	0.89	0.92	0.79	x	1		
Sn	x	0.81	0.87	x	0.97	0.89	0.92	0.79	x	0.98	1	
Zn	x	0.84	0.85	0.61	0.97	0.93	0.88	0.85	x	0.98	0.97	1
Mud	0.63	0.81	x	0.74	0.63	0.86	x	0.85	x	0.62	x	0.72
OM	x	0.87	0.81	0.61	0.93	0.95	0.83	0.84	x	0.95	0.95	0.96

n = 35; mud n =30
For $p \leq 0.001$ x = not significant
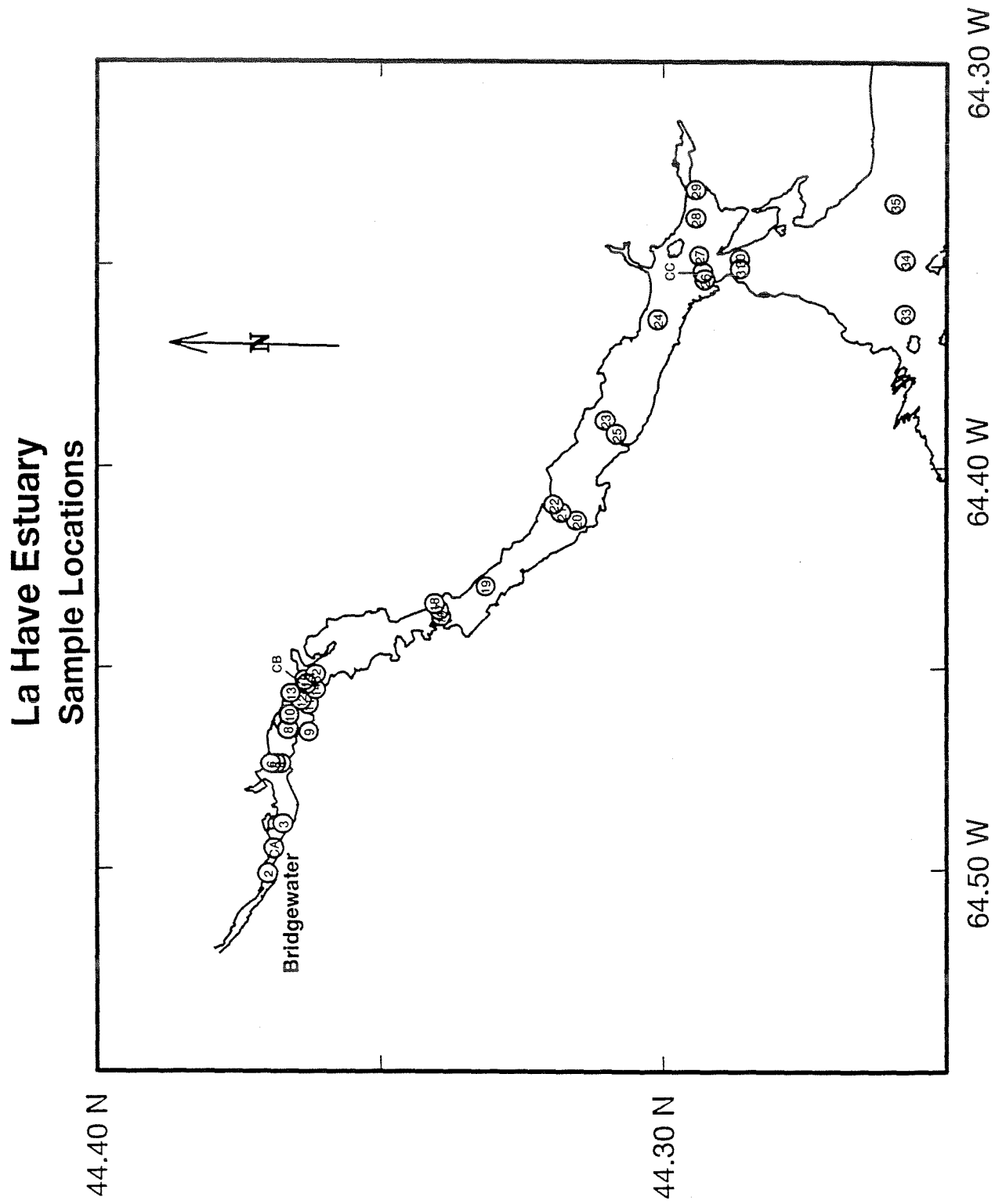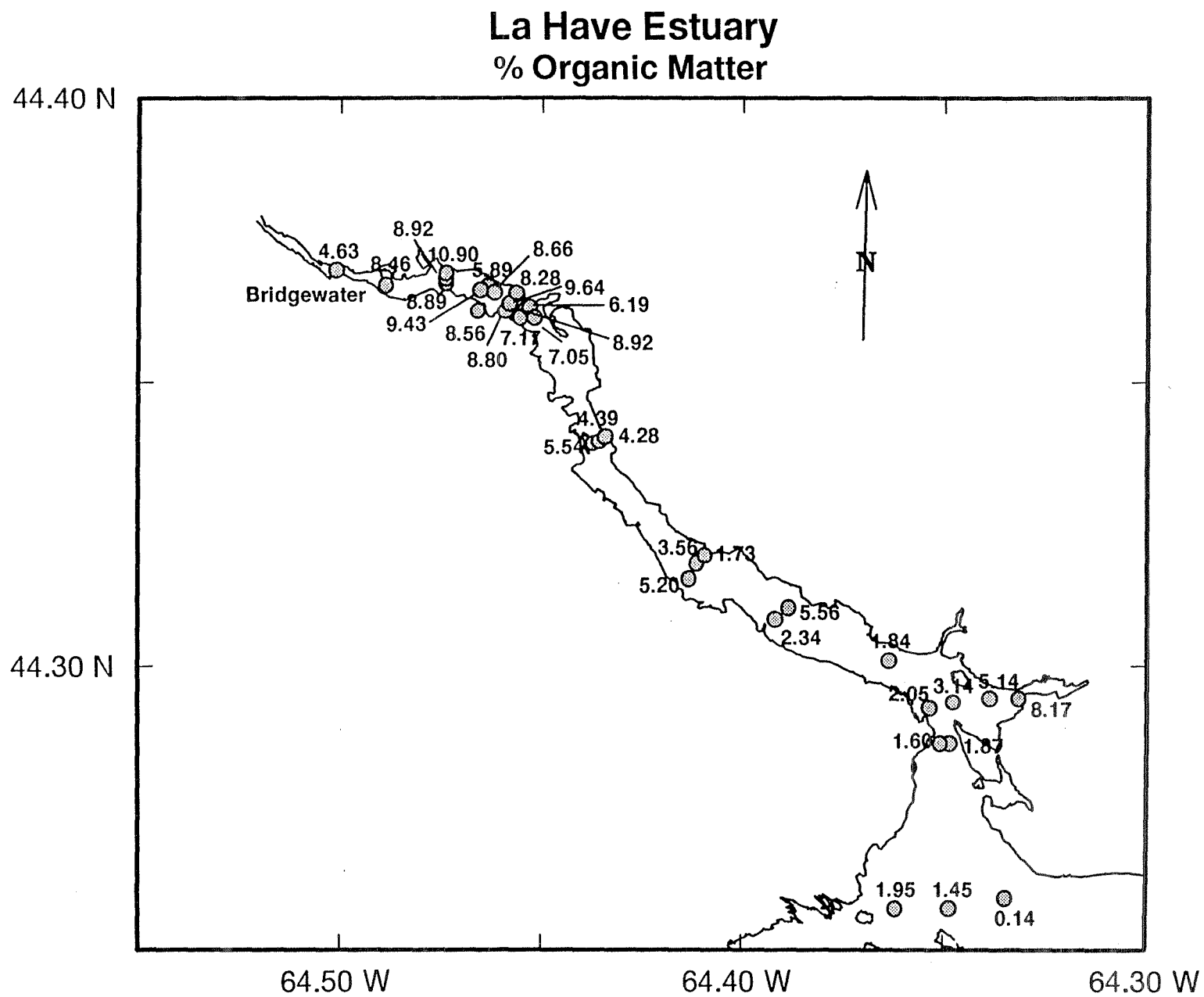mud = > 70% by weight material<63µm
OM = % by weight organic matter

Figure 54. Sample locations for La Have Estuary

La Have Estuary
% Organic Matter

44.40 N

8.92

4.63

8.46 10.90

5.89   8.66

Bridgewater   8.89   8.28

9.64

9.43   6.19

8.56   7.1

8.80   7.05   8.92

4.39

5.54   4.28

3.56   1.73

5.20

5.56

2.34

1.84

44.30 N

2.05 3.1   5.14

8.17

1.6   1.8

1.95   1.45

0.14

64.50 W

64.40 W

64.30 W

Figure 55. Organic matter concentrations in surficial sediments
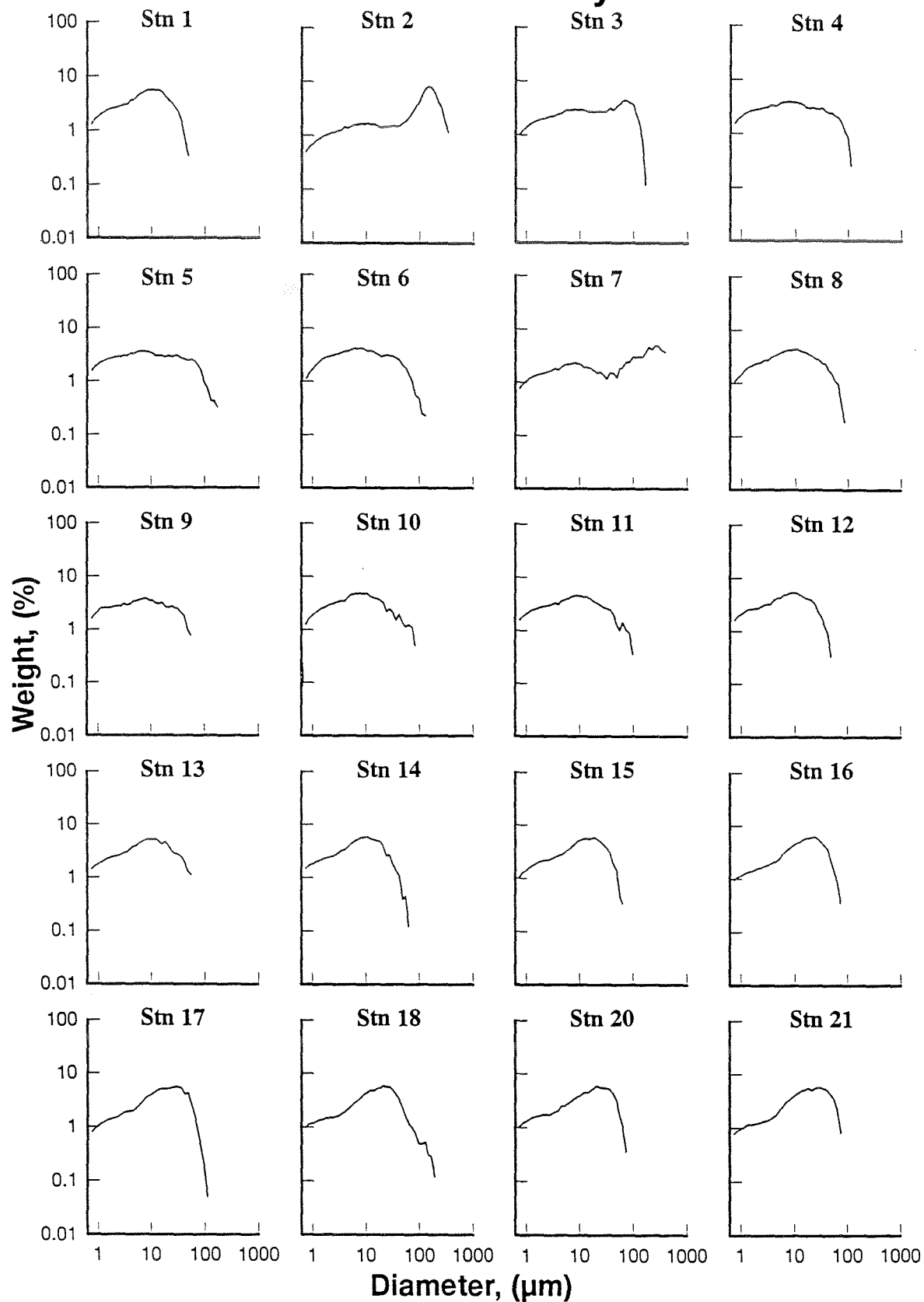
La Have Estuary

Figure 56. Disaggregated inorganic grain size distributions

La Have Estuary
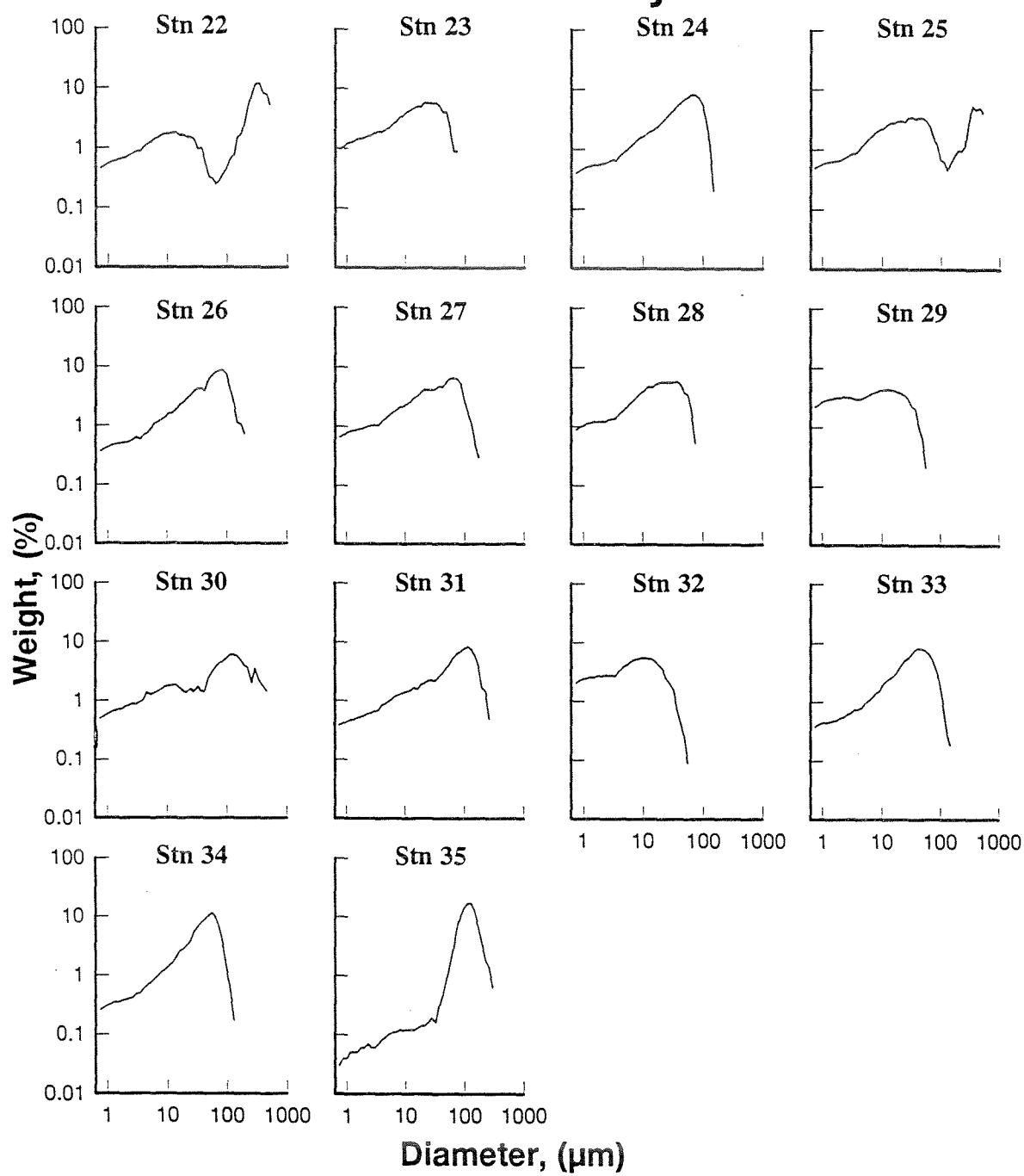
Figure 56. Disaggregated inorganic grain size distributions
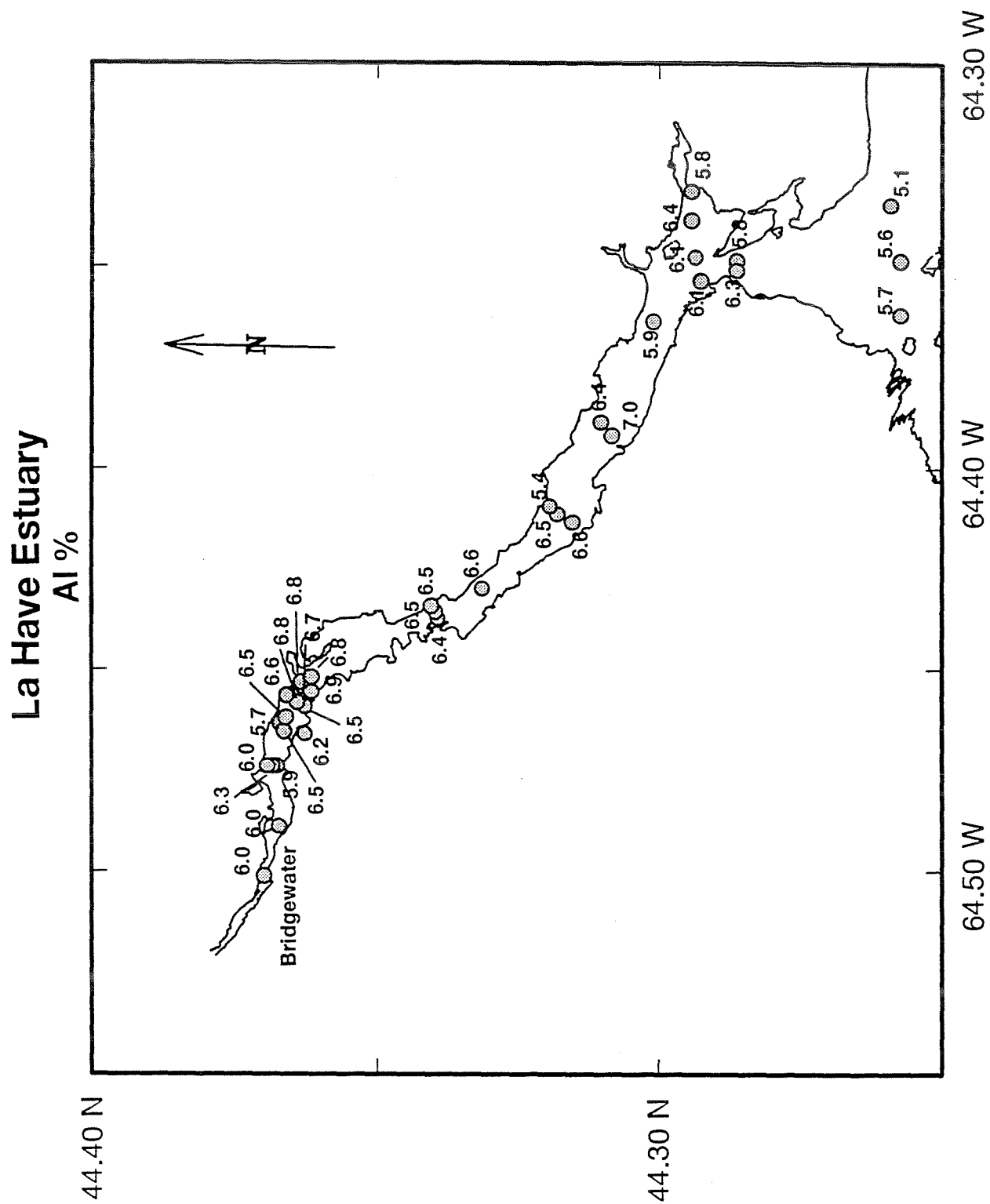
Figure 57. Aluminium concentrations in surficial sediments

La Have Estuary
Fe %

44.40 N

2.9
Bridgewater
4.4
4.0
4.2
3.4
4.5
4.3
4.1
4.8
4.4
4.1
4.2
4.5
4.8
4.4
4.4
4.4

3.6
3.3
3.9
3.8

3.1
2.1
3.7
3.5
2.5
2.2
44.30 N
2.6
3.1
2.1
3.9
2.3
2.0

2.2
2.1
1.6

64.50 W
64.40 W
64.30 W

N

Figure 58. Iron concentrations in surficial sediments

La Have Estuary
As mg/kg

44.40 N

15
29
29
26
20   36
Bridgewater   31   20   20   42
20   27   23
28   23   25   32

23
33   20

20

17   8
22

22
11

11

11   12   21
32

10   10   10

9   10   6

64.50 W   64.40 W   64.30 W
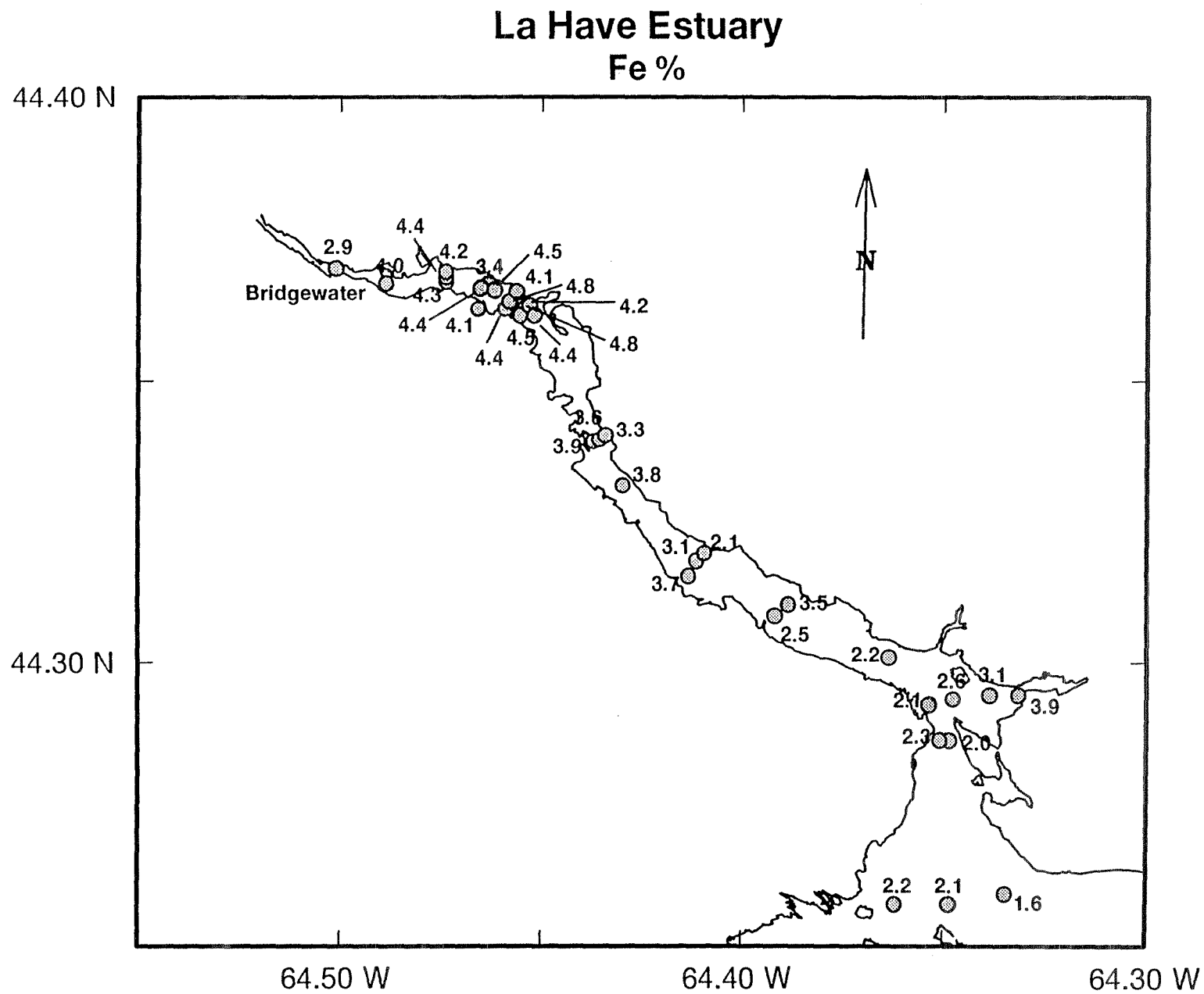
Figure 59. Arsenic concentrations in surficial sediments

La Have Estuary
Cd mg/kg

44.40 N

0.33
0.44
0.44 0.49 0.39
Bridgewater 0.22
0.46 0.32 0.24
0.35 0.28
0.43 0.39
0.36 0.27 0.23

0.22
0.25 0.23

0.22

0.23 0.11
0.25

0.27
0.18 0.18
44.30 N
0.32 0.21
0.19 0.48
0.23 0.1

0.21 0.15
0.02

64.50 W   64.40 W   64.30 W
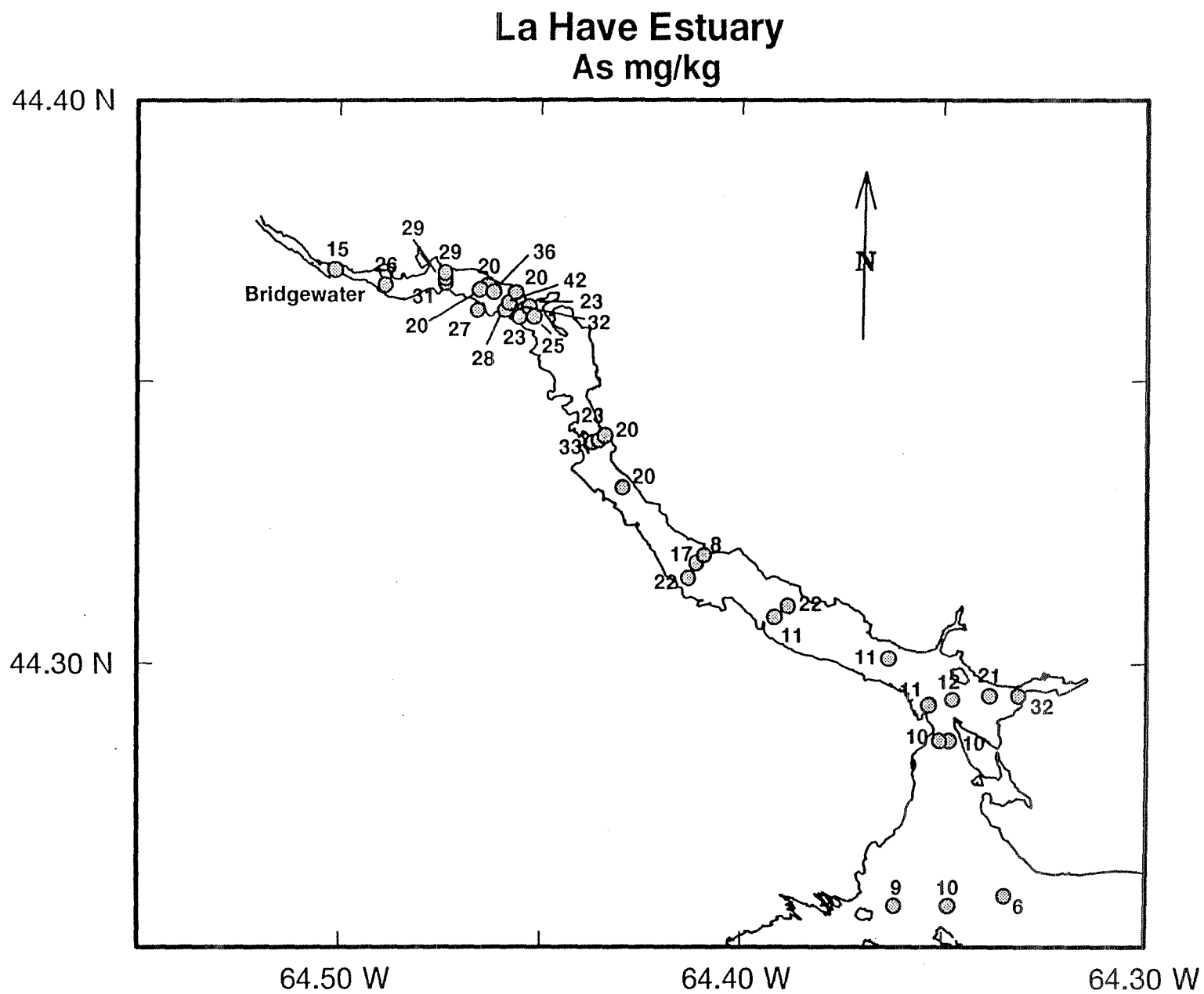
Figure 60. Cadmium concentrations in surficial sediments

La Have Estuary
Cr mg/kg

N

62 76 83 79 65 84
Bridgewater 75 81 86
79 82 96 82
85 89 84

78 76
84

84

79 52
128
78
71

57

57 65 71
77

62 52

56 54 55

44.40 N

44.30 N

64.50 W   64.40 W   64.30 W
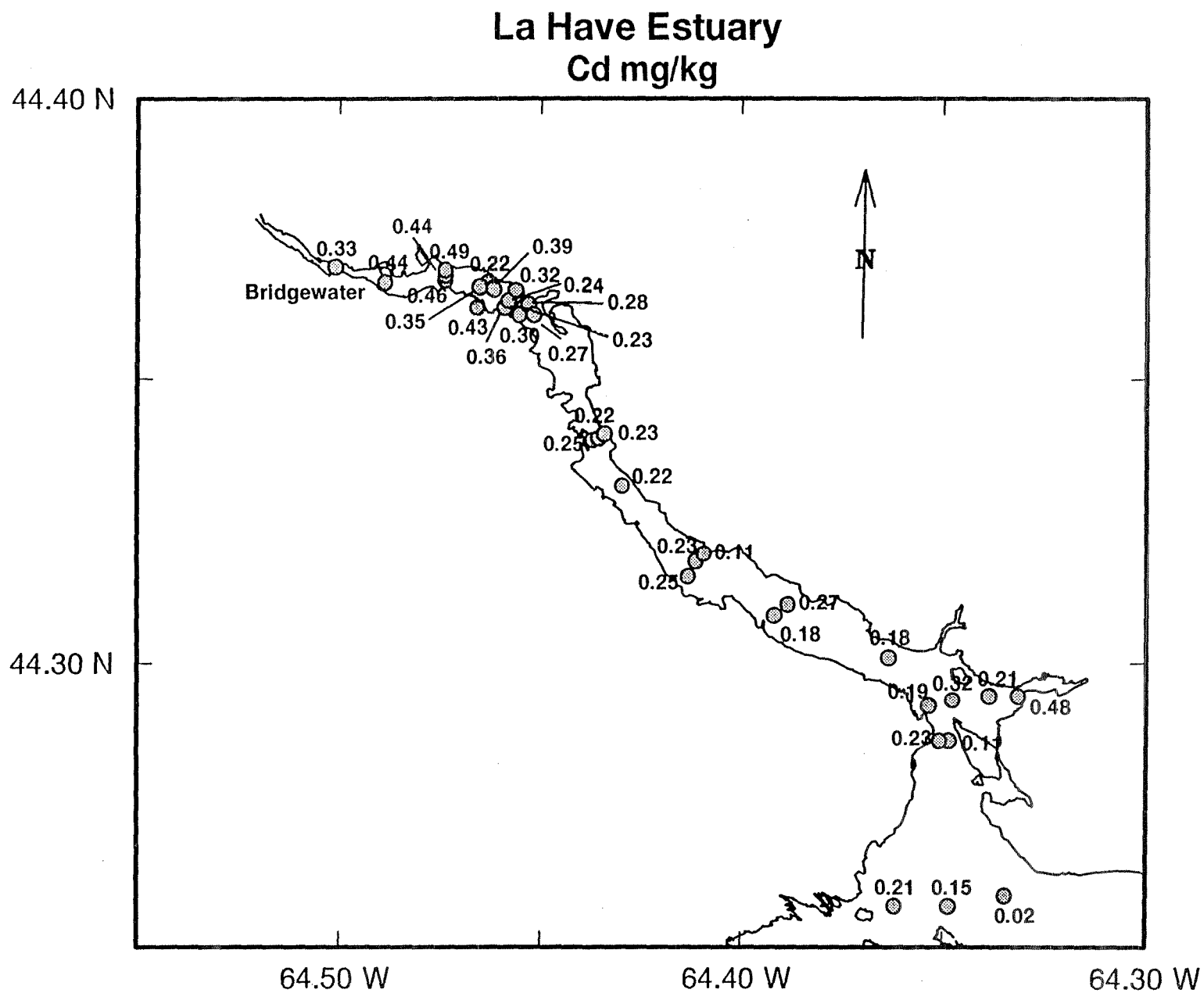
Figure 61. Chromium concentrations in surficial sediments

La Have Estuary
Cu mg/kg
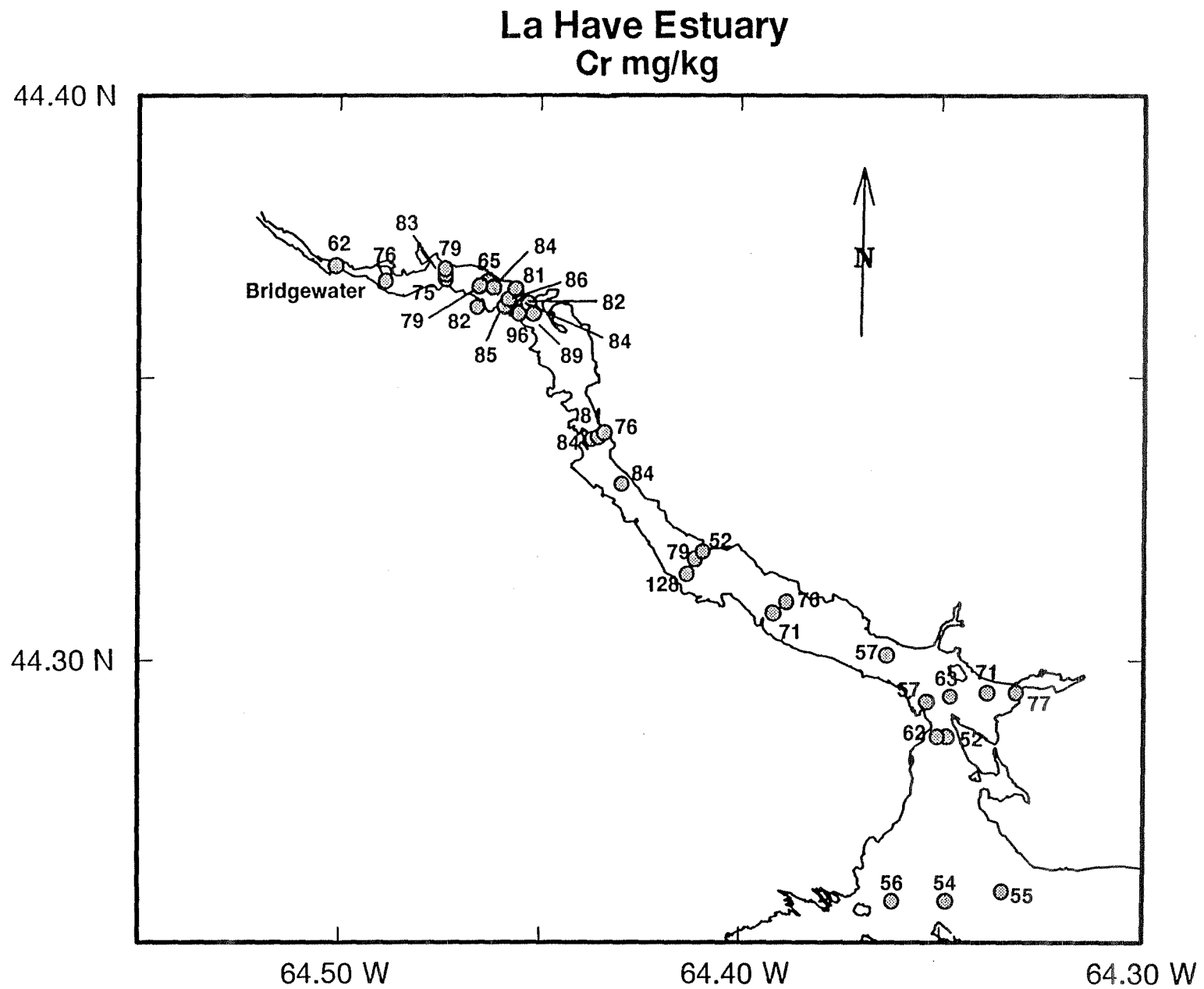
Figure 62. Copper concentrations in surficial sediments

La Have Estuary
Hg mg/kg

Figure 63. Mercury concentrations in surficial sediments

93

La Have Estuary
Li mg/kg
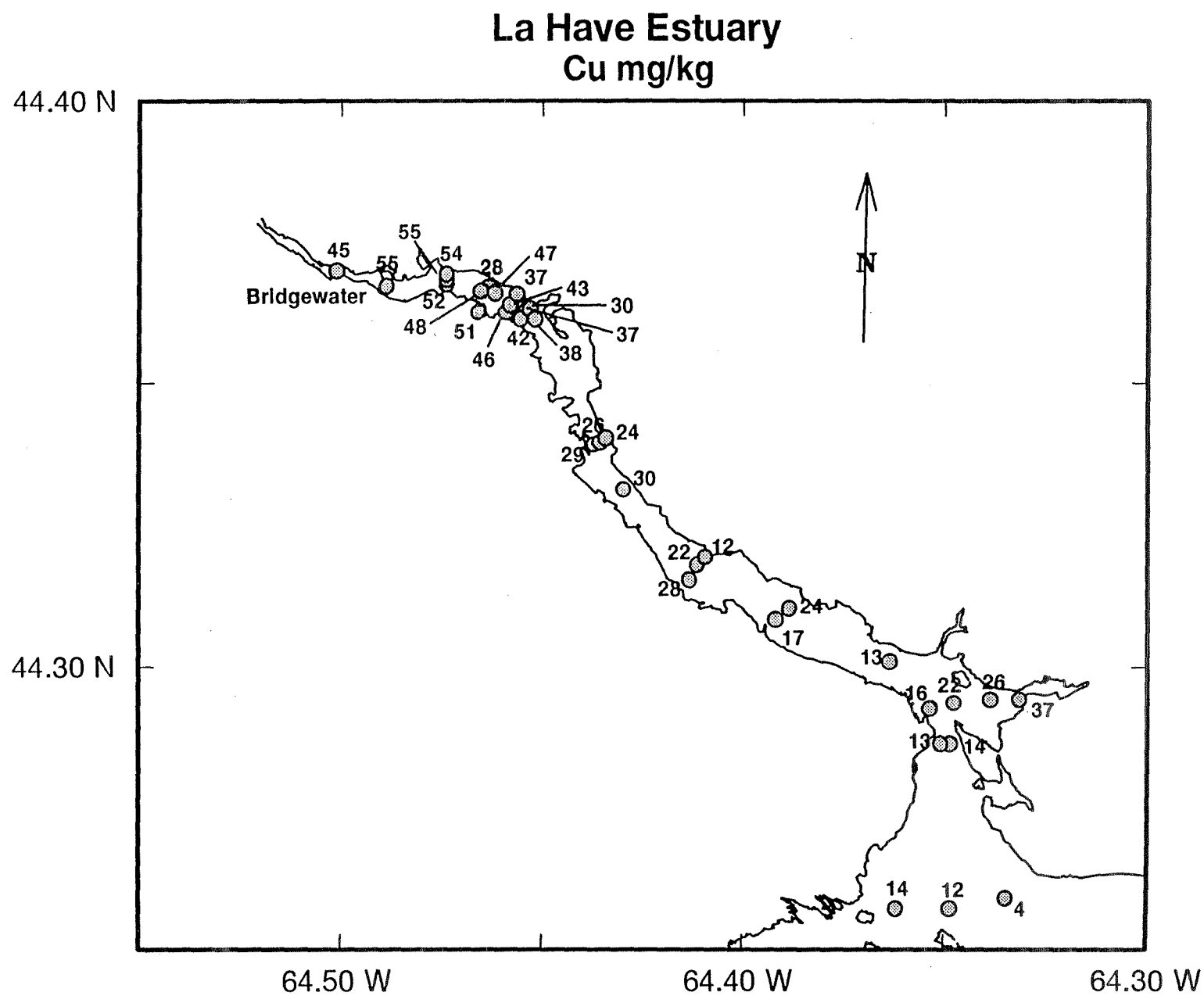
Figure 64. Lithium concentrations in surficial sediments

La Have Estuary
Mn mg/kg
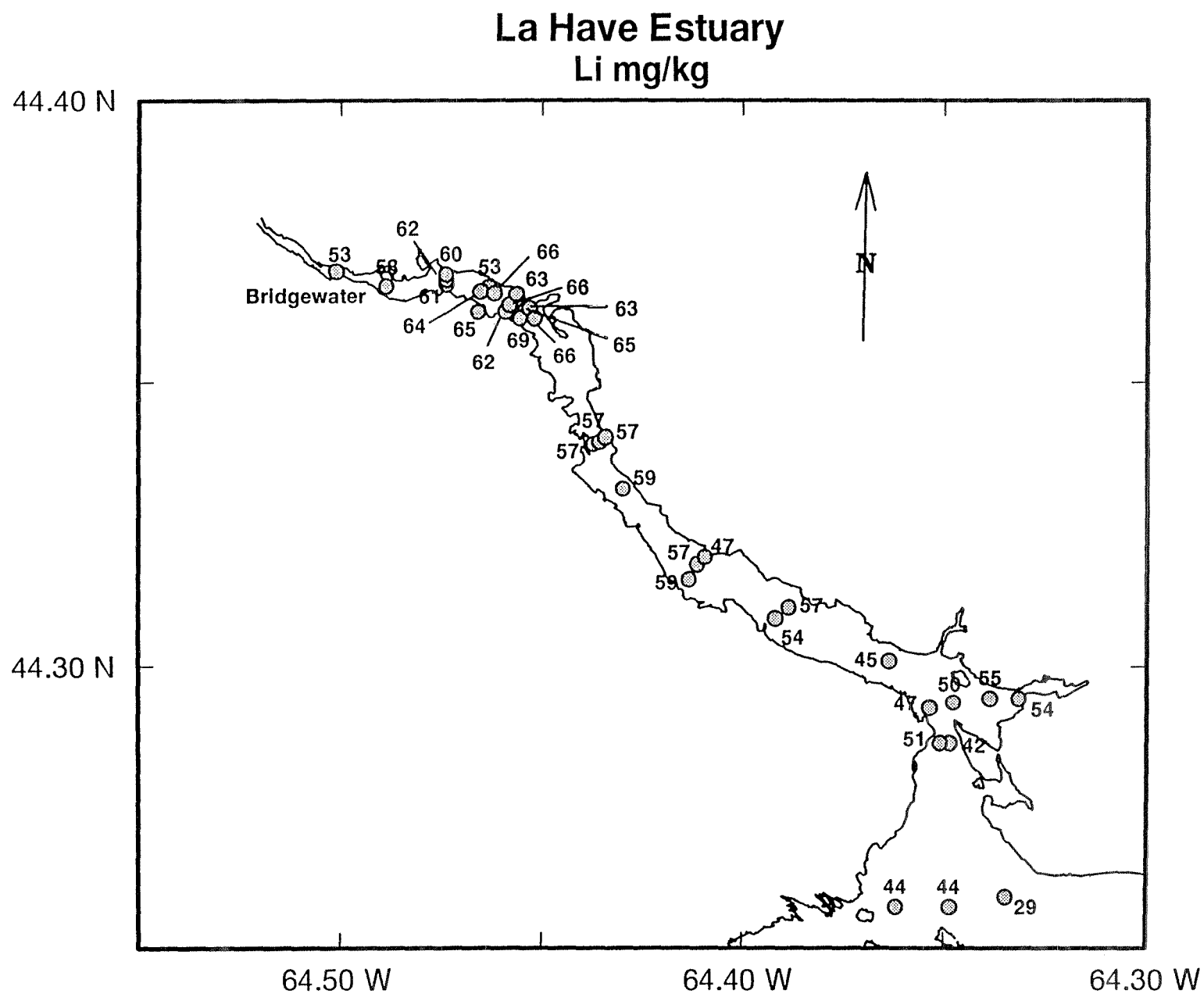
Figure 65. Manganese concentrations in surficial sediments

La Have Estuary
Ni mg/kg
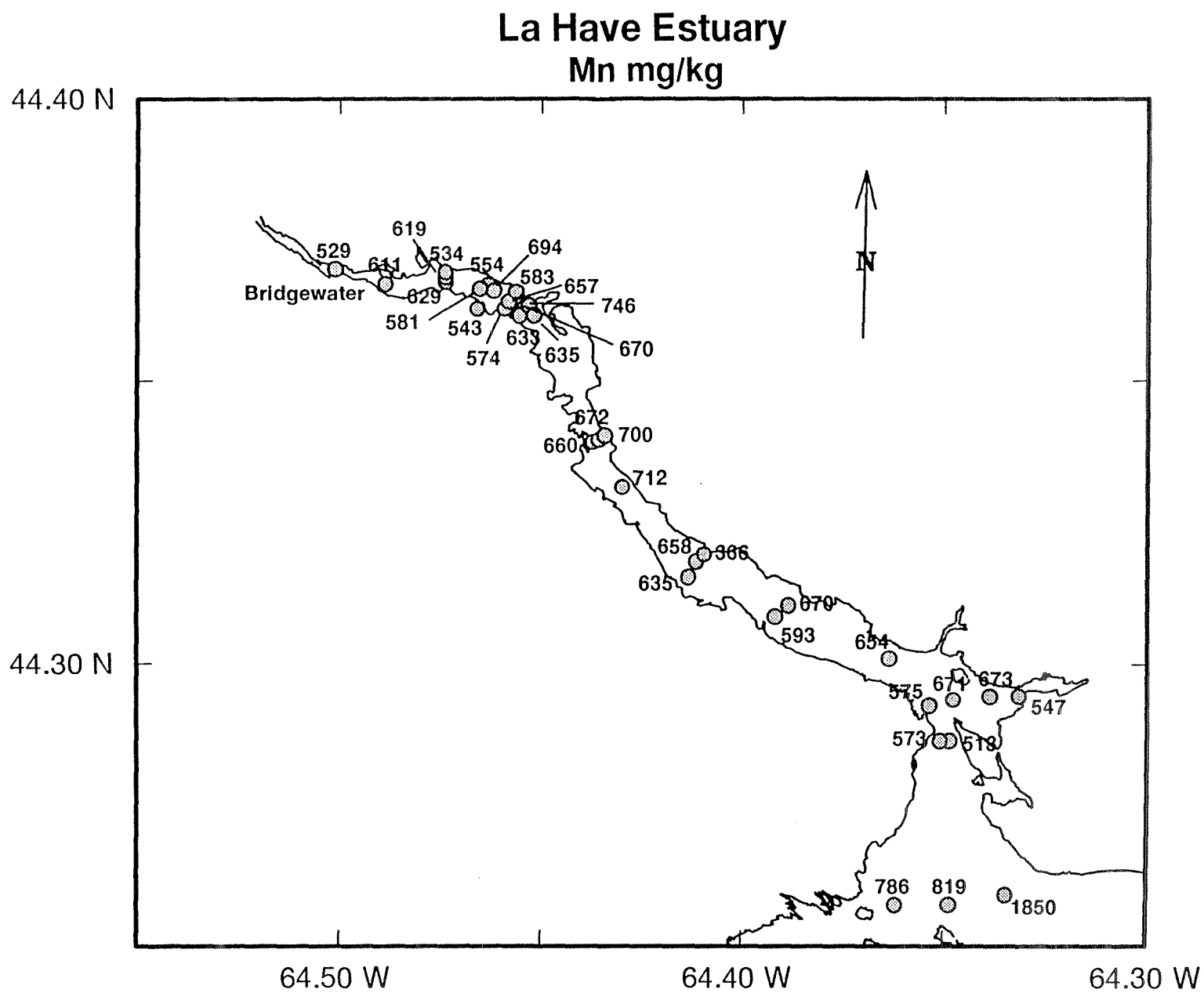
Figure 66. Nickel concentrations in surficial sediments

La Have Estuary
Pb mg/kg

44.40 N

75
55
77 78
74
45 60
Bridgewater 77 70
69 49
74 67 59
74 62

38 34
39

39

28 18
35

29
24

44.30 N
19
26 32
50
20
20 19

19 18
15

64.50 W   64.40 W   64.30 W
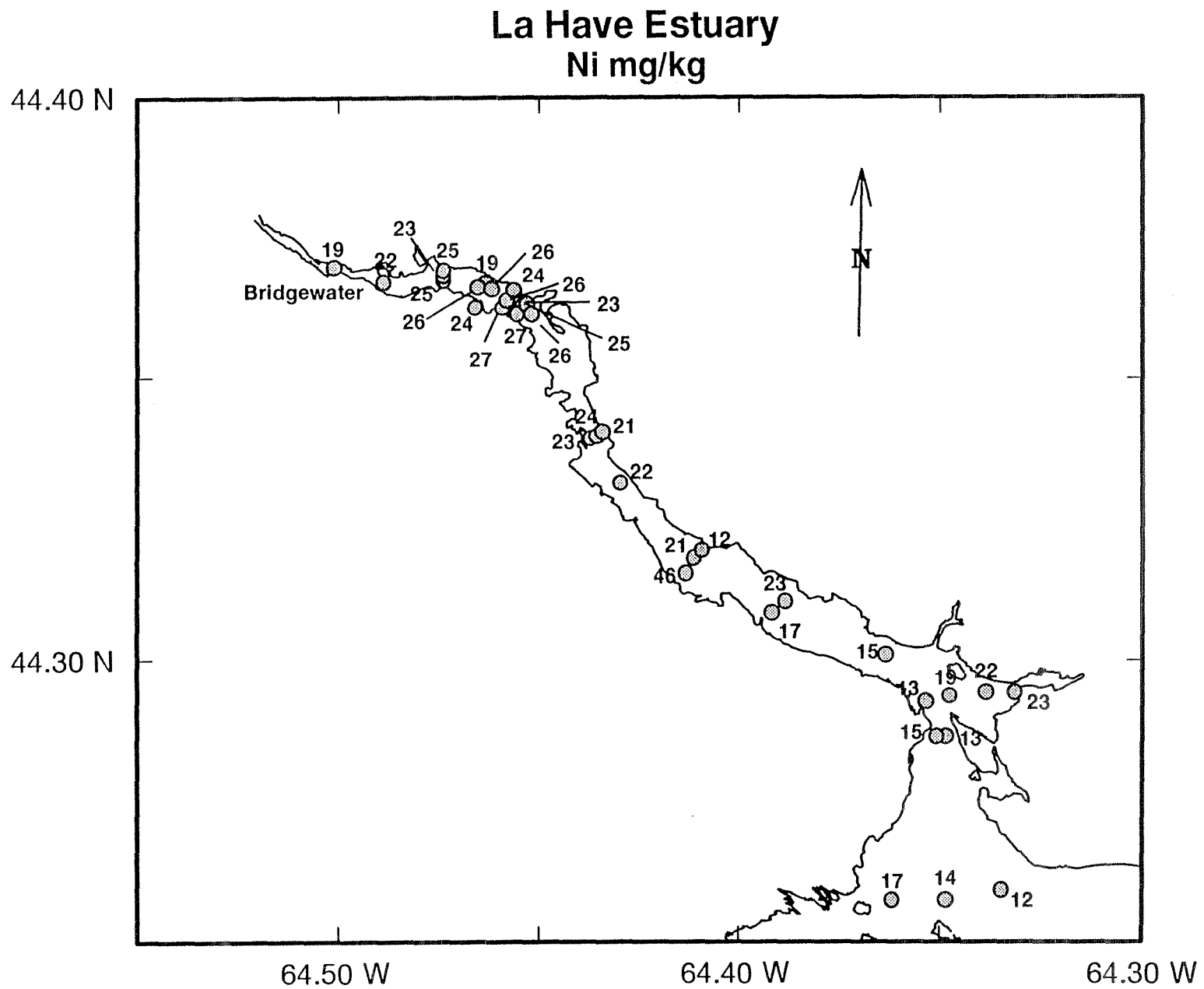
Figure 67. Lead concentrations in surficial sediments

La Have Estuary
Sn mg/kg
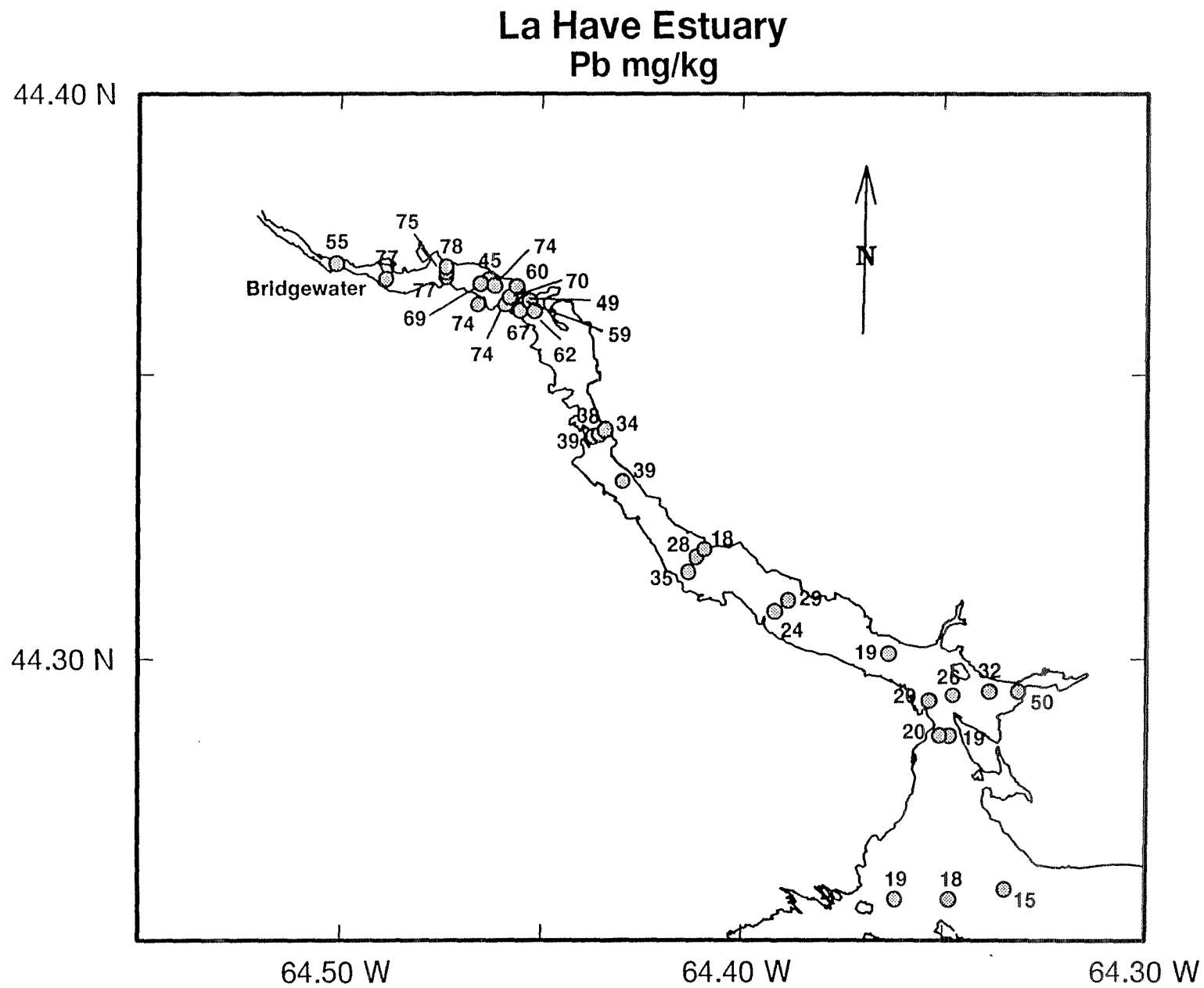
Figure 68. Tin concentrations in surficial sediments

La Have Estuary
V mg/kg
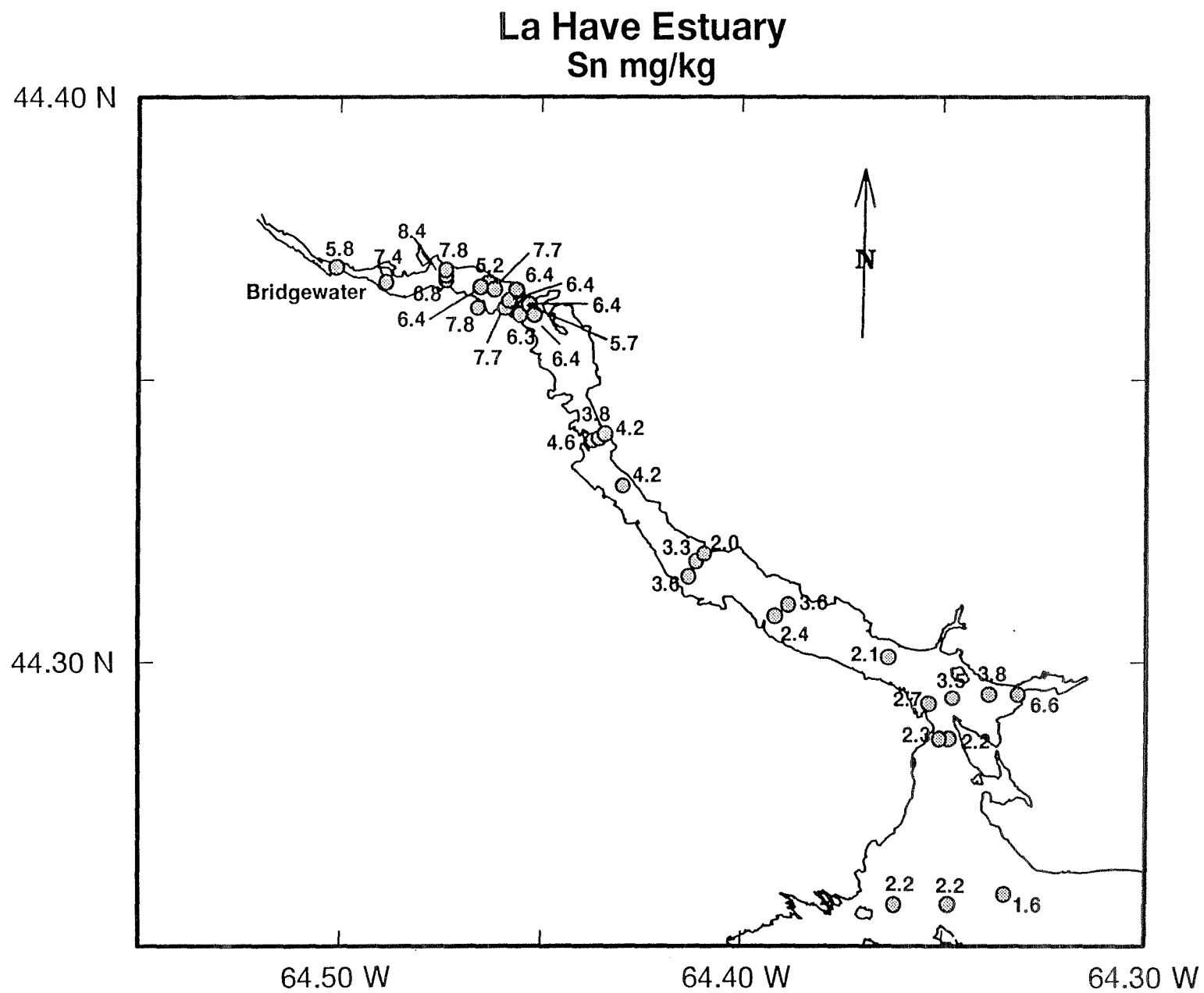
Figure 69. Vanadium concentrations in surficial sediments

La Have Estuary
Zn mg/kg

44.40 N

133
150 134
110 150 90
Bridgewater 119 131
148 104
134 144 128 122
144 128 128

92
84
98

103

78 41
85

77
57

50
44.30 N
47 69 76
56 43 119

46 46
24

64.50 W   64.40 W   64.30 W
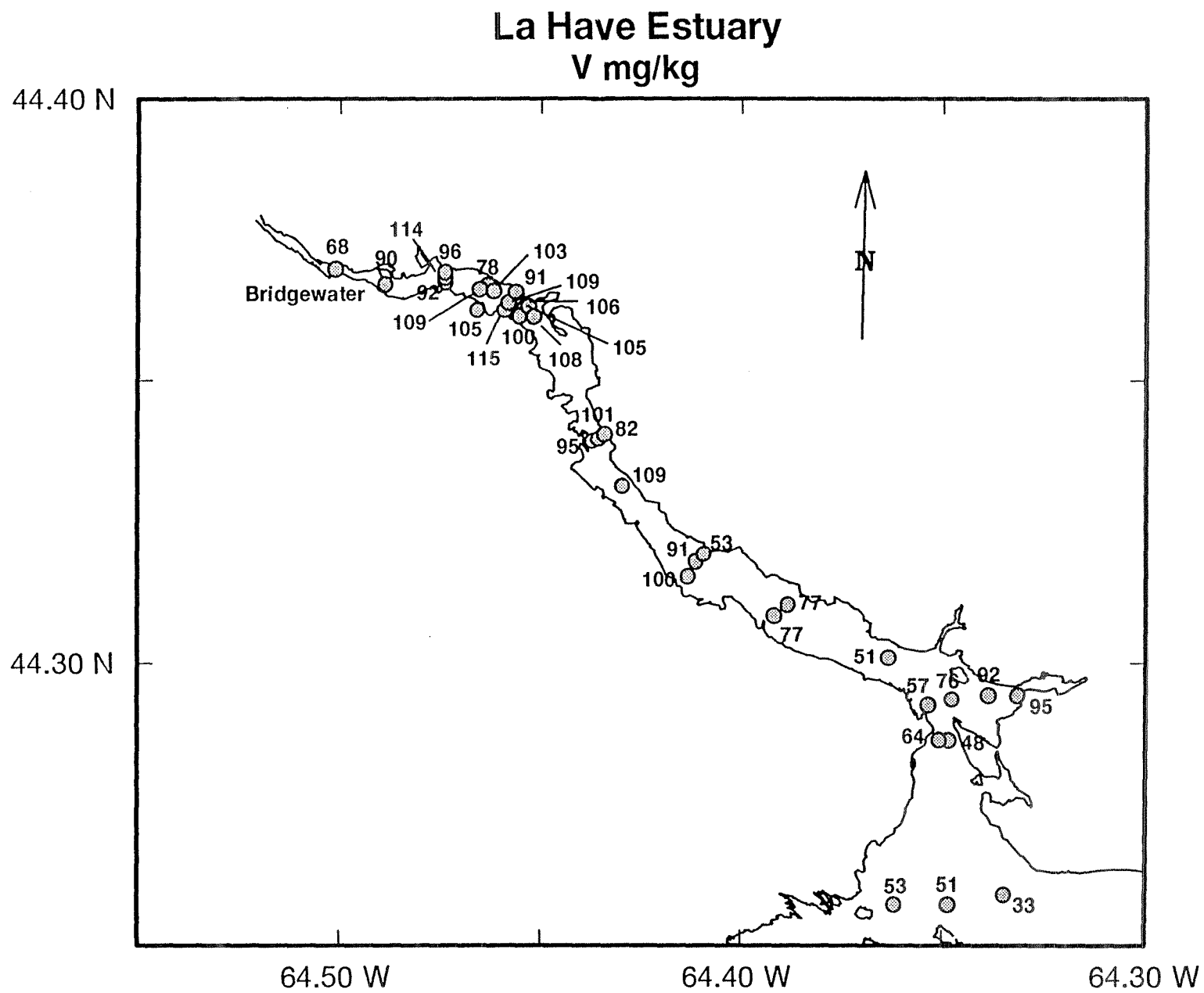
Figure 70. Zinc concentrations in surficial sediments
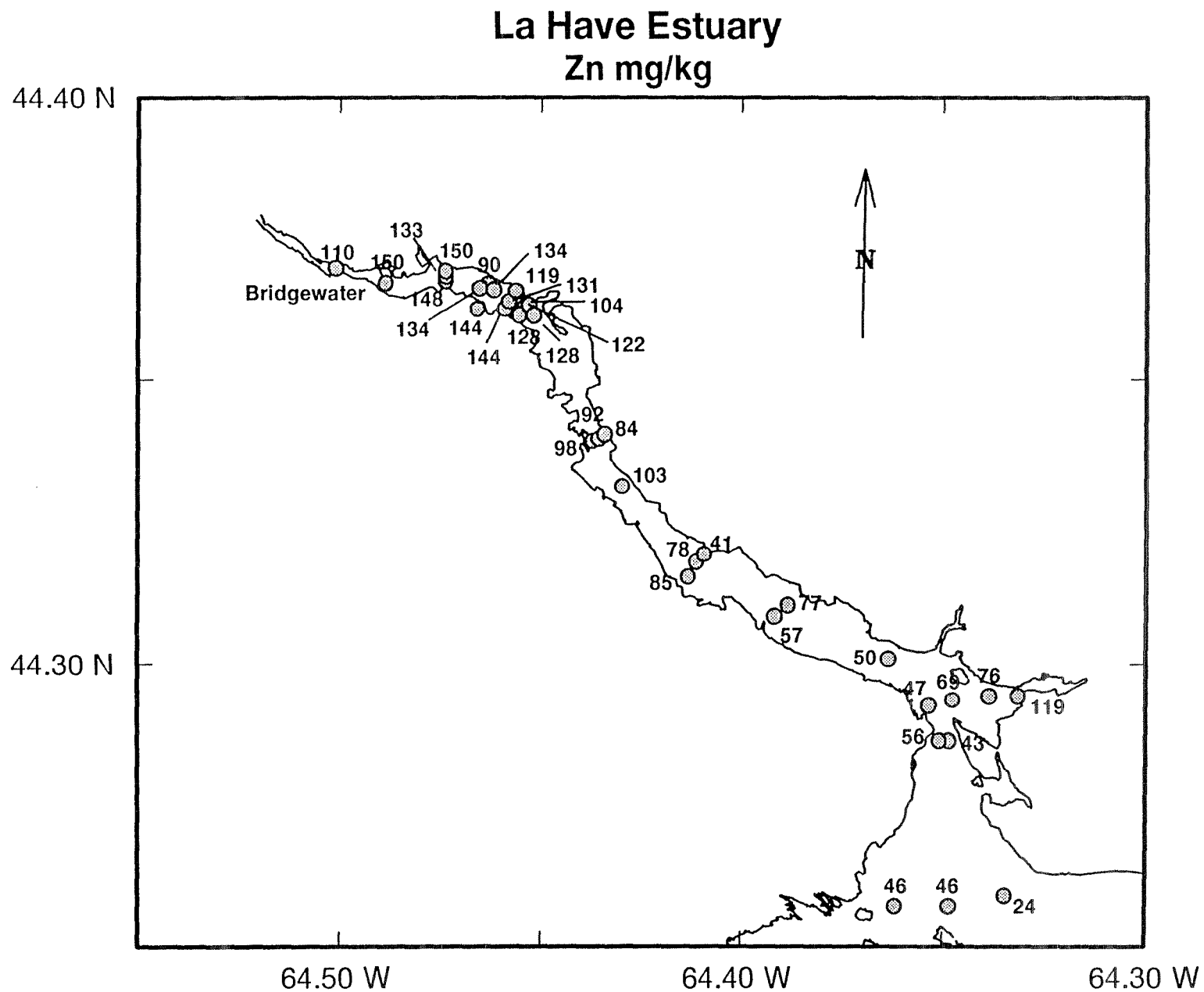
La Have Estuary

Figure 71. La Have Estuary core samples

Core CA

Core CB

Core CC

As
Sn

101
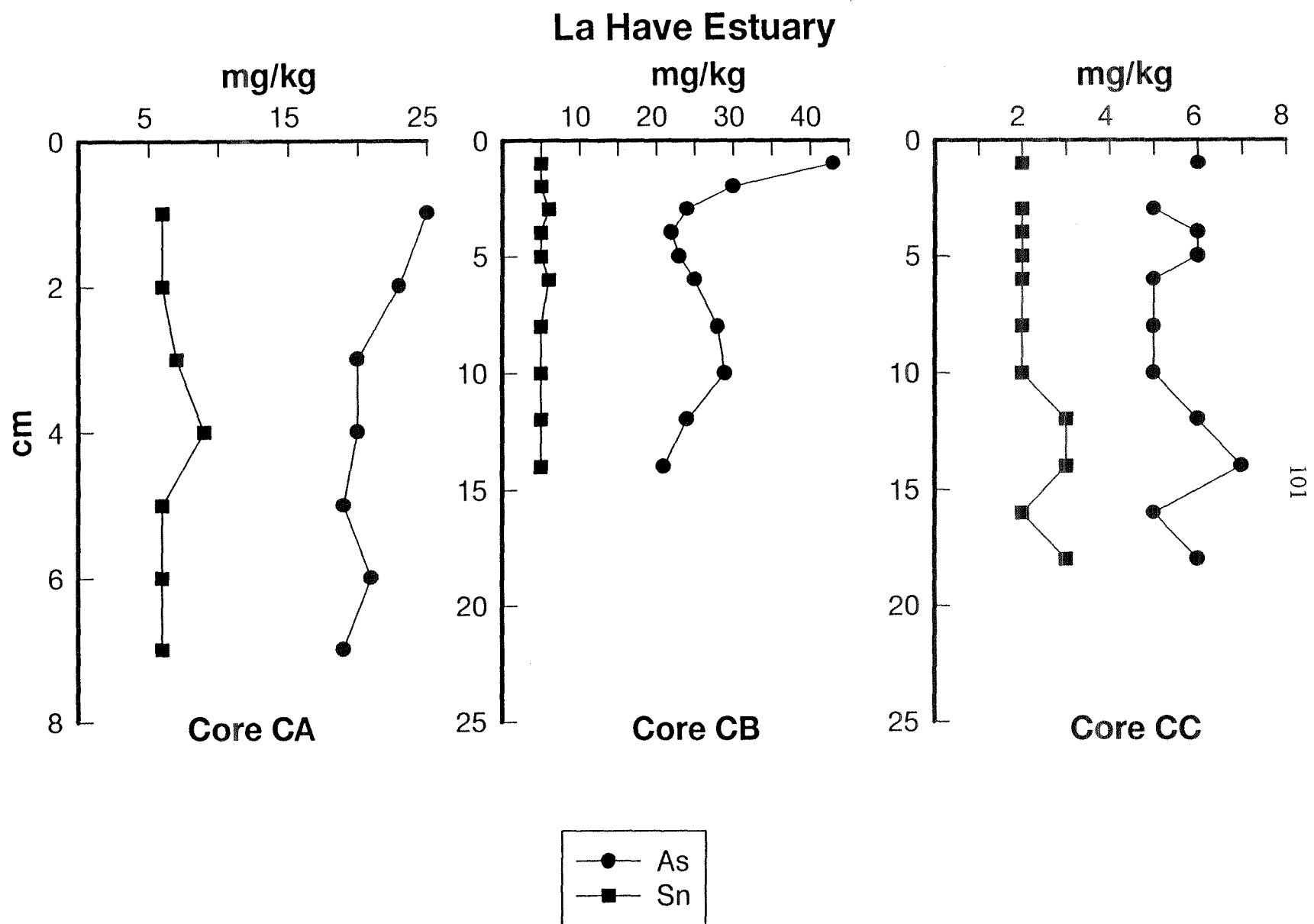
La Have Estuary

Figure 72. La Have Estuary core samples

102
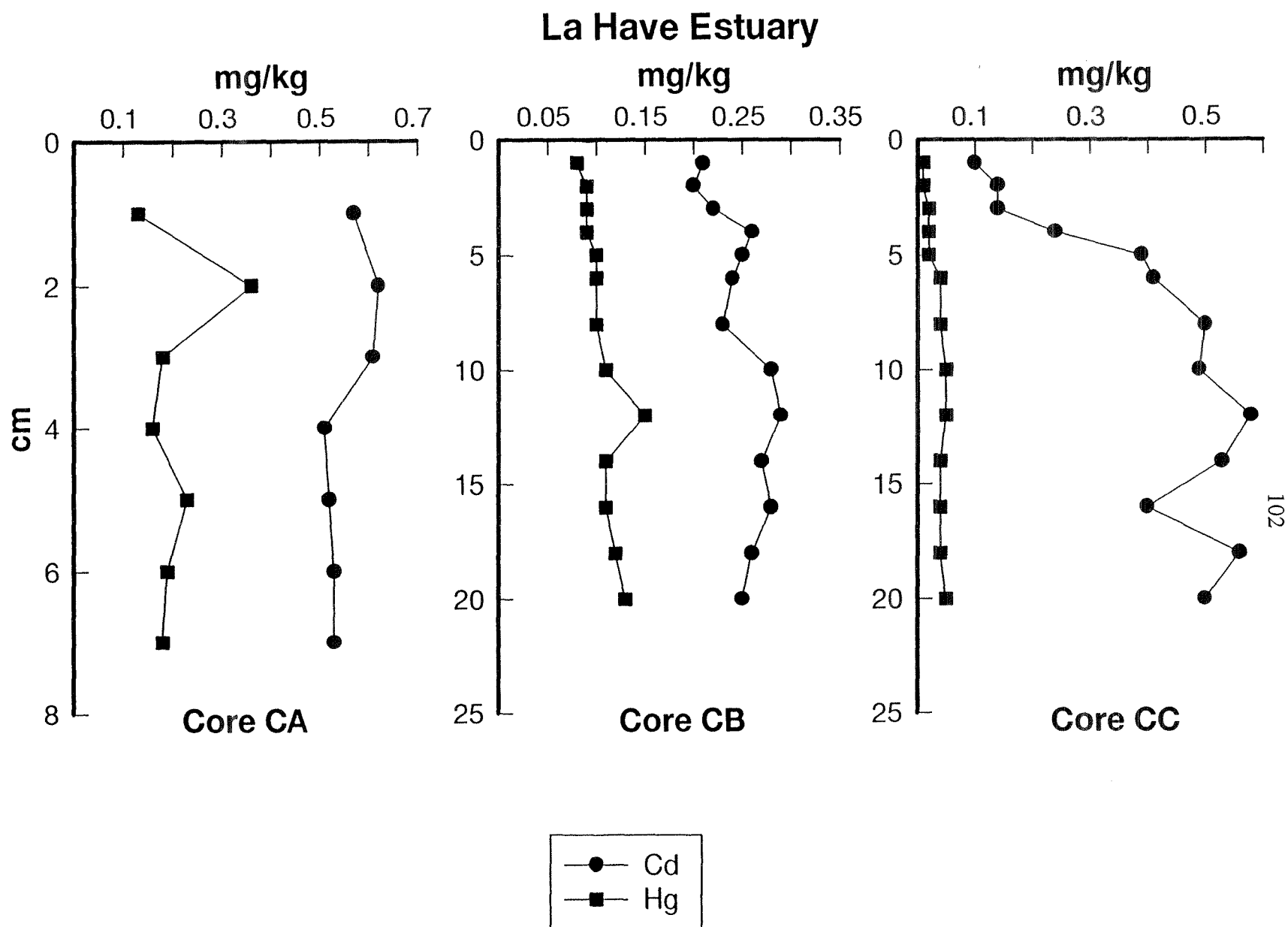
La Have Estuary

Figure 73. La Have Estuary core samples

Core CA

Core CB

Core CC

mg/kg

cm

Zn
Cu
Pb

103
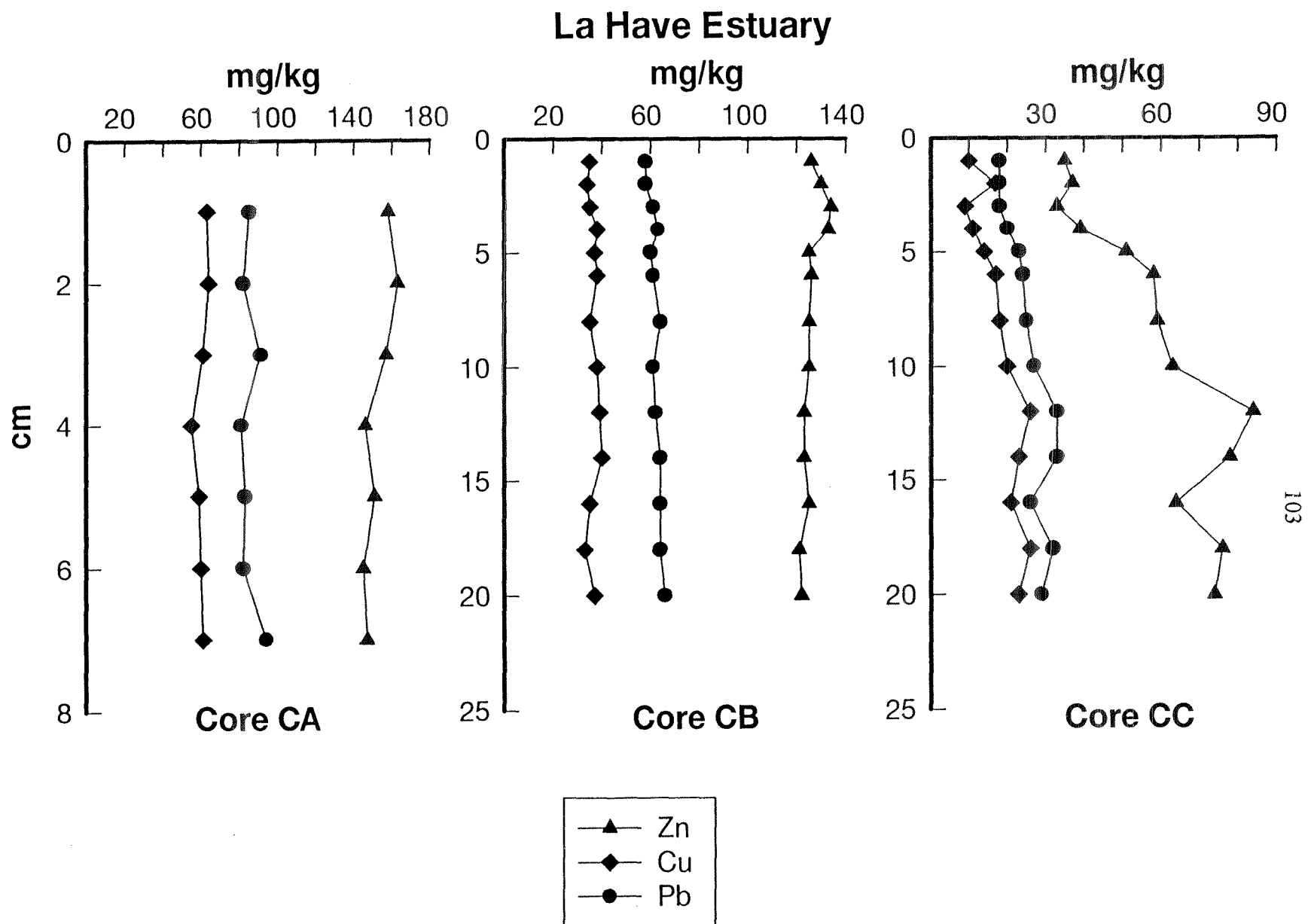
LIVERPOOL HARBOUR

Liverpool Bay, which forms the harbour of Liverpool, occupies a small embayment (7.4 km^2 in area) about 9 km long with a maximum depth of 19.2 m on the southern coast of Nova Scotia about 160 km southwest of Halifax. The Bay receives drainage via the Mersey River from an area of 2015.4 km^2. The head of the Bay is mainly occupied by the town of Liverpool, the village of Brooklyn, and cultivated land developed on a thin mantle of glacial till underlain primarily by and Precambrian quartzites and slates. The limited cultivated land supports mixed farming.

POTENTIAL SOURCES OF CONTAMINATION

Since 1759, the town of Liverpool, which has a population of approx. 3,300, has contributed organic wastes and some metallic wastes to the Bay from the pulp and paper industry, ship building, fishing activities, and urban sewage disposal. Industrial and urban discharges are, therefore, the main sources of metallic and organic contaminants.

RESULTS

Sediment Samples and Composition

The locations of the sampling stations (n=12) are shown in Figure 74. Sediments of Liverpool Bay are mainly sands and gravels except for organic-rich sandy muddy sediments (Fig. 75) containing wood fibers found near the dredged area around the Mersey Bowater Pulp and Paper Mill wharf at the head of the Harbour and in the dredged channel leading to the Public Wharf in Liverpool.

Abundance and Distribution of Metals

The abundance and distribution of the metals in Liverpool Harbour are shown in Figures 76 to 89. The range of total metal concentrations in the sediments (n=12) are: As, 2-7 mg·kg^{-1}; Cd, 0.02-0.90 mg·kg^{-1}; Cr, 20-41 mg·kg^{-1}; Cu, 2-16 mg·kg^{-1}; Hg, 0.01-0.11 mg·kg^{-1}; Ni, 9-17 mg·kg^{-1}; Pb, 12-21 mg·kg^{-1}: Sn, 1-3 mg·kg^{-1}; V, 19-39 mg·kg^{-1}; and Zn, 15-59 mg·kg^{-1} (Table 13). The data (Table 2) indicate that the trace metal concentrations are at, or near, natural levels in the Harbour sediments except for the cases of five of the twelve samples (42%) that contain values >0.3 mg·kg^{-1} Cd and one sample (8%) that contains >0.1 mg·kg^{-1} Hg. The relatively high concentrations of Cd were found in very sandy muds. One of these samples was obtained from the dredged channel leading to the Public Wharf (Station 74) and the other from near the dredged area around the Mersey Bowater wharf (Station 52).

Potential Bioavailability of Metals

Chemical partitioning of selected samples indicates that most (57-67%) of the total Cd, 17-21% of the total Cu, 20-29% of the total Pb, and 13 -39% of the total Zn are potentially bioavailable. The concentrations of acid-soluble Cd Cu, Pb, and Zn are lower than those found elsewhere. This implies that only relatively small proportions of the Cu, Pb, and Zn are held in the HOAc-insoluble detrital form.

Metal Carriers and Sources

The positive covariance of Cd, Cu, and Pb with the <63 μm fraction suggests that these metals are associated to varying degrees with the fine-grained fraction (Table 14). The proportion of the metal variability explained by the granular variability of the <63 μm fraction decreases in the order: Pb (86%) > Cd (83%) > Cu (77%) > Sn (65%) > Zn (56%) > As (48%) > Hg (34%) > Cr (30%). In contrast to other harbours, neither Al or Li can be used for normalization of the trace metal distributions. There are, however, strong correlations ($p \leq 0.001$) of As, Cd, and Pb with organic matter which implies that these metals are associated with the fine-grained organic-rich fraction of the sediments. Nevertheless, the absence of any strong covariance of the metals with either Li or Al indicates that the metals are not directly associated with the fine-grained aluminosilicate fraction. This suggests that the main metal carriers are discrete particles of detrital oxides (V, Ni) and metal fragments and/or are of non-detrital origin such as Fe-sulphides formed *in situ* in the organic-rich sediments. The amounts of the metals associated with these carriers are in addition to the small amounts of these metals naturally carried in the lattices of the aluminosilicate minerals.

There is no evidence of significant industrial input to Liverpool Harbour except for the anomalous Cd concentrations found in ship channels near to the wharves that are probably related to the accumulation of waste products from the nearby paper mill.

Table 13

Textural and metal statistics[a] for the Liverpool Harbour sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	11	23.5	± 22.1	2-66	OM%	12	3.22 ±	5.12	0.15-17.7
Metal					Metal				
Al%	12	4.35	± 0.43	3.10-4.70	Fe%	12	1.22 ±	0.25	0.90-1.70
As	12	3.7	± 1.4	2-7	Li	12	22.2 ±	3.7	17-28
Cd	12	0.30	± 0.28	0.02-0.90	Ni	12	12.3 ±	3.1	9-17
Cr	12	30.2	± 6.1	20-41	Pb	12	14.8 ±	3.3	12-21
Cu	12	6.7	± 4.3	2-16	V	12	26.7 ±	6.9	19-39
Hg	12	0.05	±.0.03	0.01-0.11	Zn	12	32.3	± 14.8	15-59
Mn%	12	0.073	± 0.032	0.036-0.145	Sn	10	1.6 ±	0.6	1-3

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM), Al, Fe, and Mn

Table 14

Correlation Matrix Liverpool Harbour

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	x	x	1									
Cr	x	x	x	1								
Cu	x	x	0.97	x	1							
Fe	x	x	x	x	x	1						
Hg	x	x	x	x	0.81	x	1					
Li	x	x	x	x	x	x	x	1				
Mn	x	x	x	x	x	x	x	x	1			
Pb	x	x	0.96	x	0.93	0.88	x	x	x	1		
Sn	x	x	0.94	x	0.96	x	0.88	x	x	0.89	1	
Zn	x	x	0.91	x	0.89	0.83	0.89	x	x	0.90	0.91	1
mud	x	x	0.91	x	0.88	x	x	x	x	0.93	0.81	x
OM	x	0.86	0.82	x	x	x	x	x	x	0.83	x	x

n = 12 (Sn:n = 10; mud:n = 11)
For p $\leq$ 0.001 x= not significant
mud = >70% by weight material<63 μm
OM = % by weight organic matter
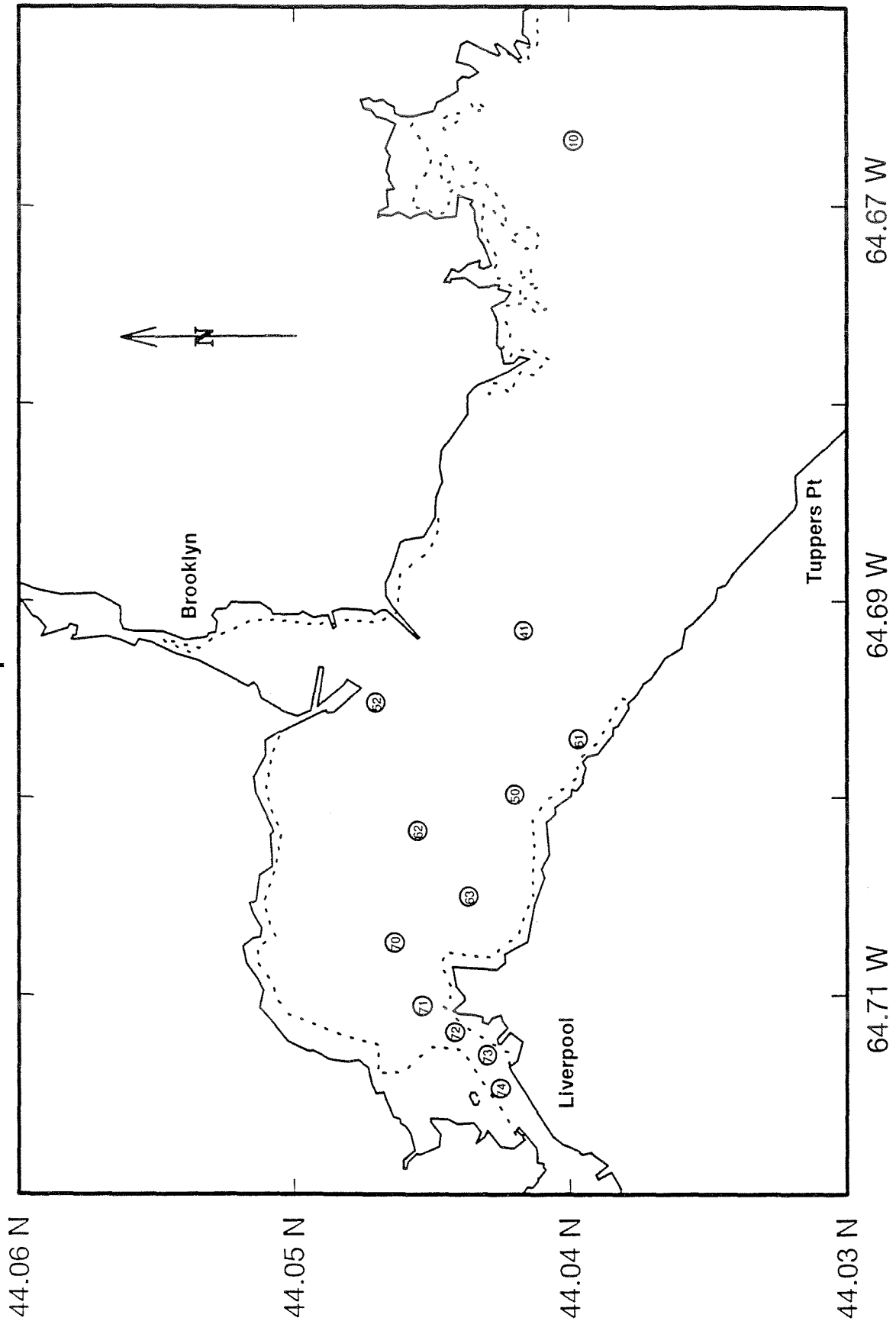
Figure 74. Sample locations for Liverpool Harbour

Liverpool Harbour
% Organic Matter

Brooklyn

N

0.15

2.50

1.54

17.70

1.94

8.11 4.44

0.54

0.96

0.36

0.21

Liverpool

0.20

Tuppers Pt

44.06 N

44.05 N

44.04 N

44.03 N

64.71 W   64.69 W   64.67 W

Figure 75. Organic matter concentrations in surficial sediments

Liverpool Harbour
Al %
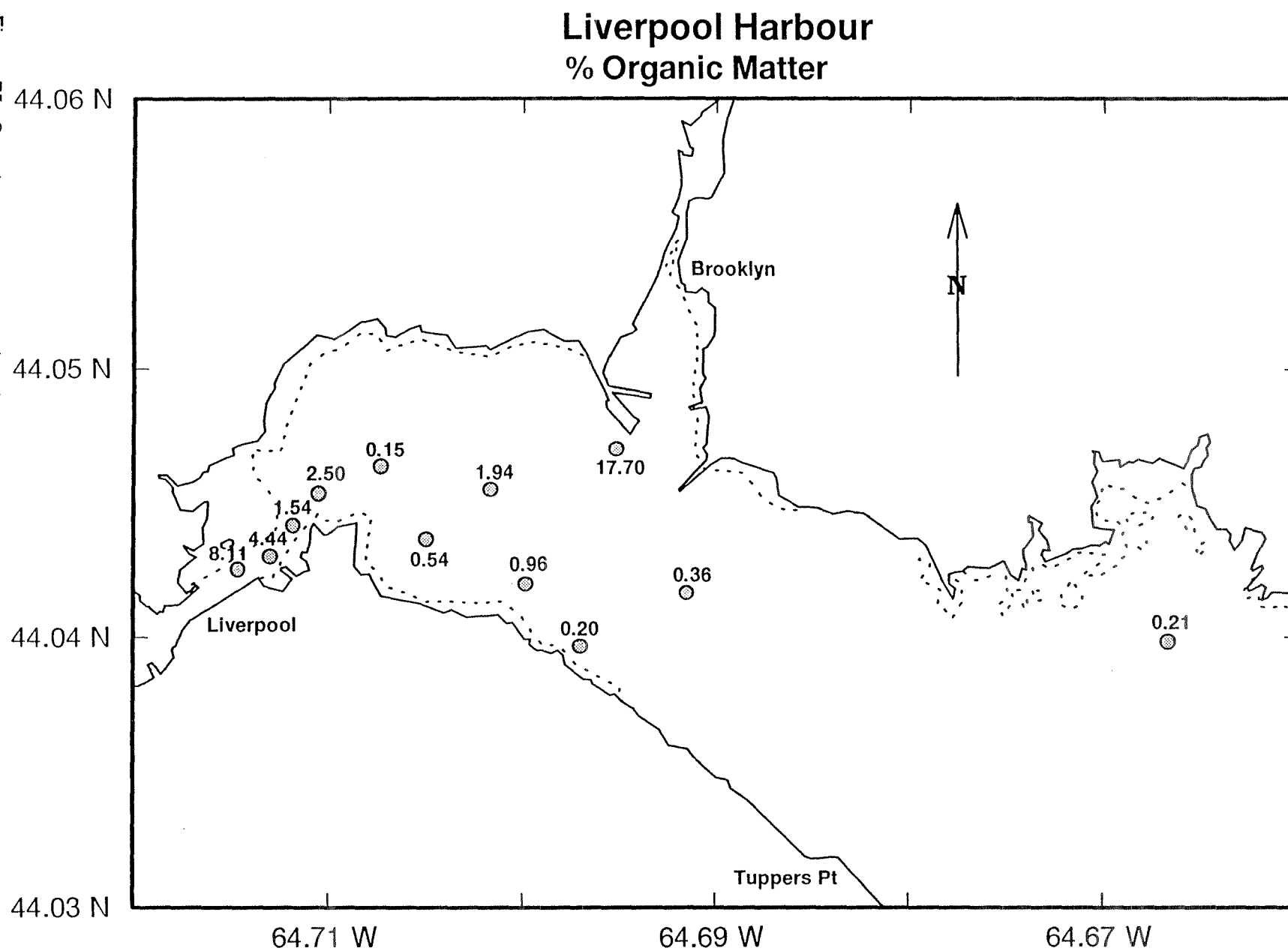
Figure 76. Aluminium concentrations in surficial sediments

44.06 N

44.05 N

44.04 N

44.03 N

64.71 W

64.69 W

64.67 W

Brooklyn

N

4.4

4.5

3.1

4.5

4.6

4.7

4.4

4.5

4.4

4.6

4.0

4.5

Liverpool

Tuppers Pt

Liverpool Harbour
Fe %

44.06 N

44.05 N

44.04 N

44.03 N

Brooklyn

N

1.0

1.2

1.2

1.4

1.7

0.9

1.5

1.4

1.2

0.9

1.2

Liverpool

1.0

Tuppers Pt

64.71 W

64.69 W

64.67 W
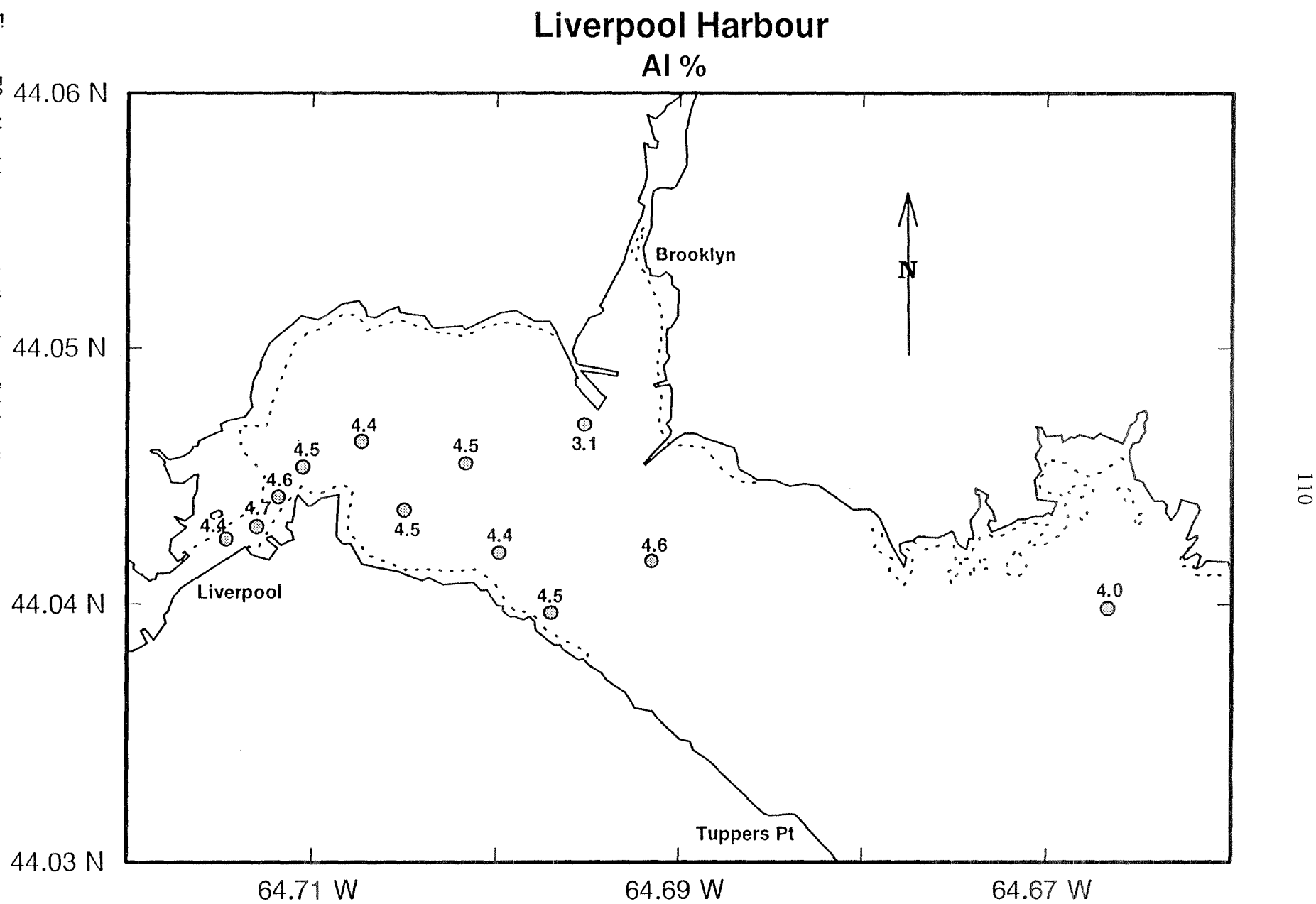
Figure 77. Iron concentrations in surficial sediments

Liverpool Harbour
As mg/kg

N

Brooklyn

7

4

3

4

4

2

2

4

3

8

5

3

Liverpool

Tuppers Pt

64.67 W

64.69 W

64.71 W

44.06 N

44.05 N

44.04 N

44.03 N
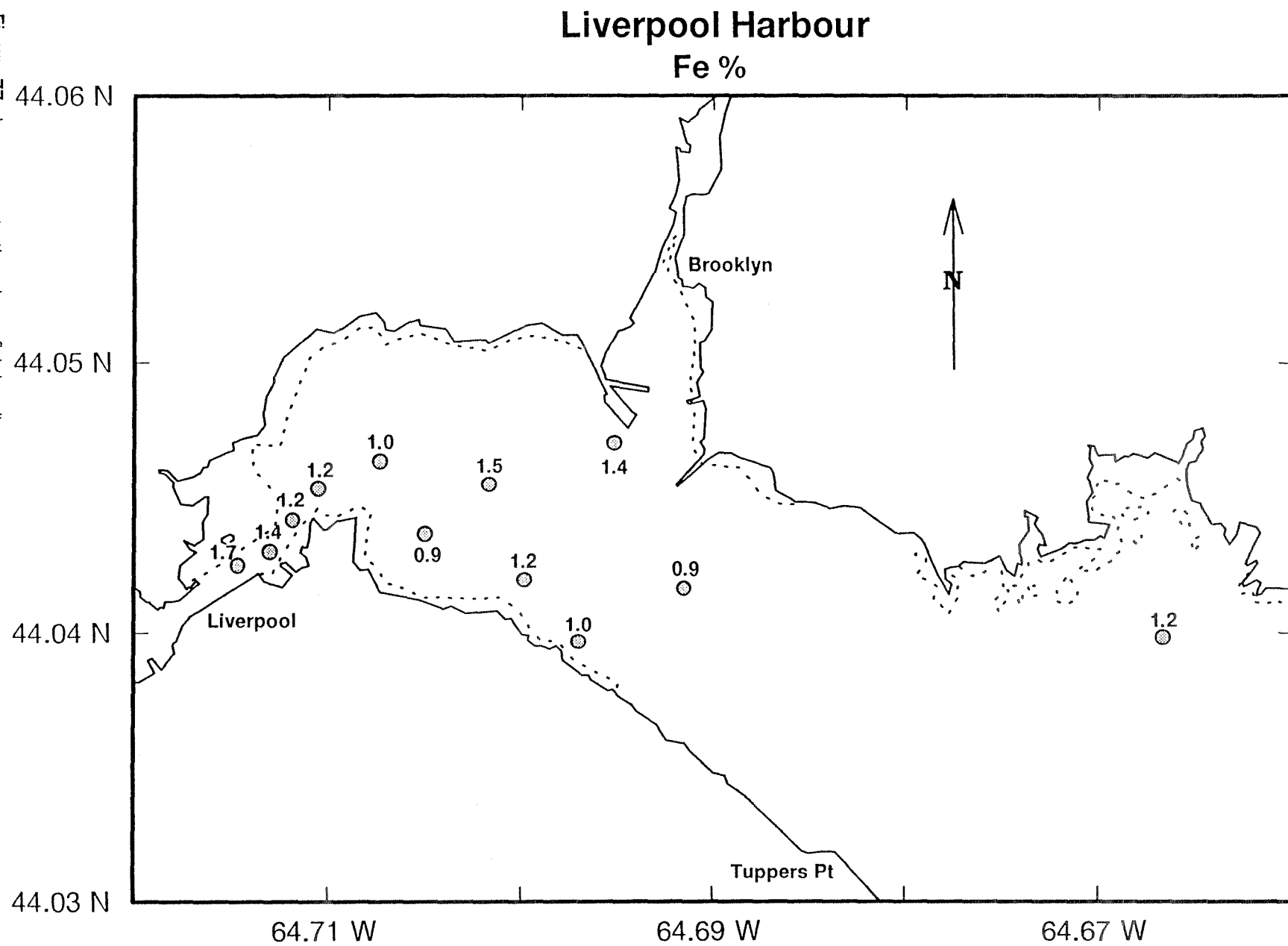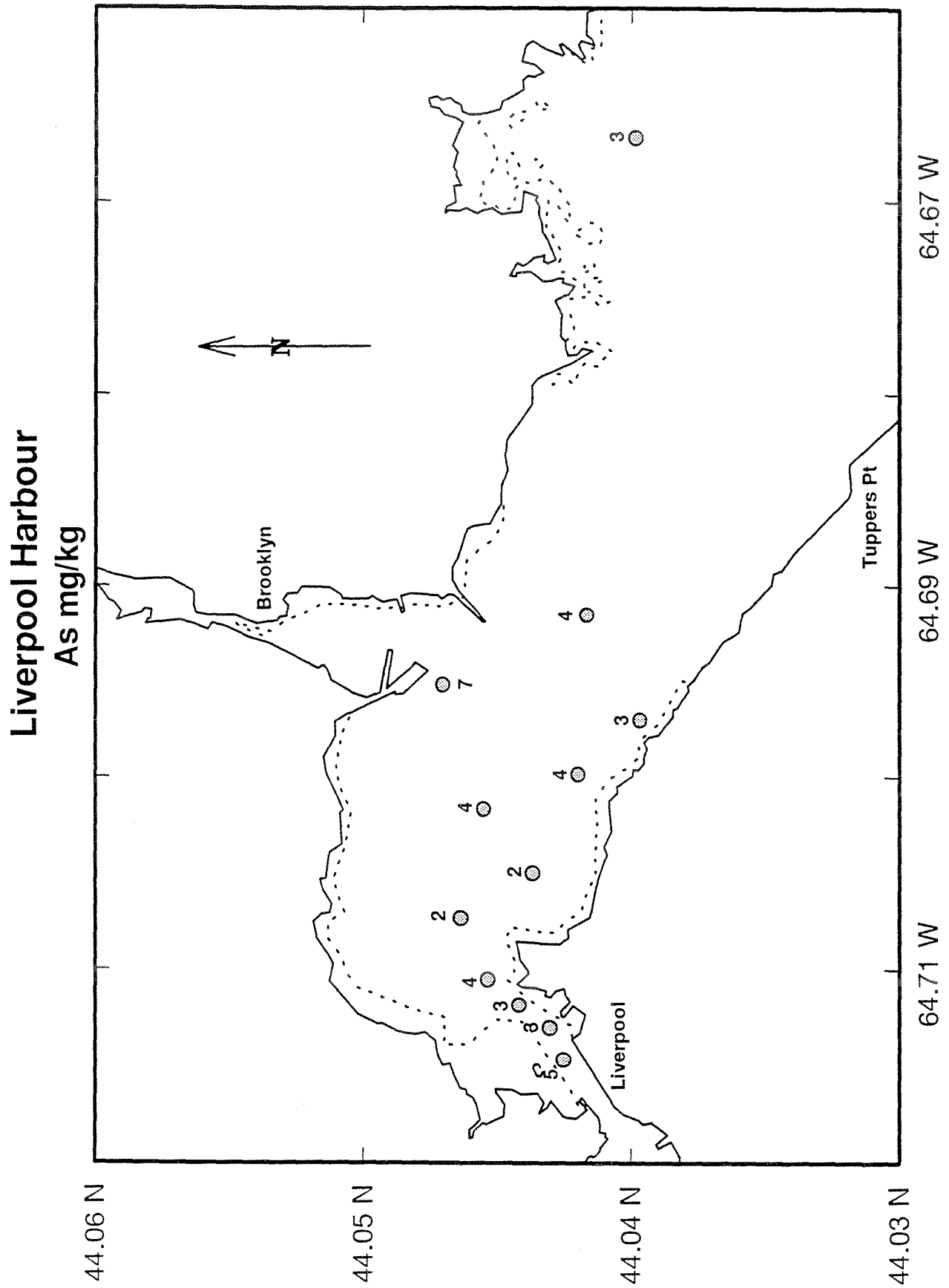
Figure 78. Arsenic concentrations in surficial sediments

Liverpool Harbour
Cd mg/kg

44.06 N

44.05 N

Brooklyn

N

0.09

0.28

0.31

0.73

0.39

0.19

0.42

0.90

0.12

0.06

0.09

0.02

44.04 N

Liverpool

Tuppers Pt

44.03 N

64.71 W

64.69 W

64.67 W

Figure 79. Cadmium concentrations in surficial sediments

Liverpool Harbour
Cr mg/kg

44.06 N

Brooklyn

N

44.05 N

31
26
34

27

20

37
34

33
23

44.04 N

25

31

Liverpool

Tuppers Pt

44.03 N

64.71 W   64.69 W   64.67 W
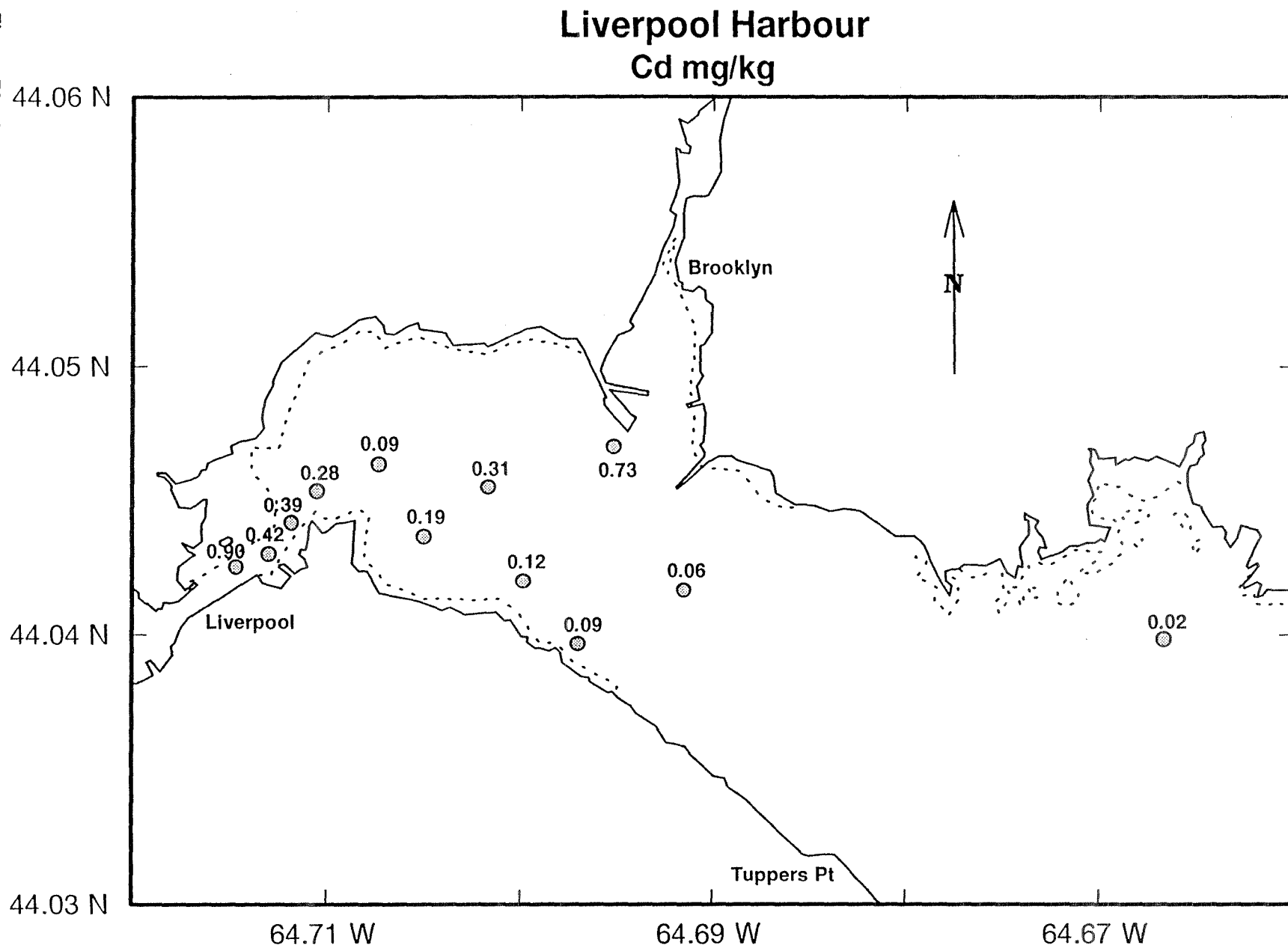
Figure 80. Chromium concentrations in surficial sediments

Liverpool Harbour
Cu mg/kg

44.06 N

Brooklyn

N

44.05 N

3

7

12

8

7

7

9

4

2

16

44.04 N

Liverpool

3

2

Tuppers Pt

44.03 N

64.71 W   64.69 W   64.67 W
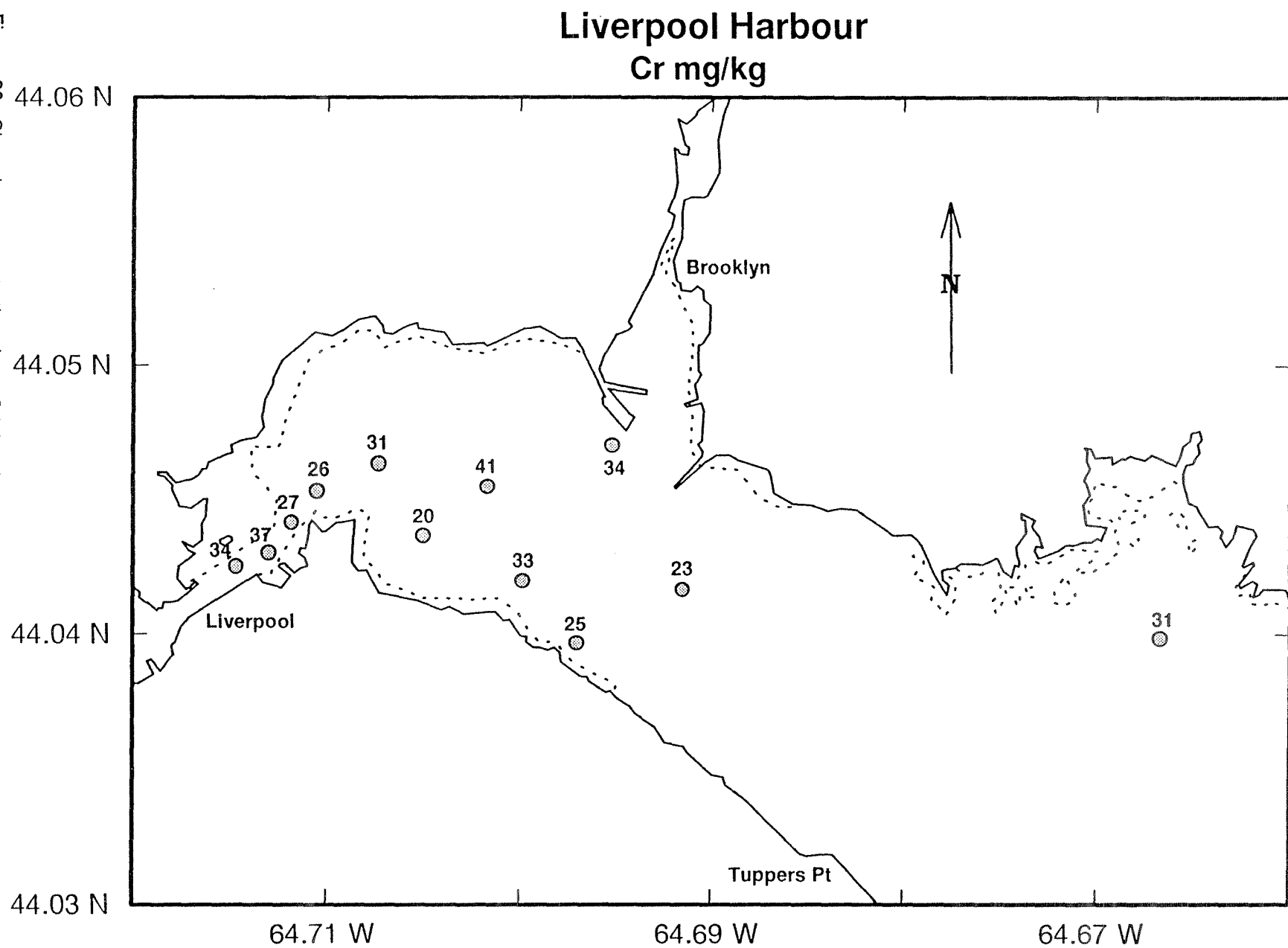
Figure 81. Copper concentrations in surficial sediments

115
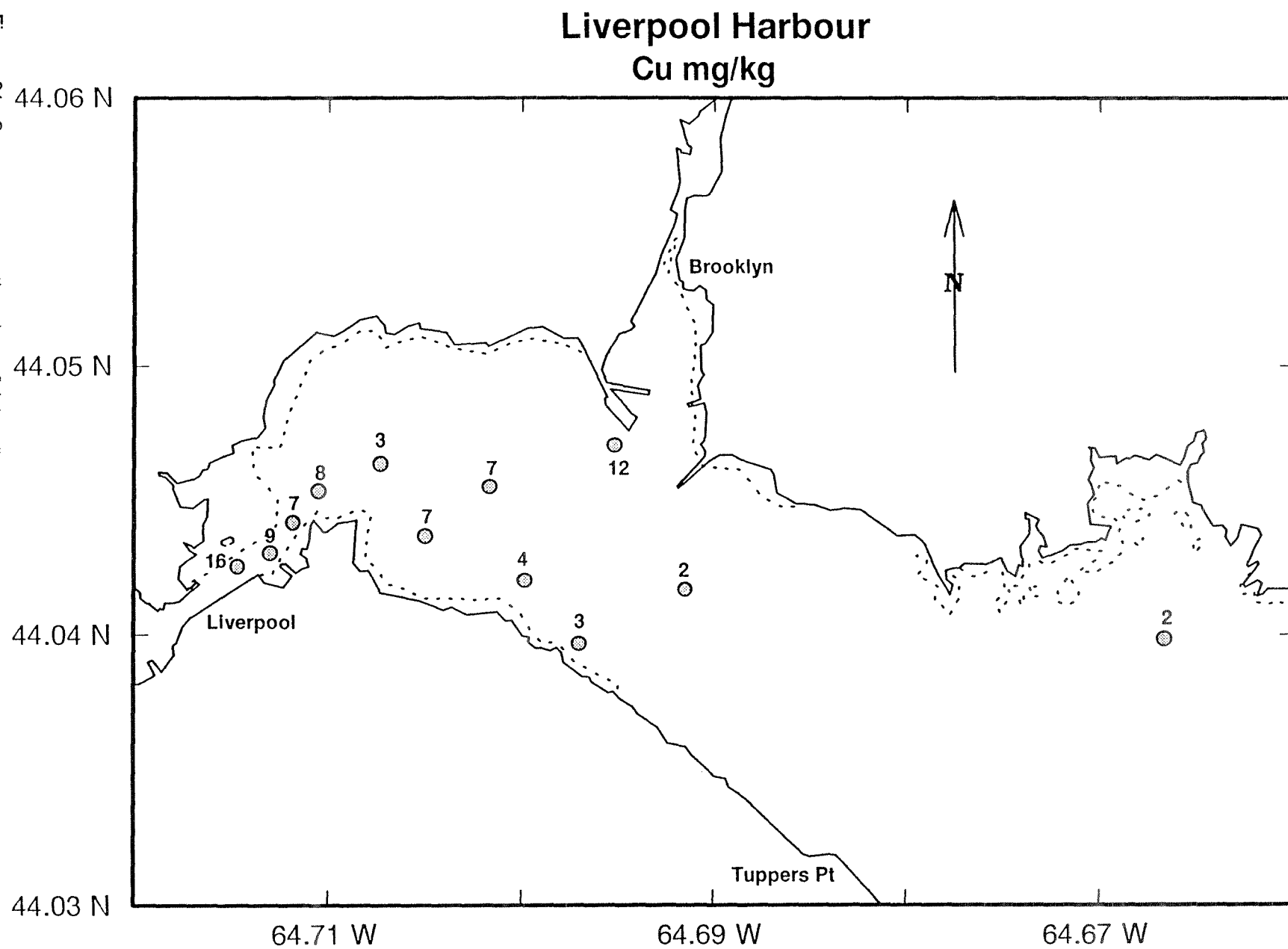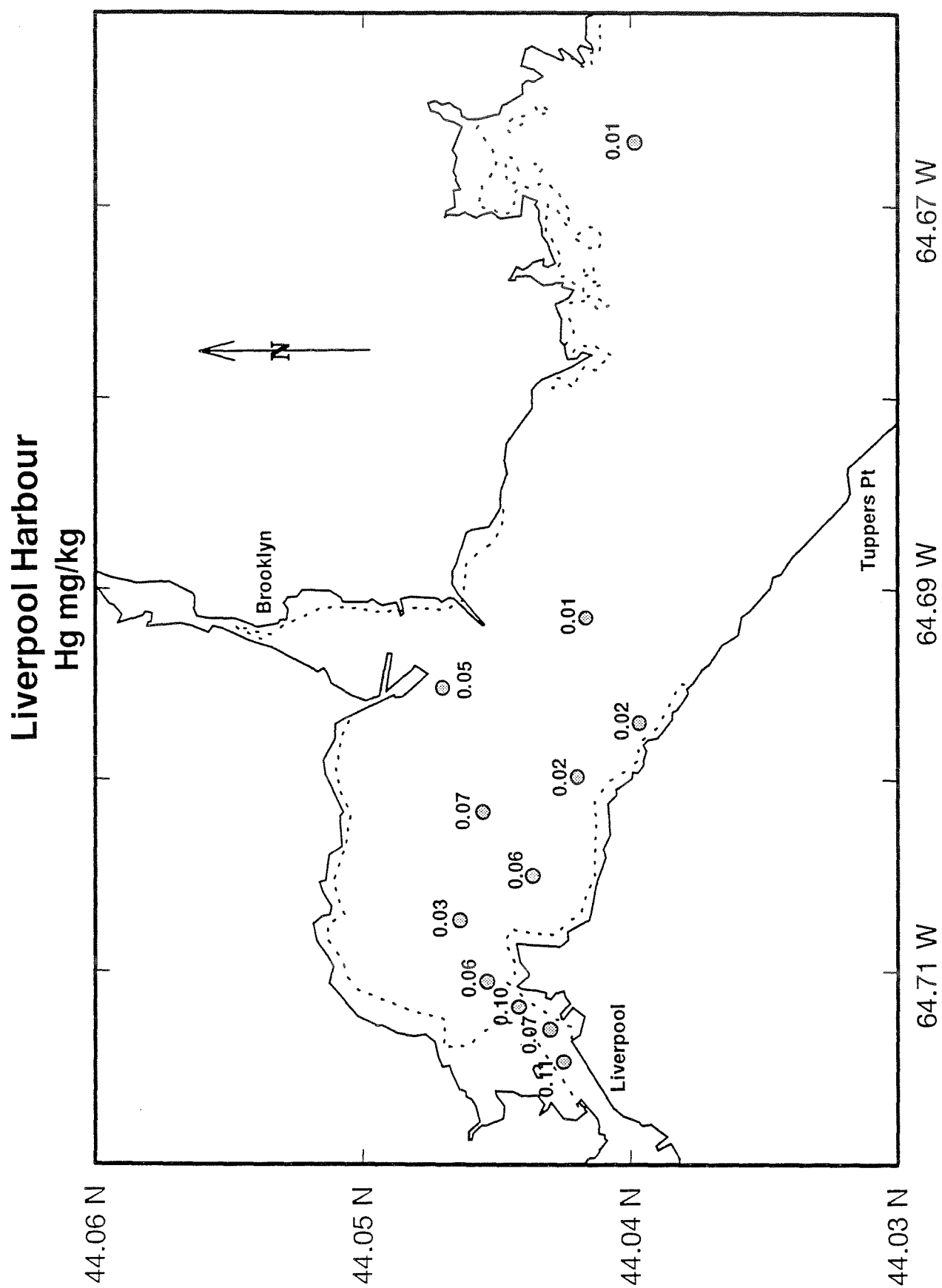
Figure 82. Mercury concentrations in surficial sediments

Liverpool Harbour
Li mg/kg

Figure 83. Lithium concentrations in surficial sediments

Liverpool Harbour
Mn mg/kg

44.06 N

44.05 N

Brooklyn

N

1110

673

552

546

590

357

677

427

1070

578

Liverpool

753

1450

44.04 N

Tuppers Pt

44.03 N

64.71 W   64.69 W   64.67 W
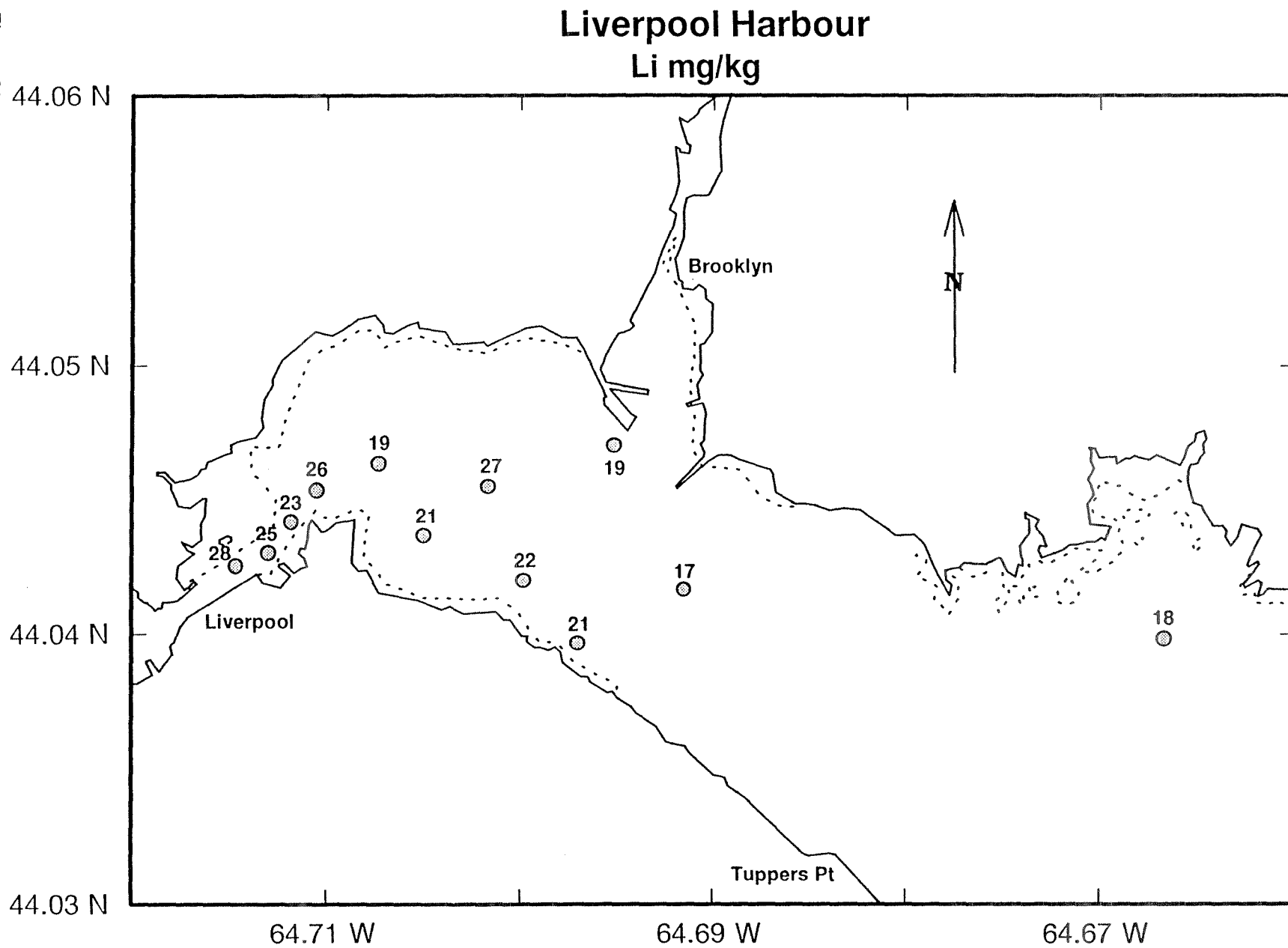
Figure 84. Manganese concentrations in surficial sediments
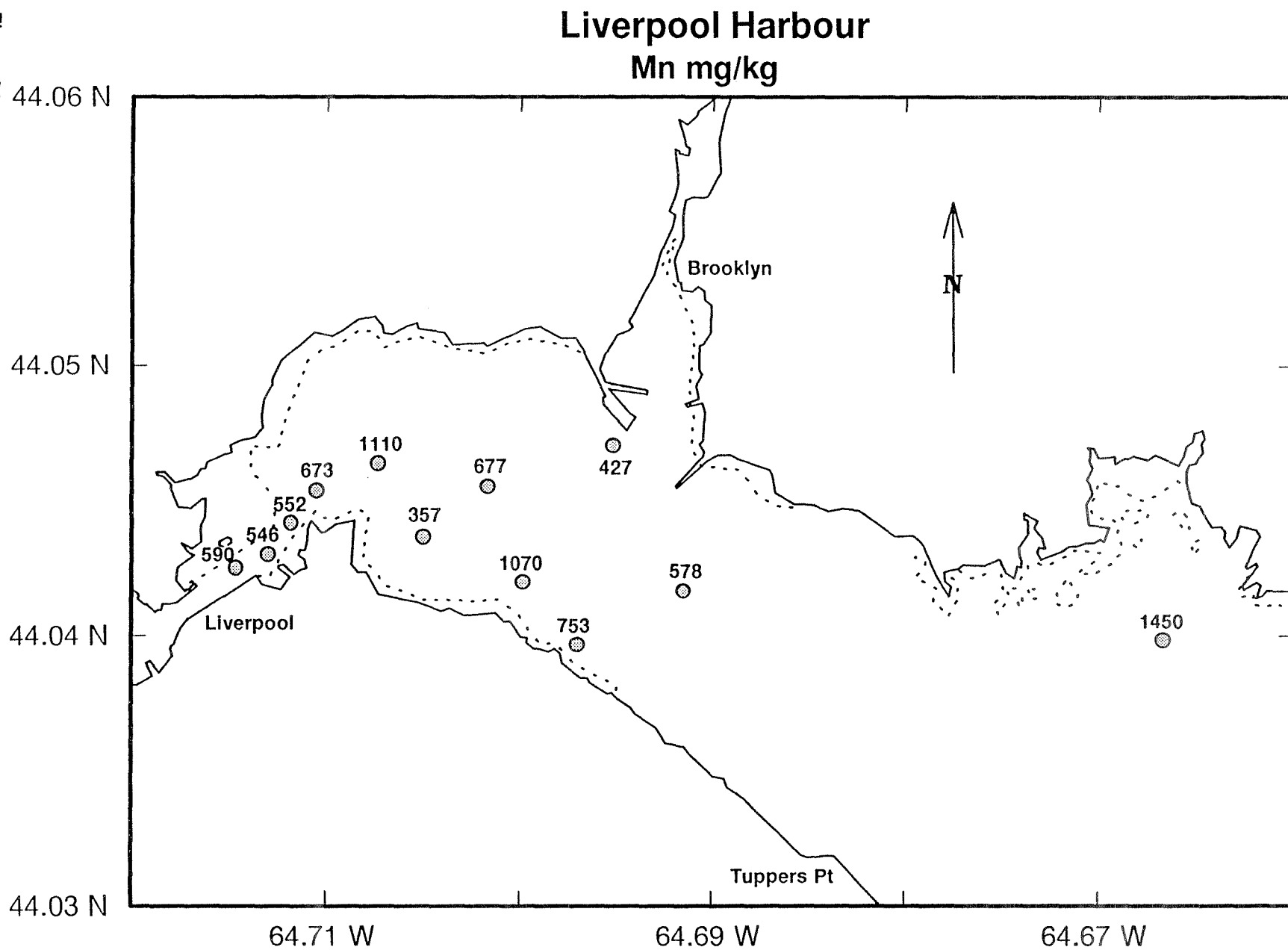
Figure 85. Nickel concentrations in surficial sediments

Liverpool Harbour
Ni mg/kg

44.06 N

Brooklyn

N

44.05 N

9
10
16
17

13
10

16
16

12
10

Liverpool

9
10

44.04 N

Tuppers Pt

44.03 N

64.71 W   64.69 W   64.67 W

Liverpool Harbour
Pb mg/kg

Brooklyn

N

Liverpool

Tuppers Pt

12
15
15
16
18
21
12
20
12
13
12
12
12

44.06 N
44.05 N
44.04 N
44.03 N

64.71 W
64.69 W
64.67 W
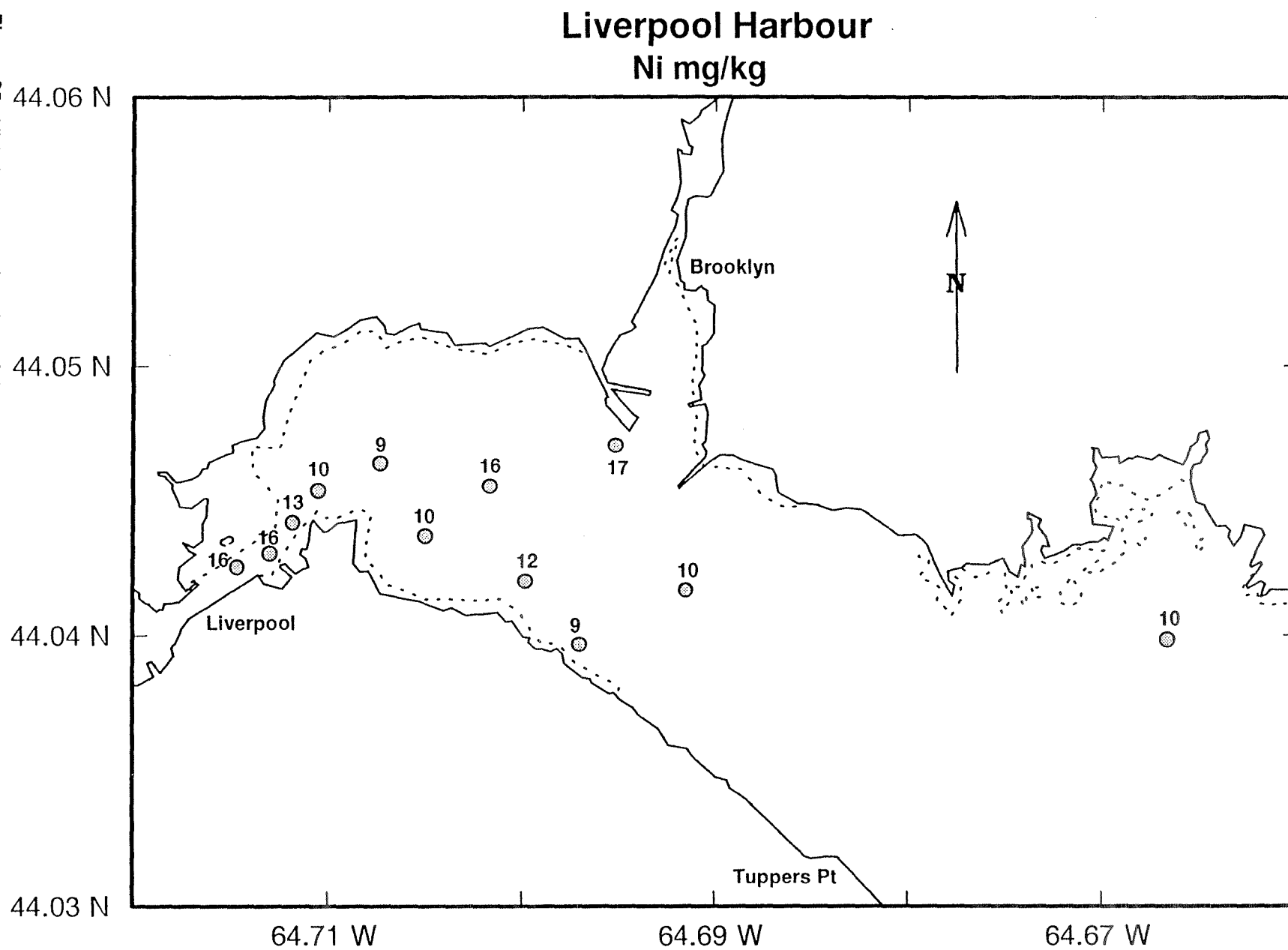
Figure 86. Lead concentrations in surficial sediments
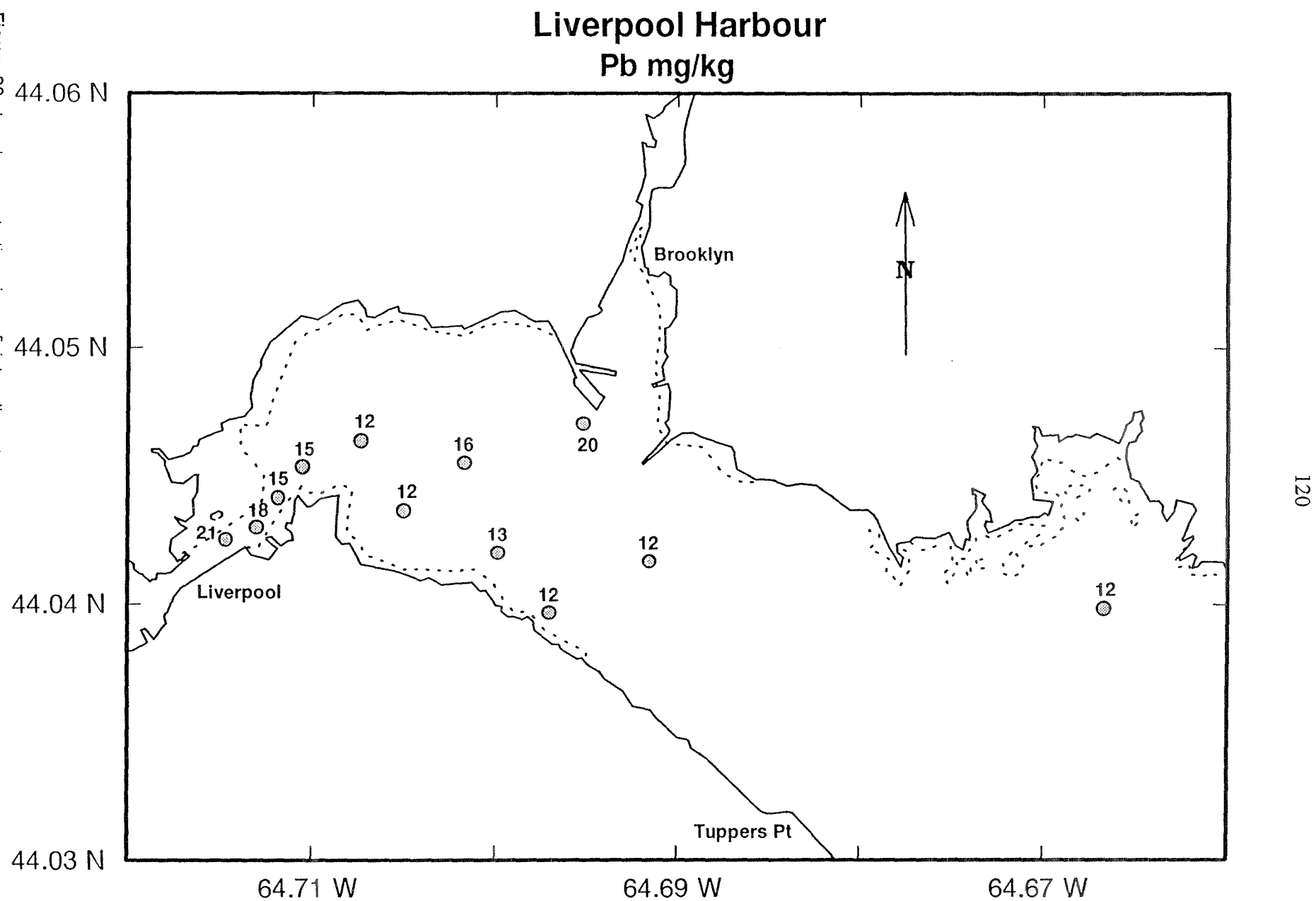
Figure 87. Tin concentrations in surficial sediments
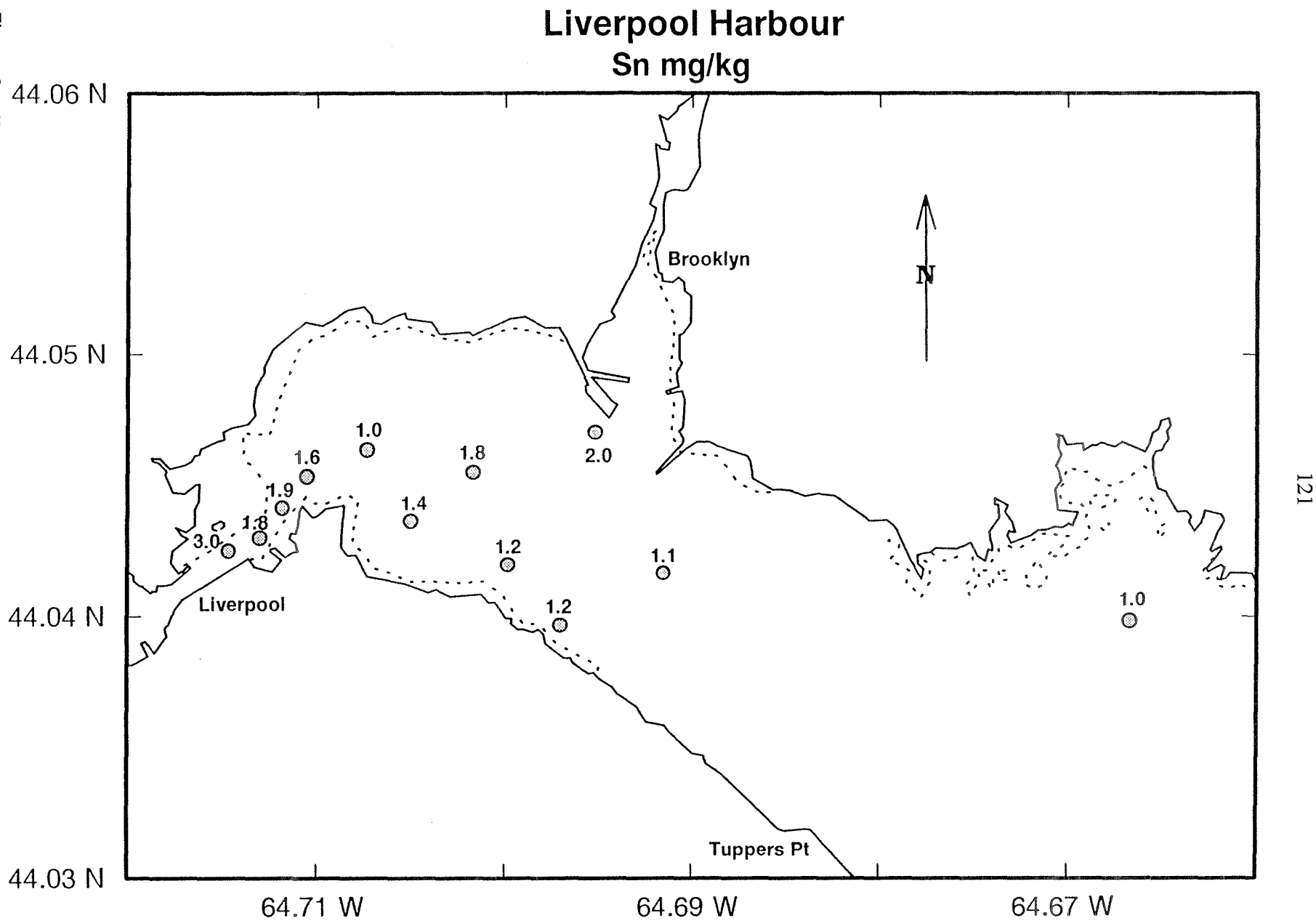
Figure 88. Vanadium concentrations in surficial sediments

Liverpool Harbour
V mg/kg

Liverpool Harbour
Zn mg/kg

44.06 N

Brooklyn

N

44.05 N

17

36

38

46

51

22

40

59

25

15

44.04 N

Liverpool

18

20

Tuppers Pt

44.03 N

64.71 W   64.69 W   64.67 W
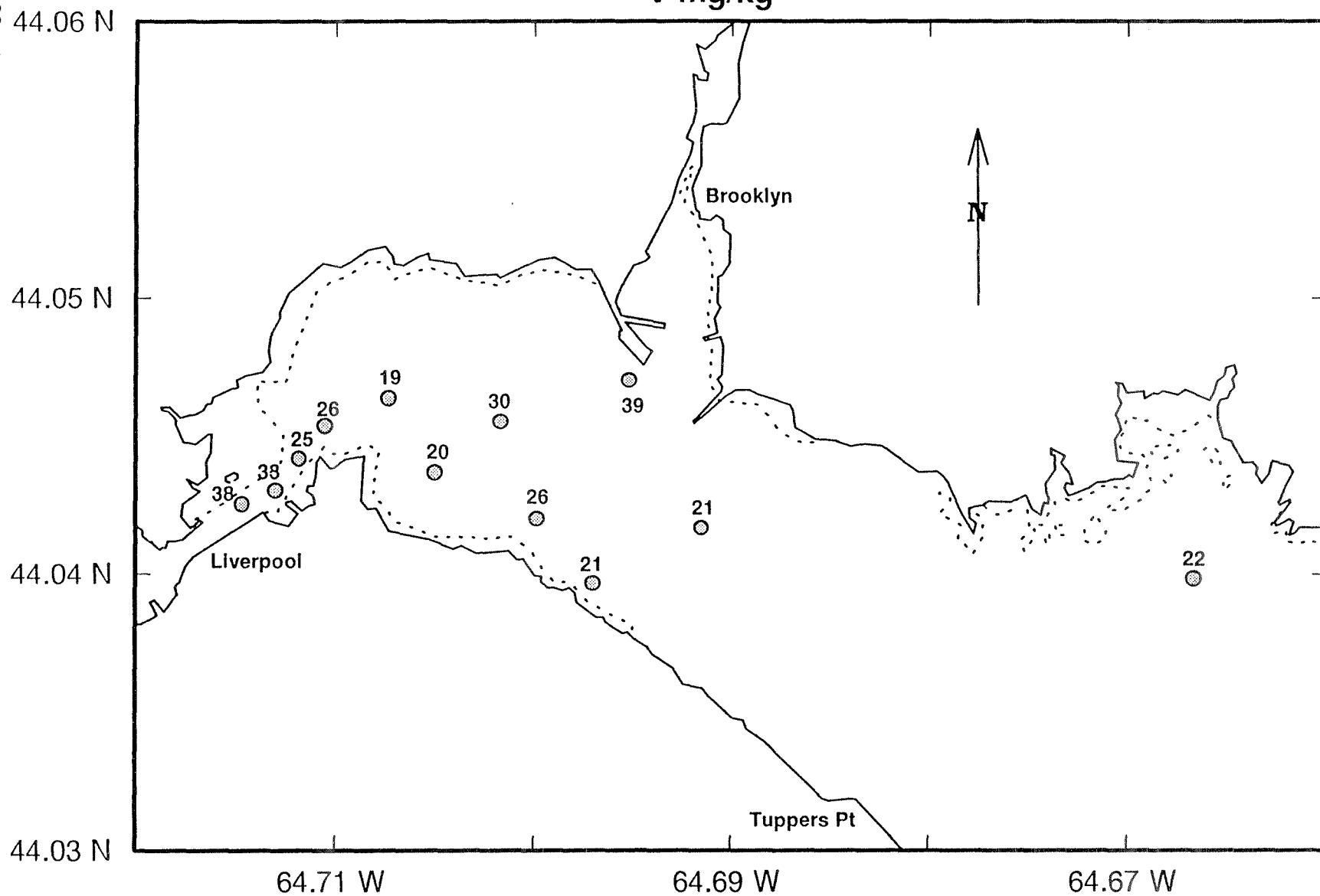
Figure 89. Zinc concentrations in surficial sediments
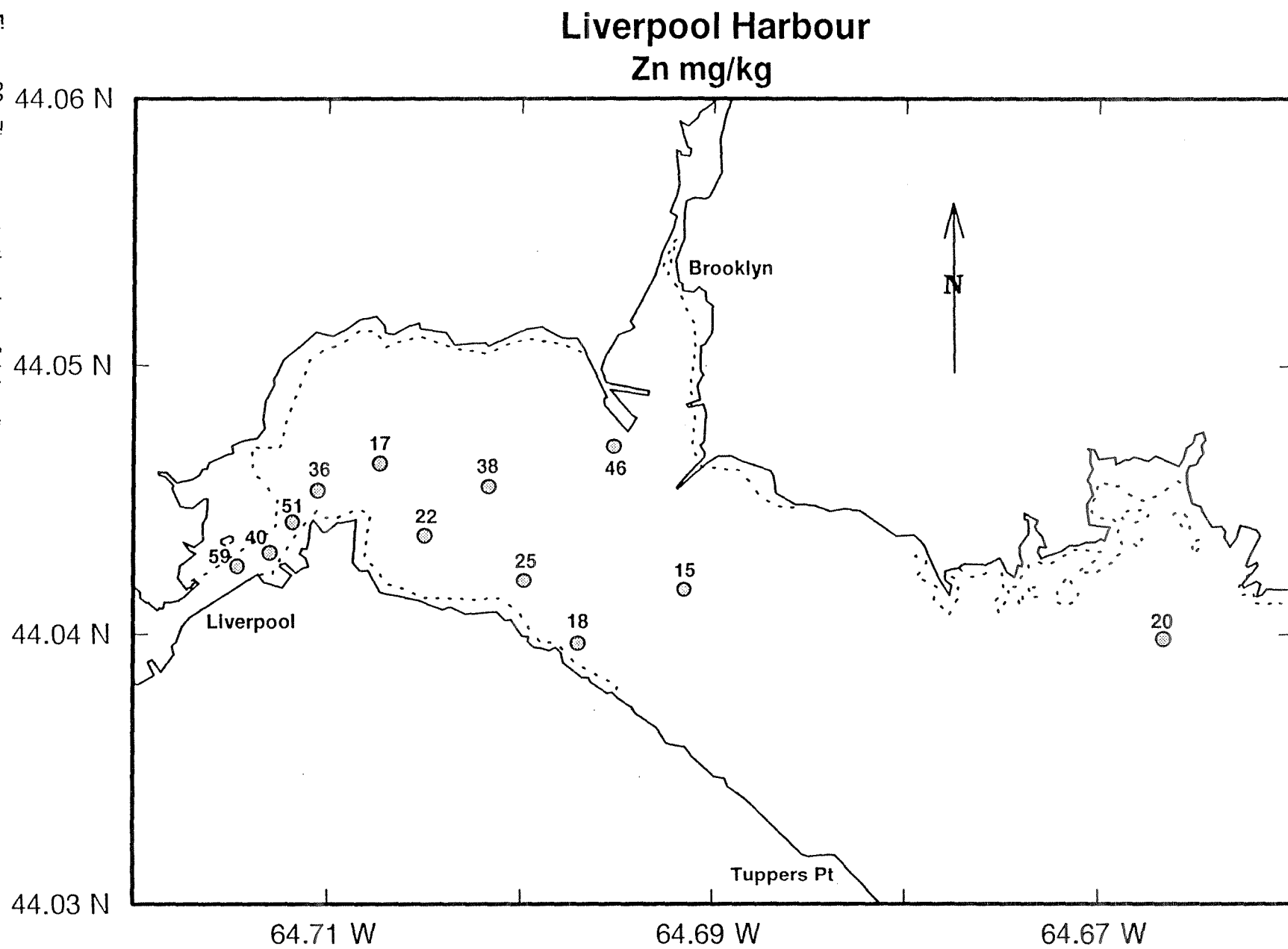
LUNENBURG HARBOUR

Lunenburg Harbour occupies a small embayment (22.7 km² in area) with a maximum depth of 19.2 m on the southern coast of Nova Scotia about 100 km southwest of Halifax. The Harbour receives drainage from a small area of 127 km² mainly occupied by the town of Lunenburg and cultivated land developed on a thin mantle of glacial till underlain primarily by Precambrian quartzites and slates. This limited area of cultivated land supports mixed farming.

POTENTIAL SOURCES OF CONTAMINATION

Since 1753, the town of Lunenburg, which has a population of approx. 3,000, has contributed metallic and organic wastes to the Harbour from its intensive ship-building (wooden and iron), foundry, and fishing activities. Until recently, sewage disposal, industrial, and urban discharges were potentially the main sources of metallic and organic contaminants. A recent underwater survey by Scarratt et al. (1994) indicated that parts of the muddy/sandy floor of the Harbour contained abandoned steel cables, fishing debris, and much garbage (bottles, scrap metal, and other wastes).

RESULTS

Sediment Samples and Composition

Surface Sediments: The locations of the sampling stations (n=14) are shown in Figure 90. Brownish-black to black, sometimes anoxic, organic sandy muds and muds (Fig. 91) occupy most the floor of the Harbour with the occasional patch of muddy sands, sands, and gravels that become more prevalent toward its mouth.

Samples collected in Lunenburg Harbour, for the most part, have broad modal peaks and constant source slopes with a mean value of 0.353 (Fig. 92). Inside of Kaulbach Head, modal diameters are less than 20 μm and the floc portion of the sediment ranges from 15-25%. At the two outermost stations, which are exposed to wave action, the floc portion drops dramatically to less than 5%, and the modal diameter and degree of sorting increase. The three stations closest to the western side of the Harbour show enrichment with coarser material which results in anomalously low concentrations of floc-settled material, especially at Station 9. Sources of the coarse material could be shore erosion or dredging.

Lunenburg Harbour is therefore typical of a quiet area in which trapping fine sediments occurs. The size spectra clearly show the transition in bottom energy which occurs as bottom turbulence, in this case wave-generated, increases.

Core Sediments: Sediment cores, ranging in length from 14 to 20 cm, were obtained at three stations (Fig. 90). The core obtained at Station LU1, which was 14 cm in length, was

obtained from a depth of 3 m in the dredged ship channel near the head of the Harbour. It comprised black organic-rich (8-9% OM) sandy muds. The core obtained at Station LU3 is 20 cm in length and was obtained seaward at a depth of 2 m on the western side of the Harbour. It comprises black organic-rich (9-10% OM) muds. The core obtained at Station LU6 is 20 cm in length and was obtained in 4 m of water seaward of the other cores on the eastern side of Harbour about 400 m east of the Government Wharf at the National Seafood plant. This also comprises organic-rich (8-14% OM) sandy muds and muds.

Abundance and Distribution of Metals in Surface and Subsurface Sediments

The abundances and distributions of metals in Lunenburg Harbour are shown in Figures 93 to 106. Lunenburg Harbour sediments contain anomalously high concentrations of Cd, Cr, Cu, Hg, Pb, Sn, and Zn with the highest concentrations of these metals being found in the sediments adjacent to the local foundry and engineering plants and wharves, in the dredged ship channel, and in the shallow parts on the western side of the Harbour. Lower concentrations tend to occur in sediments toward the mouth of the Harbour and beyond. The levels of As, Ni, and V appear to be at, or near, natural concentrations. The range of total metal concentrations in Lunenburg Harbour sediments (n=17) are: As, 5-20 $mg \cdot kg^{-1}$; Cd, 0.24-1.71 $mg \cdot kg^{-1}$; Cr, 55-97 $mg \cdot kg^{-1}$; Cu, 11-108 $mg \cdot kg^{-1}$; Hg, 0.03-0.39 $mg \cdot kg^{-1}$; Ni, 16-36 $mg \cdot kg^{-1}$; Pb, 16-73 $mg \cdot kg^{-1}$; Sn, 1.9-10.2 $mg \cdot kg^{-1}$; V, 50-100 $mg \cdot kg^{-1}$; and Zn, 49-304 $mg \cdot kg^{-1}$ (Table 15). The data (Table 2) indicate that 86% of the samples contain Cd concentrations exceeding background levels (i.e., >0.3 $mg \cdot kg^{-1}$) and 86% exceed the limit for ocean dumping of 0.6 $mg \cdot kg^{-1}$. Of these, 50% exceed 1.5 $mg \cdot kg^{-1}$. In addition, 71% of the samples contain >40 $mg \cdot kg^{-1}$ Cu, 71% >0.1 $mg \cdot kg^{-1}$ Hg, 64% >40 $mg \cdot kg^{-1}$ Pb, 57% >5 $mg \cdot kg^{-1}$ Sn, and 57% >150 $mg \cdot kg^{-1}$ Zn.

Subsurface Sediments: The means, standard deviations, and ranges of the metals in the core sediments are shown in Table 16. The vertical distributions of As, Cd, Cu, Hg, Pb, Sn, and Zn in each of the cores is shown in Figures 107 to 109. These data indicate that the subsurface sediments (n=78) are highly contaminated with Cd, Cu, Hg, Sn, and Zn over the entire lengths of all the cores.

Potential Bioavailability of Metals

Chemical partitioning of selected samples reveals that most (51-79%) of the total Cd, 0-19% of the total Cu, 22-49% of the total Pb, and 24-59% of the total Zn are potentially bioavailable. The high concentrations of Cd, and significant amounts of Pb and Zn, in the non-detrital fraction imply that these metals have been supplied in solution or weakly attached to particulate matter, indicating a significant anthropogenic contribution to the sediments. Although the concentrations of acid-soluble Cd are relatively high, the proportion of Cd in the non-detrital fraction (% of total) is slightly lower than that found in the LaHave estuary and Country Harbour. This implies that a significant amount of Cd is also in the detrital fraction. Chemical partitioning of two subsamples

taken from depths of 1 and 14 cm in the core obtained at Station LU1 showed that 70-79% of the total Cd, 6-12% of the total Cu, 18-30% of the total Pb, and 51% of the total Zn are weakly held in the core sediments. Similar partitioning of two other subsamples taken from depths of 1 and 6 cm in the core obtained at Station LU3 also showed that 62-75% of the total Cd, 9-15% of the total Cu, 22-29% of the total Pb, and 45-46% of the total Zn are weakly bound. Finally, partitioning of two samples taken from depths of 1 and 18 cm in the core obtained at Station LU6 again confirmed that 67-68% of the total Cd, <1 % of the total Cu, 17-18% of the total Pb, and 17-43% of the total Zn are weakly bound.

Metal Carriers and Sources

The significant positive covariances ($p < 0.001$) of As and Cr with the <63 μm fraction suggest that their metal carriers are closely associated with the fine-grained organic-rich sediments (Table 17). However, Cd, Cu, Pb, Zn, and Sn, which are present in anomalous concentrations, do not covary significantly with changes in the proportion of the fine fraction of the sediments, even though the highest concentrations do occur in the fine-grained sediments. However, the significant positive covariances ($p < 0.01$) of As, Cd, Cr, Cu, Hg, Pb, Sn, and Zn with Li (Table 8) show that Li normalizes for varying amounts of the granular and mineralogical variability of these metals in the surface sediments. The proportion of the metal variability explained by the granular and mineralogical variability of Li decreases in the order: Cr (91%) > Cd (85%) > Cu (78%) > Hg (75%) > Sn (68%) = Pb (68%) > As (63%) > Zn (60%). Inspection of the correlation matrix indicates strong correlations of Cd with Cr, Cu, Zn, Pb with Cu, Hg, and Sn, and all metals, excepting Zn, with Fe. This suggests that important carriers of the metals include discrete fine-grained iron-bearing particles of either detrital or non-detrital origin. This would include the natural iron oxide minerals carrying Cr, metallic fragments carrying Cd, Cu, Hg, Pb, Sn, and Zn, as well as the non-detrital metallic sulphides that are formed *in situ* in the organic-rich sediments. The high concentrations of Cd in the non-detrital fraction and its strong correlation ($p \geq 0.001$ $r = 0.96$) with organic matter imply that Cd has also been supplied in solution and subsequently become weakly attached to particulate matter. This points to a significant anthropogenic contribution of this metal. Amounts of the metals associated with these carriers are in addition to those naturally carried in the lattices of the aluminosilicate minerals. Arsenic is not greatly enriched in these sediments and is at, or near, natural levels. It appears to be associated with the fine-grained iron-rich aluminosilicate fraction (most likely chorite).

The main sources of the anomalous levels of Cd, Cr, Cu, Hg, Pb, Sn, and Zn appear to be industrial inputs of scrap metallic fragments from local foundry and engineering plants, the ship-building industry, and organic fish and sewage waste from the town surrounding the Harbour. Inventory estimates, based on an area of 0.74 km^2 for the Harbour and the average concentrations of the metals over the core depth of 20 cm, suggest that Lunenburg Harbour contains about 0.14 t of Cd, 3.8 t of Cu, 0.02 t of Hg, 2.4 t of Pb, 0.2 t of Sn, and 4.8 t of Zn in excess of normal background levels.

Table 15

Textural and metal statistics[a] for the Lunenburg Harbour sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	11	82.0	±22.6	24-96	OM%	14	6.69 ± 2.69		0.86-8.96
Metal					Metal				
Al%	14	6.24	± 0.52	5.13-6.99	Fe%	14	3.45 ± 0.79		1.97-4.
As	14	14.1	± 4.9	5-20	Li	14	55.1	± 8.5	38-66
Cd	14	1.31	± 0.50	0.24-1.71	Ni	14	26.7	± 5.7	16-73
Hg	14	0.22	± 0.12	0.03-0.39	V	14	80.5	±15.4	50-100
Mn%	14	0.061	± 0.01	0.054-0.068	Zn	14	158.6	±70.1	49-304

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM) Al, Fe, and Mn

Table 16

Statistical data for trace element, Al and Fe concentrations (mg kg^{-1} except % for Al and Fe) in Lunenburg Harbour subsurface sediments

Core 1 n=10	As	Cd	Cr	Cu	Hg	Li	Mn
Mean	11	1.61	88	98	0.38	67	625
SD	2	0.14	2	3	0.04	1	15
CV%	14	9	2	3	26	1	2
	Ni	Pb	Sn	V	Zn	Al%	Fe%
Mean	38	85	9.6	201	260	6.93	4.33
SD	2	2	0.7	6	13	0.14	0.07
CV%	6	3	7	3	5	2	2
Core 3 n=18	As	Cd	Cr	Cu	Hg	Li	Mn
Mean	12	1.68	85	76	0.35	64	629
SD	2	0.18	2	4	0.07	2	11
CV%	7	10	2	5	19	3	2
	Ni	Pb	Sn	V	Zn	Al%	Fe%
Mean	34	66		201	193	6.69	3.96
SD	3	3		6	10	0.07	2.26
CV%	8	4		3	5	1	3
Core 6 n=12	As	Cd	Cr	Cu	Hg	Li	Mn
Mean	12	1.55	83	55	0.12	62	613
SD	0.4	0.08	3	4	0.01	1	21
CV%	12	5	3	8	11	2	2
	Ni	Pb	Sn	V	Zn	Al%	Fe%
Mean	32	40	5	89	142	6.46	3.60
SD	2	2	0.5	3	8	0.11	0.11
CV%	5	6	12	4	6	2	3

n = number of samples:
SD = standard deviation.
CV% = coefficient of variation = standard deviation/mean X100

Table 17

Correlation Matrix Lunenburg Harbour

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	0.89	x	1									
Cr	0.95	x	0.94	1								
Cu	0.86	0.82	0.83	0.84	1							
Fe	0.97	0.82	0.90	0.97	0.87	1						
Hg	0.86	0.86	0.76	0.80	0.96	0.88	1					
Li	0.97	0.79	0.92	0.98	0.88	0.99	0.87	1				
Mn	x	x	x	x	x	x	x	x	1			
Pb	0.83	0.77	x	x	0.93	0.82	0.96	0.82	x	1		
Sn	0.83	x	x	x	0.90	0.80	0.92	0.83	x	0.98	1	
Zn	x	x	0.80	x	0.82	x	0.78	0.78	x	0.84	0.82	1
mud	x	0.94	x	0.86	x	0.93	0.83	0.89	x	x	x	x
OM	0.85	x	0.96	0.91	x	0.88	x	0.90	x	x	x	x

n = 14 (<63; n = 11)
For p ≤0.001 x = not significant
mud = >70% by weight material<63μm
OM = % by weight organic matter

Lunenburg Harbour
Sample Locations
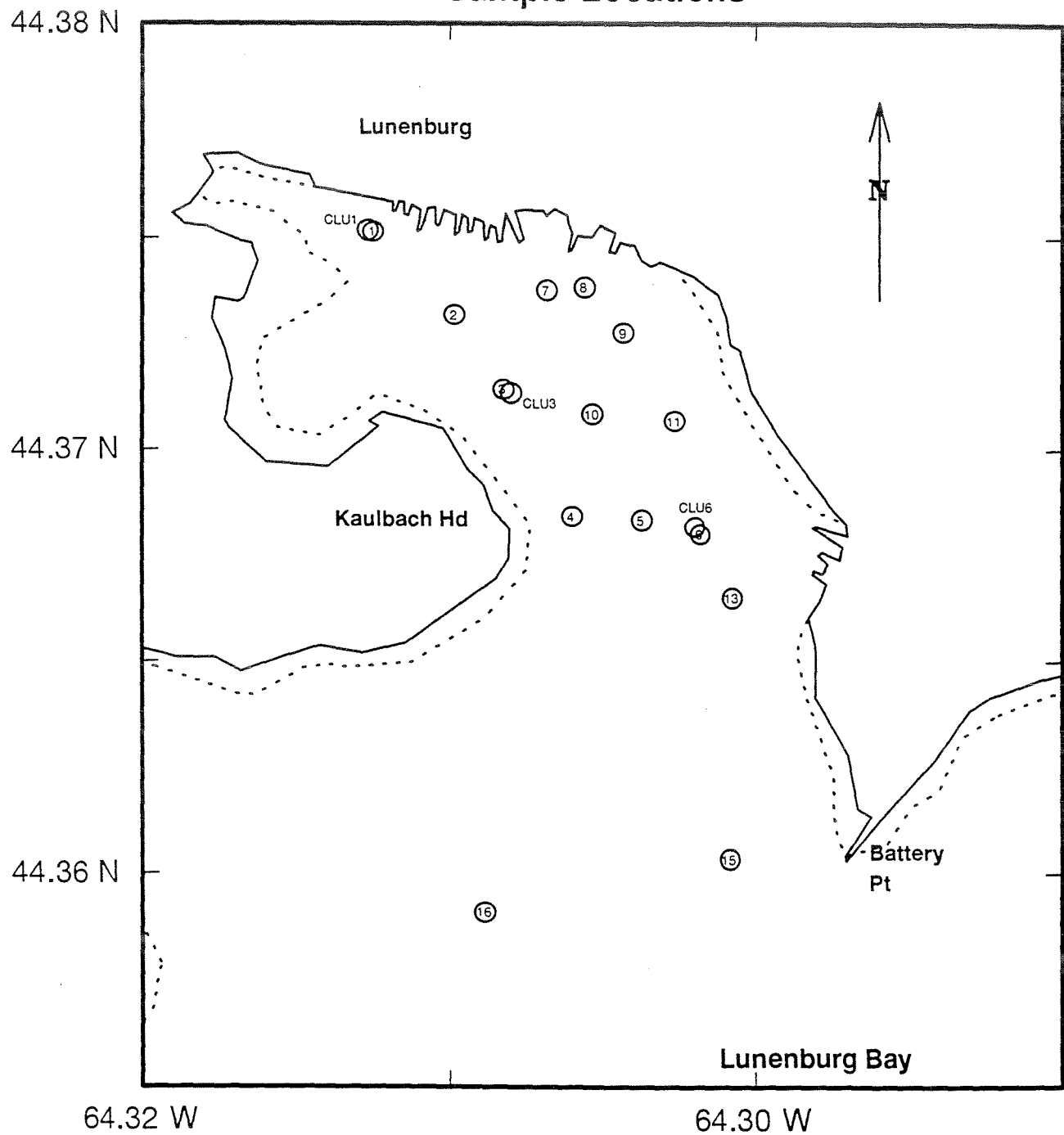
Figure 90. Sample locations for Lunenburg Harbour

Lunenburg Harbour
% Organic Matter
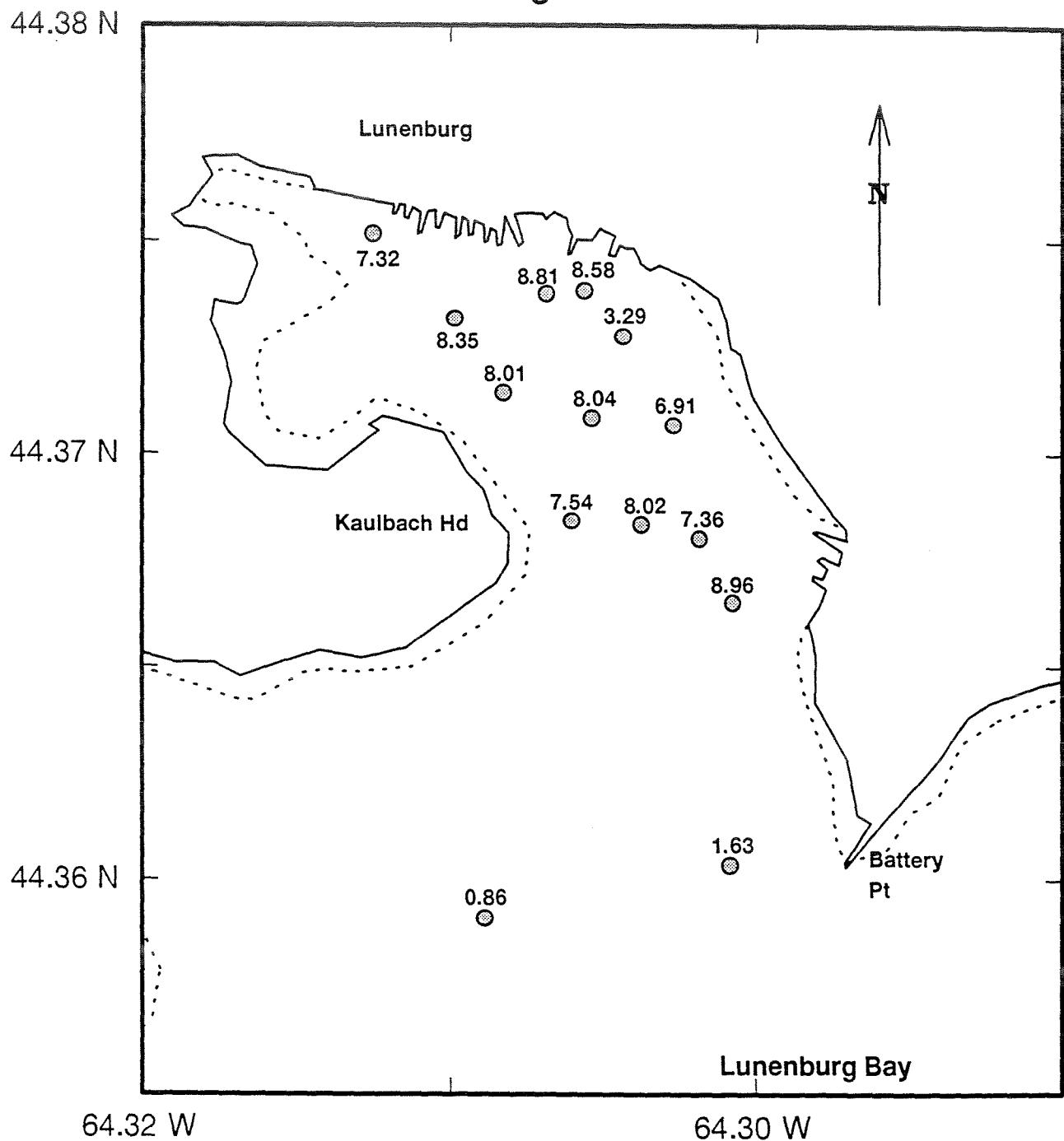
Figure 91. Organic matter concentrations in surficial sediments
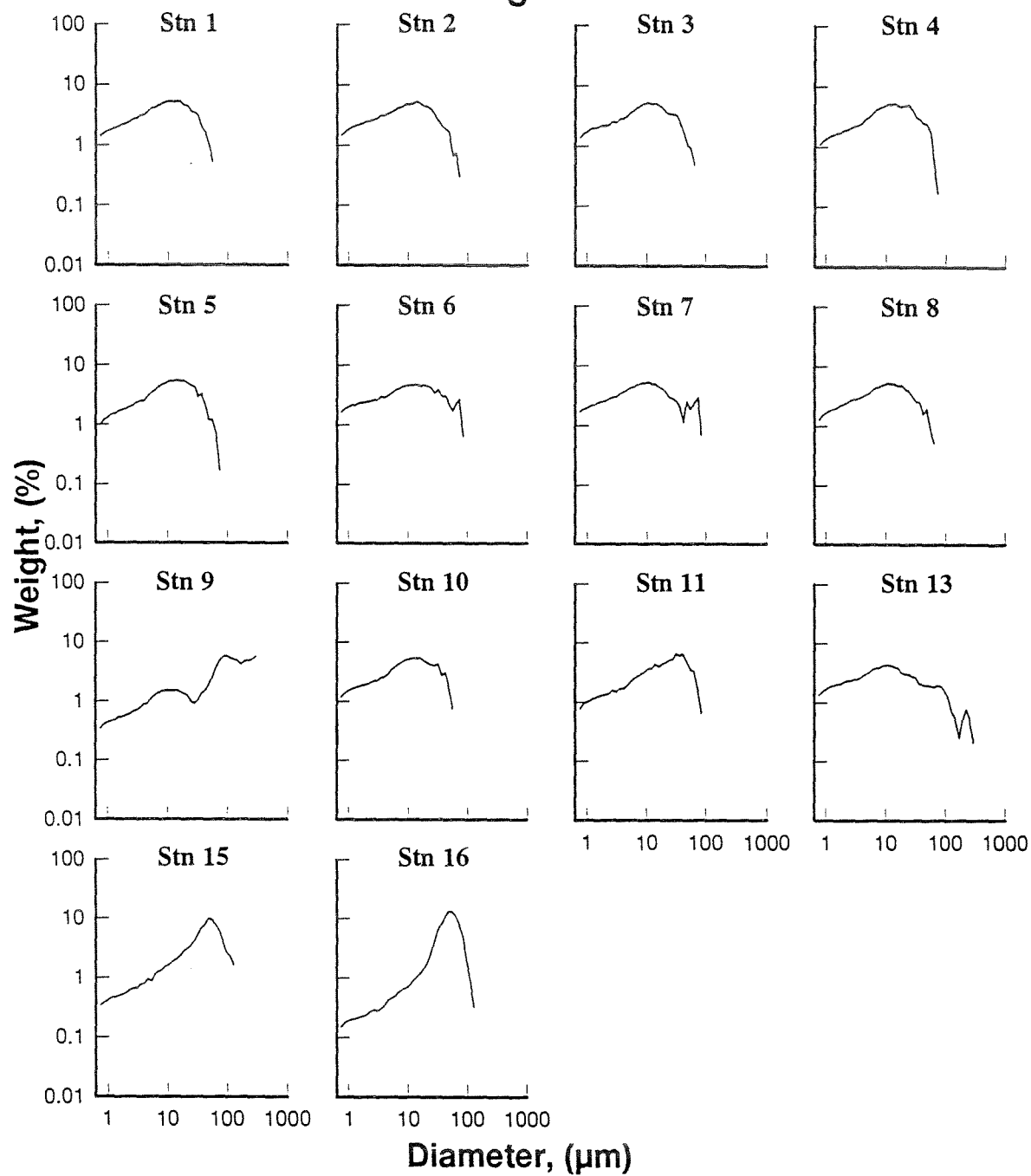
Lunenburg Harbour

Figure 92. Disaggregated inorganic grain size distributions

Lunenburg Harbour
Al %
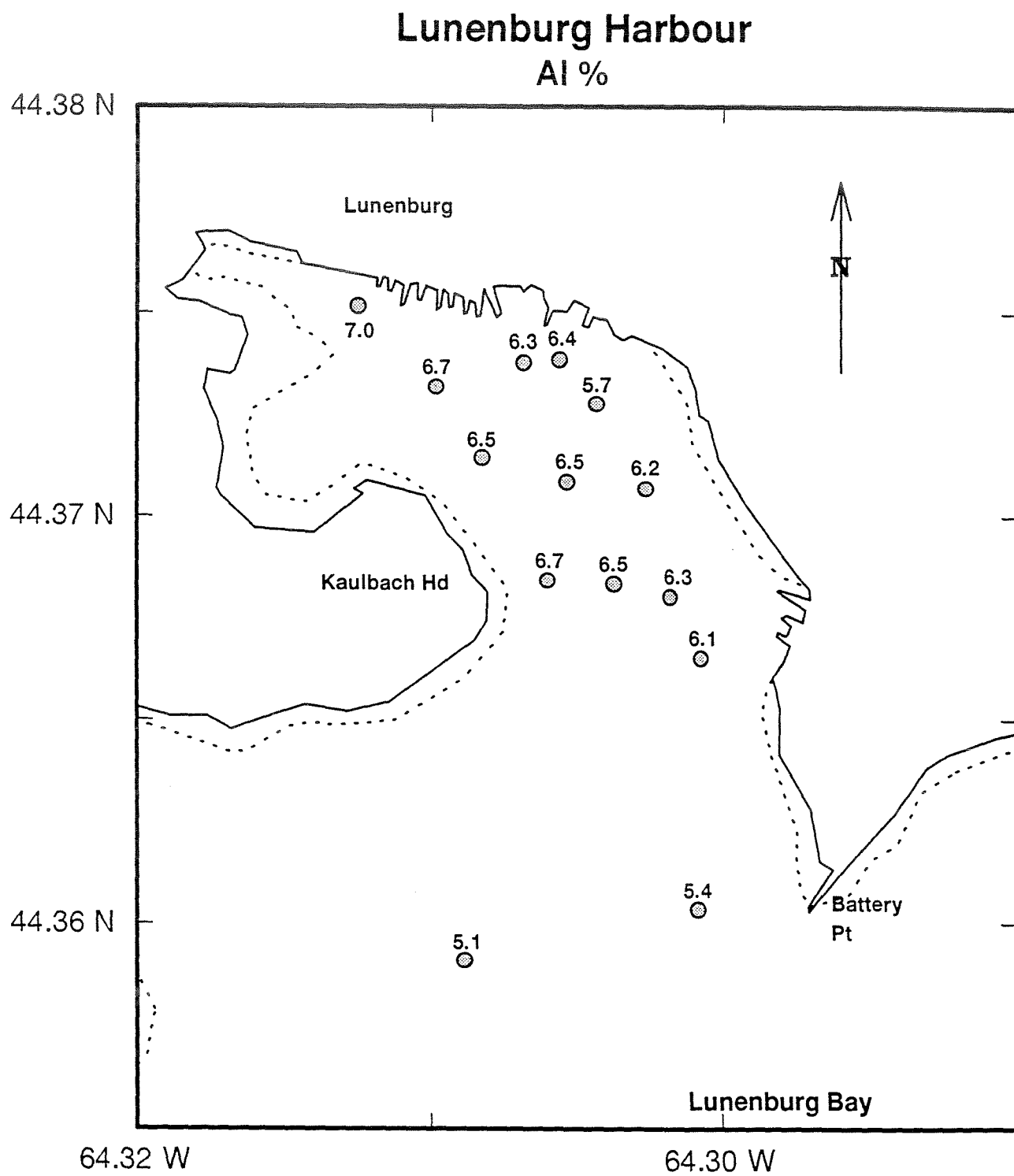
Figure 93. Aluminium concentrations in surficial sediments

Lunenburg Harbour
Fe %
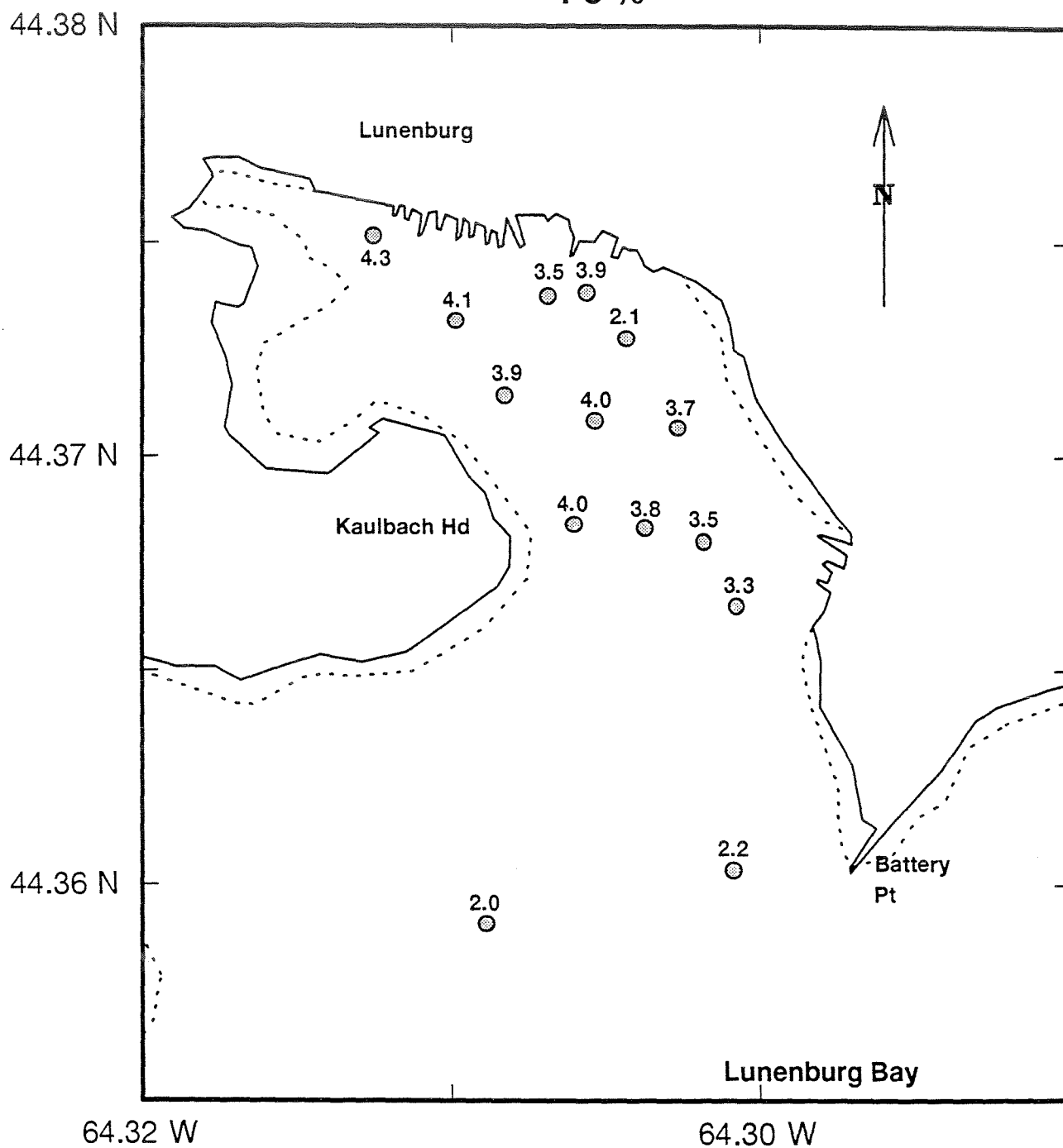
Figure 94. Iron concentrations in surficial sediments

Lunenburg Harbour
As mg/kg
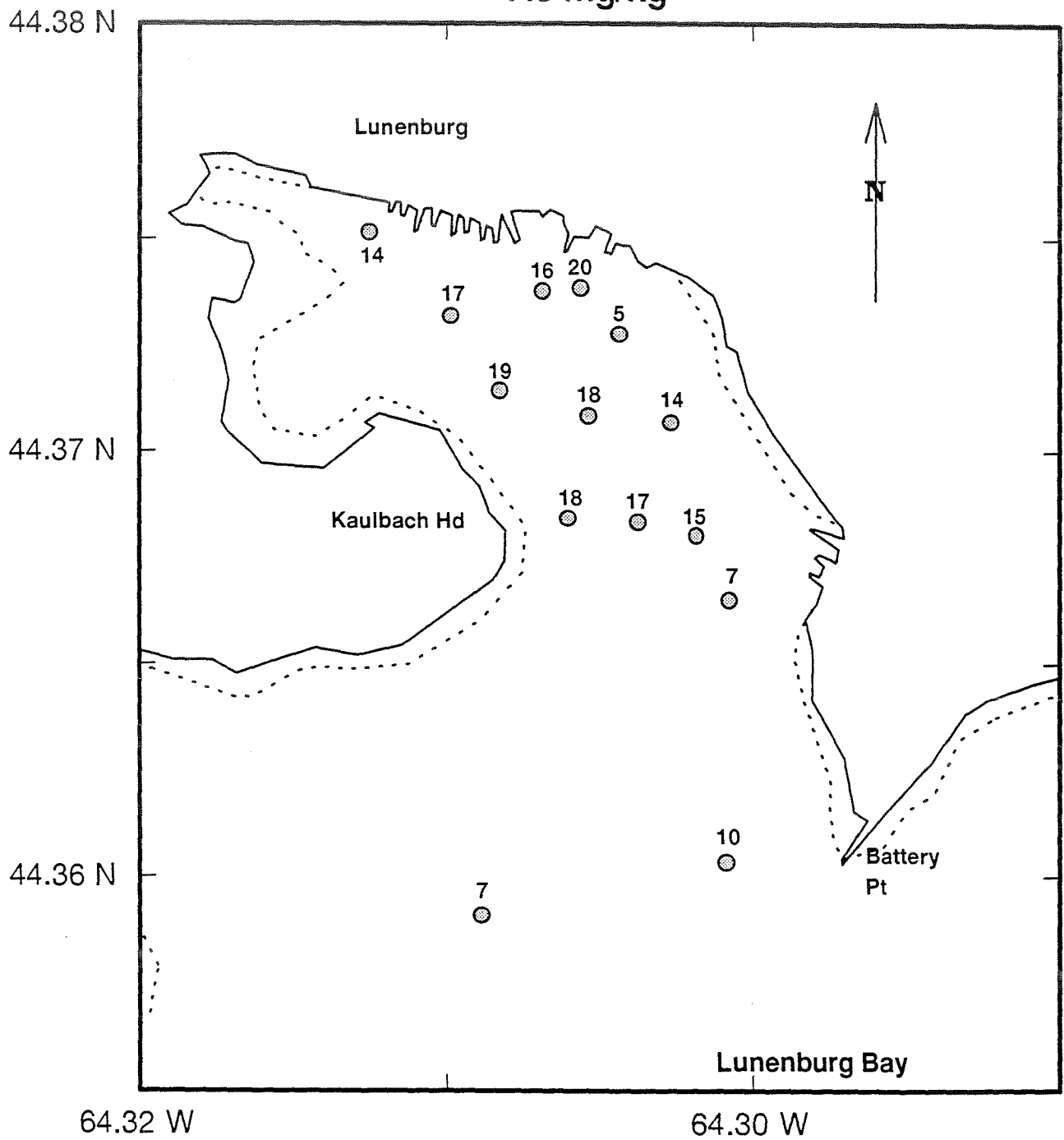
Figure 95. Arsenic concentrations in surficial sediments
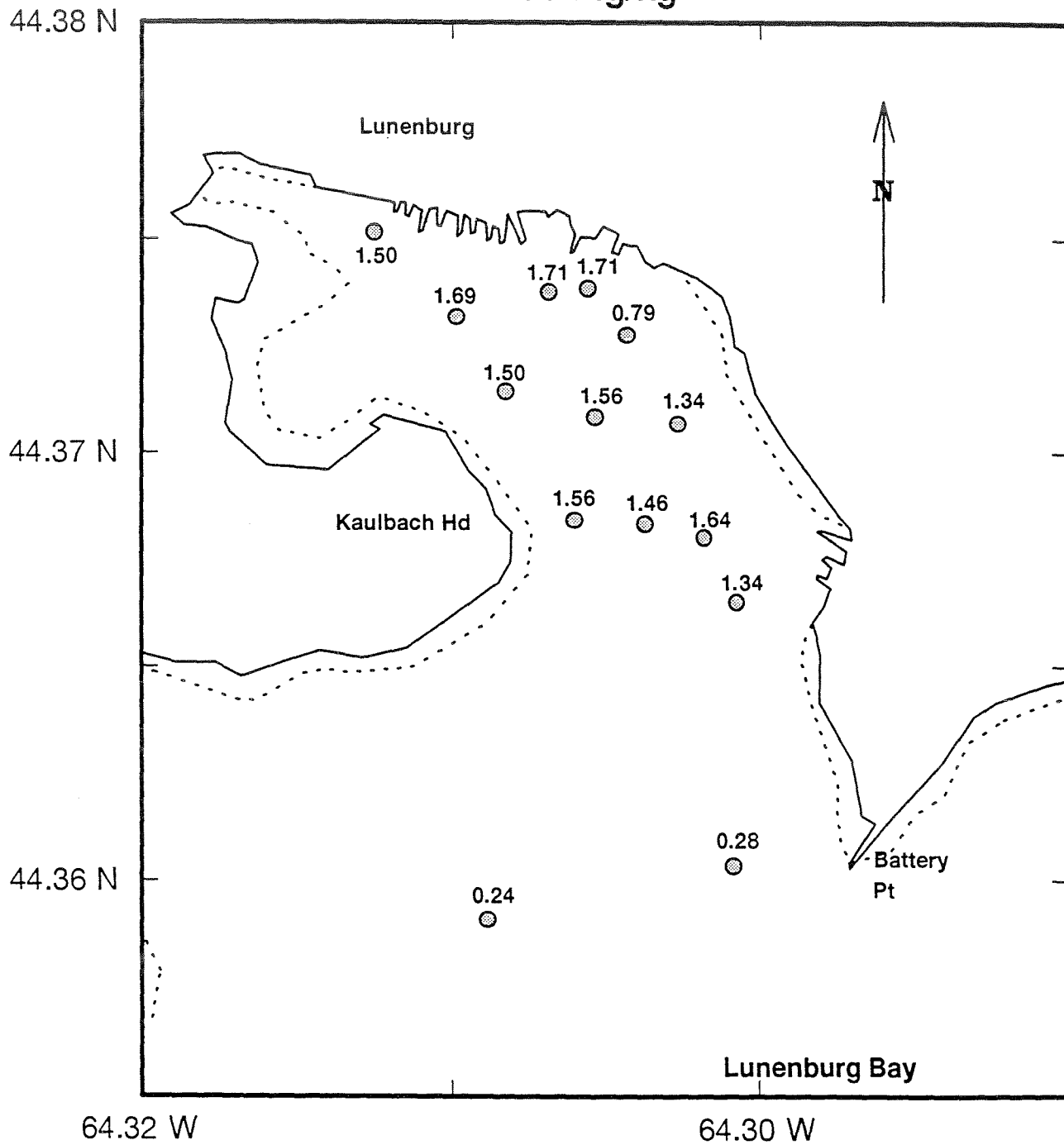
Figure 96. Cadmium concentrations in surficial sediments
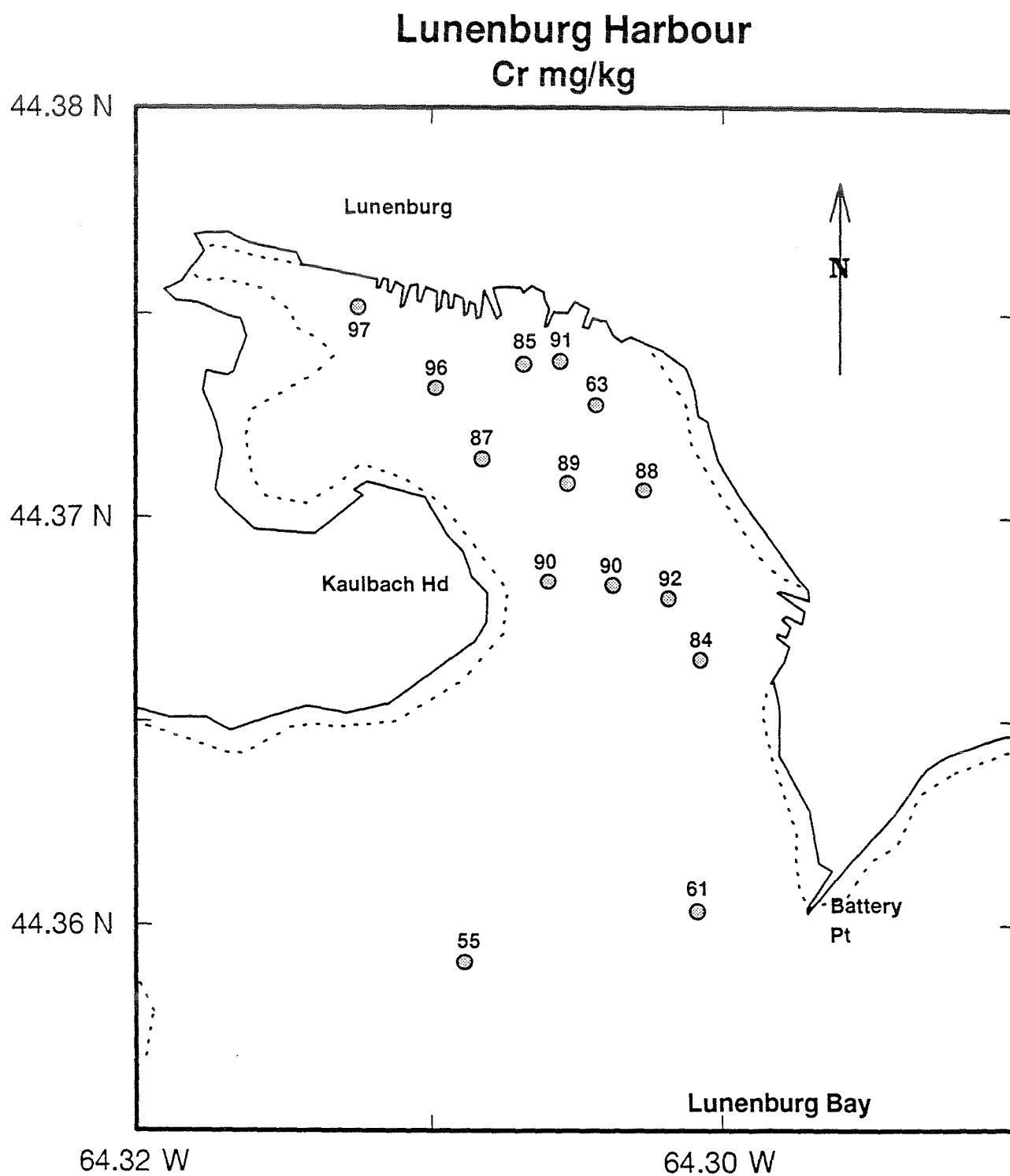
Figure 97. Chromium concentrations in surficial sediments

Lunenburg Harbour
Cu mg/kg
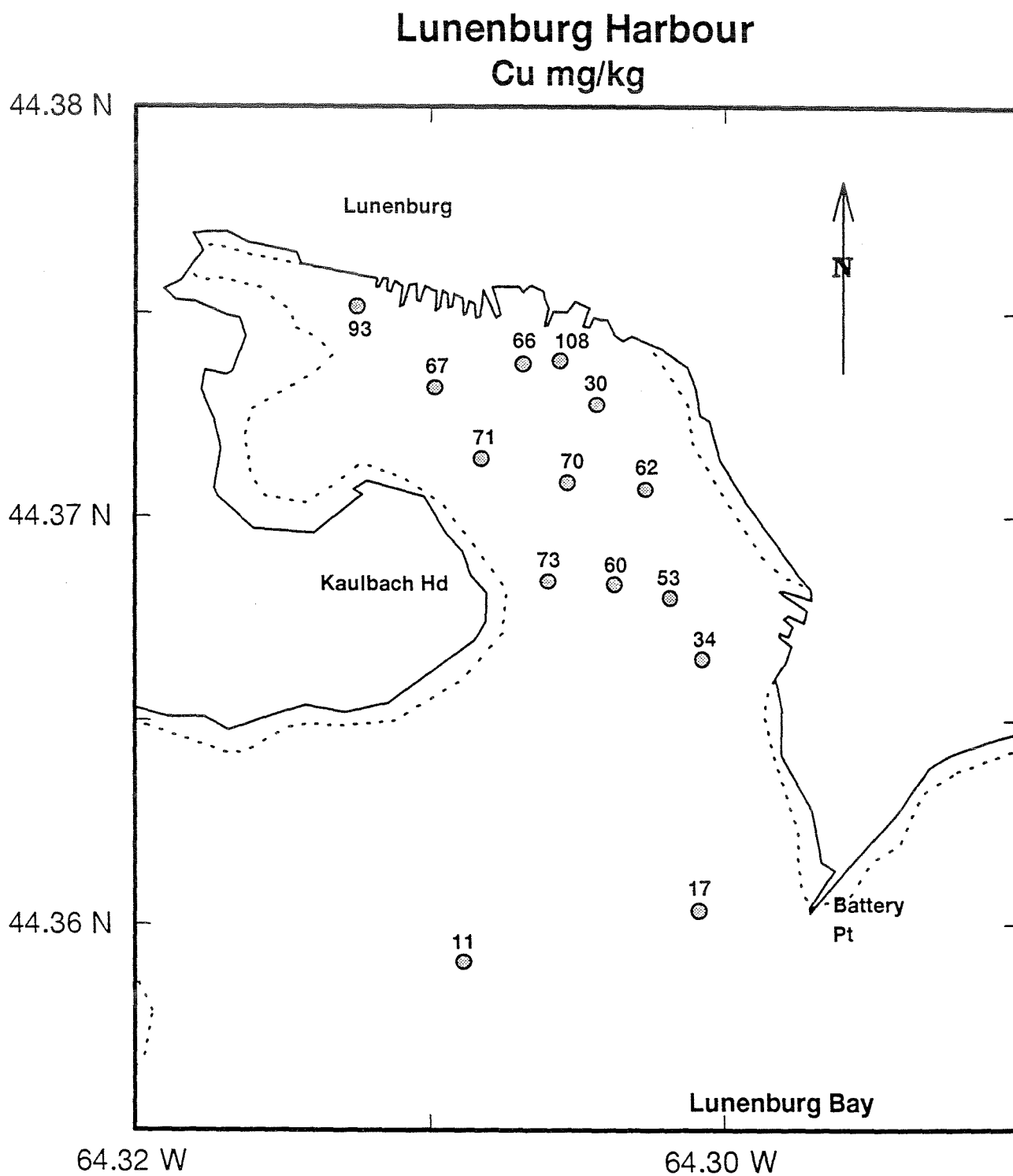
Figure 98. Copper concentrations in surficial sediments

Lunenburg Harbour
Hg mg/kg

44.38 N

Lunenburg

N

0.38

0.23 0.39

0.28

0.09

0.33

0.31   0.26

44.37 N

0.30   0.25

0.16

Kaulbach Hd

0.06

0.05

Battery
Pt

44.36 N

0.03

Lunenburg Bay

64.32 W   64.30 W
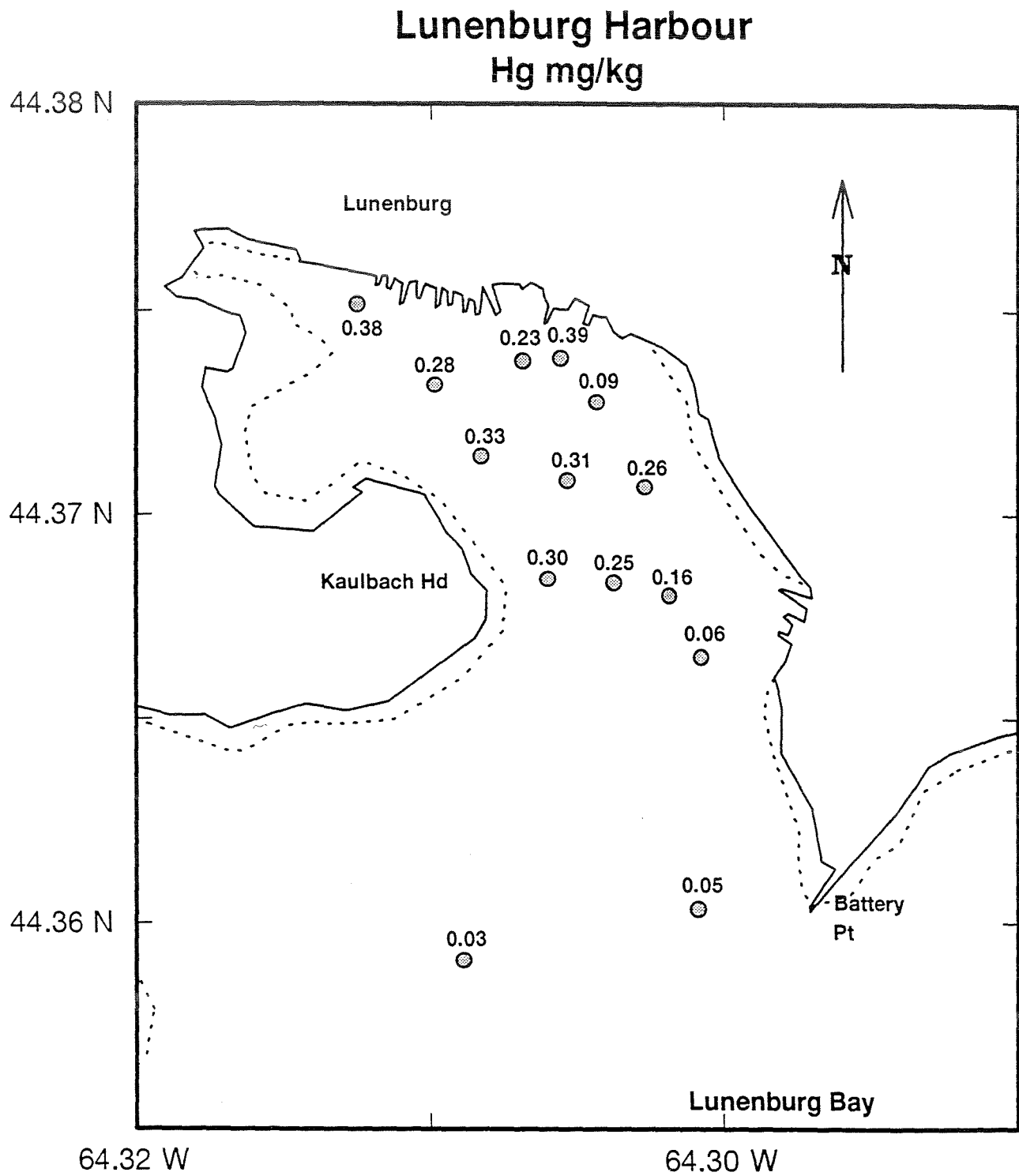
Figure 99. Mercury concentrations in surficial sediments

Lunenburg Harbour
Li mg/kg
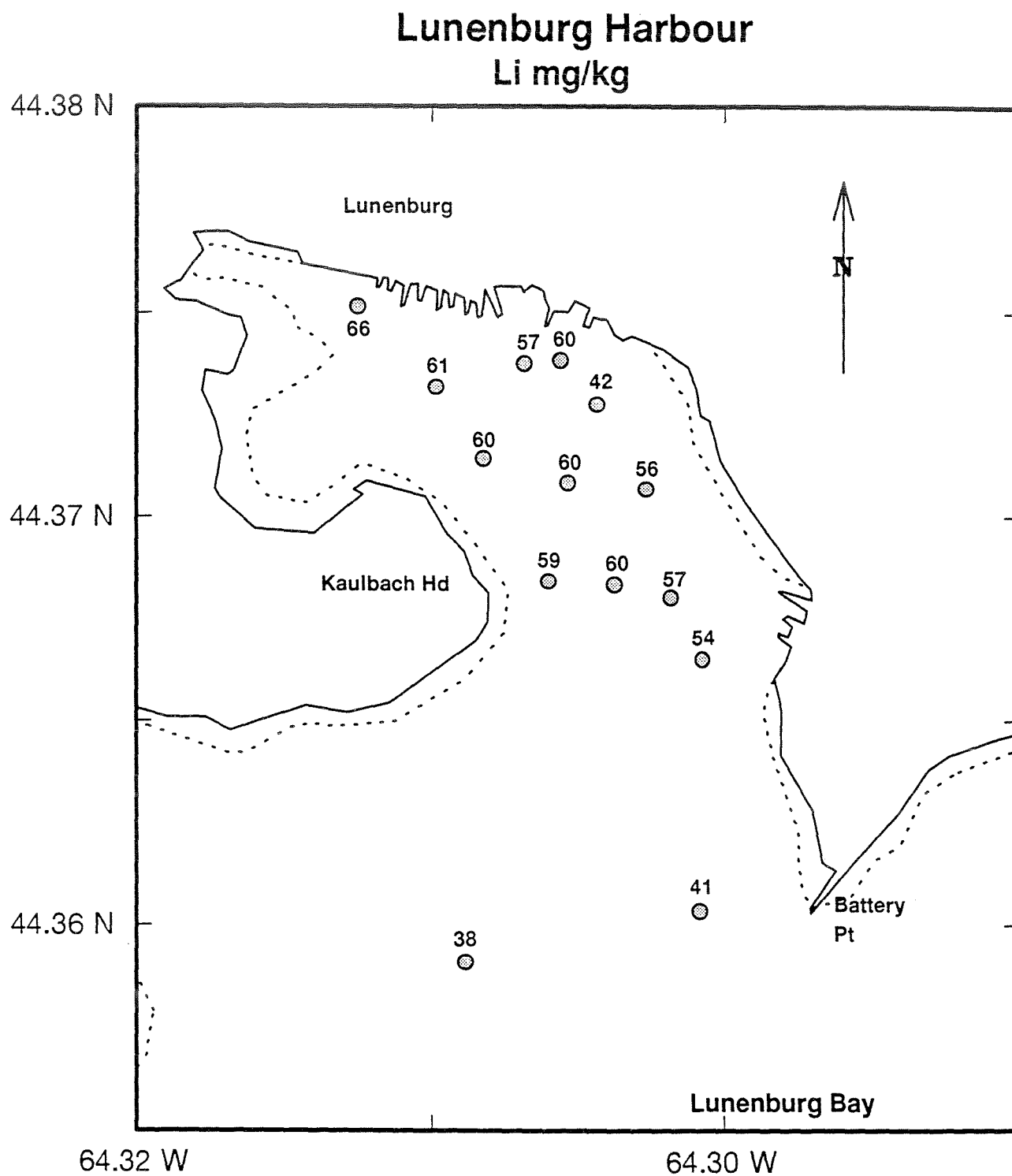
Figure 100. Lithium concentrations in surficial sediments

Lunenburg Harbour
Mn mg/kg
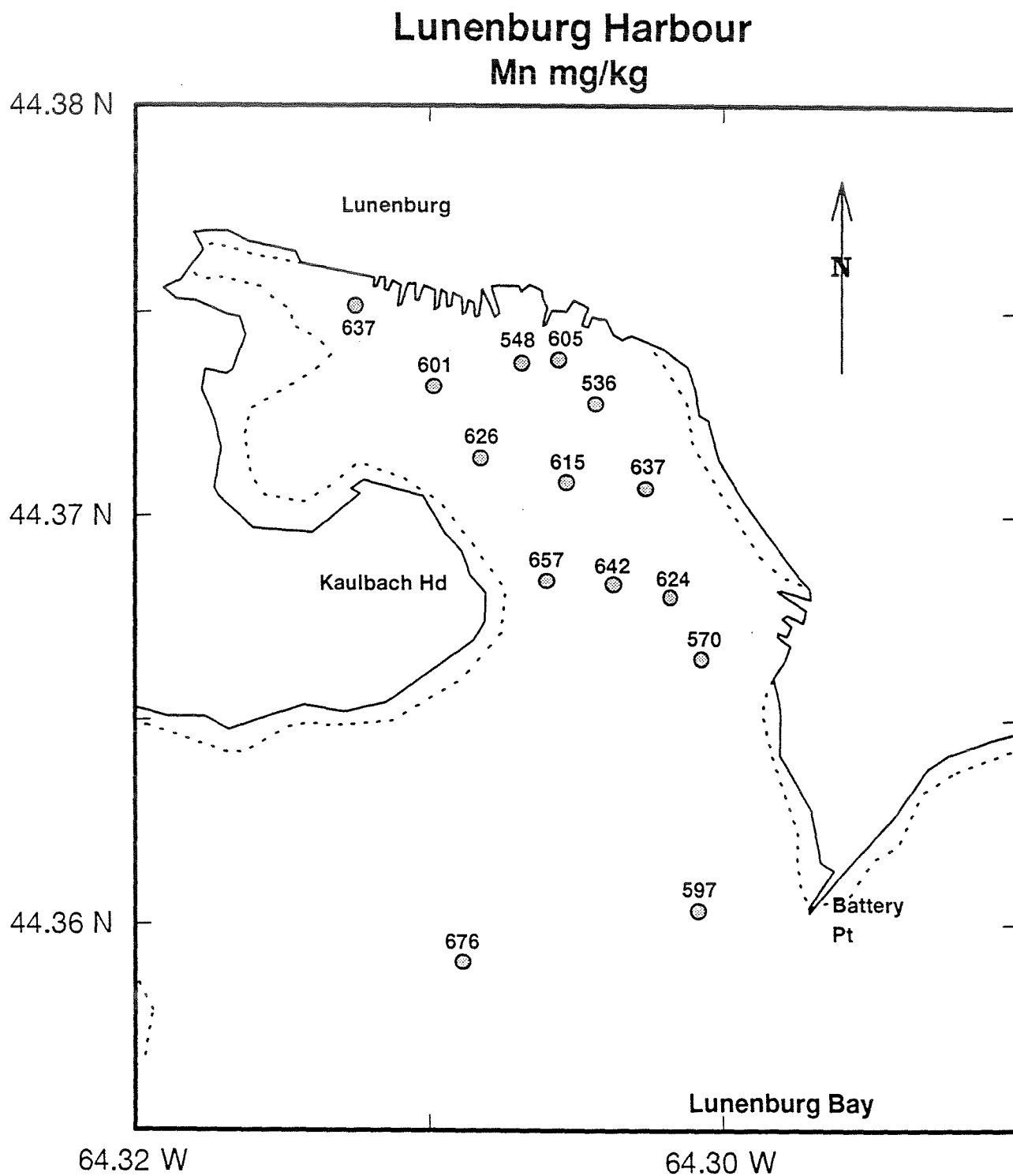
Figure 101. Manganese concentrations in surficial sediments

Lunenburg Harbour
Ni mg/kg
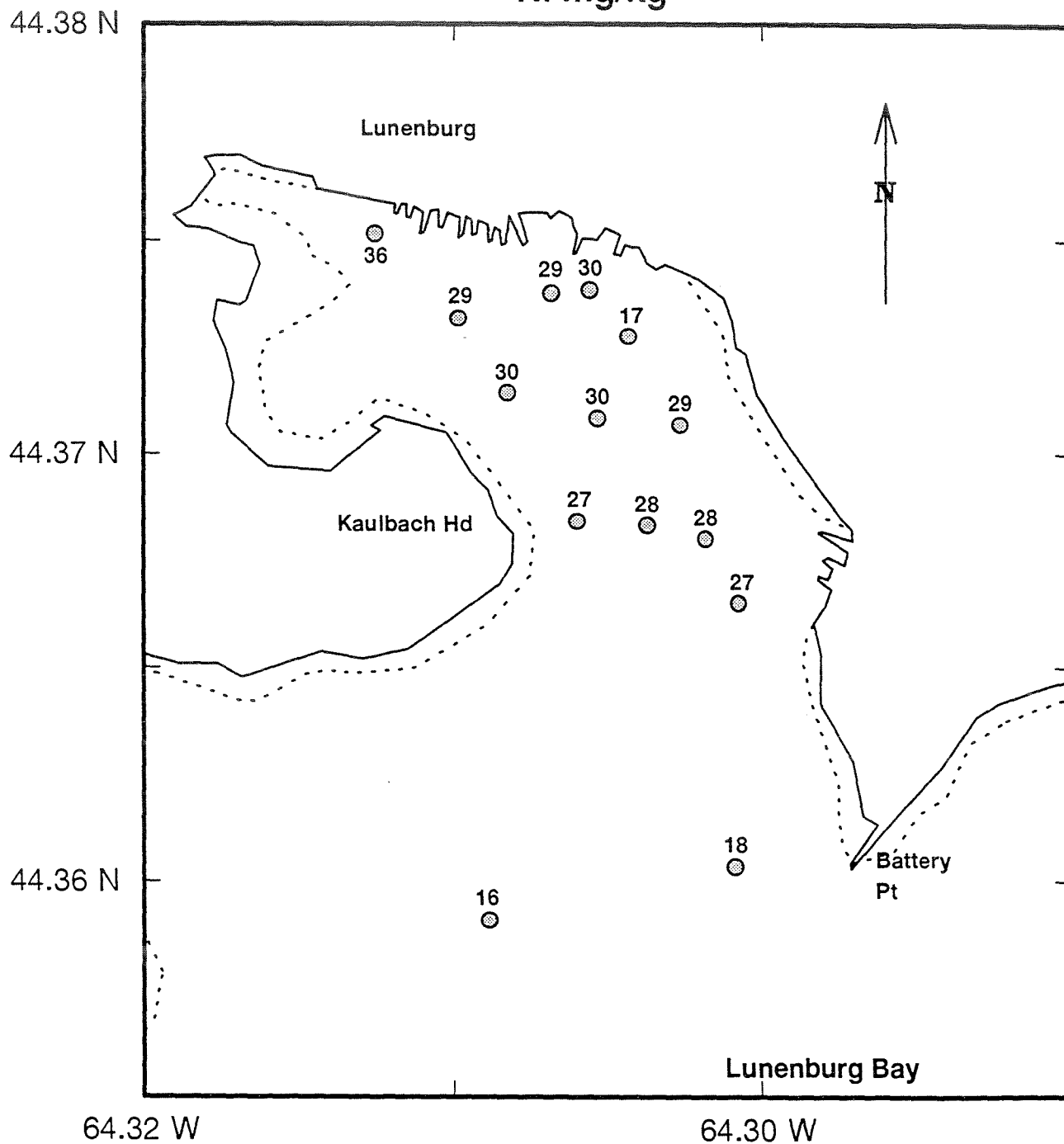
Figure 102. Nickel concentrations in surficial sediments

Lunenburg Harbour
Pb mg/kg
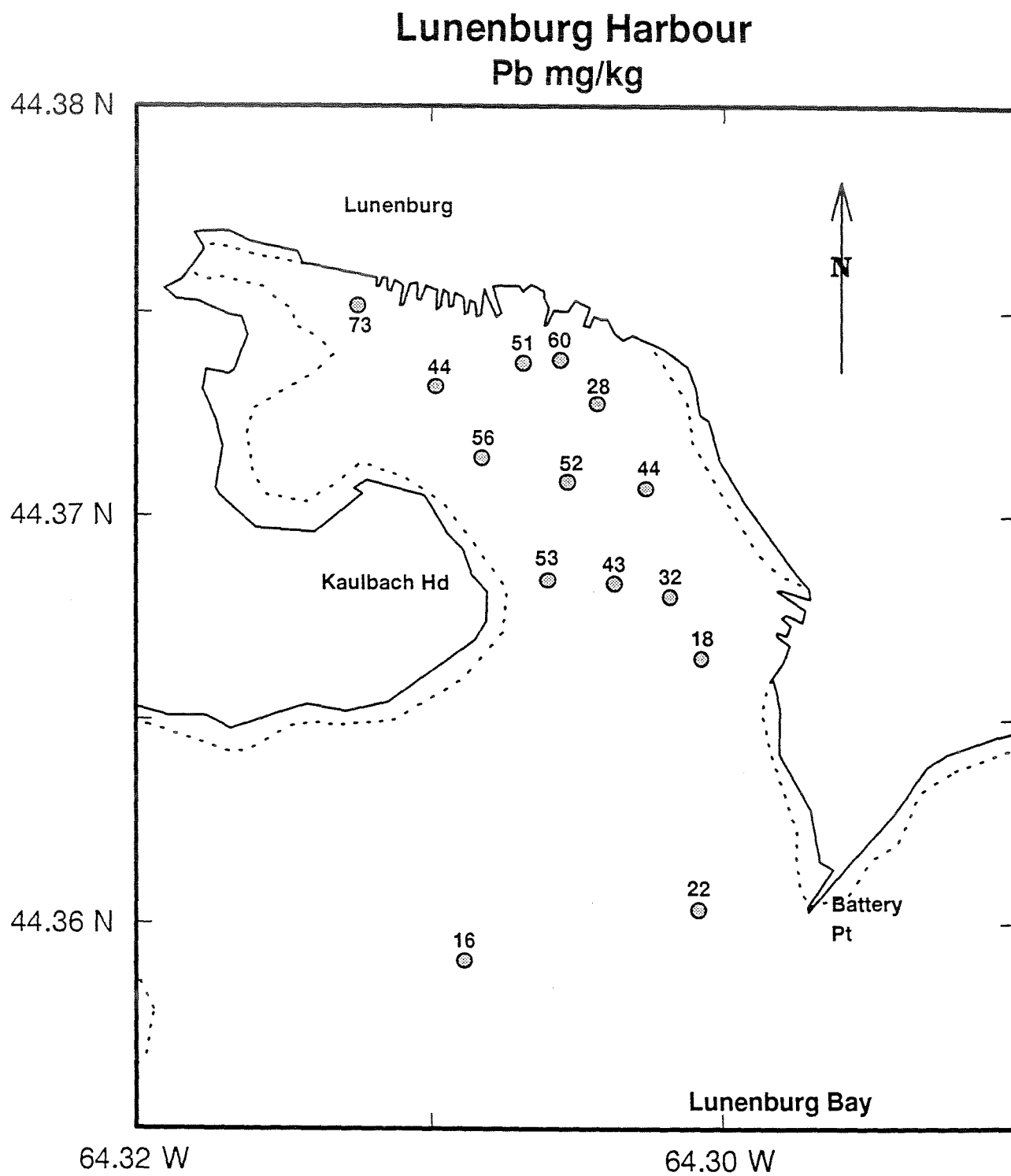
Figure 103. Lead concentrations in surficial sediments

Lunenburg Harbour
Sn mg/kg
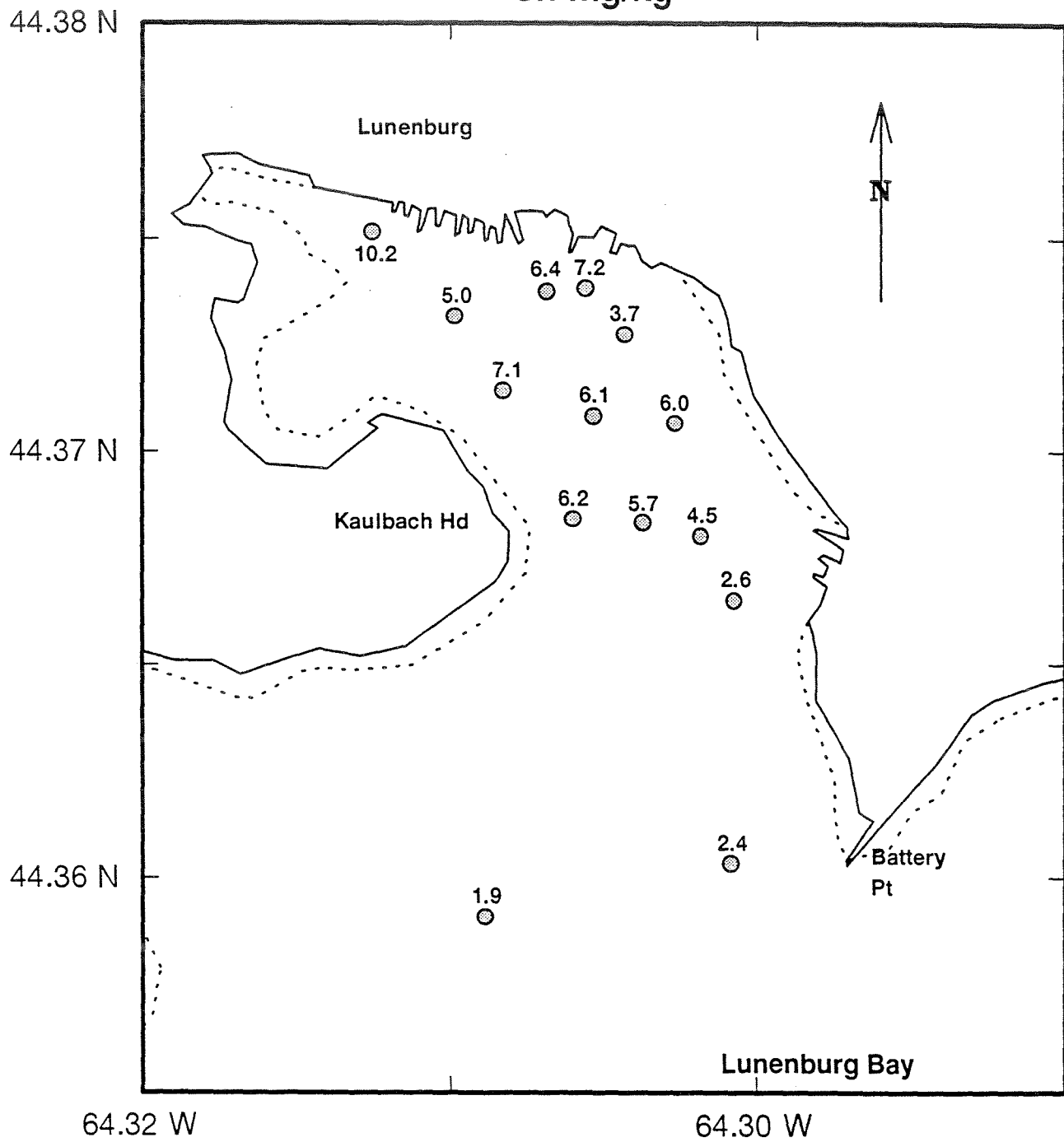
Figure 104. Tin concentrations in surficial sediments

Lunenburg Harbour
V mg/kg
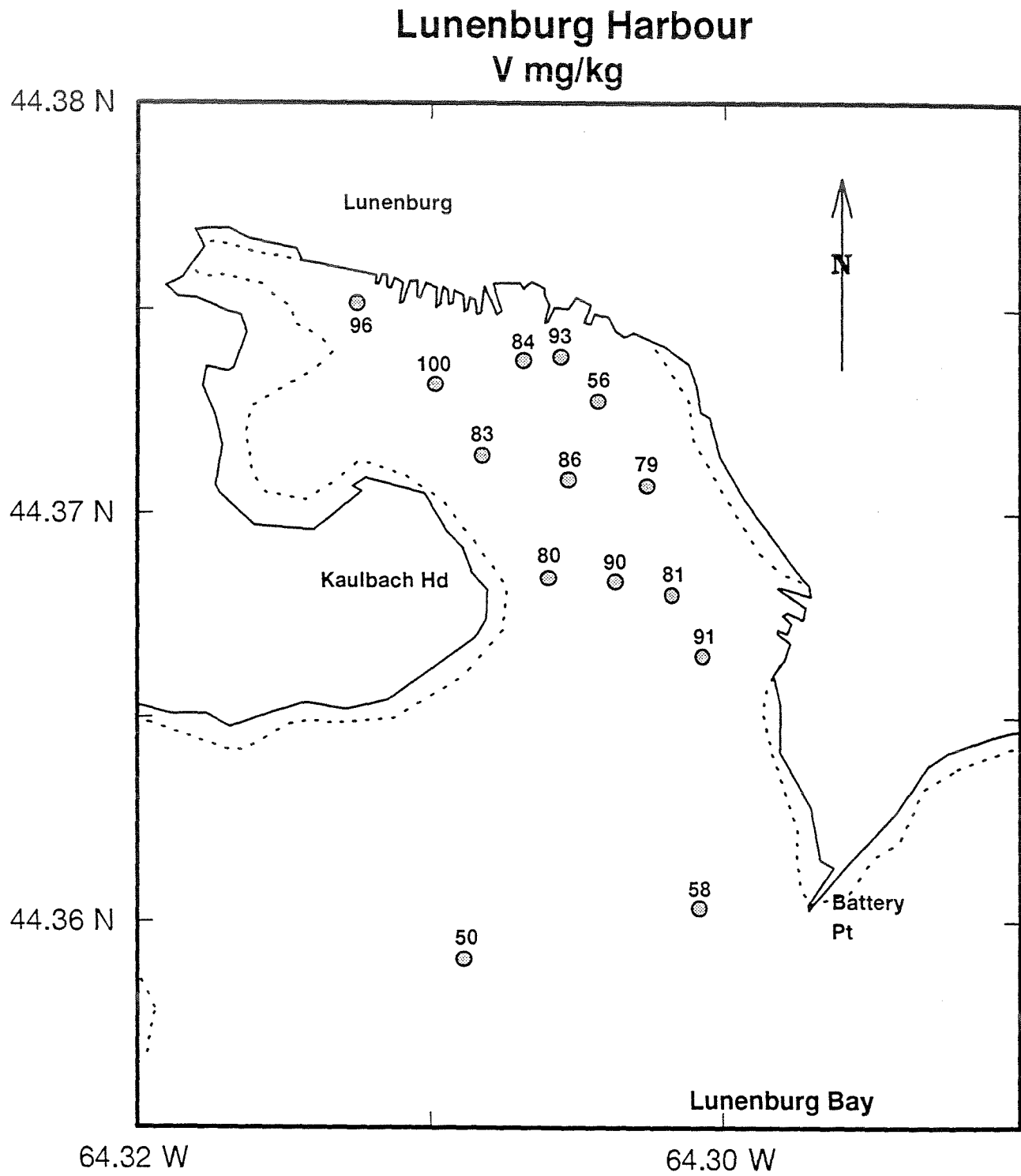
Figure 105. Vanadium concentrations in surficial sediments

Lunenburg Harbour
Zn mg/kg
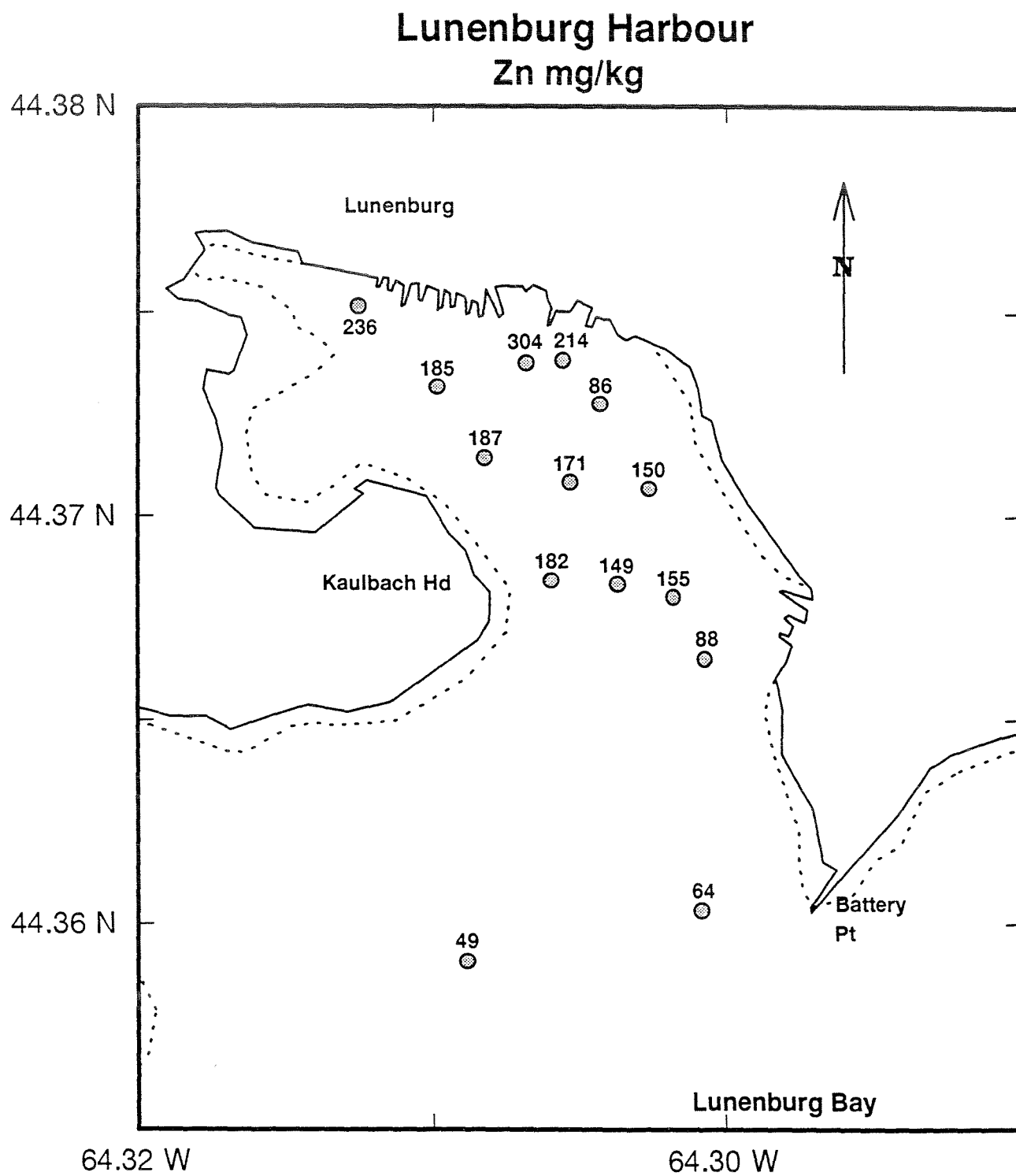
Figure 106. Zinc concentrations in surficial sediments

Lunenburg Harbour

Figure 107. Lunenburg Harbour core samples

147
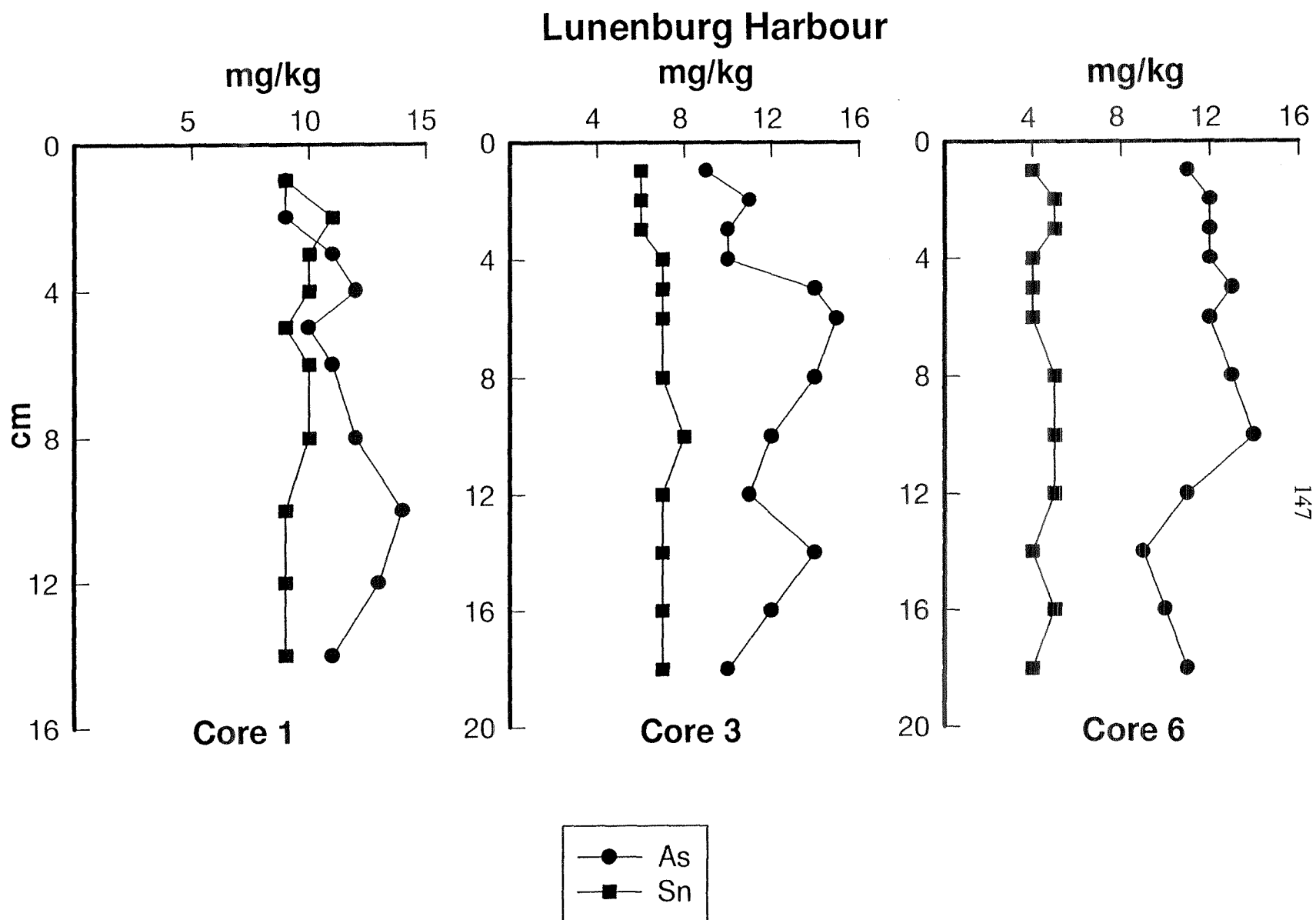
Lunenburg Harbour

Figure 108. Lunenburg Harbour core samples
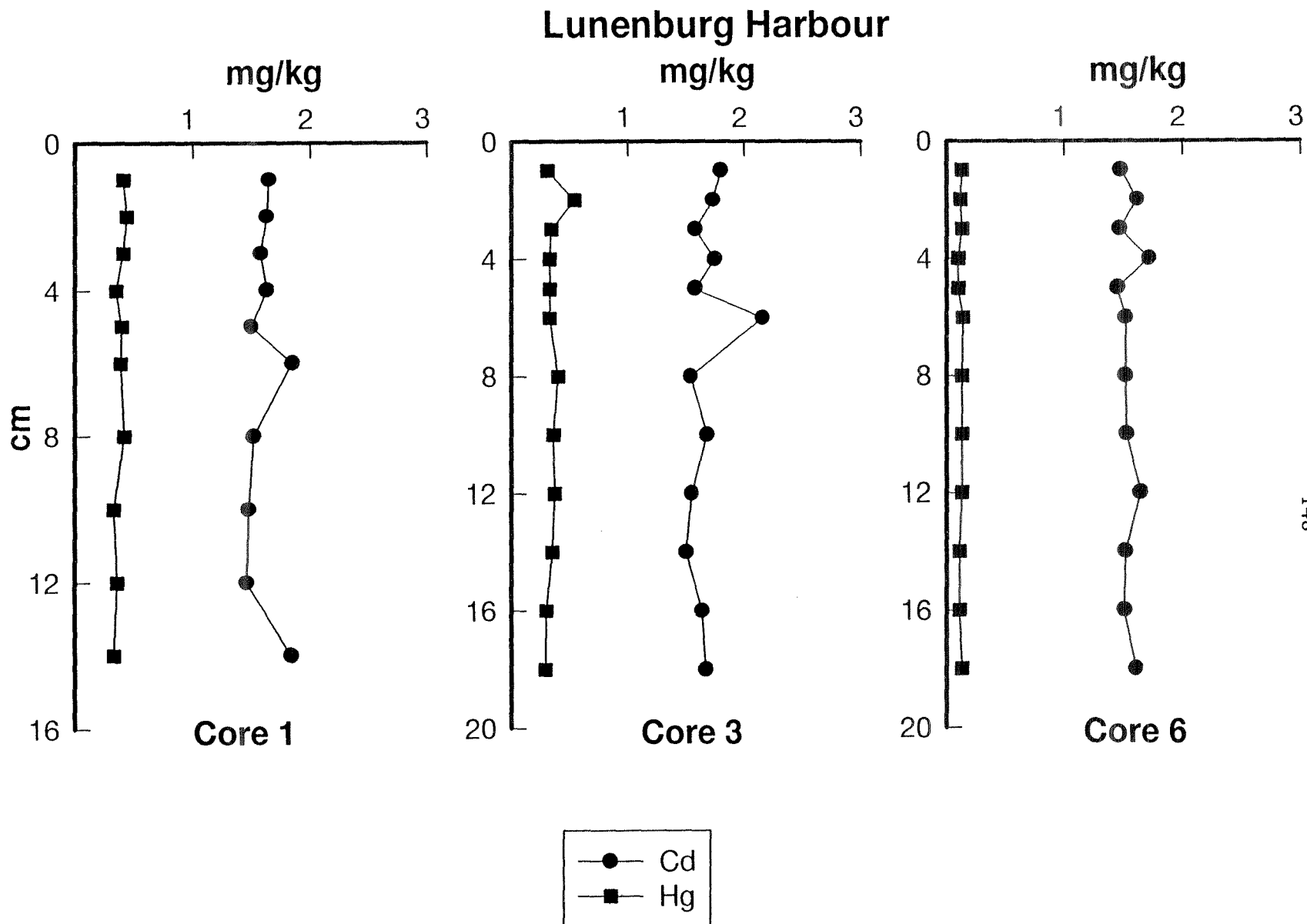
Lunenburg Harbour

Figure 109. Lunenburg Harbour core samples

149
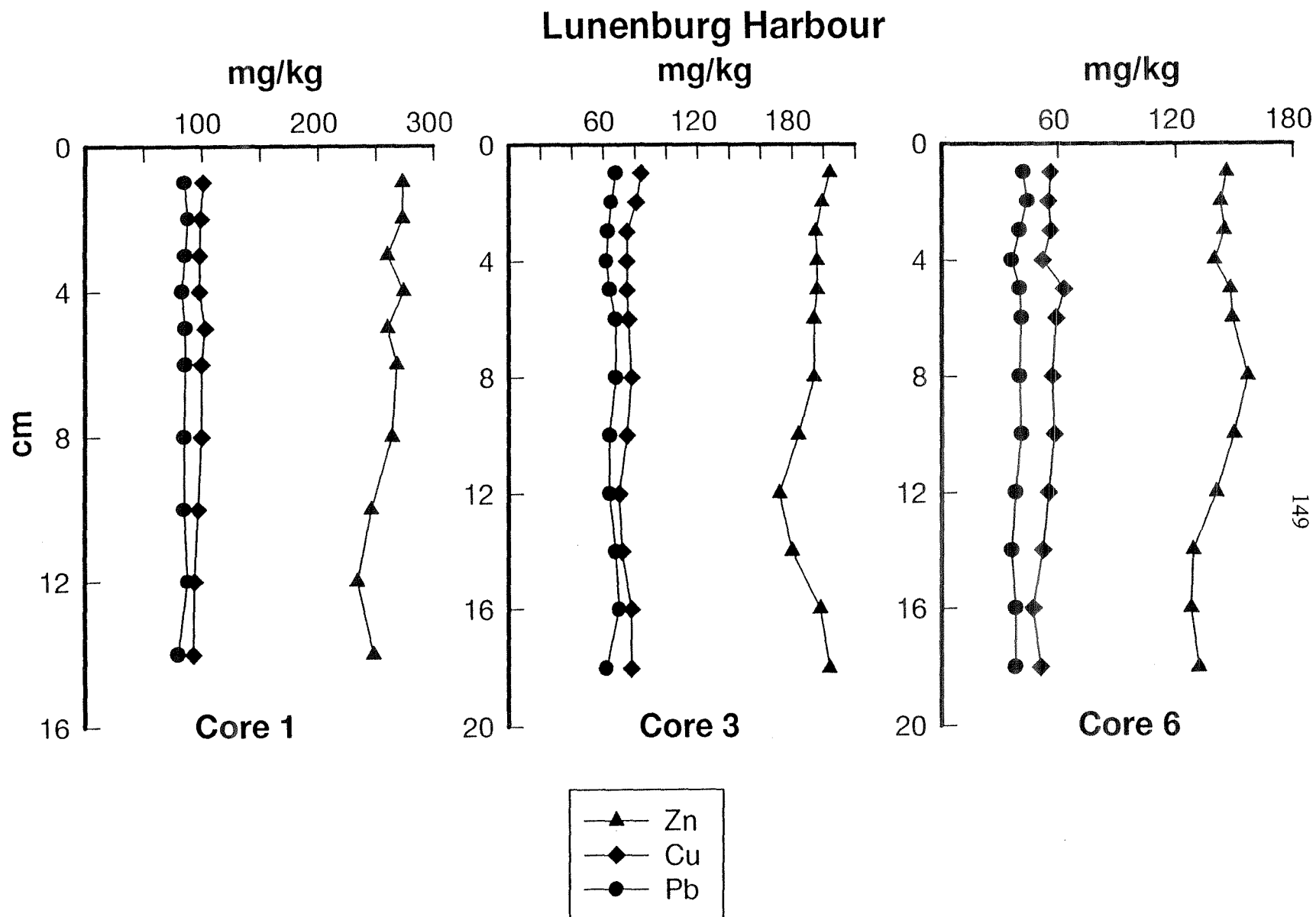
PETPESWICK INLET

Petpeswick Inlet is a long (16.7 km), narrow (0.1-2.4 km), shallow (depths 0.3-10 m) inlet running into the eastern shore of Nova Scotia about 45 km north of Halifax. At its head, the Inlet receives drainage via a small stream draining an area of 1512 km^2. This drainage area is mainly wooded with the vegetation developed on a thin mantle of glacial till underlain by Precambrian quartzites and slates. A narrow strip of cleared land occupied by cottages and permanent residences borders the inlet.

POTENTIAL SOURCES OF CONTAMINATION

The main sources of contaminants are organic waste discharged from local habitations.

RESULTS

Sediment Samples and Composition

Fourteen sampling stations were occupied in Petpeswick Inlet (Fig. 110). Fine-grained black muds, containing varying amounts of organic matter (Fig. 111), occupy the head of the Inlet and become more sandy toward its mouth where tidal currents prevent the accumulation of fine-grained material.

Samples collected in Petpeswick Inlet range from very well sorted sands with modal diameters greater than 100 μm to poorly sorted muds with modal sizes less than 25 μm at the head (Fig. 112). The source slope is constant throughout the area with a mean value of 0.45. The floc portion of the size distribution is below 10% in the lower reaches of the Inlet and only starts to increase at the very head of the Inlet where it reaches a maximum of 24%. Throughout the Inlet, there is evidence of reworking of the sediment with higher round peaks occurring at all stations. Petpeswick Inlet is subject to high tidal currents due to its shape. About one-half of the water in the Inlet is exchanged on each tide, and speeds can reach 1 m.s^2 (Kranck 1980). Floc-dominated sedimentation is restricted to the deep basin at the head of the Inlet. Kranck (1980) suggested that a net inward flux of particulate material results from material being trapped on the spartina beds at the side of the channel and in the basin at the head of the Inlet.

Abundance and Distribution of Metals

The concentrations of As, Cd, Cr, Cu, Pb, and Zn at the individual sampling stations are shown in Figures 113 to 126. The ranges of total metal concentration measured in Petpeswick Inlet sediments are: As, 2.5-14 mg·kg^{-1}; Cd, 0.03-1.22 mg·kg^{-1}; Cr, 24-73 mg·kg^{-1}; Cu, 6-24 mg·kg^{-1}; Hg, 0.01-0.07 mg·kg^{-1}; Ni, 6-27 mg·kg^{-1}; Pb, 8-37 mg·kg^{-1}; Sn, 2-3 mg·kg^{-1}; V, 23-90 mg·kg^{-1}; and Zn, 20-105 mg·kg^{-1} (Table 18). All of the metals, except Cd, are at or near

natural concentrations. Of the 15 samples obtained, 9 (60%) contained > 0.3 mg·kg^{-1} Cd with the high concentrations occuring in the fine-grained organic-rich sediments in the upper part of the Inlet. A 20-cm long sediment core obtained from near the head of the Inlet in 1993 contained high concentrations of Cd (0.85-1.50 mg. kg^{-1}) and Pb (42-70 mg.mg^{-1}) over its entire length.

Potential Bioavailability of Metals

Chemical partitioning of selected samples indicates that most (>90%) of the total Cd, 4-18% of the total Cu, 13-22% of the total Pb, and 21-32% of the total Zn are potentially bioavailable. Thus, only normal amounts of Cu, Pb, and Zn are potentially bioavailable.

Metal Carriers and Sources

The strong positive correlations of the metals, excepting Mn and Sn, with increasing mud (material <63 μm) indicate that the metal carriers are predominantly fine-grained (Table 19). The strong positive correlations of all the metals, excepting Mn and Sn, with Li indicate the inclusion and/or association of these metals with fine-grained aluminophyllosilicate minerals such as the micas, illite, chlorite, and kaolinite. The positive covariance (p<0.01) of As, Cd, Cr, Cu, Hg, Pb, and Zn with Li (Table 19) demonstrates that lithium normalizes for granular and mineralogical variability in the surficial sediments. The proportions of the metal variances explained by granular variability decreases in the order: Cu (94%) > Cr (91%) > Zn (87%) > Pb (81%) > As (67%) > Hg (64%) > Cd (62%) >> Sn (19%). Factor analyses indicate that the deposition of fine-grained organic material accounts for 66% of the variance of all the metals except Mn and Sn. The small amounts of Sn present are most likely associated with the aluminosilicates. The strong correlations of Cu, Pb, and Zn with Fe, as well as organic matter, suggest that these metals are held in metal-bearing iron monosulphides and/or pyrite formed *in situ* in the organic-rich fine-grained sediments. The anomalous Cd and Hg are probably associated with the trapping and deposition of organic-rich particles derived from local sewage disposal at the head of the Inlet.

Table 18

Textural and metal statistics[a] for the Petpeswick Inlet sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
mud(%)	15	57.4	±35.6	3-96	OM(%)	15	5.56	± 3.86	0.21-12.5
Metal					Metal				
Al%	15	4.29	± 0.83	2.88-5.47	Fe%	15	2.25	± 0.68	1.02-3.01
As	13	8.4	± 3.5	3-14	Li	15	33.1	±11.2	15-46
Cd	15	0.41	± 0.35	0.03-1.22	Ni	15	19.7	± 7.9	6-27
Cr	15	52.5	±15.6	24-73	Pb	15	18.9	± 8.7	8-37
Cu	15	15.7	± 6.4	6-24	Sn	10	2.7	± 0.5	2-3
Hg	15	0.03	± 0.02	0.01-0.07	V	15	58.6	±20.8	23-90
Mn%	15	0.050	± 0.02	0.035-0.125	Zn	15	57.4	±27.9	20-105

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM), Al, Fe, and Mn

Table 19

Correlation Matrix Petpeswick Inlet

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	x	x	1									
Cr	0.96	0.83	x	1								
Cu	0.93	0.84	0.76	0.96	1							
Fe	0.91	x	x	0.96	0.93	1						
Hg	x	x	0.85	x	0.83	x	1					
Li	0.95	0.82	0.79	0.95	0.97	0.93	0.80	1				
Mn	x	x	x	x	x	x	x	x	1			
Pb	0.78	x	0.82	0.86	0.94	0.86	0.96	0.90	x	1		
Sn	x	x	x	x	x	x	x	x	x	x	1	
Zn	0.80	0.82	0.90	0.87	0.93	0.87	0.95	0.93	x	0.98	x	1
Mud	0.95	0.86	0.77	0.96	0.98	0.94	0.80	0.99	x	0.90	x	0.93
OM	0.82	0.78	0.85	0.86	0.91	0.84	0.88	0.95	x	0.93	x	0.96

n = 24; mud ;n = 30
For $p \leq 0.001$ x = not significant
mud = >70% by weight material <63μm
OM = % by weight organic matter

Petpeswick Inlet
Sample Locations
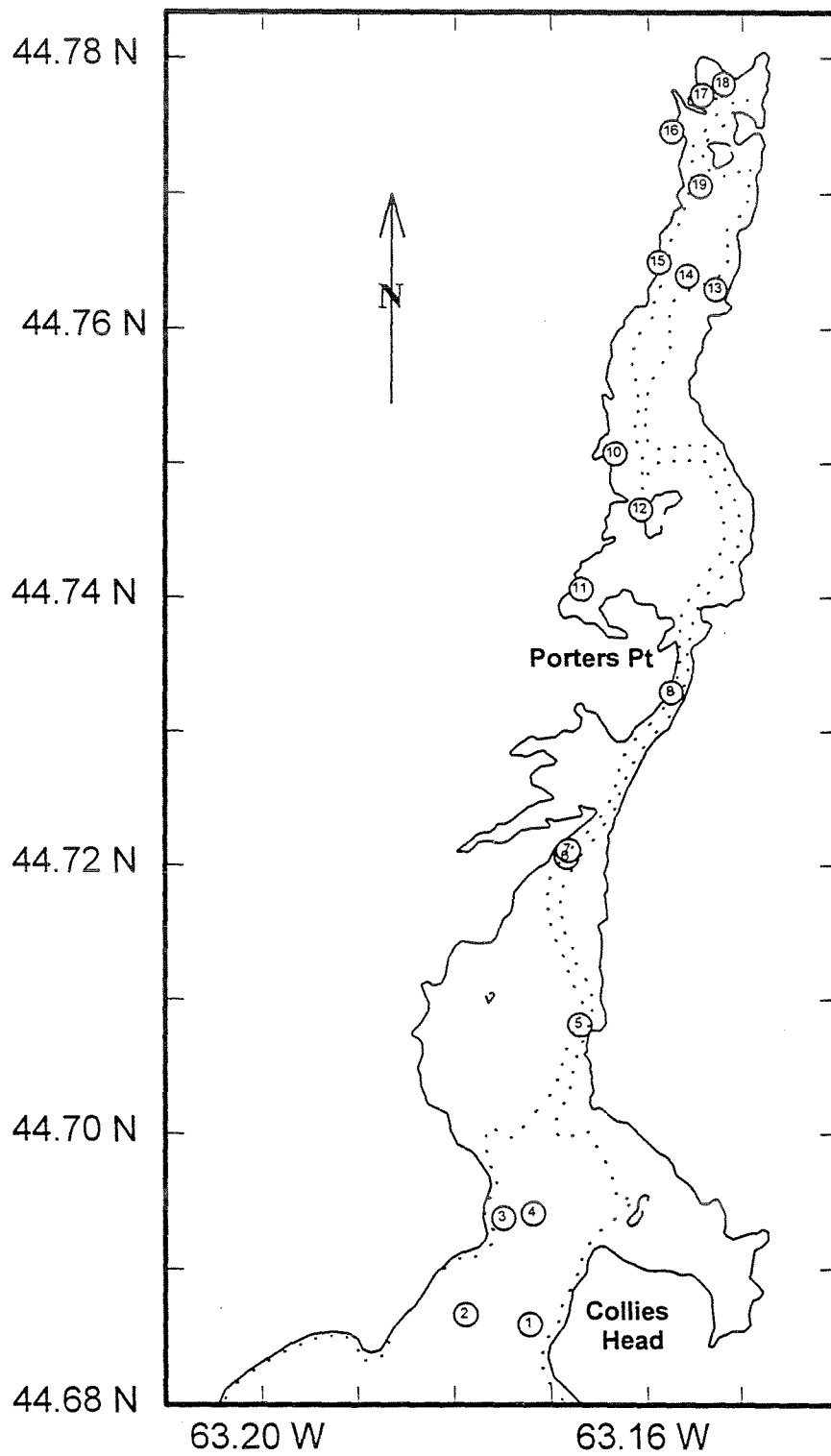
Figure 110. Sample locations for Petpeswick Inlet

Petpeswick Inlet
% Organic Matter
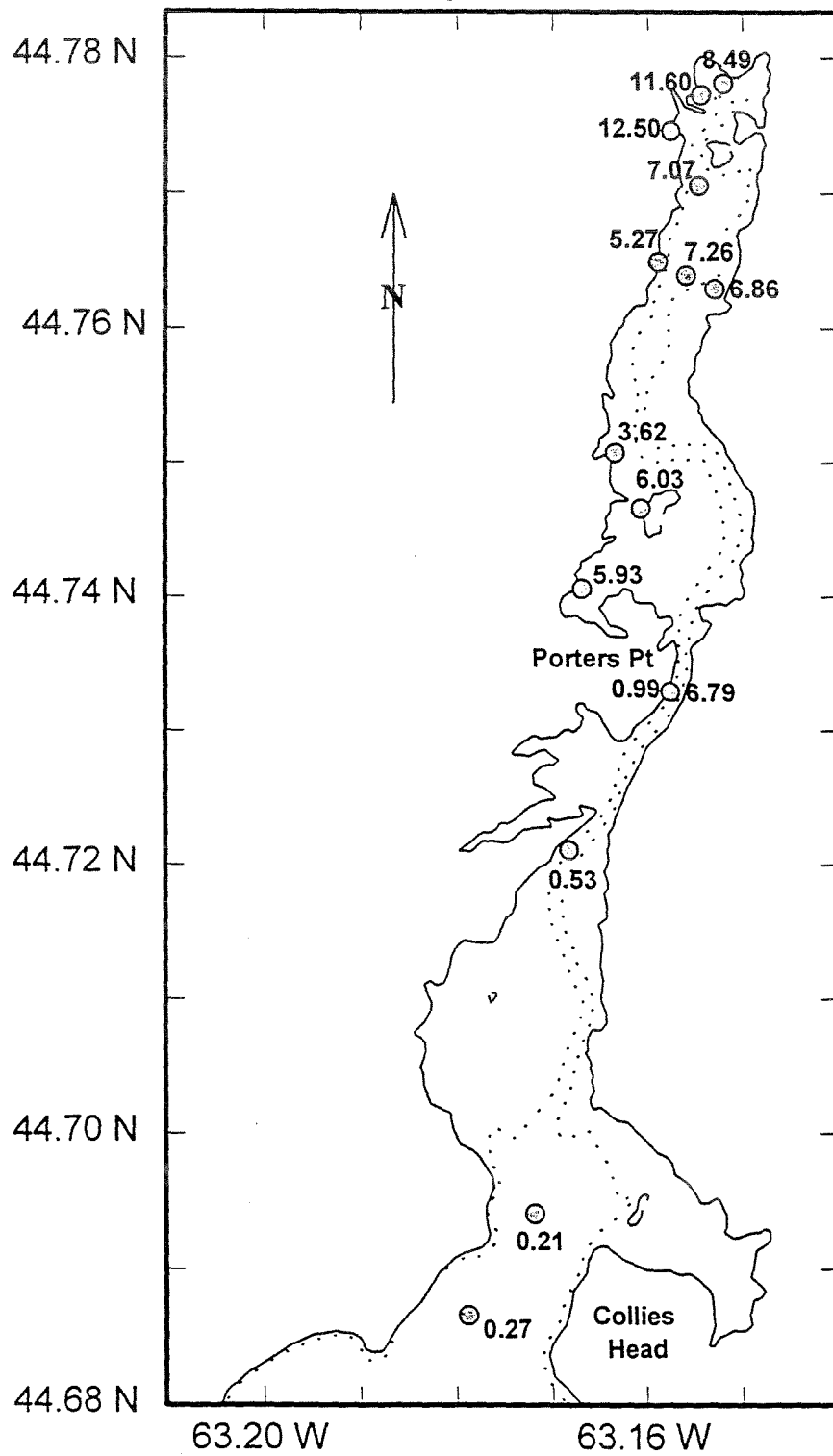
Figure 111. Organic matter concentrations in surficial sediments
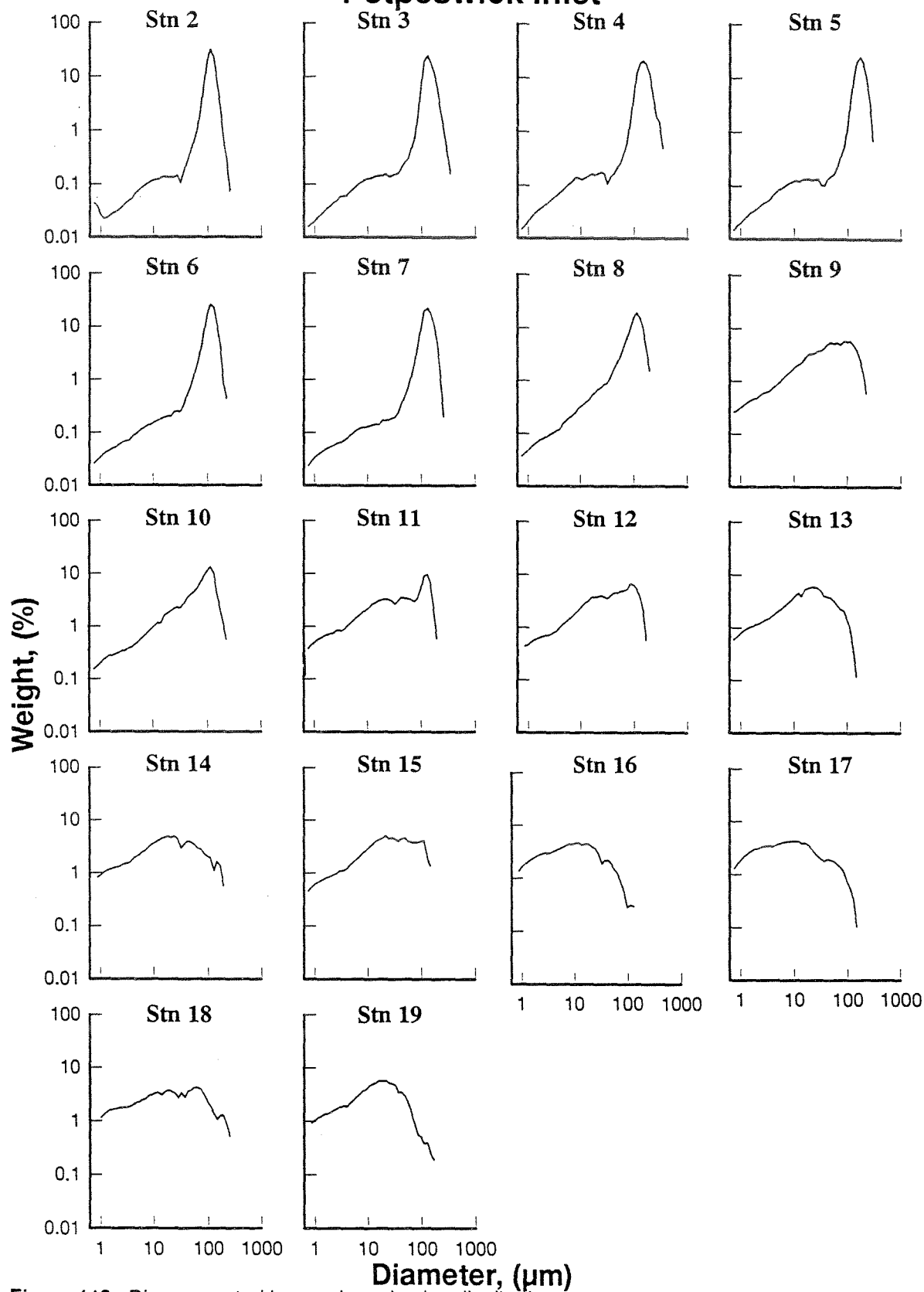
Petpeswick Inlet

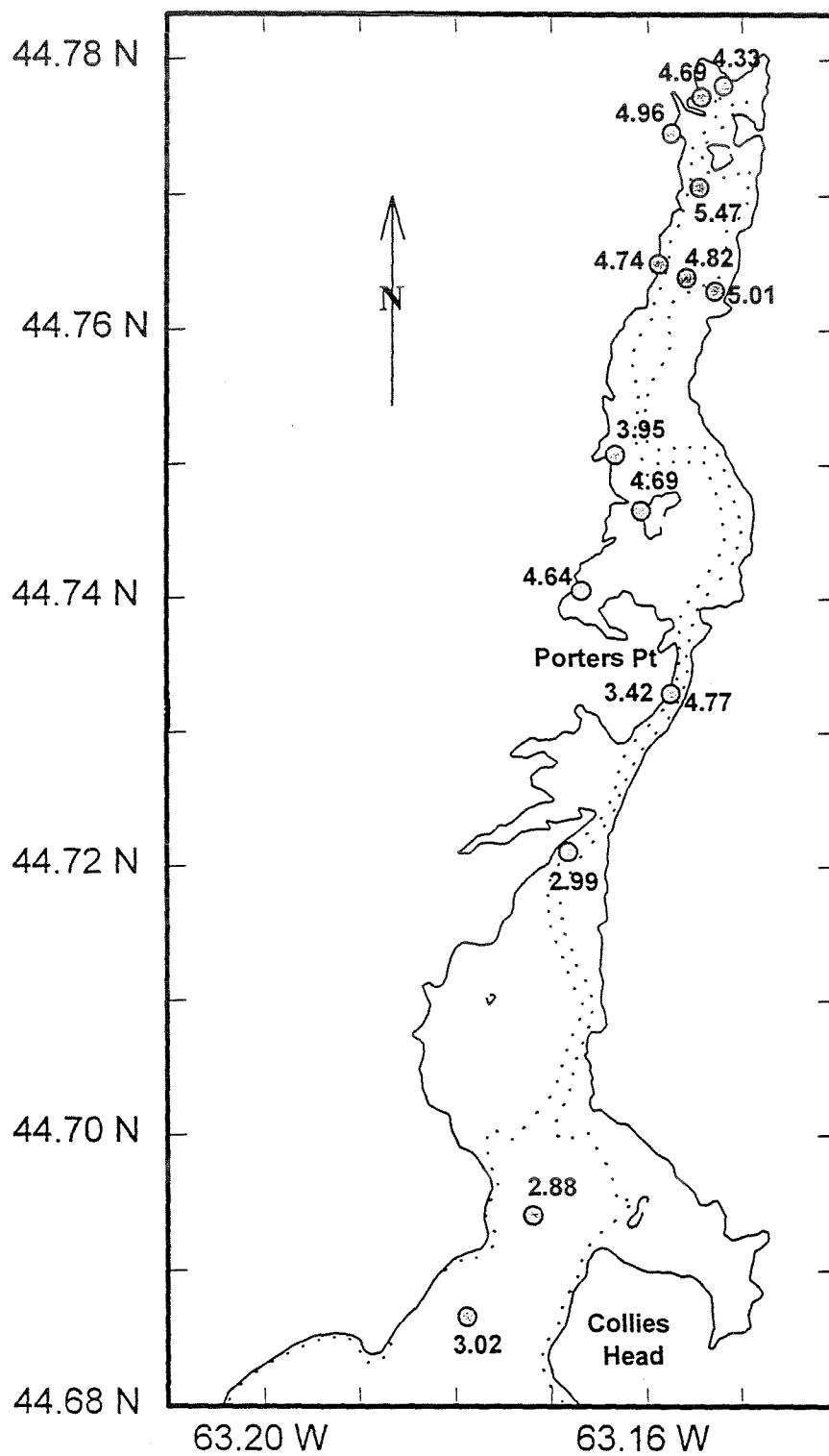**Figure 112.** Disaggregated inorganic grain size distributions

Petpeswick Inlet
Al %

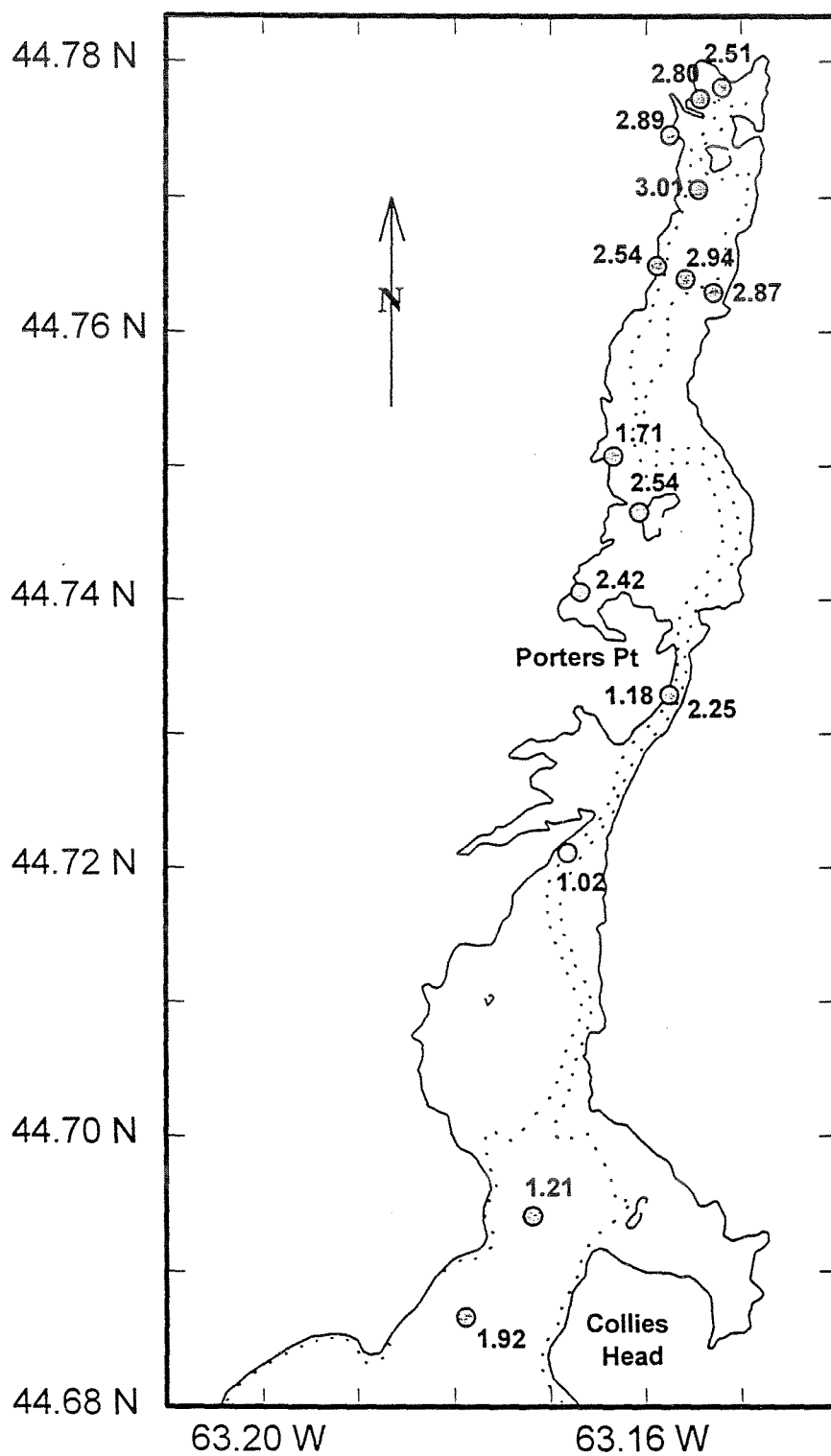**Figure 113.** Aluminium concentrations in surficial sediments

Petpeswick Inlet
Fe %

Figure 114. Iron concentrations in surficial sediments

Petpeswick Inlet
As mg/kg
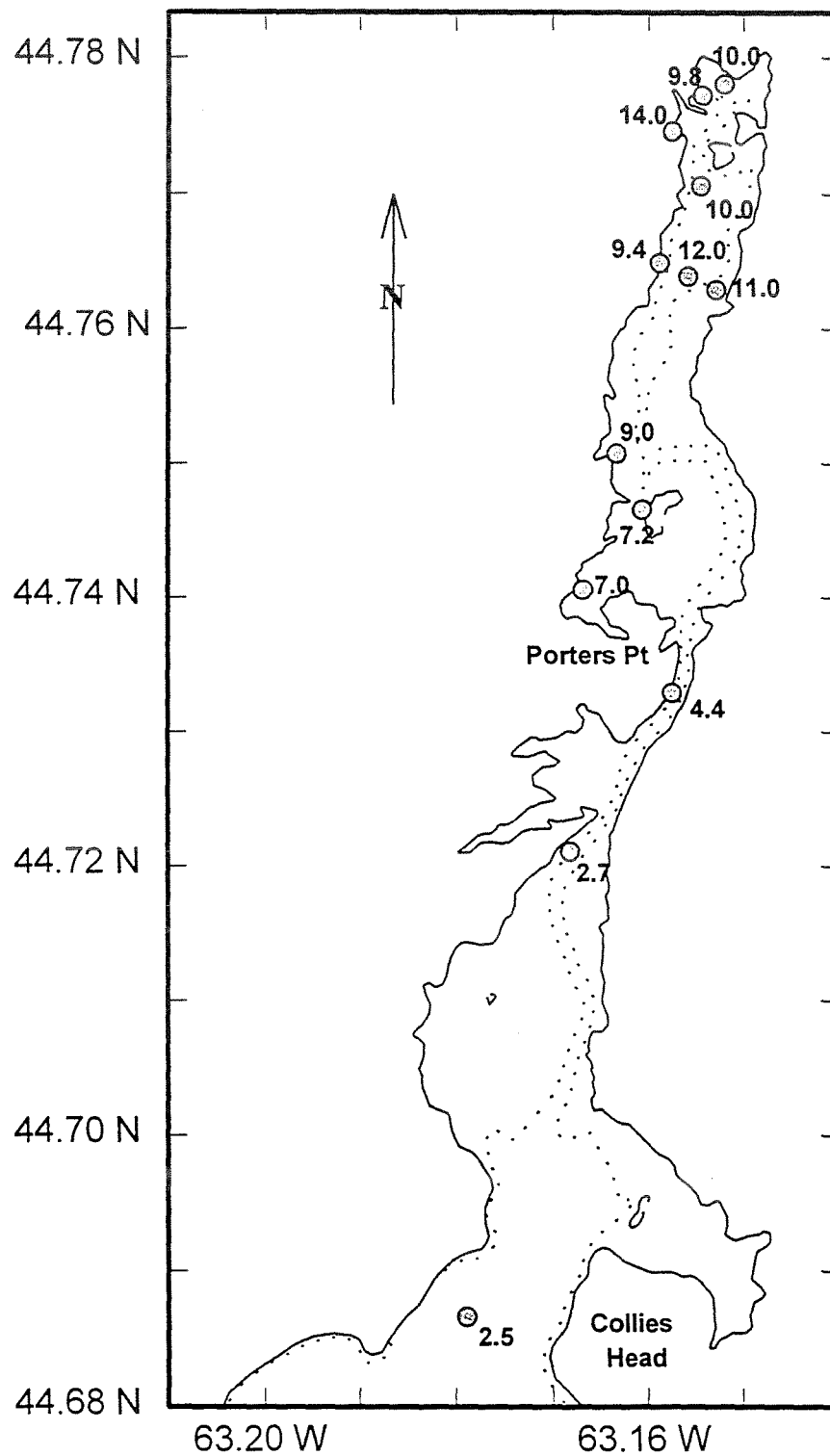
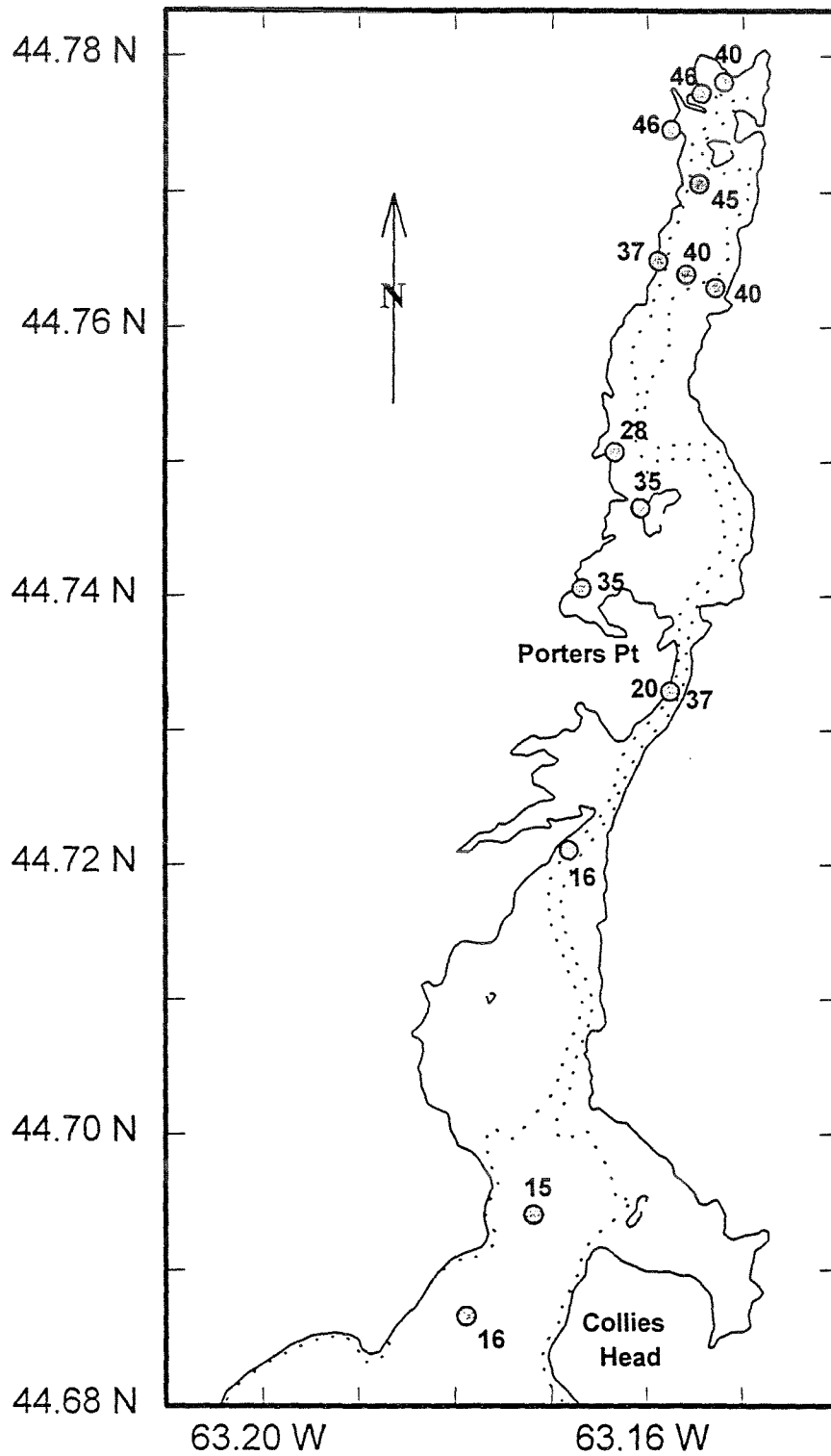**Figure 115.** Arsenic concentrations in surficial sediments
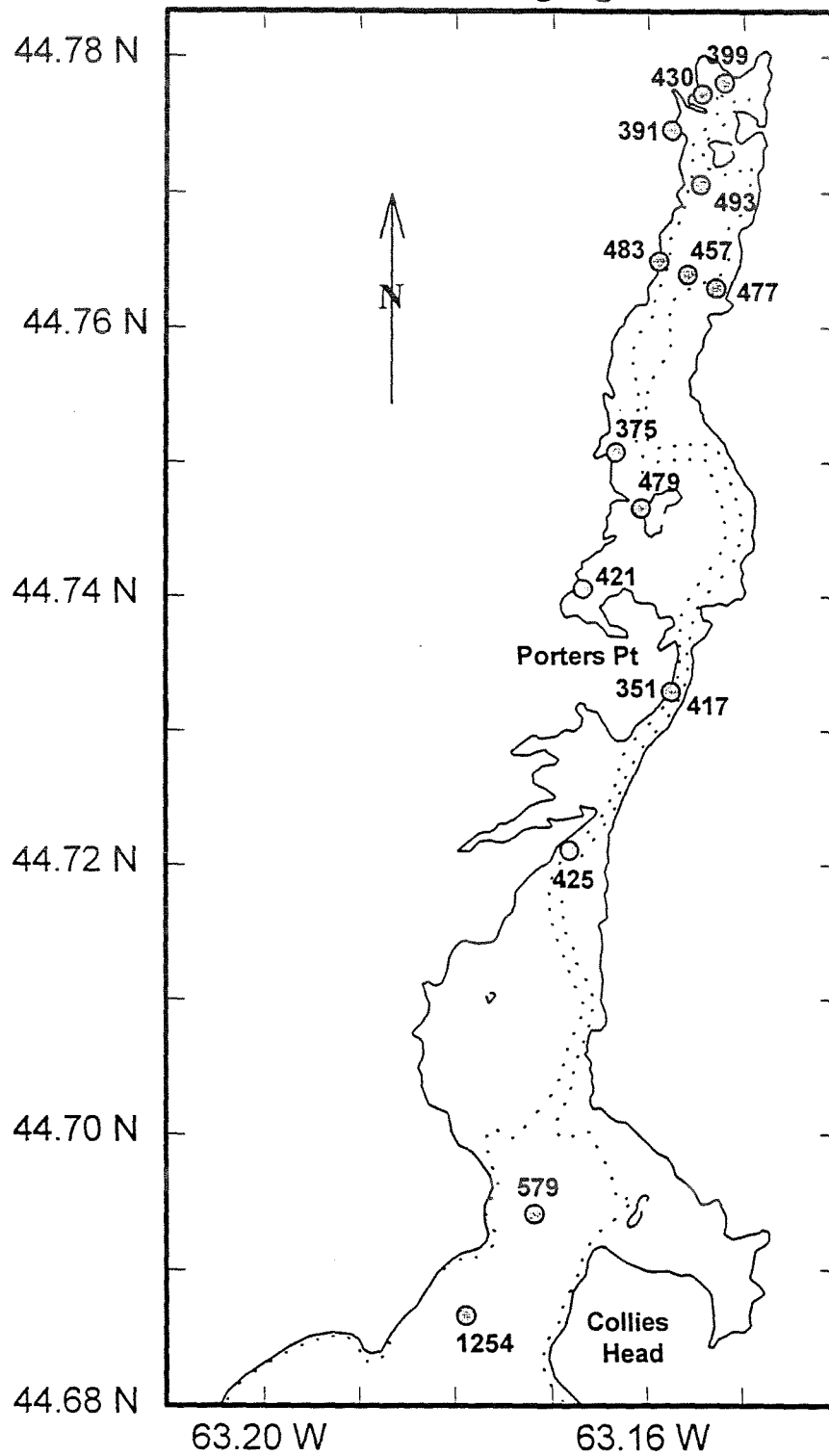
Petpeswick Inlet
Cd mg/kg

44.78 N

1.22
0.91
0.83
0.58
0.35 0.47
0.42

44.76 N

N

0.24
0.36

44.74 N

0.38

Porters Pt
0.08 0.19

44.72 N

0.04

44.70 N

0.03

0.03

Collies
Head

44.68 N

63.20 W   63.16 W
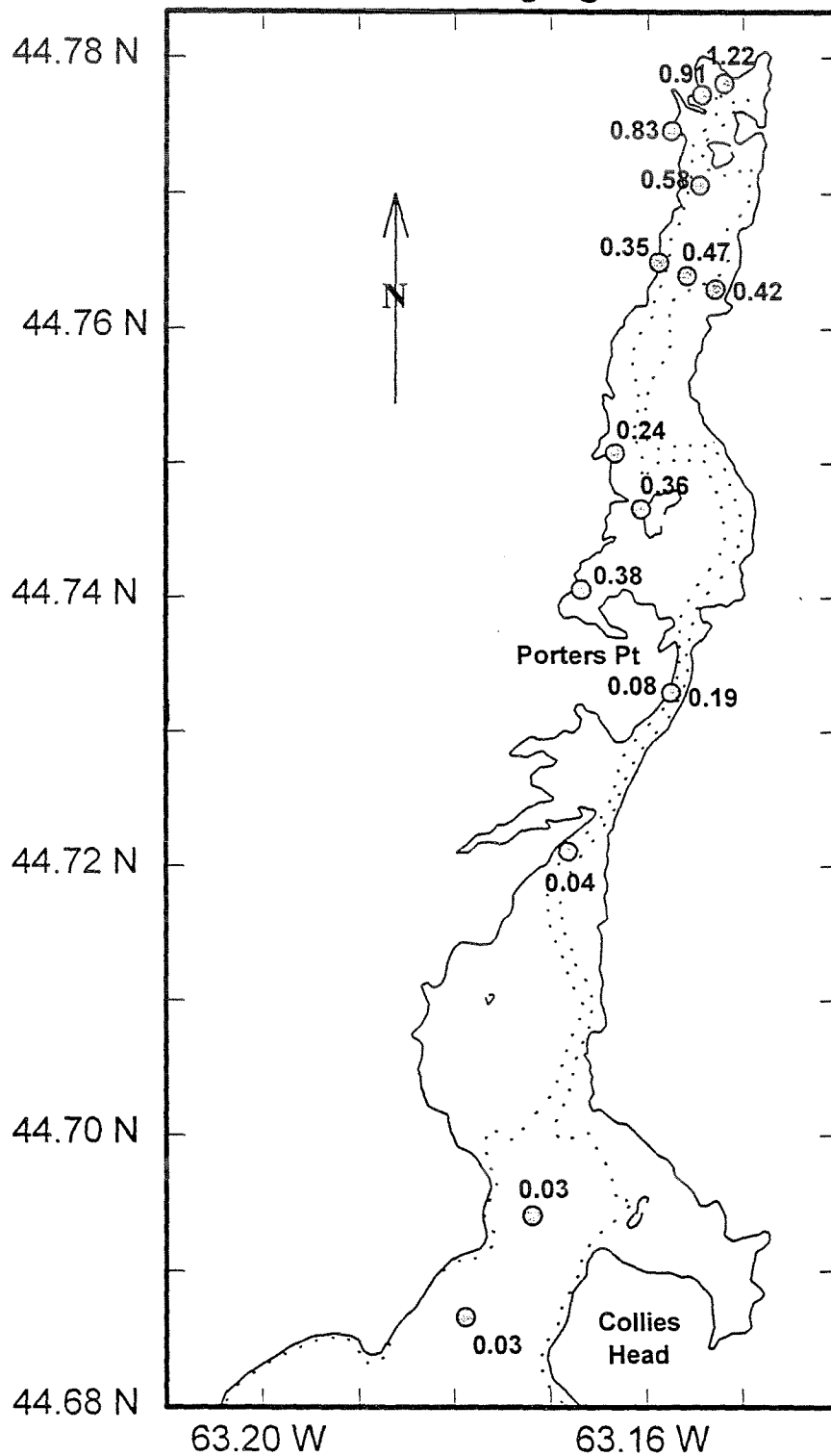
Figure 116. Cadmium concentrations in surficial sediments

Petpeswick Inlet
Cr mg/kg
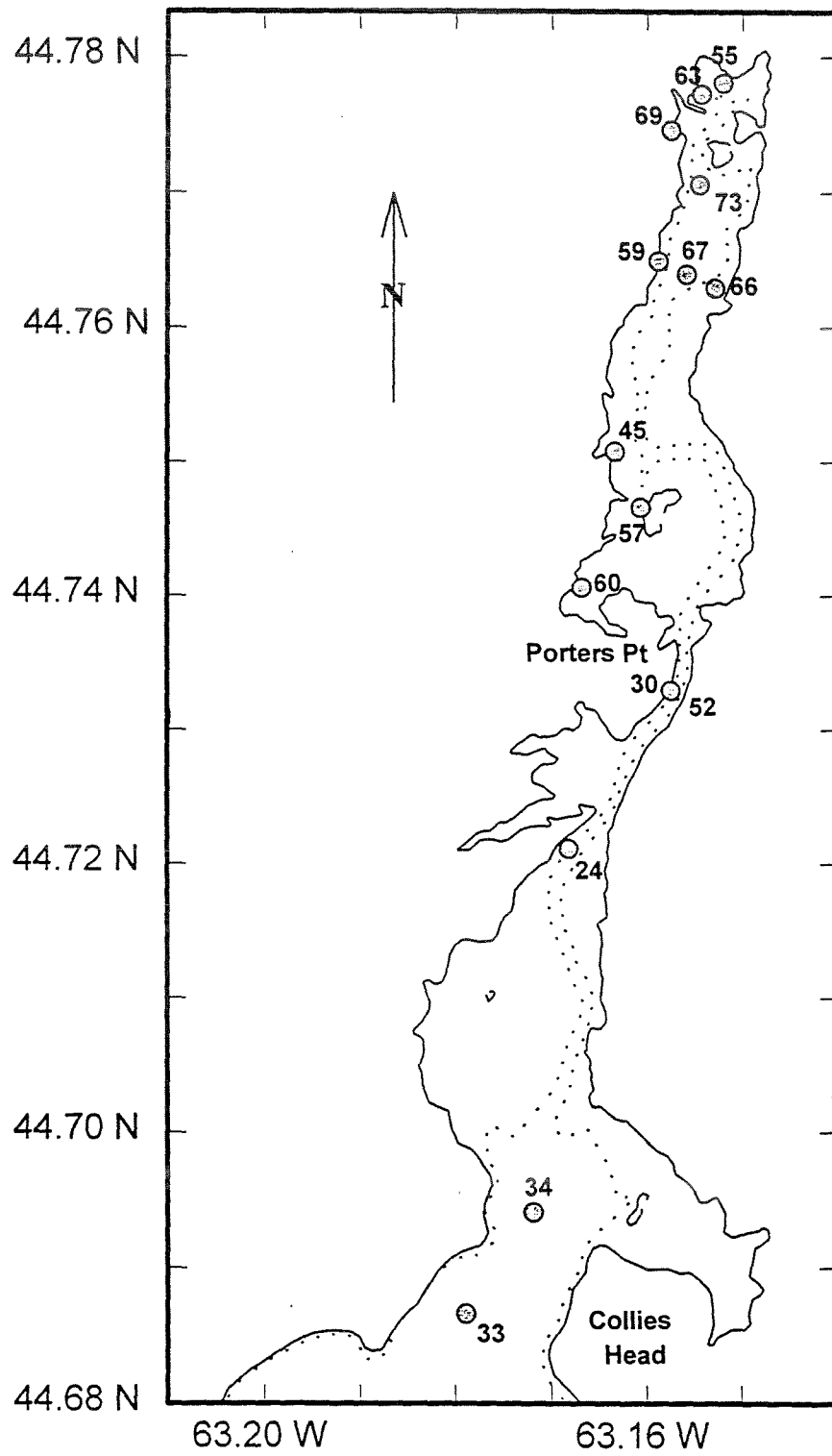
Figure 117. Chromium concentrations in surficial sediments

Petpeswick Inlet
Cu mg/kg
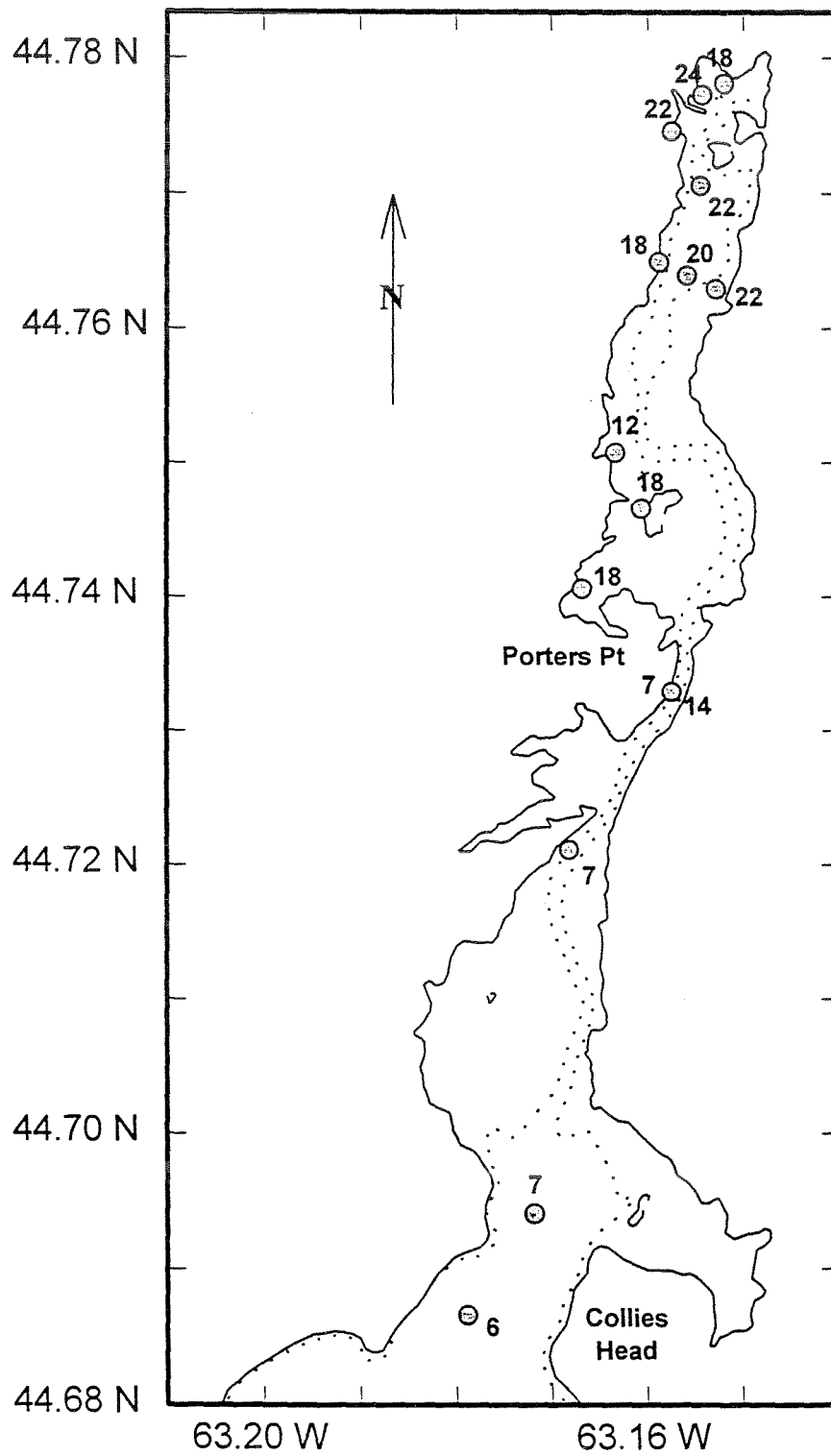
Figure 118. Copper concentrations in surficial sediments

Petpeswick Inlet
Hg mg/kg
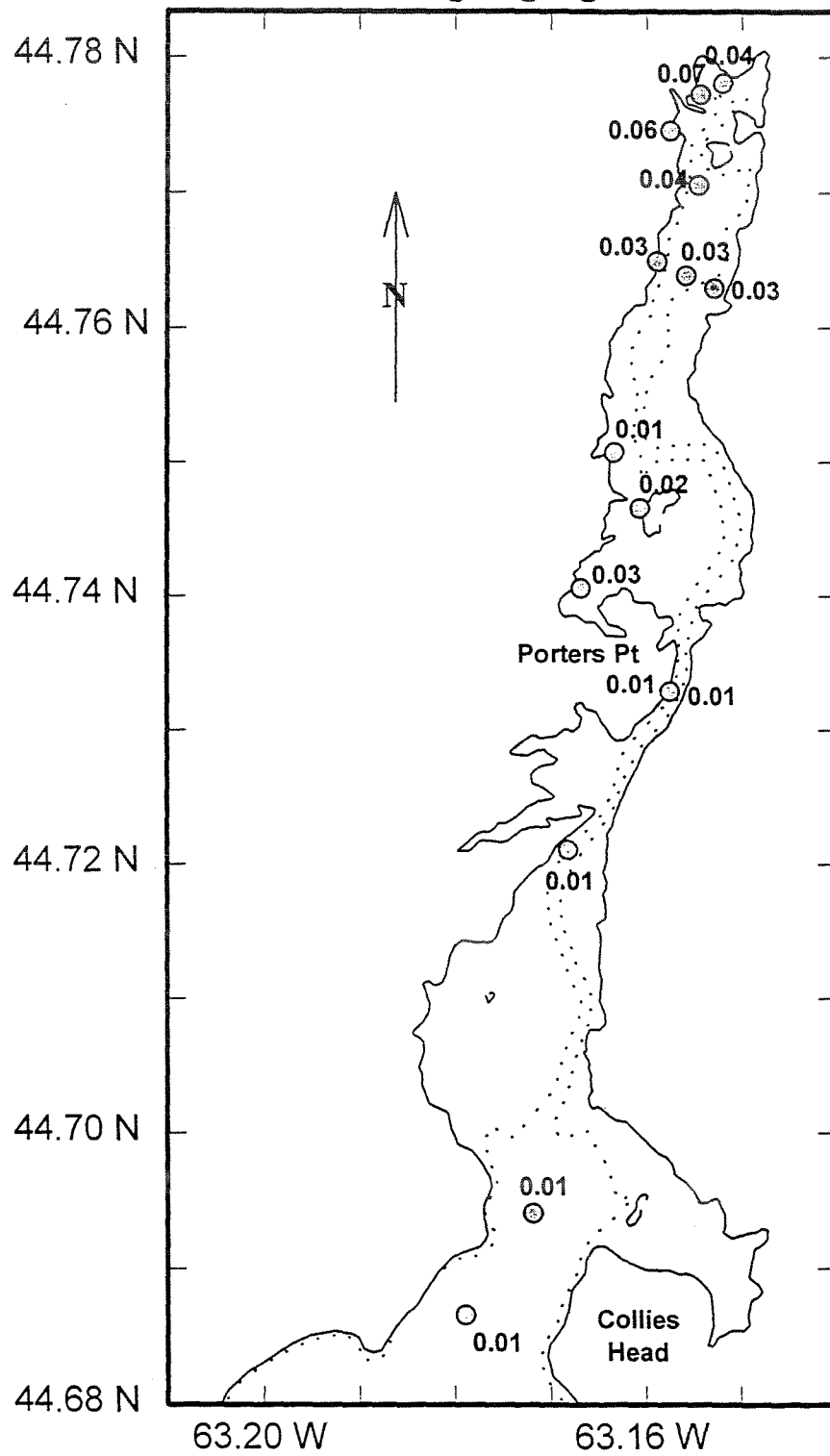
Figure 119. Mercury concentrations in surficial sediments

Petpeswick Inlet
Li mg/kg

Figure 120. Lithium concentrations in surficial sediments

Petpeswick Inlet
Mn mg/kg

Figure 121. Manganese concentrations in surficial sediments

Petpeswick Inlet
Ni mg/kg
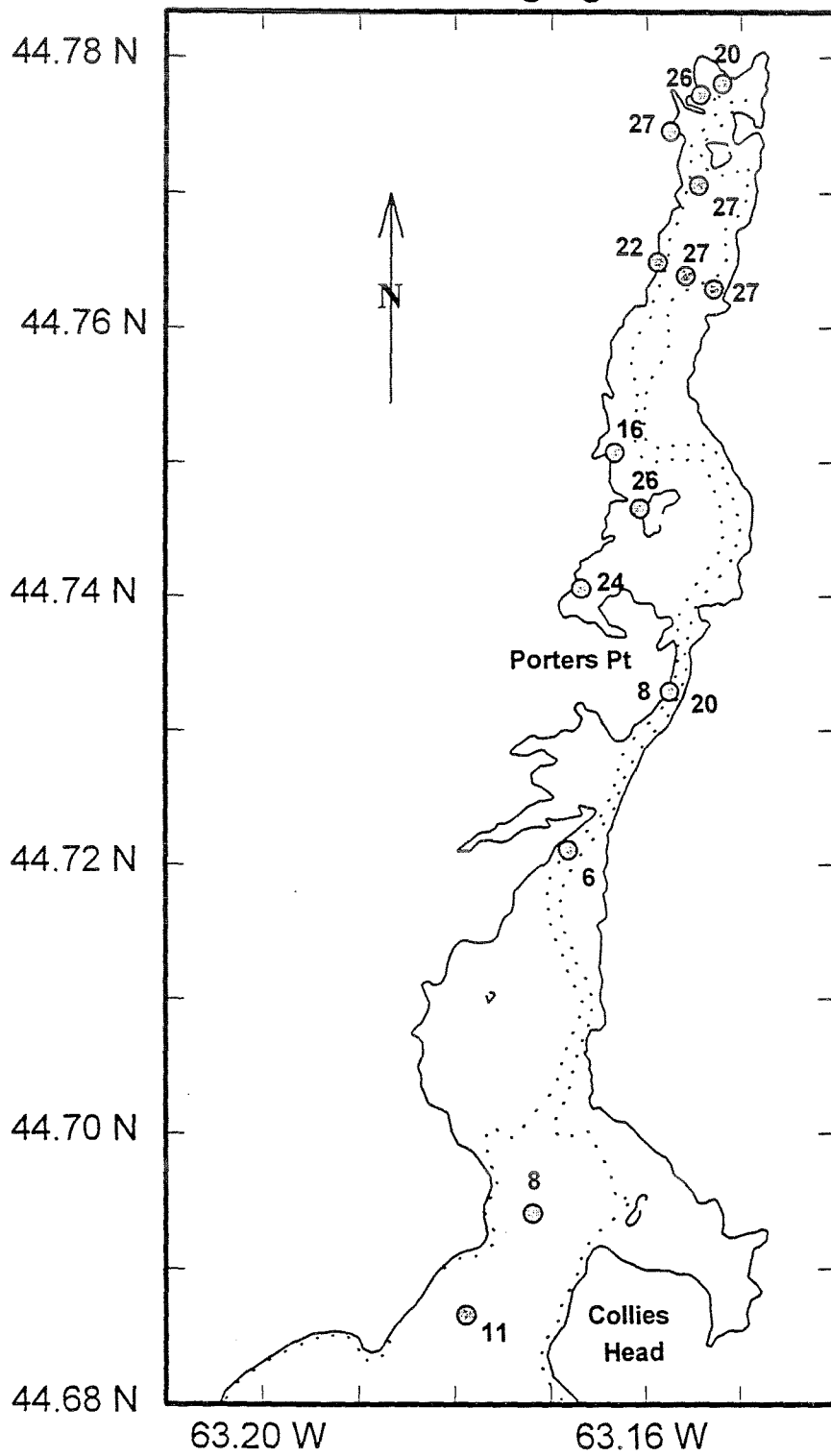
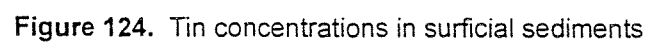**Figure 122.** Nickel concentrations in surficial sediments

Petpeswick Inlet
Pb mg/kg
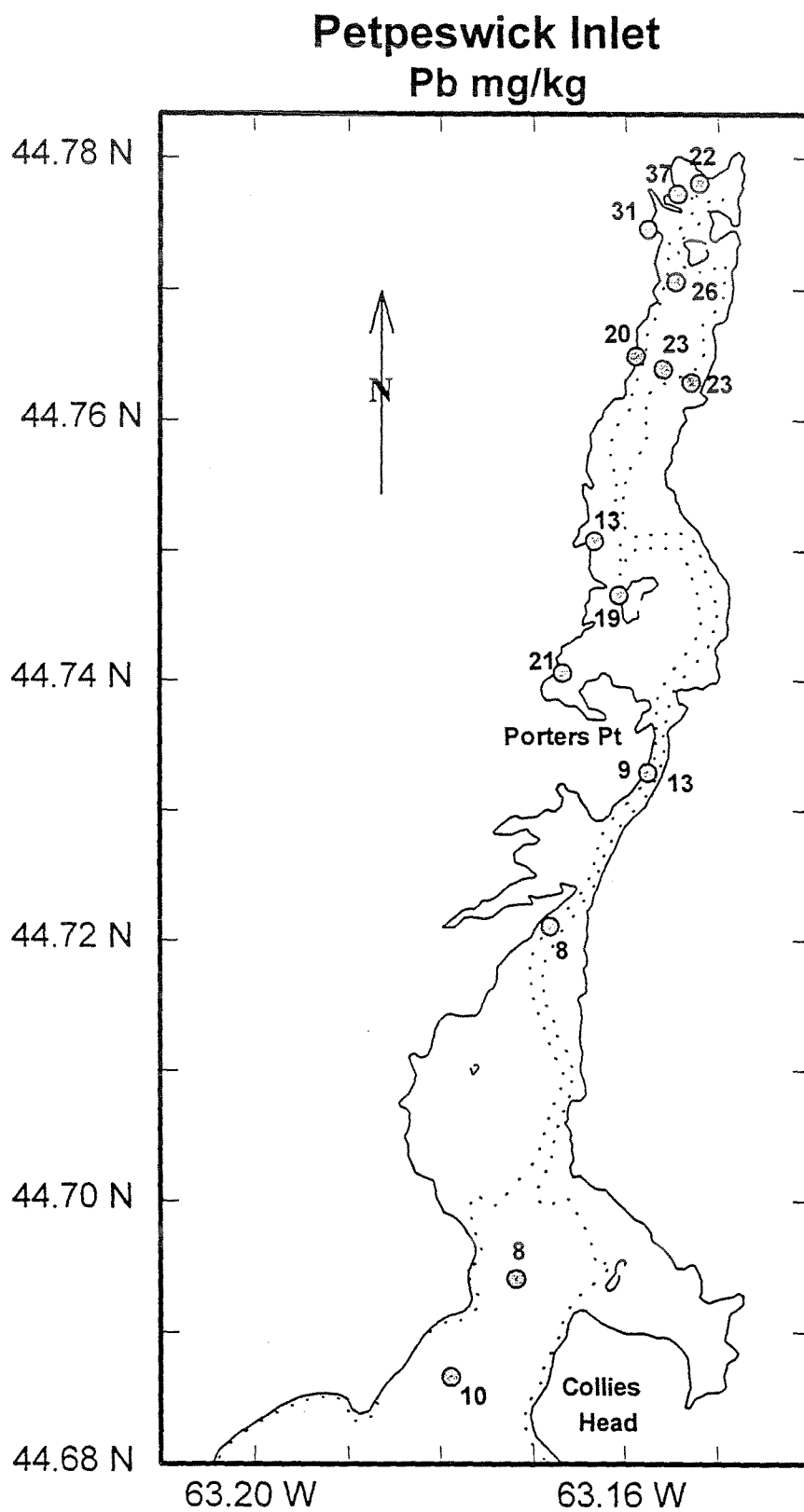
Figure 123. Lead concentrations in surficial sediments

Petpeswick Inlet
Sn mg/kg

Figure 124. Tin concentrations in surficial sediments

Petpeswick Inlet
V mg/kg
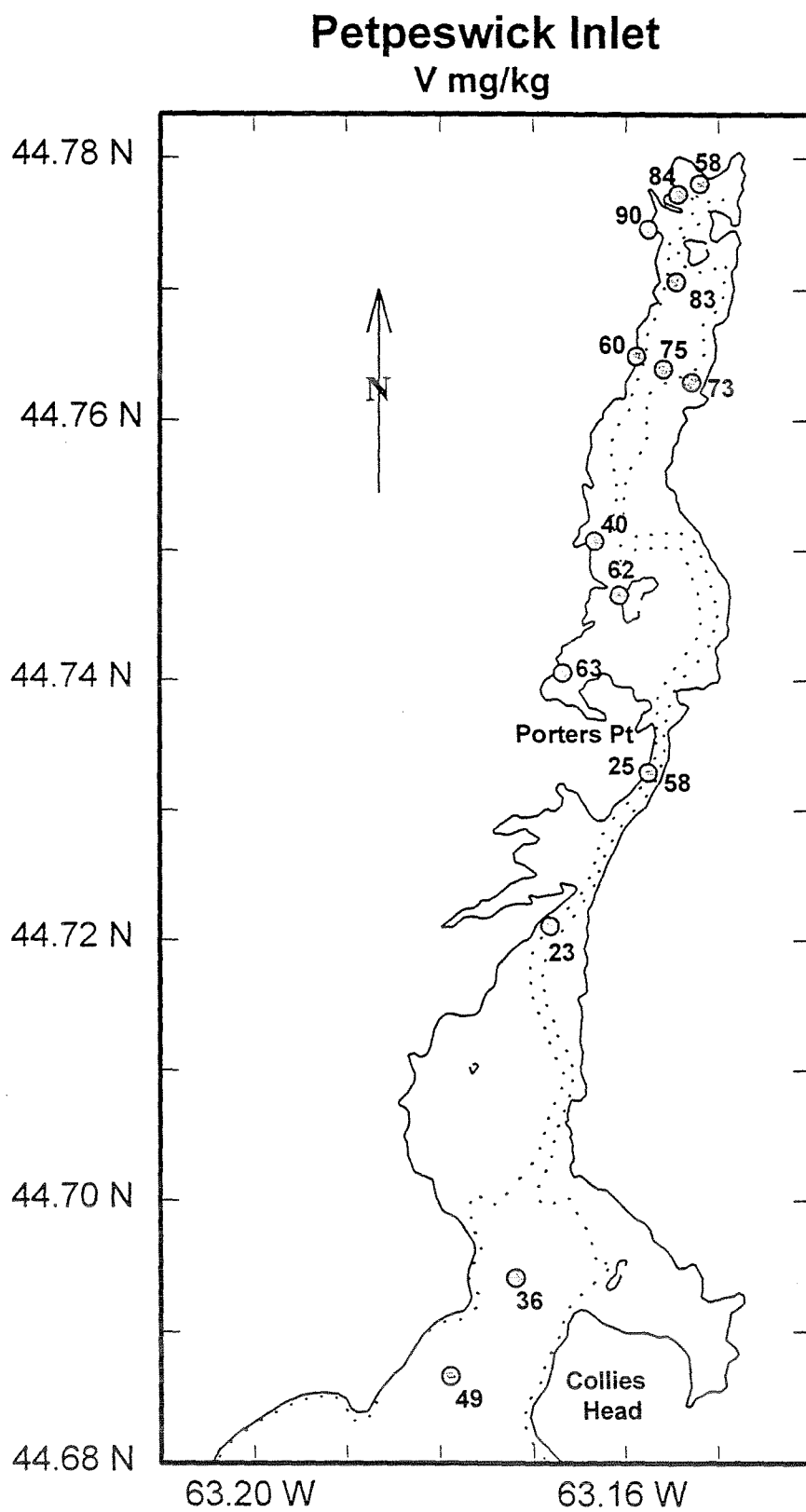
Figure 125. Vanadium concentrations in surficial sediments
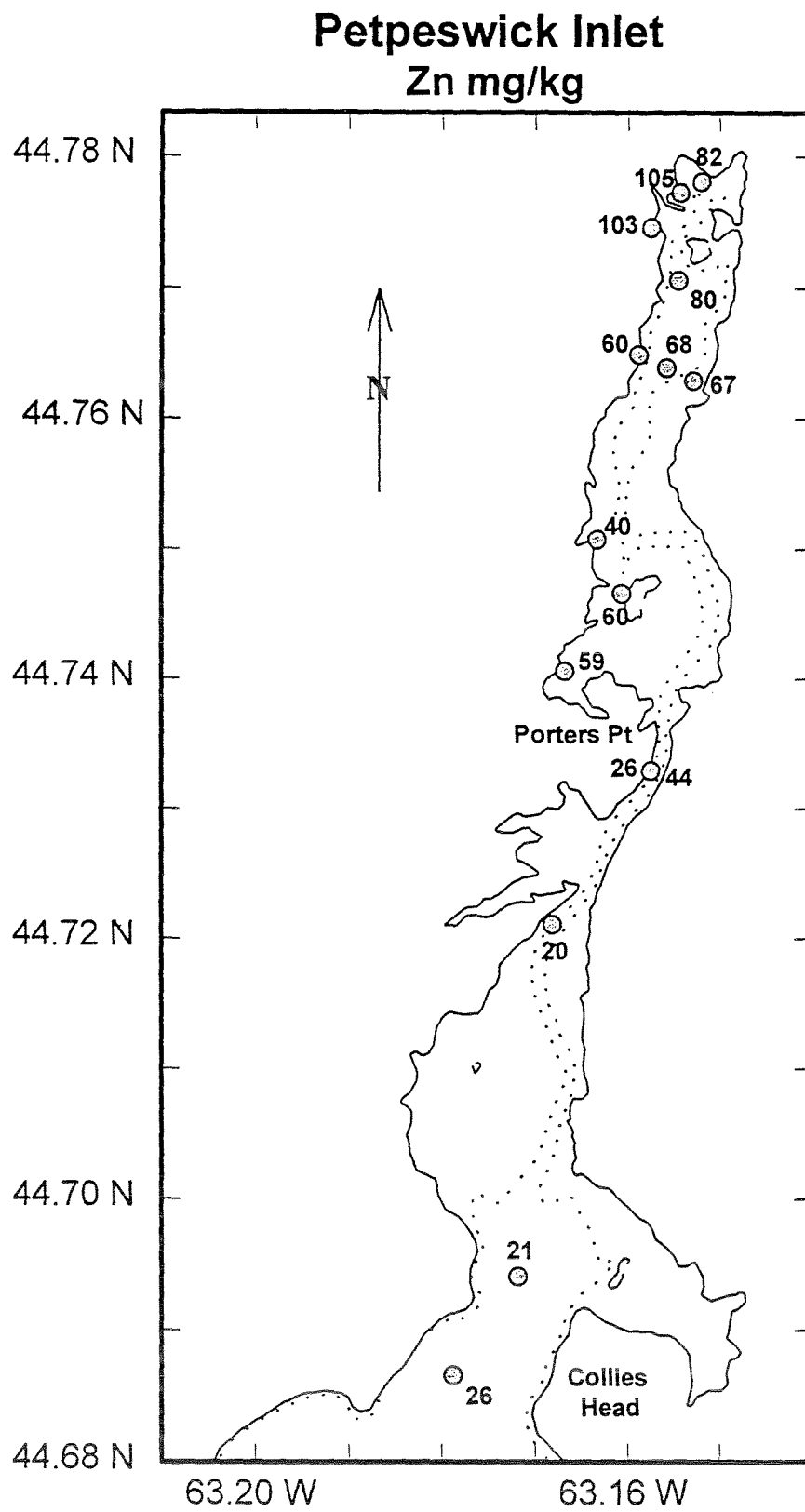
Petpeswick Inlet
Zn mg/kg

Figure 126. Zinc concentrations in surficial sediments

PUBNICO HARBOUR

Pubnico Harbour occupies a long (3.7 km) narrow (1.7 km) inlet having an area of 20.5 km² with a maximum depth of 22.1 m on the southern coast of Nova Scotia about 260 km southwest of Halifax. The Harbour receives limited drainage via a number of small brooks from an area of 148.8 km². The surrounding land is developed on a thin mantle of glacial till underlain primarily by Precambrian quartzites and slates.

POTENTIAL SOURCES OF CONTAMINATION

The Harbour is used by fishing boats, and the adjacent land is sparsely populated with no industrial development. The potential sources of contamination are restricted to the disposal of fish wastes and local residential sewage discharges.

RESULTS

Sediment Samples and Composition

The locations of the sampling stations are shown in Figure 127. Light-brown muds occupy the head of the long, narrow tidal inlet bordered by mud flats in its upper reaches. The sediments become sandy further seaward and change gradually from sandy muds to muddy sands, containing varying amounts of organic matter (Fig. 128) and thence to sands at the mouth of the Harbour.

The sediments within Pubnico Harbour all have very similar size distributions with modal diameters less than 64 μm and a mean source slope of 0.14 (Fig. 129). The concentration of floc-settled material is less than 10% at all stations, with the exception of Stations 11 and 12 located at the mouth of the Harbour. The spectra show that there is considerable low-energy sorting of the samples occurring, with the percent deposited as multi-round being in excess of 60% of the total sediment. This sorting can be seen in the steep, well defined, modal peaks at the coarse end of the spectra. In some samples, there is also some coarser material present, but this appears to be limited to the central part of the channel where current velocities are in the order of 0.20 m.s⁻² (Gregory et al. 1993). The similarity in size distributions for the sediments in Pubnico Harbour suggests that tidal velocities in this parallel-sided inlet are constant throughout. The increase in floc-settled material at the outermost stations coincides with a broadening of the inlet and decreased current speed.

Abundance and Distribution of Metals

Pubnico Harbour is the least contaminated among the areas studied. The abundance and distribution of the metals in Pubnico Harbour are shown in Figures 130 to 143. The range of total

metal concentrations measured in Pubnico Harbour sediments (n=12) are: As, 3.6-8 mg·kg^{-1}; Cd, 0.09-0.34 mg·kg^{-1}; Cr, 30-60 mg·kg^{-1}; Cu, 7-11 mg·kg^{-1}; Hg, 0.01-0.03 mg·kg^{-1}; Pb, 15-25 mg·kg^{-1}; and Znm, 30-52 mg·kg^{-1} (Table 20). The data indicate that trace metal concentrations are at, or near, natural concentrations, except for a few instances of high concentrations of Cd. The relatively high concentrations of Cd (0.28-0.34 mg·kg^{-1}) occur in organic-rich fine-grained sediments at the head of Pubnico inlet constituting 25% of the samples (Table 2).

Potential Bioavailability of Metals

Chemical partition of selected samples indicates that most (82-86%) of the total Cd, 10-30% of the total Cu, 33% of the total Pb, and 17-19% of the total Zn are potentially bioavailable.

Metal Carriers and Sources

The significant positive covariances (p<0.001) of Cd and Zn with the <63 μm fraction and Pb, Sn, and Zn with Al, indicate that metal carriers are associated only generally with the fine-grained aluminosilicate fraction of the sediments (Table 21) either structurally combined with the aluminosilicates or within discrete oxide and sulphide minerals. Significant correlations of As, Cd, and Zn with organic matter suggest that Cd as well as Zn occur in metal sulphides formed *in situ* in the organic-rich sediments near the head of the inlet. The high concentrations of Cd in the non-detrital fraction imply that Cd has been supplied in solution or weakly attached to particulate matter. Factor analyses confirm that aluminosilicate minerals account for much (41%) of the variance of Pb and Sn, as well as Ni and V, in the sediments. They also show that the association of As, Cd, and Cu with fine-grained organic-rich sediments accounts for 30% of the variance of these metals. On the whole, however, trace metal concentrations are at, or near, natural concentrations. There is no evidence, therefore, of significant anthropogenic inputs to Pubnico Harbour except in relation to the few high concentration areas for Cd in the sediments of the upper reaches of the Harbour.

Table 20

Textural and metal statistics[a] for the Pubnico Harbour sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	12	72.3	±21.1	35-98	OM%	12	2.68	± 1.09	1.18-4.48
Metal					Metal				
Al%	12	5.04	± 0.36	4.42-5.67	Fe%	12	2.14	± 0.28	1.75-2.57
As	12	5.7	± 1.3	3.6-8.0	Li	12	28.9	± 4.4	23-38
Cd	12	0.19	± 0.09	0.09-0.34	Ni	12	17.7	± 2.7	14-22
Cr	12	43.0	± 9.6	30-60	Pb	12	19.8	± 3.4	15-25
Cu	12	8.9	± 1.2	7-11	Sn	12	2.0	± 0.70	1-4
Eg	12	0.02	± 0.01	0.01-0.03	V	12	46.6	± 7.3	37-58
Mn%	12	0.060	± 0.02	0.042-0.103	Zn	12	42.3	± 7.1	30-52

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM), Al, Fe,and Mn

Table 21

Correlation Matrix Pubnico Harbour

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	x	x	1									
Cr	x	x	x	1								
Cu	x	x	x	x	1							
Fe	0.80	x	x	x	x	1						
Hg	x	x	x	x	x	x	1					
Li	x	x	x	x	x	0.90	x	1				
Mn	x	x	x	x	x	x	x	x	1			
Pb	0.84	x	x	x	x	x	x	x	x	1		
Sn	0.84	x	x	x	x	x	x	x	x	x	1	
Zn	0.88	x	x	x	x	0.84	x	x	x	0.85	x	1
mud	x	x	0.84	x	0.80	x	x	x	x	x	x	x
OM	x	0.94	0.94	x	x	x	x	x	x	x	x	0.83

n = 12
For $p \leq 0.001$ x = not significant
mud =>70% by weight material<63μm
OM = % by weight organic matter

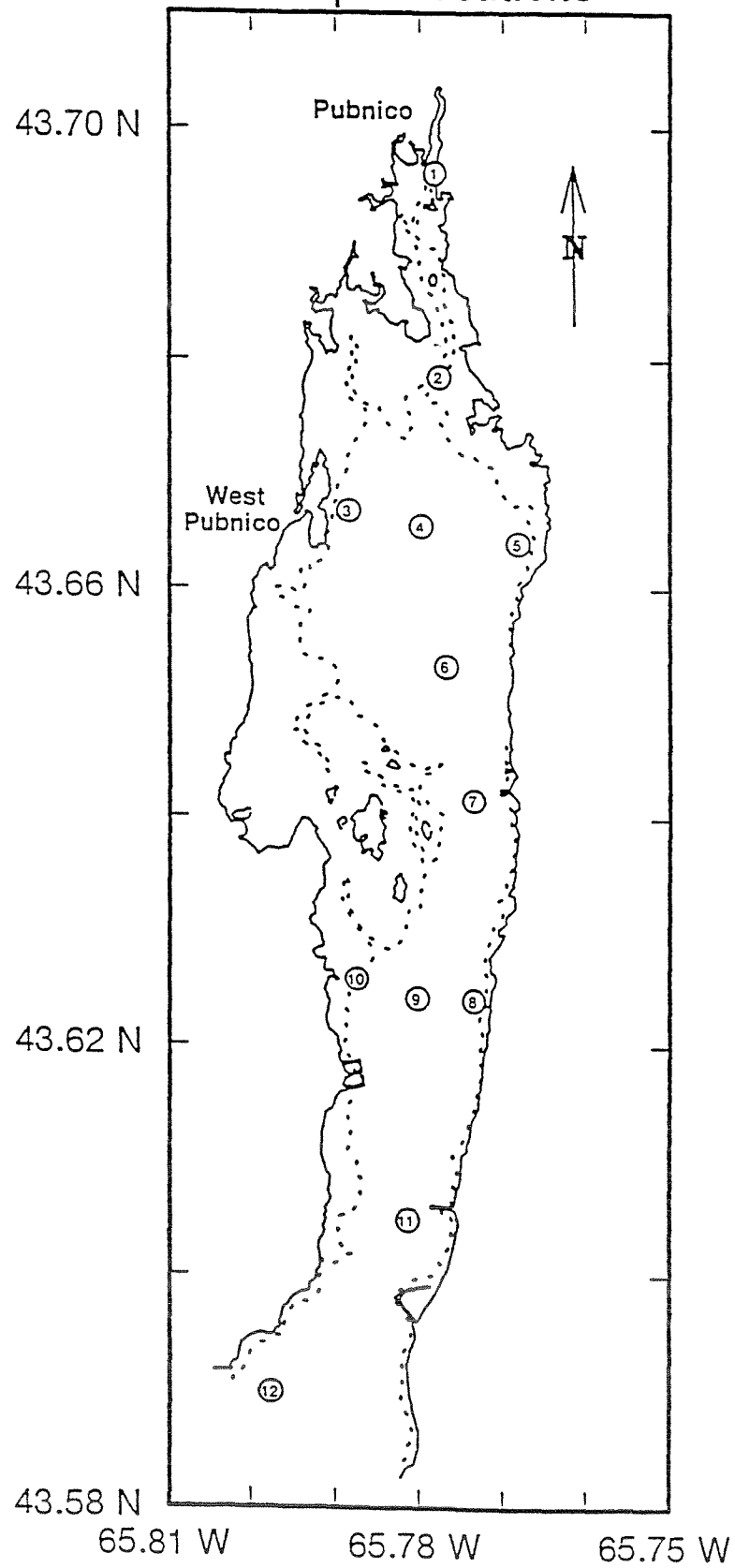# Pubnico Harbour
Sample Locations

Figure 127. Sample locations for Pubnico Harbour
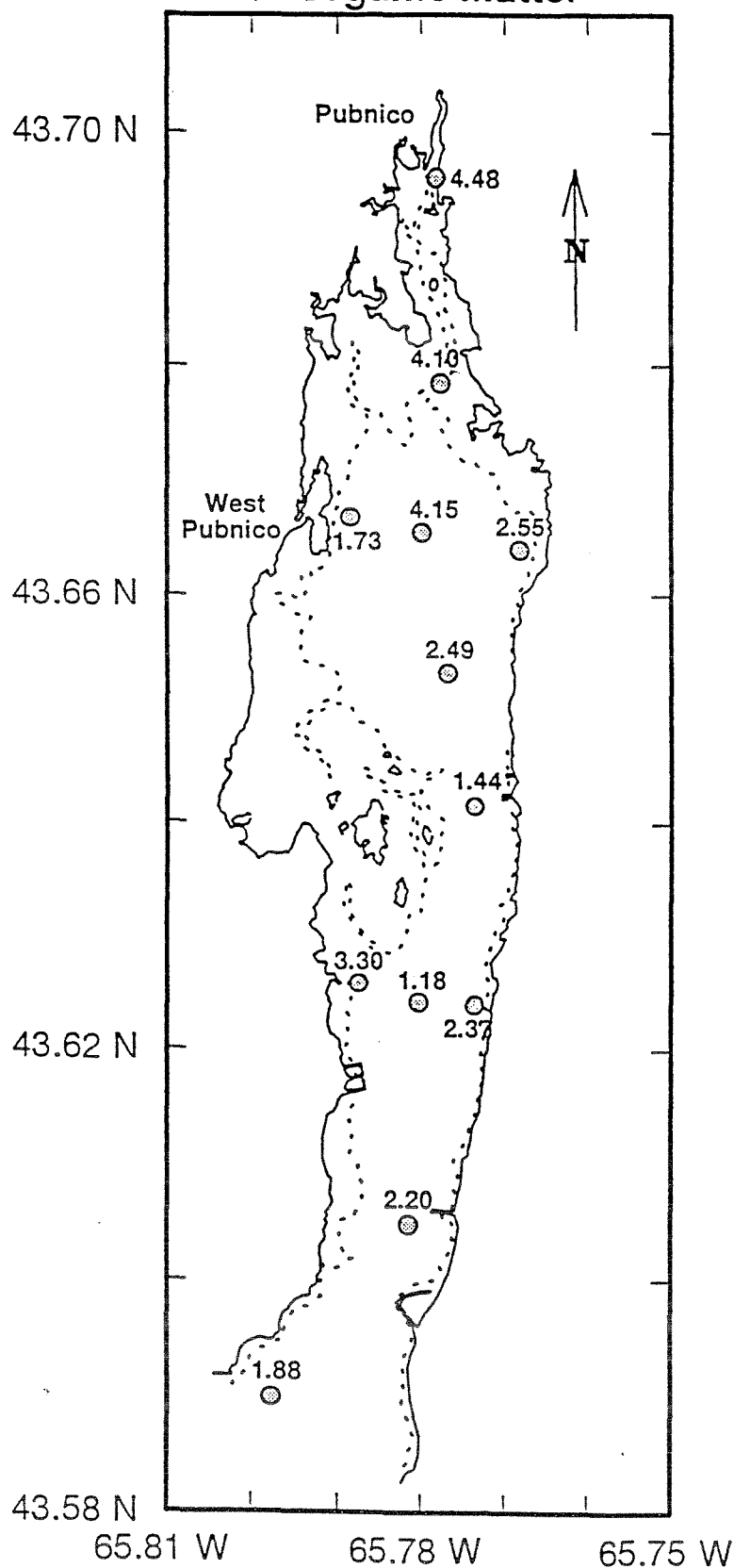
Pubnico Harbour
% Organic Matter

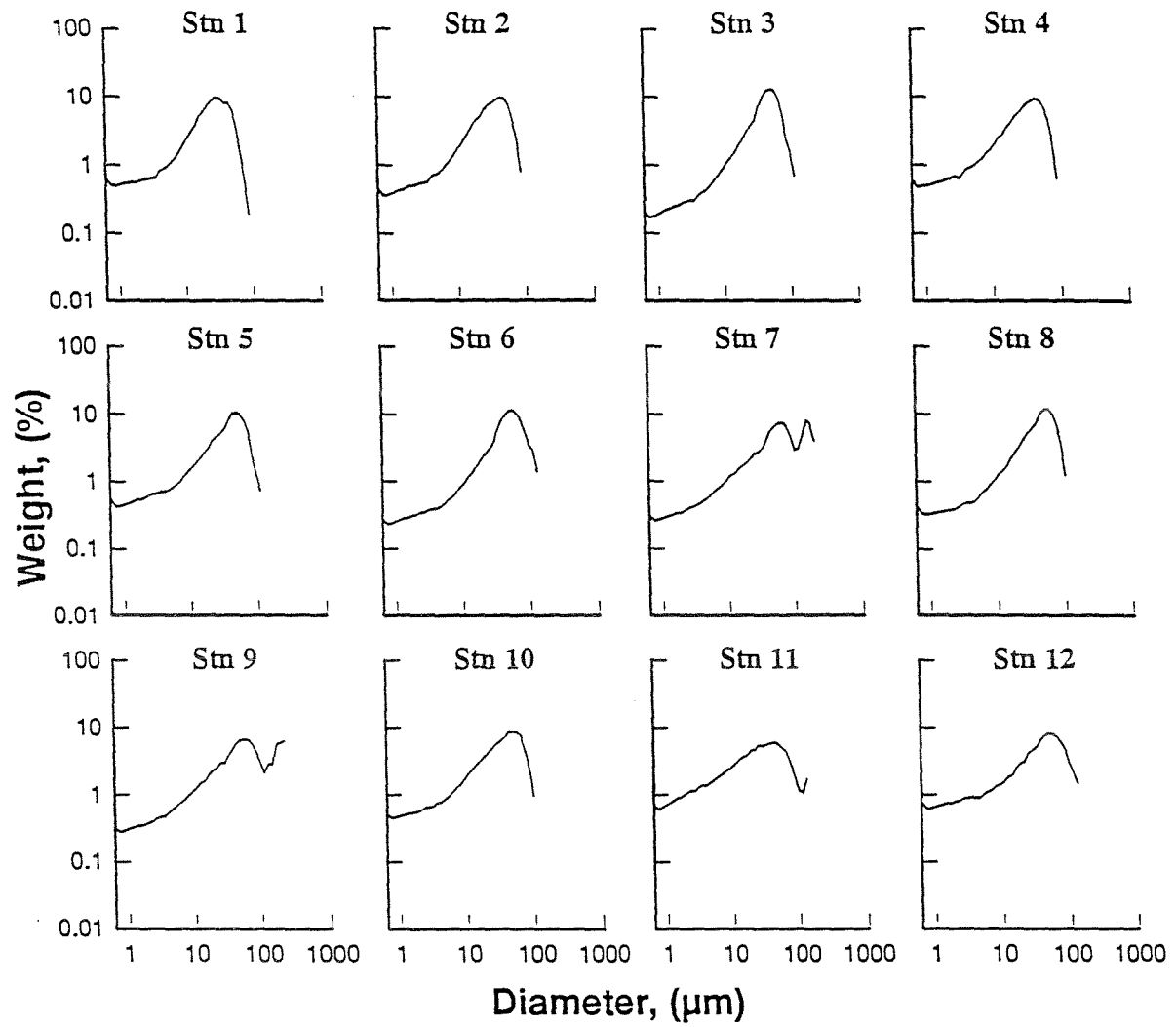Figure 128. Organic matter concentrations in surficial sediments

Pubnico Harbour

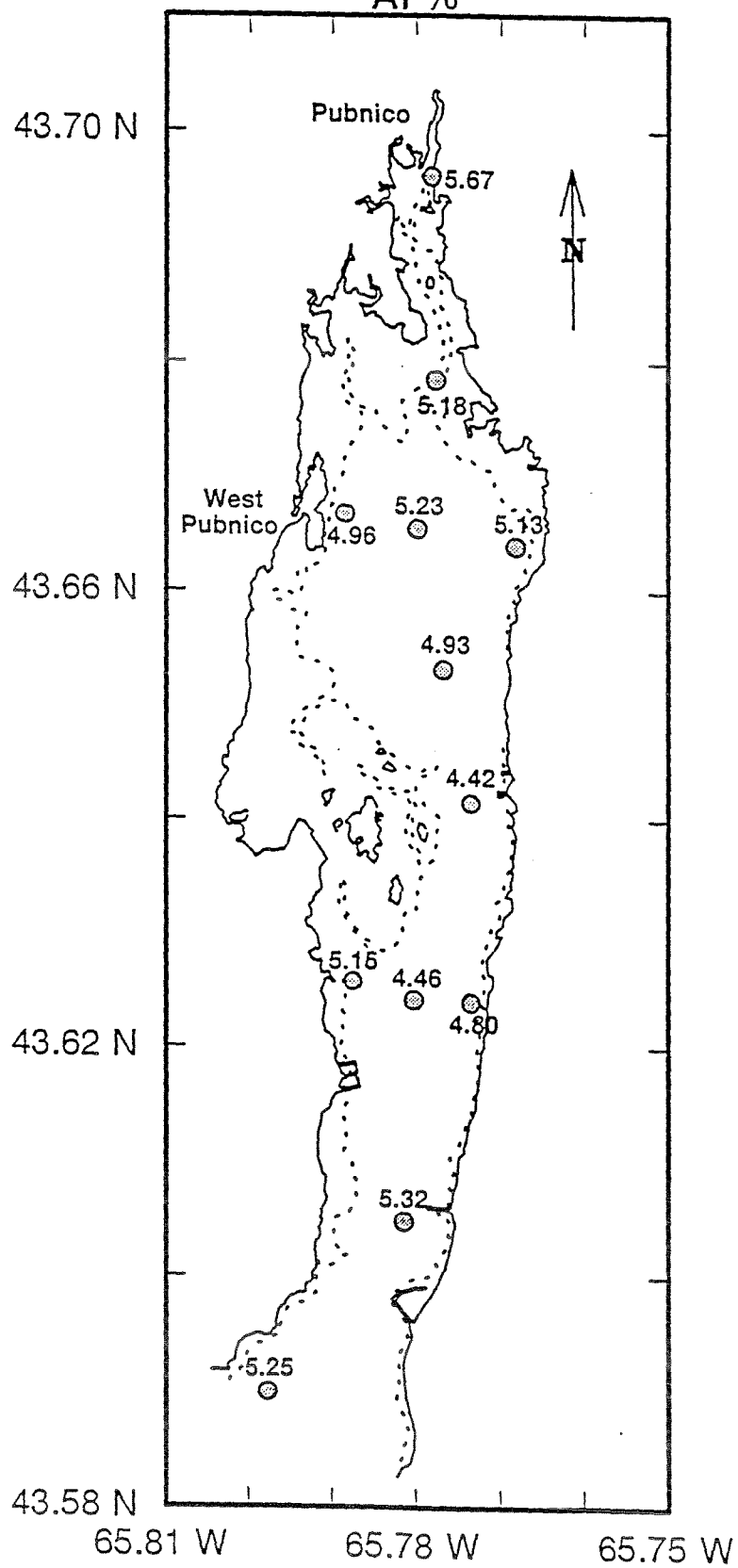Figure 129. Disaggregated inorganic grain size distributions

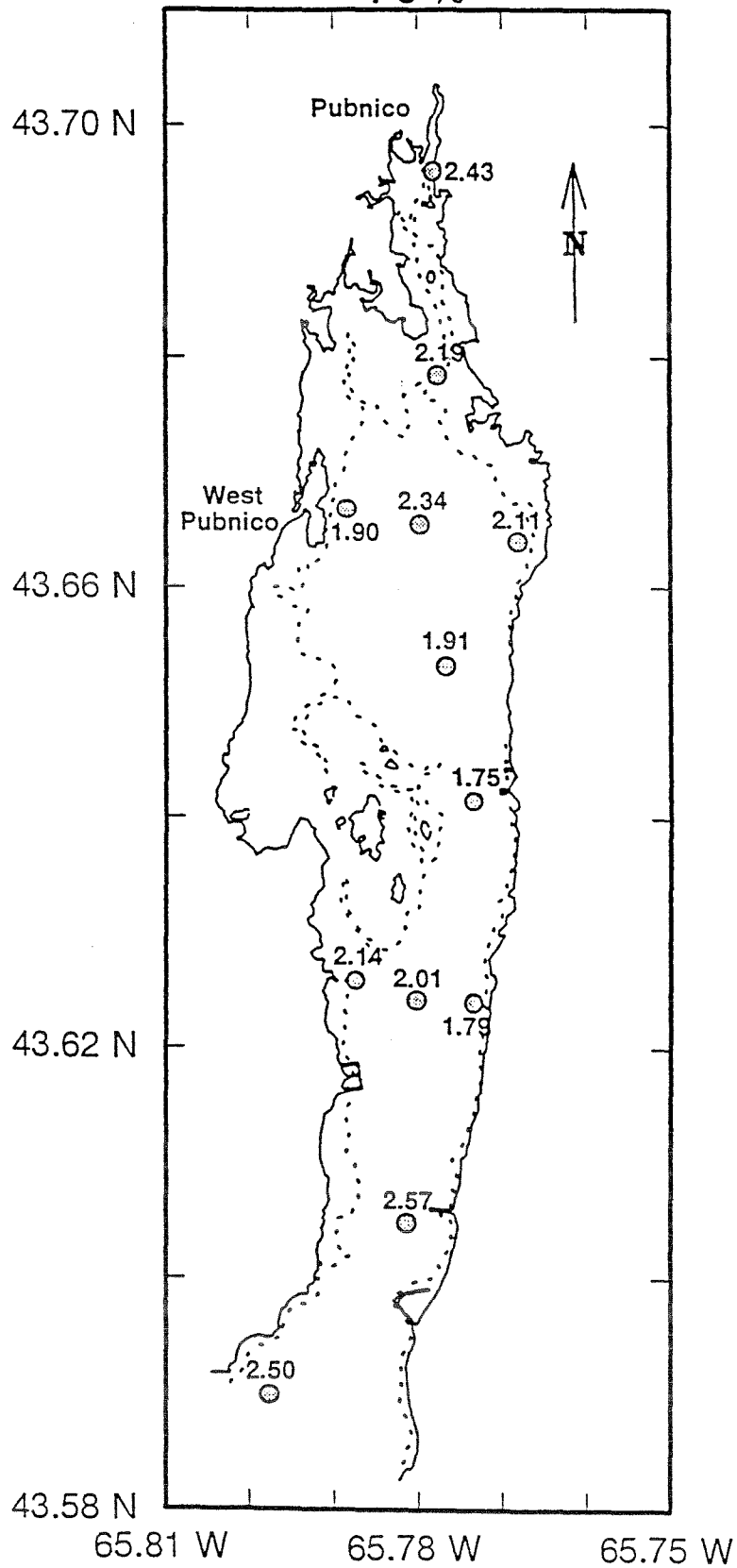Figure 130. Aluminium concentrations in surficial sediments

Pubnico Harbour
Fe %

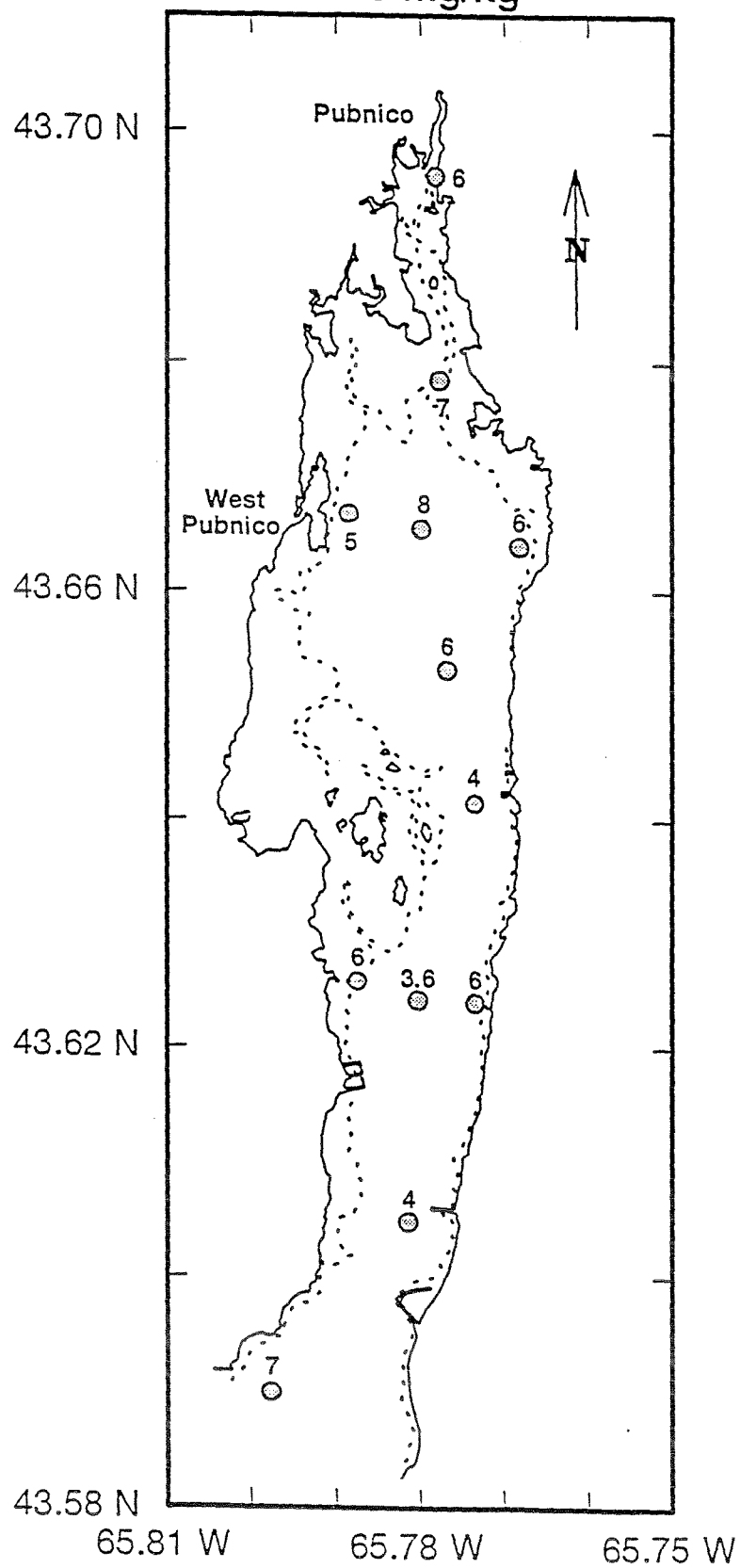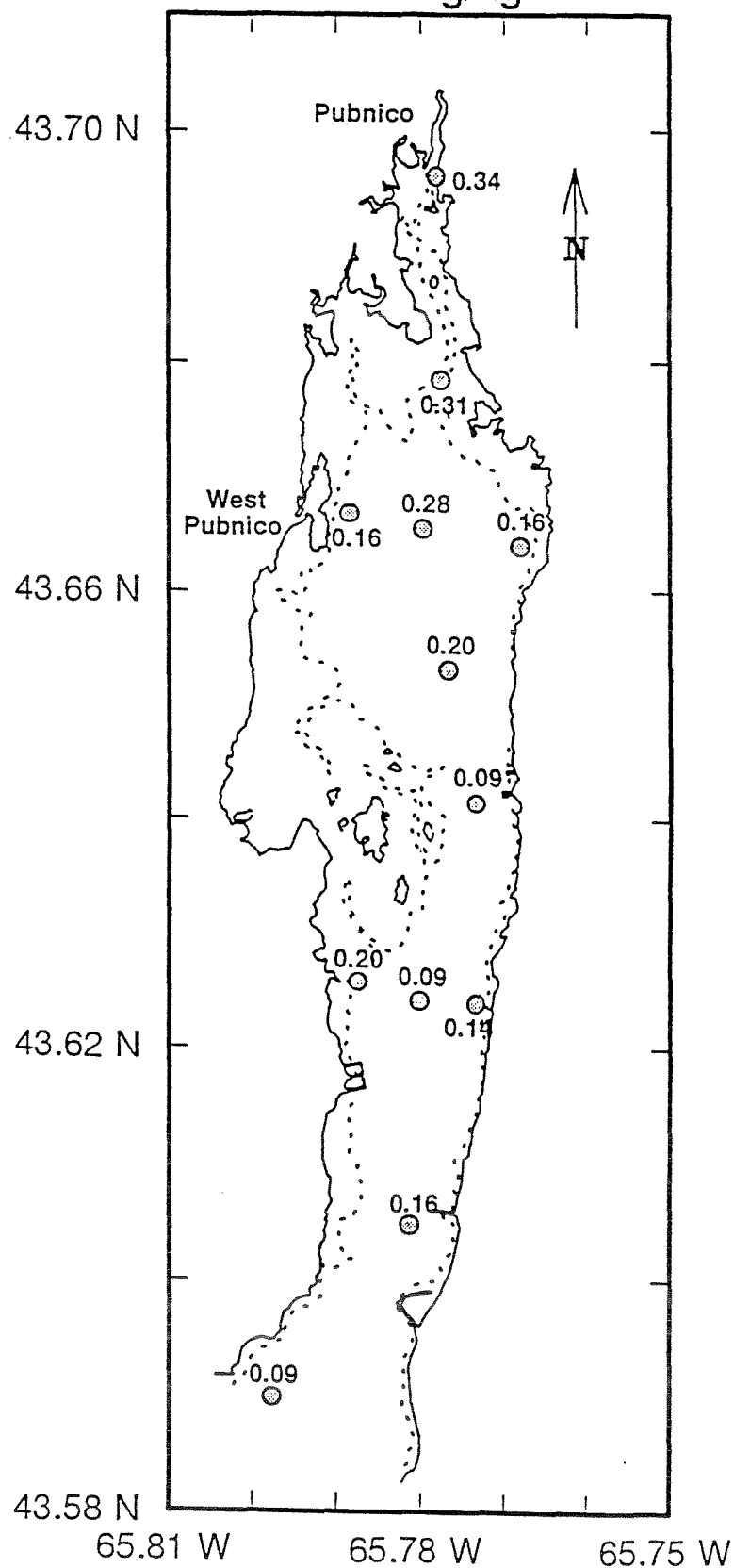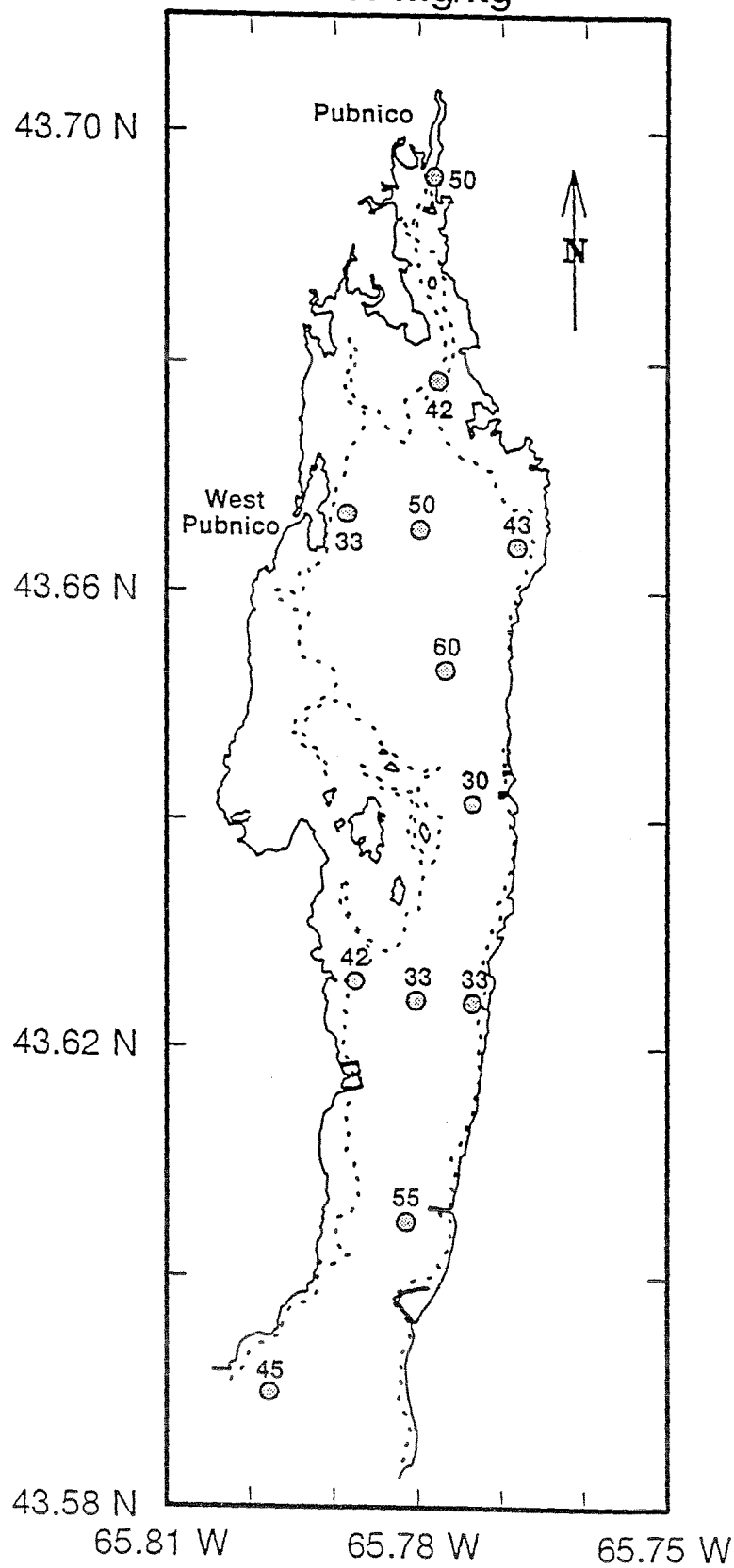Figure 131. Iron concentrations in surficial sediments

180

Pubnico Harbour
As mg/kg

Figure 132. Arsenic concentrations in surficial sediments

Pubnico Harbour
Cd mg/kg

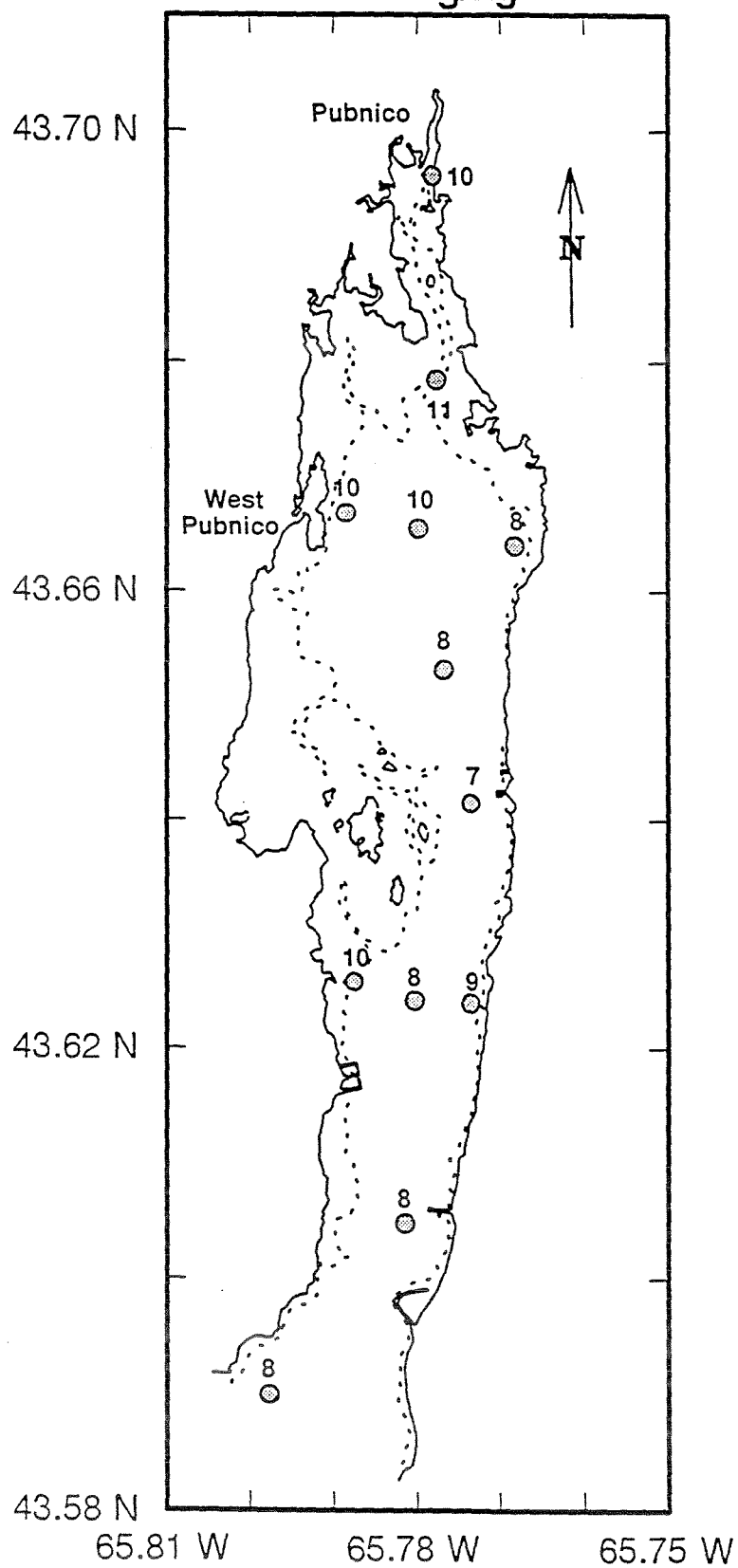Figure 133. Cadmium concentrations in surficial sediments

Figure 134. Chromium concentrations in surficial sediments

Pubnico Harbour
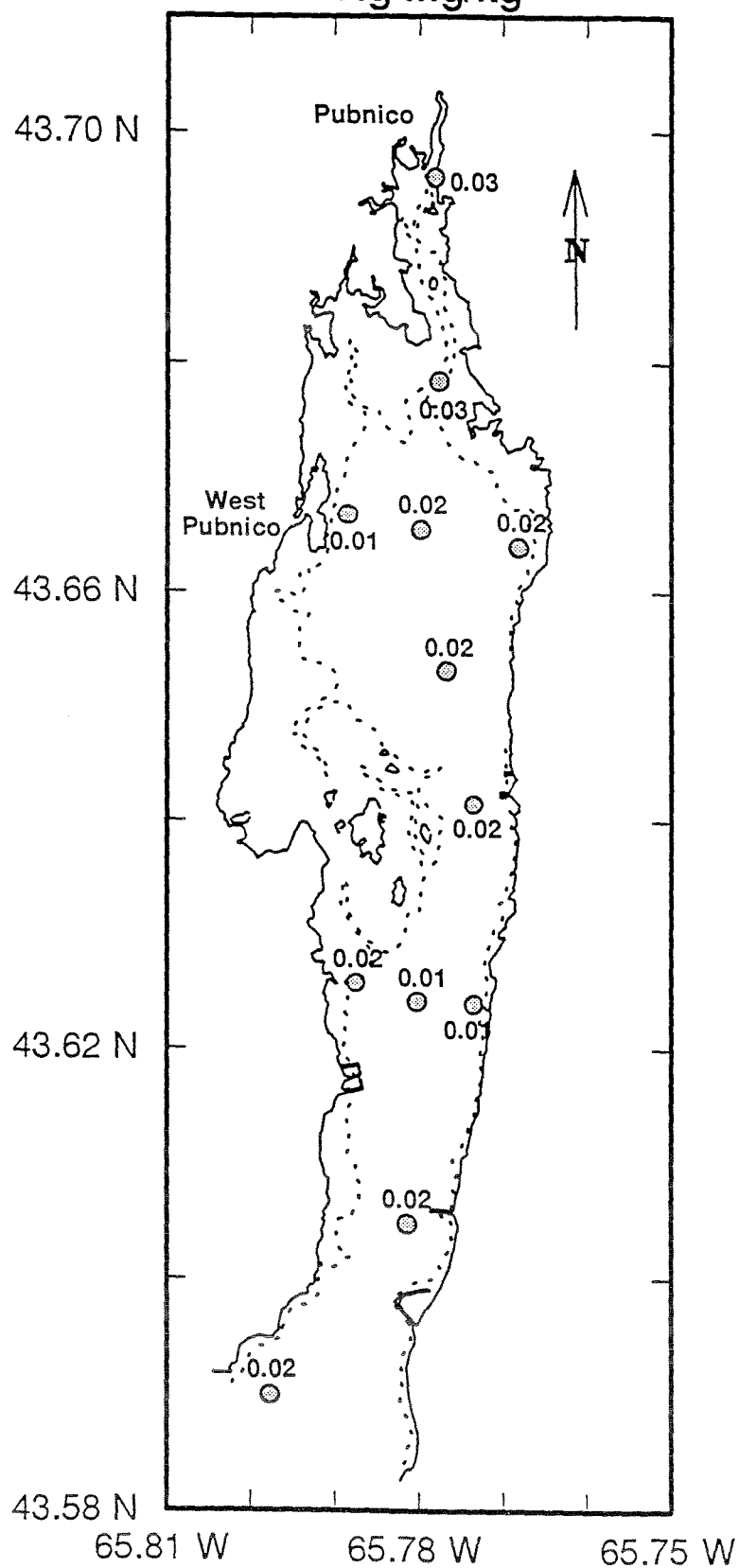## Cu mg/kg

Figure 135. Copper concentrations in surficial sediments

Pubnico Harbour
Hg mg/kg

Figure 136. Mercury concentrations in surficial sediments
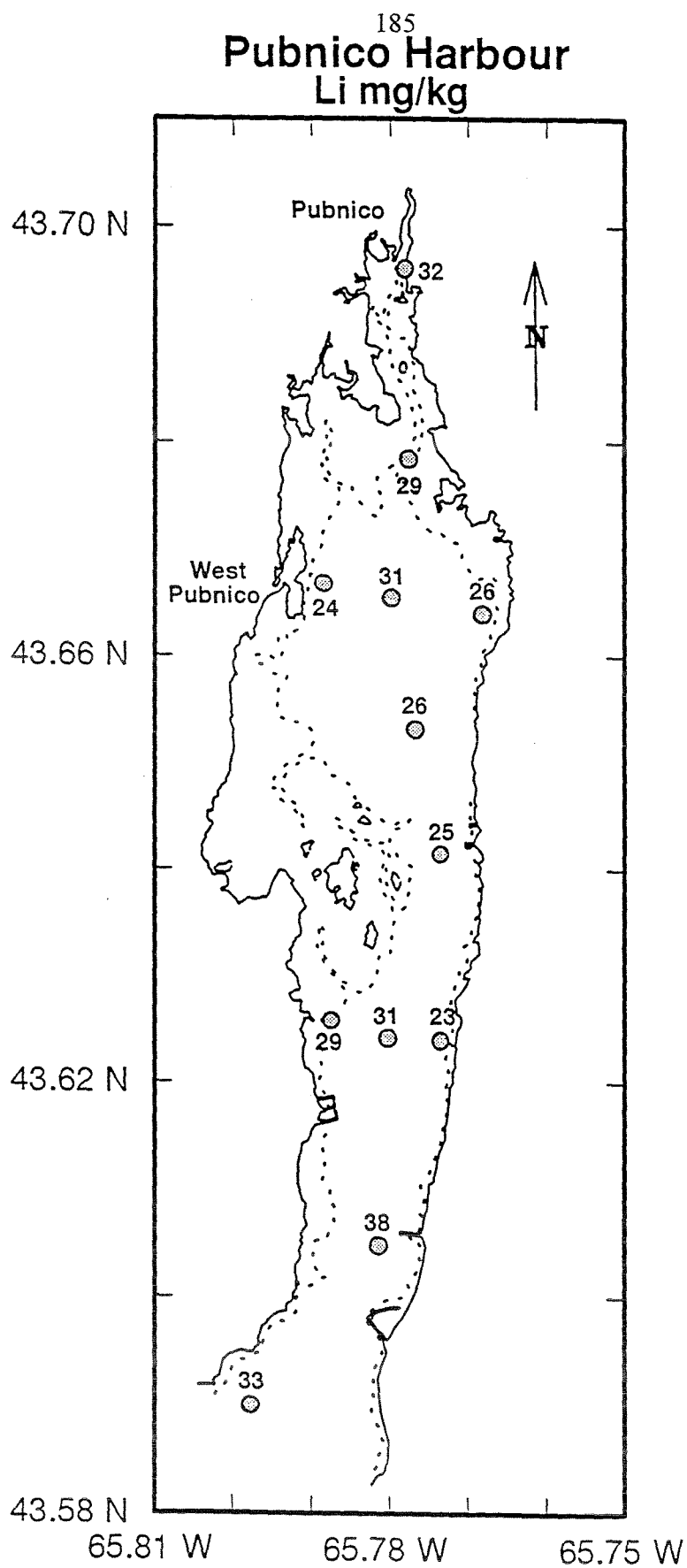
Pubnico Harbour
Li mg/kg

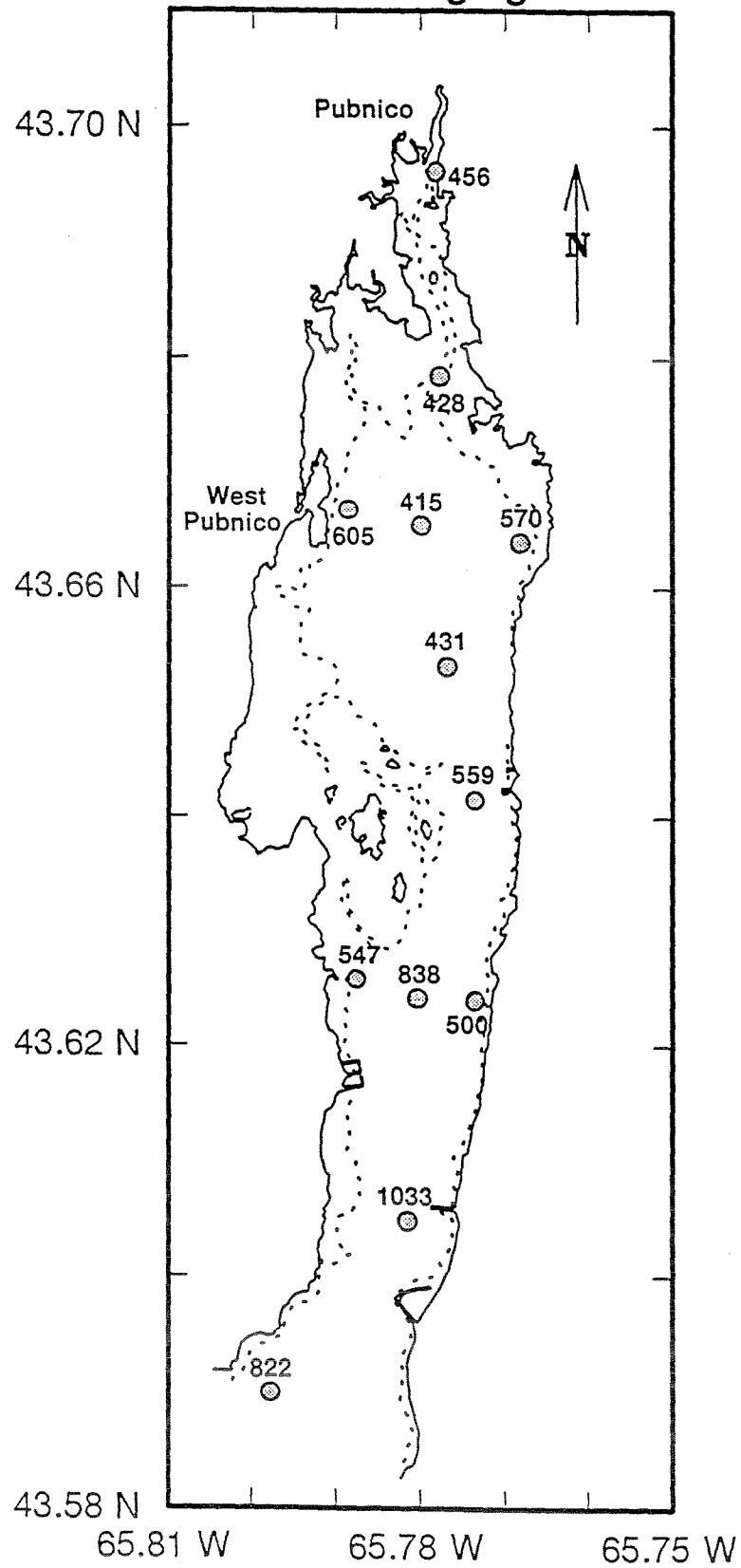**Figure 137.** Lithium concentrations in surficial sediments

Pubnico Harbour
Mn mg/kg

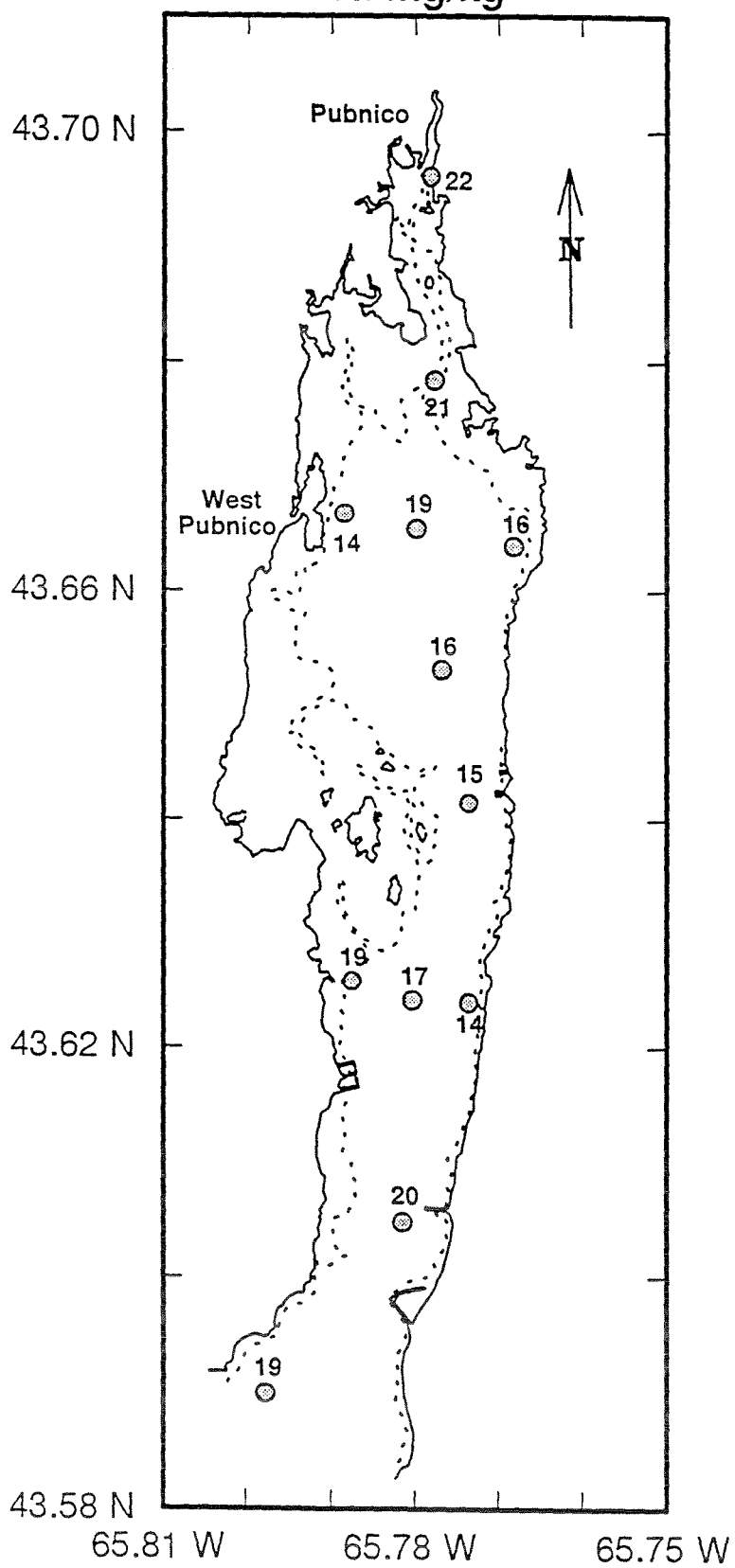Figure 138. Manganese concentrations in surficial sediments

Pubnico Harbour
Ni mg/kg

Pubnico

22

West
Pubnico

19

16

14

15

19

17

14

20

19

43.70 N

43.66 N

43.62 N

43.58 N

65.81 W   65.78 W   65.75 W

Figure 139. Nickel concentrations in surficial sediments
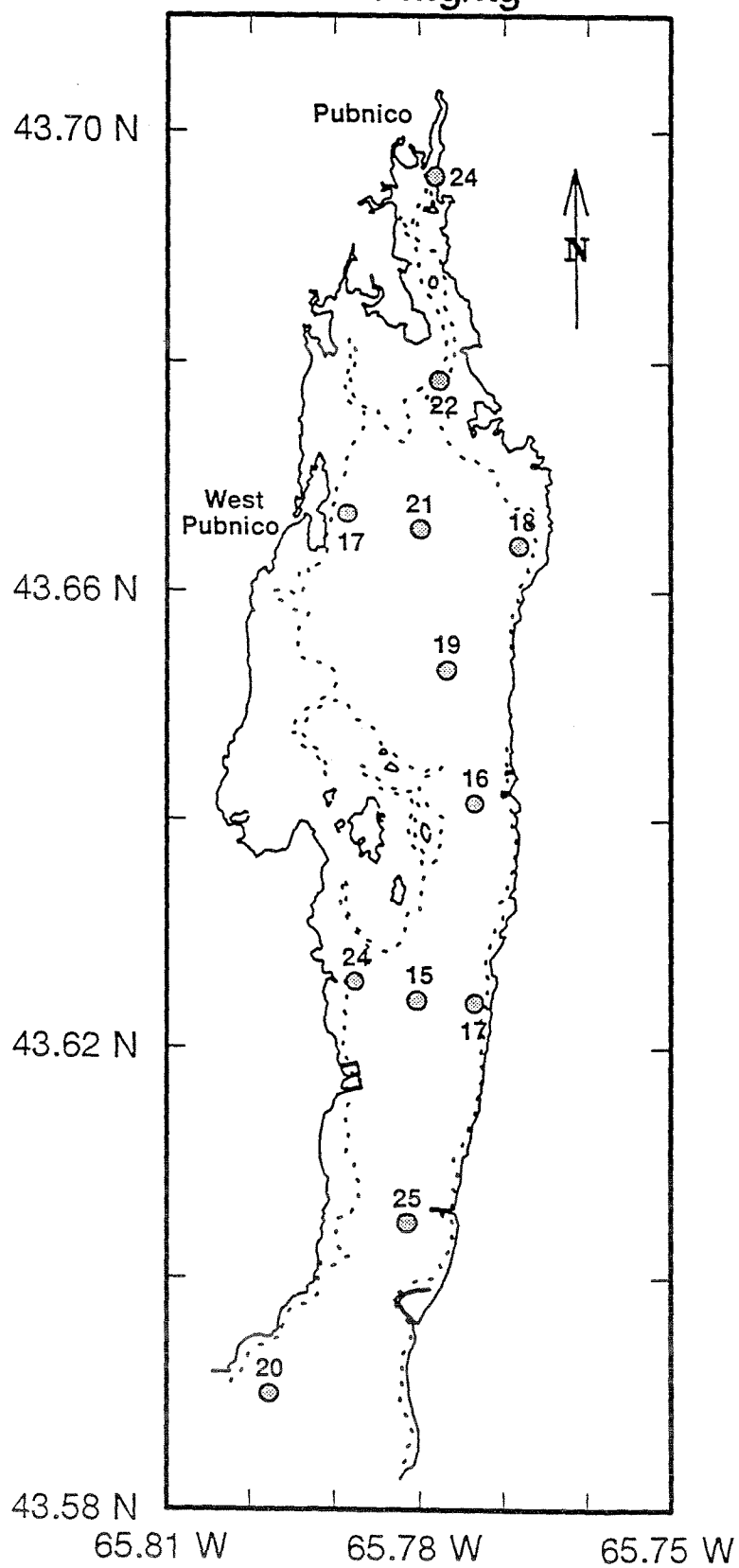
Pubnico Harbour
Pb mg/kg

Figure 140. Lead concentrations in surficial sediments
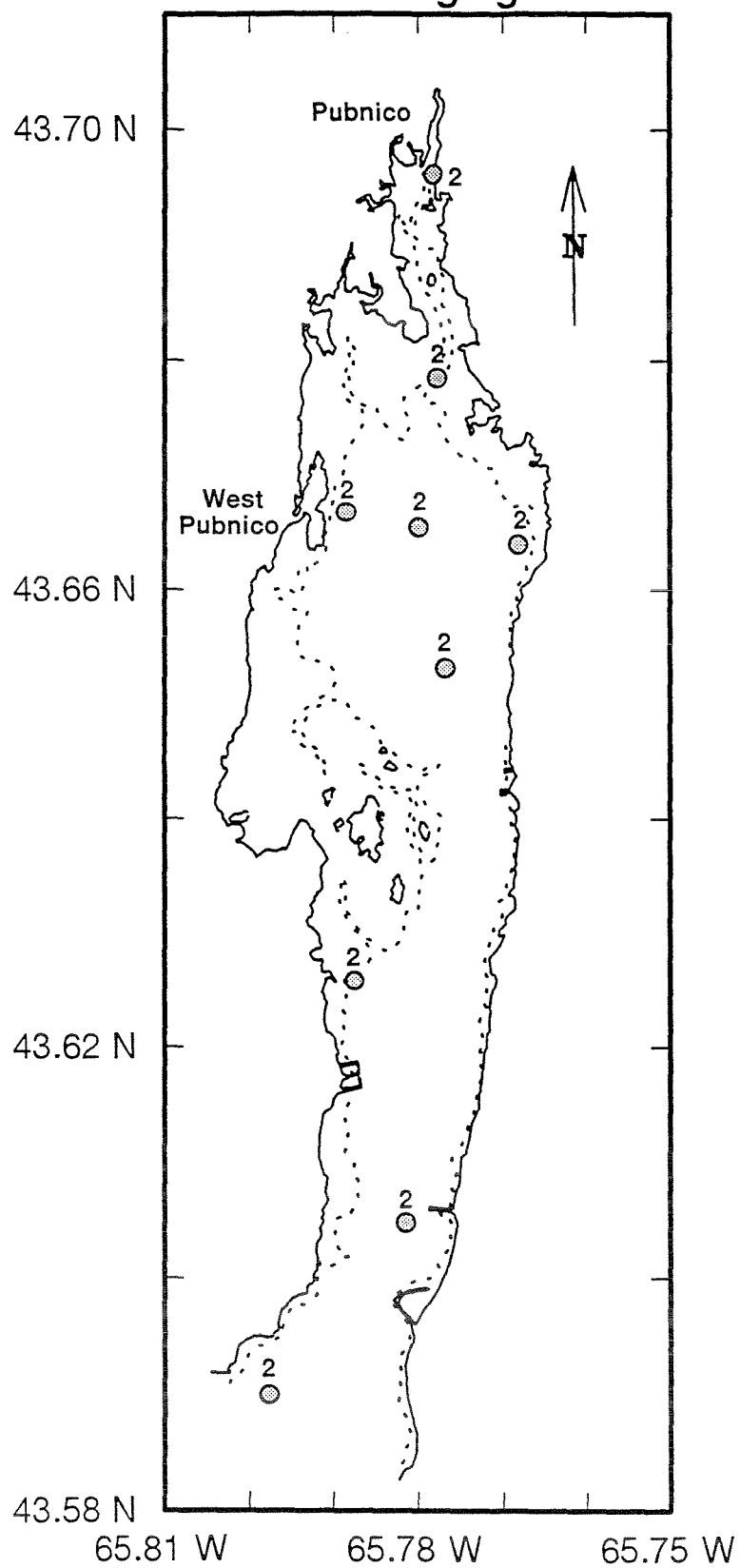
Pubnico Harbour
Sn mg/kg

Figure 141. Tin concentrations in surficial sediments
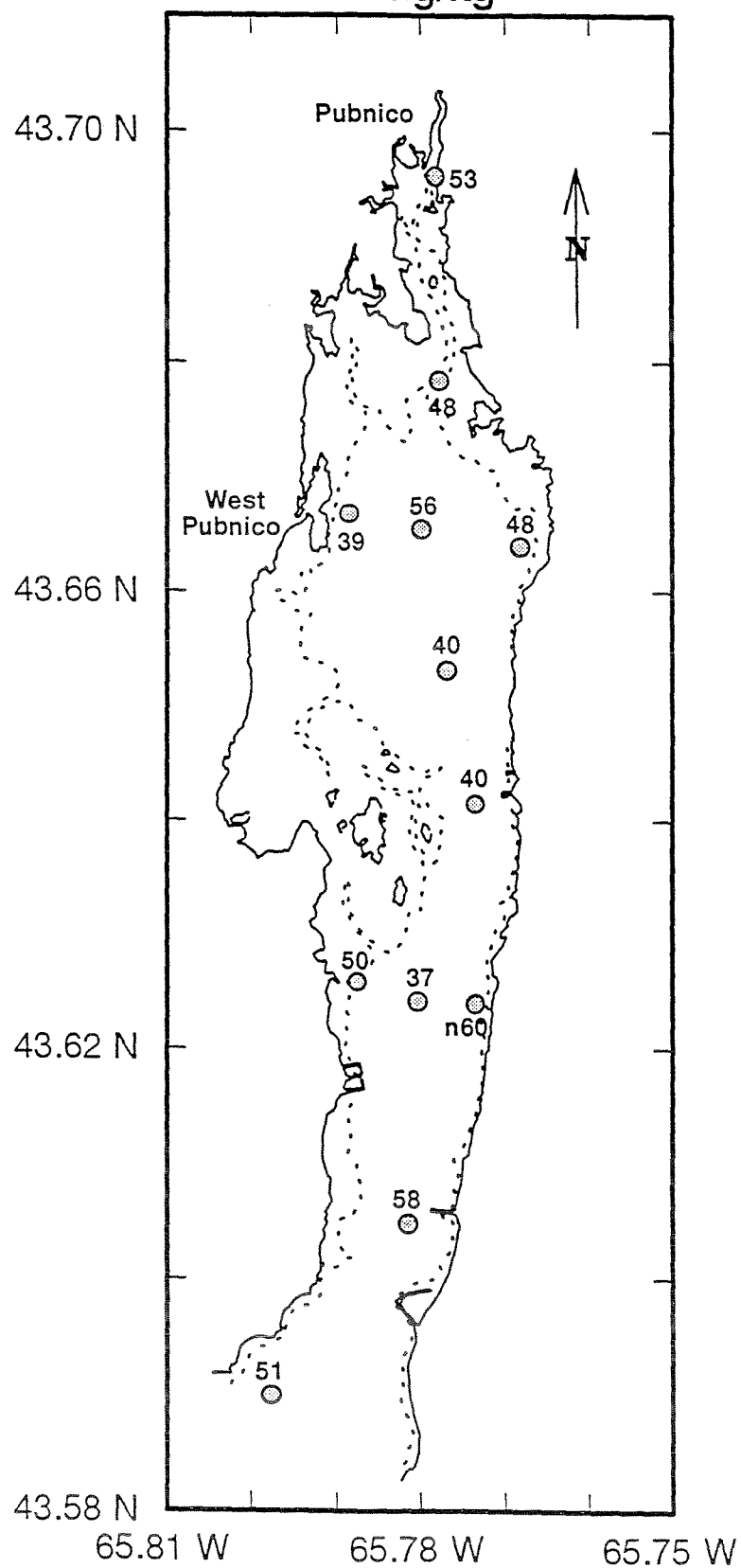
Pubnico Harbour
V mg/kg

Figure 142. Vanadium concentrations in surficial sediments
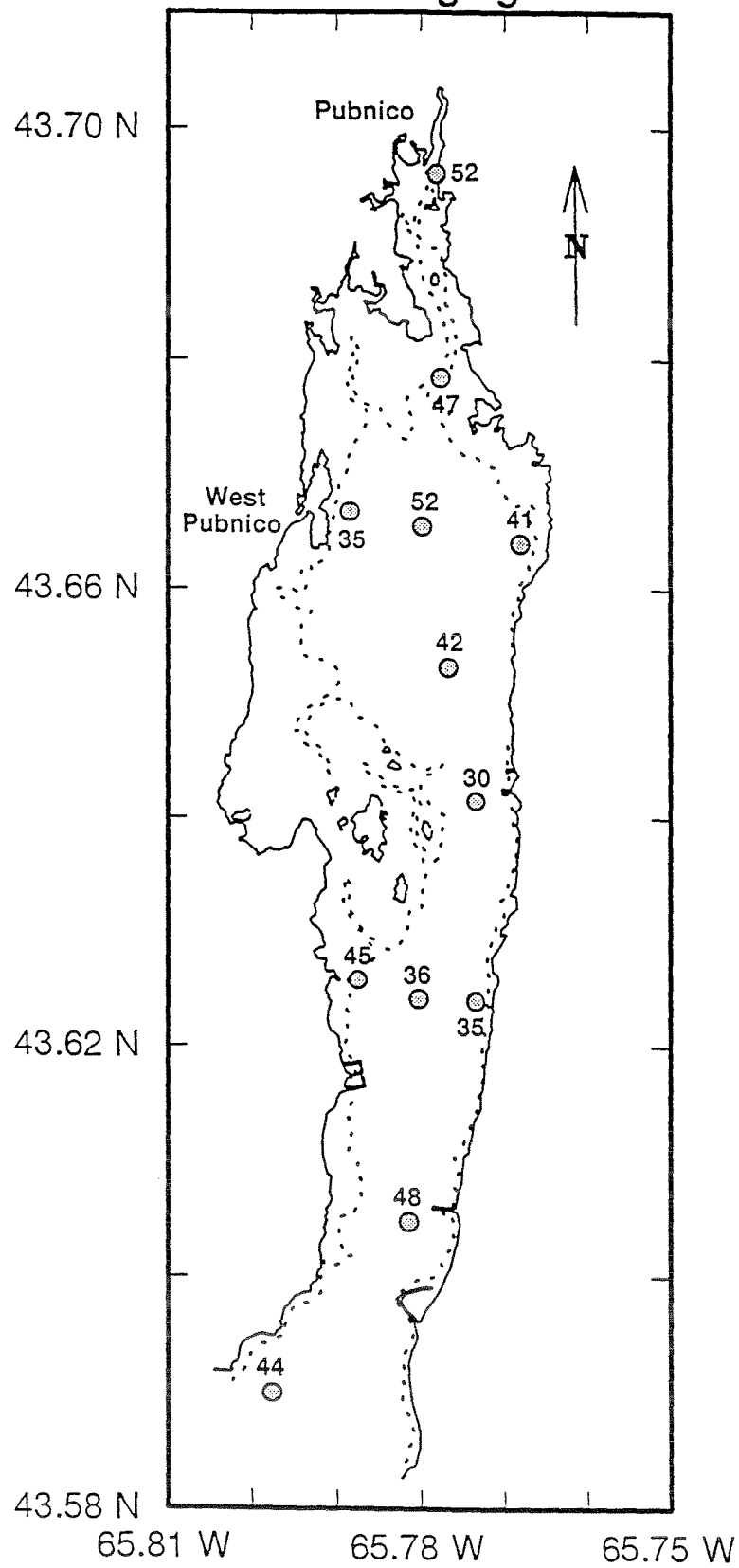
Pubnico Harbour
Zn mg/kg

Figure 143. Zinc concentrations in surficial sediments

SHELBURNE HARBOUR

Shelburne Bay occupies a long (16.2 km) elongated forked embayment of area 44.4 km^2 with a maximum depth of 16.4 m on the southern coast of Nova Scotia about 223 km southwest of Halifax. The forked inner part of the Bay, known as Shelburne Harbour (22.6 km^2), has an axial length of 9.6 km and a maximum depth of 13.1 m. The Harbour receives drainage via the Roseway River from an area of 748 km^2. The surrounding land is developed on a thin mantle of glacial till underlain primarily by Precambrian quartzites and slates. The head and northeastern arms of the Harbour are mainly occupied by the town of Shelburne and the northwestern arm by cultivated land with residential dwellings around Birchtown. The limited cultivated land supports mixed farming.

POTENTIAL SOURCES OF CONTAMINATION

Since 1780, the town of Shelburne, which has a population of approx. 2,500, has contributed organic and some metallic wastes to the Harbour from its ship building and repair, fish processing, and fishing activities as well from urban sewage disposal. Industrial and urban discharges are potentially, therefore, the main sources of metallic and organic contaminants.

RESULTS

Sediment Samples and Composition

The locations of the sampling stations (n=32) are shown in Figure 144. Sandy muds and organic-rich muds (Fig. 145) occupy the inner part of Shelburne Harbour, with the sediments becoming more sandy in the outer part and toward the seaward limits of Shelburne Bay.

Shelburne Harbour sediments are dominated by the shallow sill landward of McNutt's Island. A transition across the sill can be seen in the change in both source slope and percent floc settled concentration in the bottom sediments (Fig. 146). Station 30, located in what could be considered the transition zone, shows a decrease in source slope and has a percent floc concentration intermediate between that found in the inner and outer Harbour stations. At the seaward end of Shelburne Harbour, the sediments consist of well-sorted medium sands, mean modal diameter 170 μm, with a prominent steep floc tail with a slope of 0.58. The floc portion represents less than 6% of the total sediment and probably results from trapping of offshore fine sediment within the interstitial spaces. In more sheltered areas of the outer Harbour, floc concentrations increase slightly and are also associated with a decrease in modal size. The inner part of Shelburne Harbour consists of sediments deposited from suspension, with some reworking of the material occurring at stations approaching the transition zone. At the head of the Harbour at the mouth of the Shelburne River, sediments have source slopes in the order of 0.2 and percent floc settled concentrations of less than 20%. In addition, there are larger amounts of coarser material found at stations a short way downstream, indicating the fall off in the carrying capacity

of the inlet stream. Opposite the town of Shelburne, the source slope flattens to a mean value of 0.07, and the percent floc settled portion increases to between 25 and 44%, with the maximum value being recorded at Station 10, located within the Government Wharf. In other parts of the inner Harbour, floc concentrations drop slightly; but the source slope value is maintained. Within the inner Harbour, there are only minor amounts of higher round, sorted sediment, occurring in the samples with values increasing seaward.

Shelburne Harbour's sediment deposition patterns are controlled by a shoaling of the bottom which limits both the exchange of offshore water with the inner Harbour and the amount of resuspension. Fine sediments are being trapped within the upper reaches of the Harbour, but the presence of some higher round sediment in all sediments would indicate that there is some reworking of the bottom and that accumulation rates will be moderated by resuspension.

Abundance and Distribution of Metals

The abundance and distribution of the metals in Shelburne Harbour are shown in Figures 147 to 160. Shelburne Harbour sediments contain some anomalously high concentrations of Cd and a few high concentrations of Cu, Pb, and Sn. The range of total metal concentrations measured in Shelburne Harbour sediments (n=32) are: As (n=22), 2-28 $mg \cdot kg^{-1}$; Cd, 0.02-1.32 $mg \cdot kg^{-1}$; Cr, 3-55 $mg \cdot kg^{-1}$; Cu, 2-44 $mg \cdot kg^{-1}$; Hg, 0.01-0.23 $mg \cdot kg^{-1}$; Ni, 5-26 $mg \cdot kg^{-1}$; Pb, 10-80 $mg \cdot kg^{-1}$; Sn (n=22), 2-13 $mg \cdot kg^{-1}$; V, 8-73 $mg \cdot kg^{-1}$; and Zn, 8-90 $mg \cdot kg^{-1}$ (Table 22). These data (Table 2) indicate that 59% of the samples contain >0.3 $mg \cdot kg^{-1}$ Cd, of which 53% exceed the limit for ocean dumping of 0.6 $mg \cdot kg^{-1}$. Of these, 30% range in concentration from 1.0-1.32 $mg \cdot kg^{-1}$. The highest concentrations of Cd occur in organic-rich muds occupying the head of the northwest arm of the Harbour. Cadmium-rich muds also occur along the town's waterfront and around the Public Wharf extending across the Harbour and seaward for about 7 to 9 km, beyond which concentrations decrease as the sediments become more sandy. In addition, 3% of the samples contain >40 $mg \cdot kg^{-1}$ Cu, 25% >0.1 $mg \cdot kg^{-1}$ Hg, 19% >40 $mg \cdot kg^{-1}$ Pb, and 14% $\geq$5 $mg \cdot kg^{-1}$ Sn.

Potential Bioavailability of Metals

Chemical partitioning of selected samples indicate that most (68-83%) of the total Cd, 0-22% of the total Cu, 26-65% of the total Pb, and 12-43% of the total Zn are potentially bioavailable. The high concentrations of Cd, and Pb in the non-detrital fraction imply that they have been supplied in solution or weakly attached to particulate matter and point to a significant anthropogenic contribution of these metals to the sediments.

Metal Carriers and Sources

The significant positive covariances ($p<0.001$) to a greater or lesser degree for all the metals, excepting Sn, with the <63-μm and organic fractions and, to a lesser extent, with Al, and Li, indicate that metal carriers are associated generally with the fine-grained organic-rich aluminosilicate fraction of the sediments (Table 23). This is confirmed by the factor analyses which show that the abundance and distribution of Cd, Cr, Cu, Ni, V, and Zn are mainly controlled (65% of the total variance) by the deposition of the fine-grained organic-rich fraction. The proportion of the metal variability explained by the granular variability of the <63-μm fraction decreases in the order: Cr (87%) > Zn (76%) > Cu (69%) > Cd (64%) > Zn (76%) > As (52%) ≥ Pb (51%) >> Hg (37%) >> Sn (7%). The proportion of the metal variability explained by the granular and mineralogical variability of Li decreases in the order: Zn (84%) > Cr (74%) > Cu (70%) > Cd (60%) = Hg (60%) > Pb (56%) >> As (12%) > Sn (5%).

It is clear that a significant proportion of Cr, Cu, Pb, and Zn concentrations can be explained by the natural amounts of these metals held in fine-grained phyllosilicates and in discrete oxide minerals (Cr). This is not the case for As and Sn and for a considerable proportion of the Cd and Pb. Sn has no significant correlation with the other variables in Table 20. However, a significant correlation of Sn with Hg and OM in the fine-grained sediments (<63 μm) alone suggests that some Sn may be associated with metallic particles or sulphides formed *in situ* in the organic-rich sediments. The relatively high Sn concentration found in the sample obtained from a cove at the head of the Harbour may reflect metallic particles containing Sn. A significant correlation of As with the fine fraction and organic matter suggests that it has a more or less random distribution at or near natural levels throughout the sediments. The relatively high concentrations of Cd and Hg at many sites may also reflect their association with metallic particles or sulphides formed *in situ* in the organic rich sediments. The amounts associated with these carriers are in addition to those naturally associated with the lattices of the aluminosilicate minerals.

The main source of anomalous levels of Cd and Hg in the sediments appears to be industrial input of scrap metallic fragments from industry and from organic fish and sewage waste discharged from the town surrounding the Harbour. Relatively poor flushing of the Harbour allows for the accumulation of fine-grained organic-rich particulate matter and associated contaminants in the upper reaches of the northwestern and northeastern arms of the Harbour. After deposition, this material becomes anoxic with the attendant enrichment of metals like Cd and Pb in the form of sulphides. At present, about 75% of the floor of the Harbour contains sediments that exceed the limit for ocean dumping of 0.6 mg·kg^{-1} Cd.

Table 22

Textural and metal statistics[a] for the Shelburne Harbour sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	32	59.4	±41.2	1-99	OM%	32	6.95 ± 5.3.		0.10-16.7
Metal					**Metal**				
Al%	32	4.66	± 0.65	3.47-5.51	Fe%	32	1.80 ± 0.53		0.56-2.43
As	22	13.7	± 6.4	2-28	Li	32	32.5	±11.5	13-50
Cd	32	0.48	± 0.39	0.02-1.32	Ni	32	16.4	± 6.7	5-26
Cr	32	28.4	±18.9	3-55	Pb	32	29.3	±16.4	10-80
Cu	32	15.8	±11.3	2-44	V	32	43.1	±20.9	8-73
Hg	32	0.06	± 0.05	0.01-0.23	Zn	32	44.5	±24.7	8-90
Mn%	32	0.062 ± 0.055		0.024-0.236	Sn	21	3.9	± 2.4	2-13

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM), Al, Fe, and Mn

Table 23

Correlation Matrix Shelburne Harbour

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	0.63	x	1									
Cr	0.82	x	0.78	1								
Cu	0.67	x	0.80	0.84	1							
Fe	0.61	x	0.58	0.82	0.66	1						
Hg	x	x	0.70	0.61	0.83	x	1					
Li	0.88	x	0.78	0.86	0.84	0.68	0.77	1				
Mn	-.64	x	-0.57	x	-0.59	x	x	-.68	1			
Pb	0.56	x	0.69	0.64	0.79	x	0.79	0.75	-.58	1		
Sn	x	x	x	x	x	x	x	x	x	x	1	
Zn	0.74	x	0.87	0.87	0.96	0.70	0.86	0.92	-.62	0.80	x	1
mud	0.86	0.72	0.80	0.93	0.83	0.65	0.61	0.87	-.69	0.71	x	0.87
OM	0.60	0.82	0.84	0.79	0.87	x	0.78	0.83	-.68	0.82	x	0.90

n = 32 (As:n=22)
For p ≤0.001 x = not significant
mud = >70% by weight material<63μm
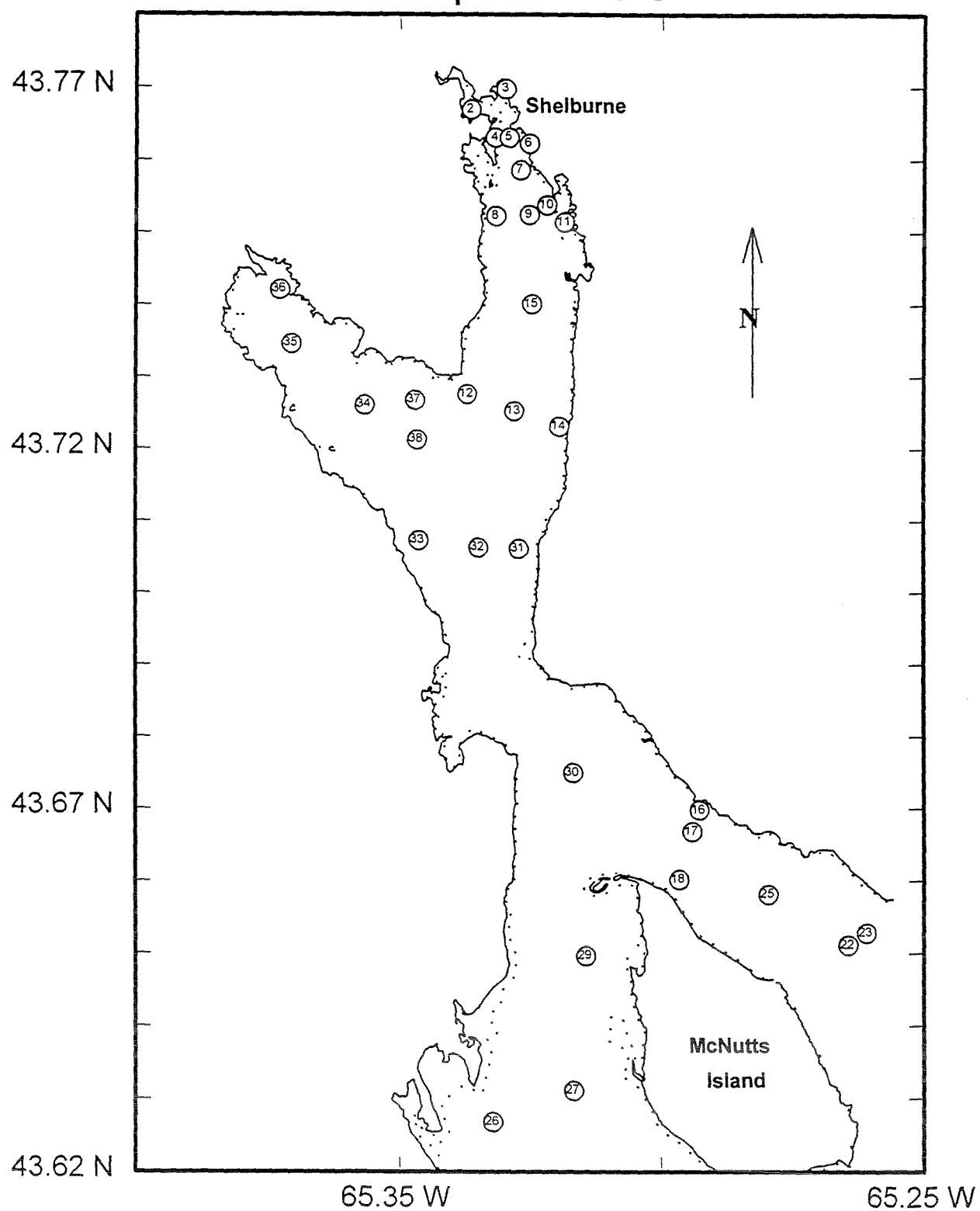OM = % by weight organic matter

Shelburne Harbour
Sample Locations

Figure 144. Sample locations for Shelburne Harbour
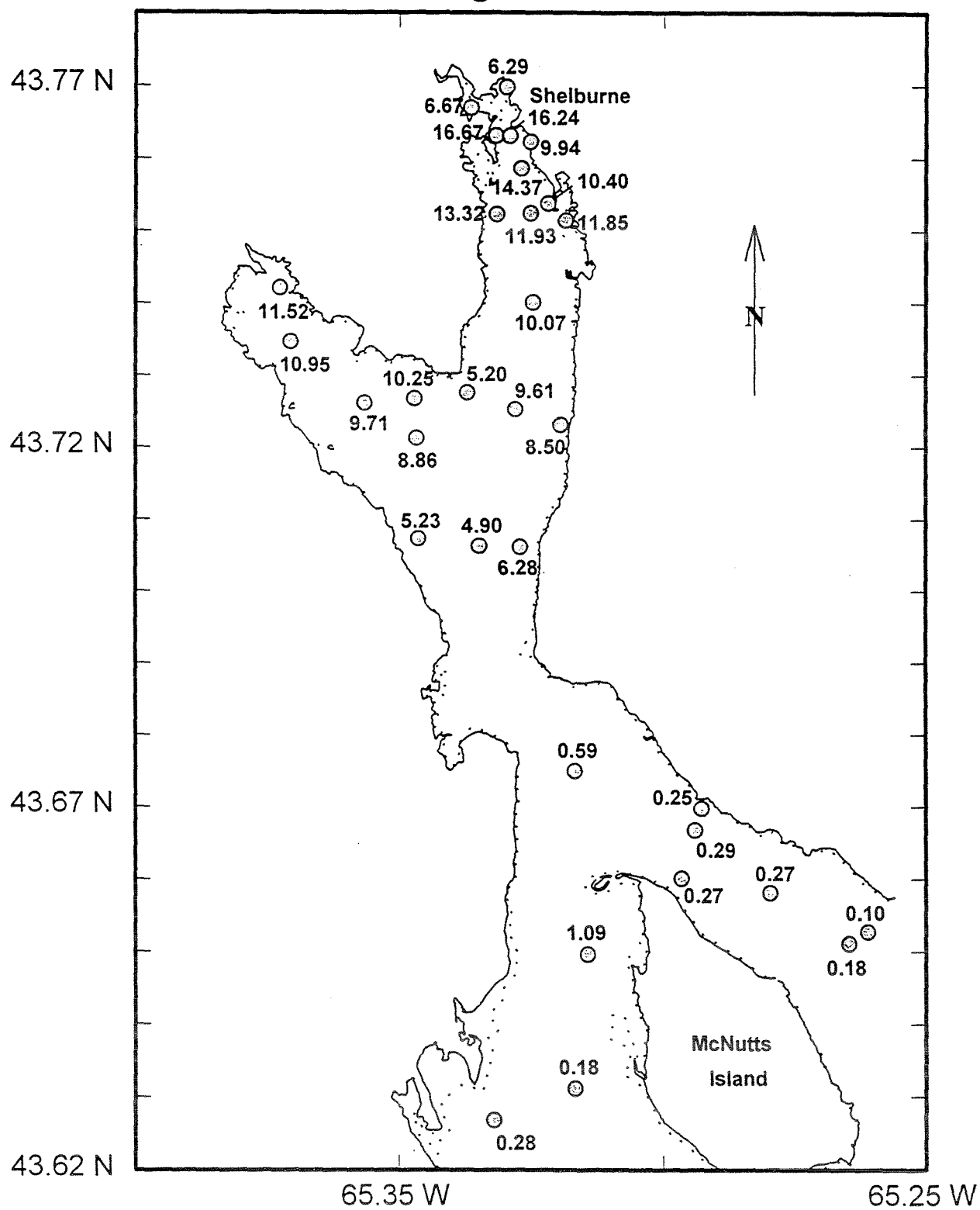
Shelburne Harbour
% Organic Matter

6.29

Shelburne

6.67

16.24

16.67

9.94

14.37

10.40

13.32

11.85

11.93

11.52

10.07

10.95

10.25

5.20

9.71

9.61

8.86

8.50

5.23

4.90

6.28

0.59

0.25

0.29

0.27

0.27

0.10

1.09

0.18

McNutts
Island

0.18

0.28

43.77 N

43.72 N

43.67 N

43.62 N

65.35 W

65.25 W

N

Figure 145. Organic matter concentrations in surficial sediments
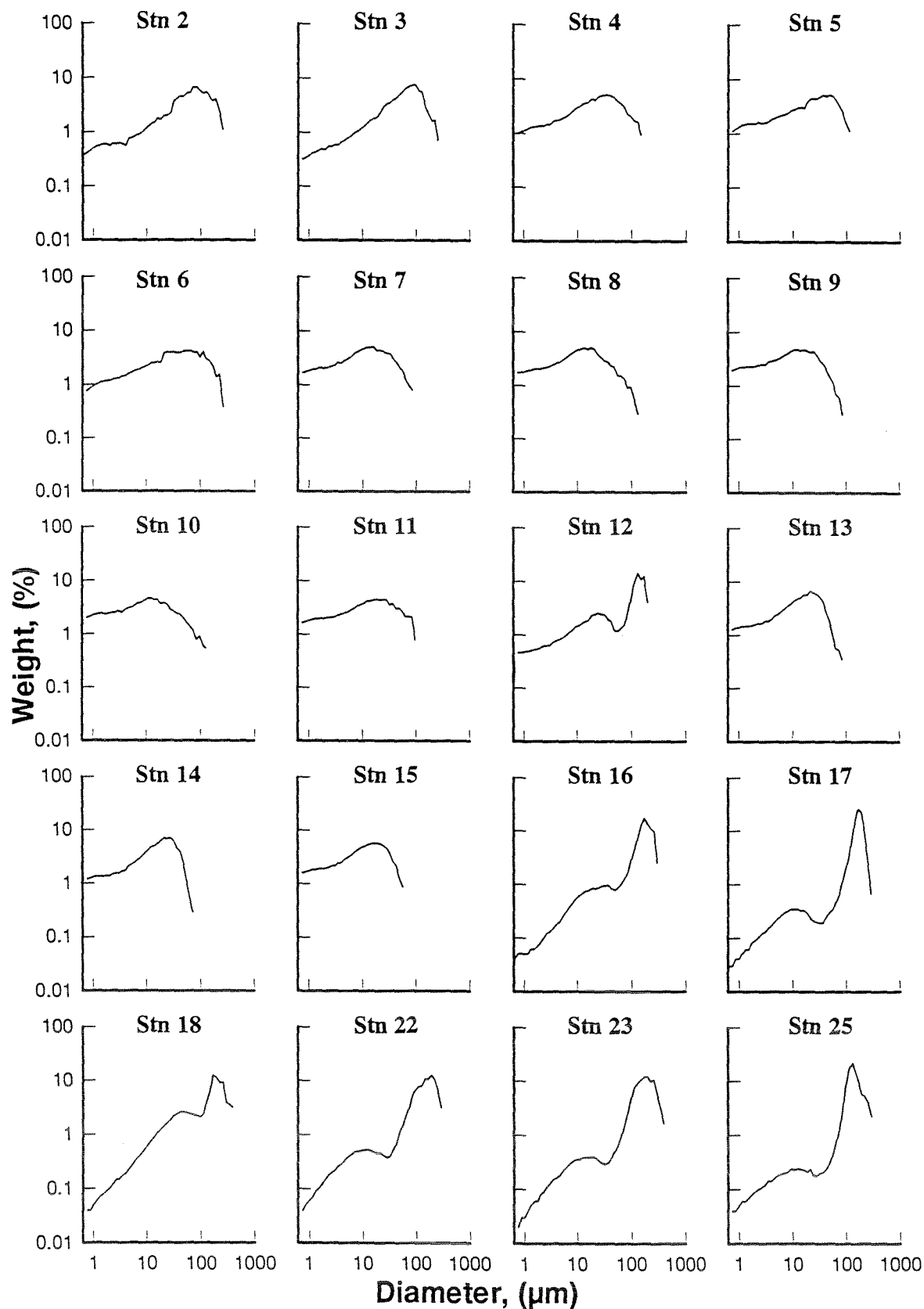
Shelburne Harbour

Figure 146. Disaggregated inorganic grain size distributions
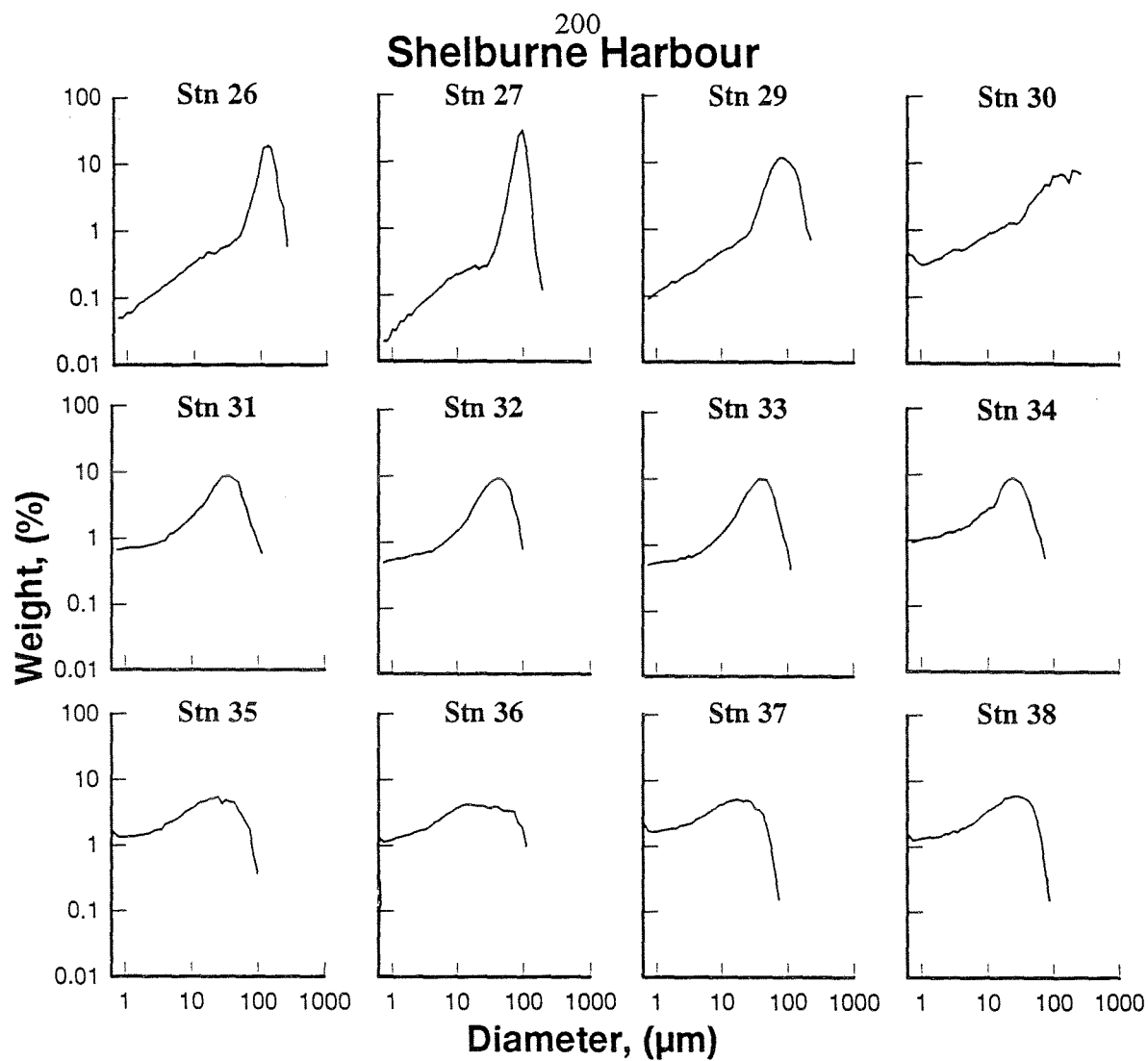
Shelburne Harbour

Figure 146. Disaggregated inorganic grain size distributions

Shelburne Harbour
Al %
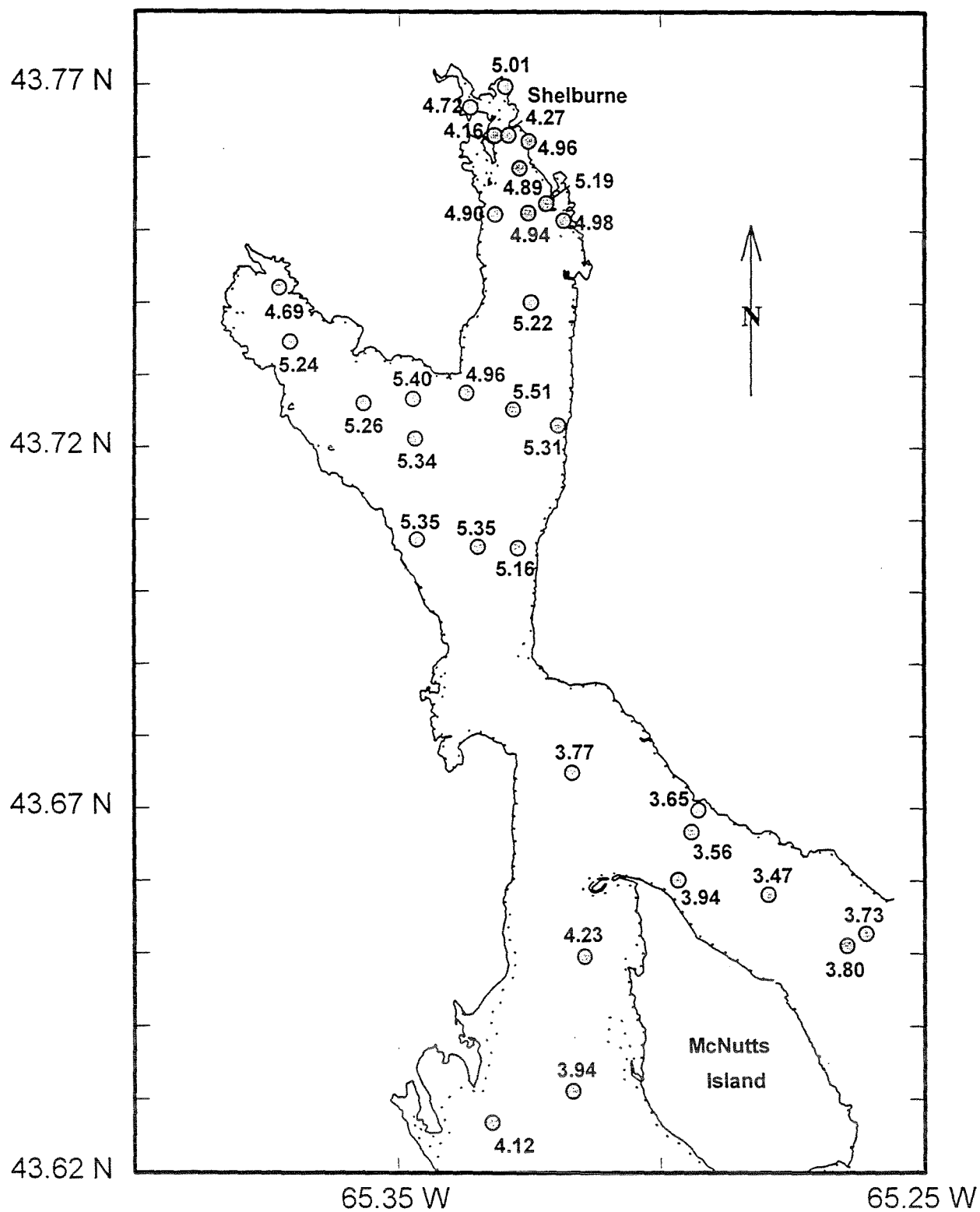
Figure 147. Aluminium concentrations in surficial sediments

202

Shelburne Harbour
Fe %
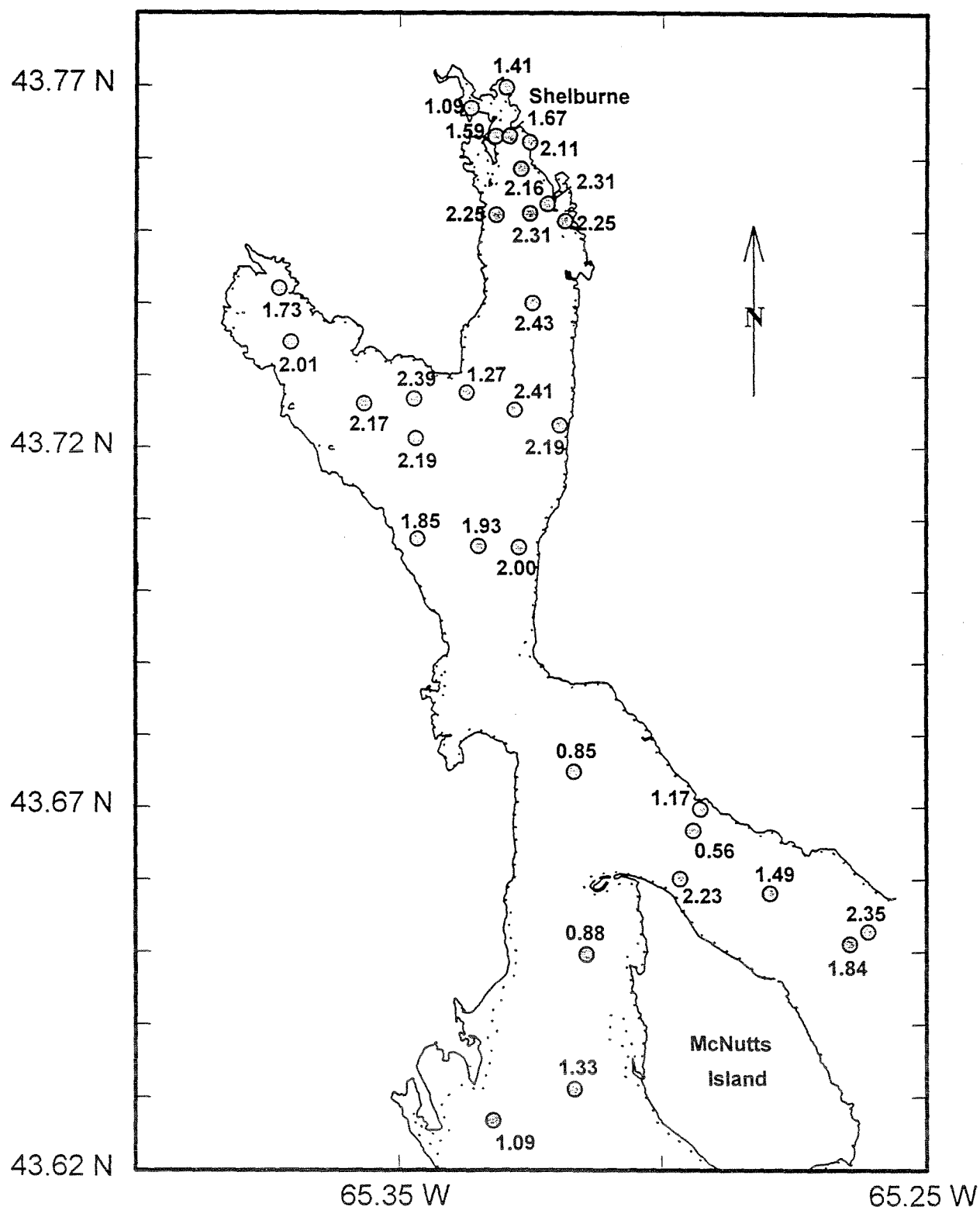
Figure 148. Iron concentrations in surficial sediments
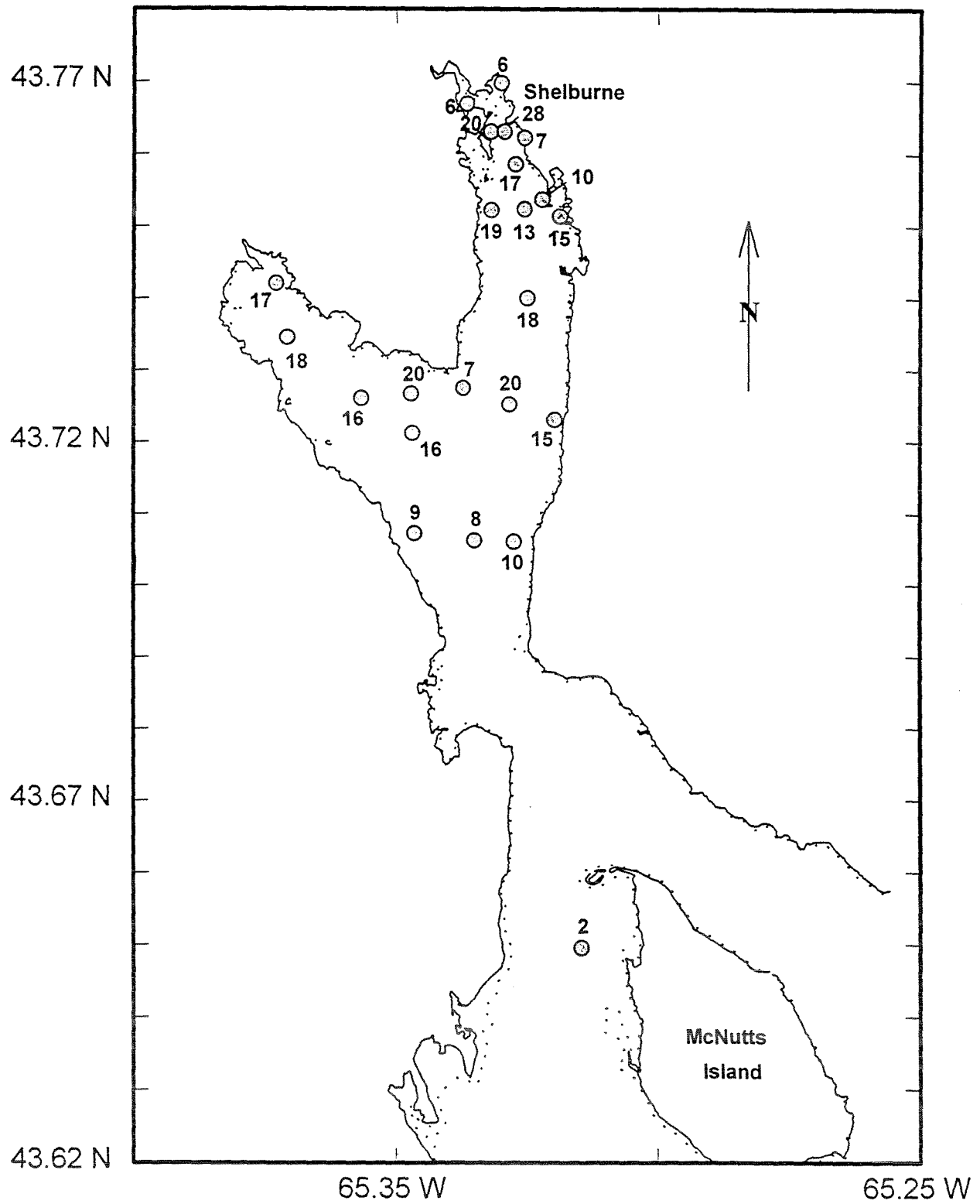
Shelburne Harbour
As mg/kg

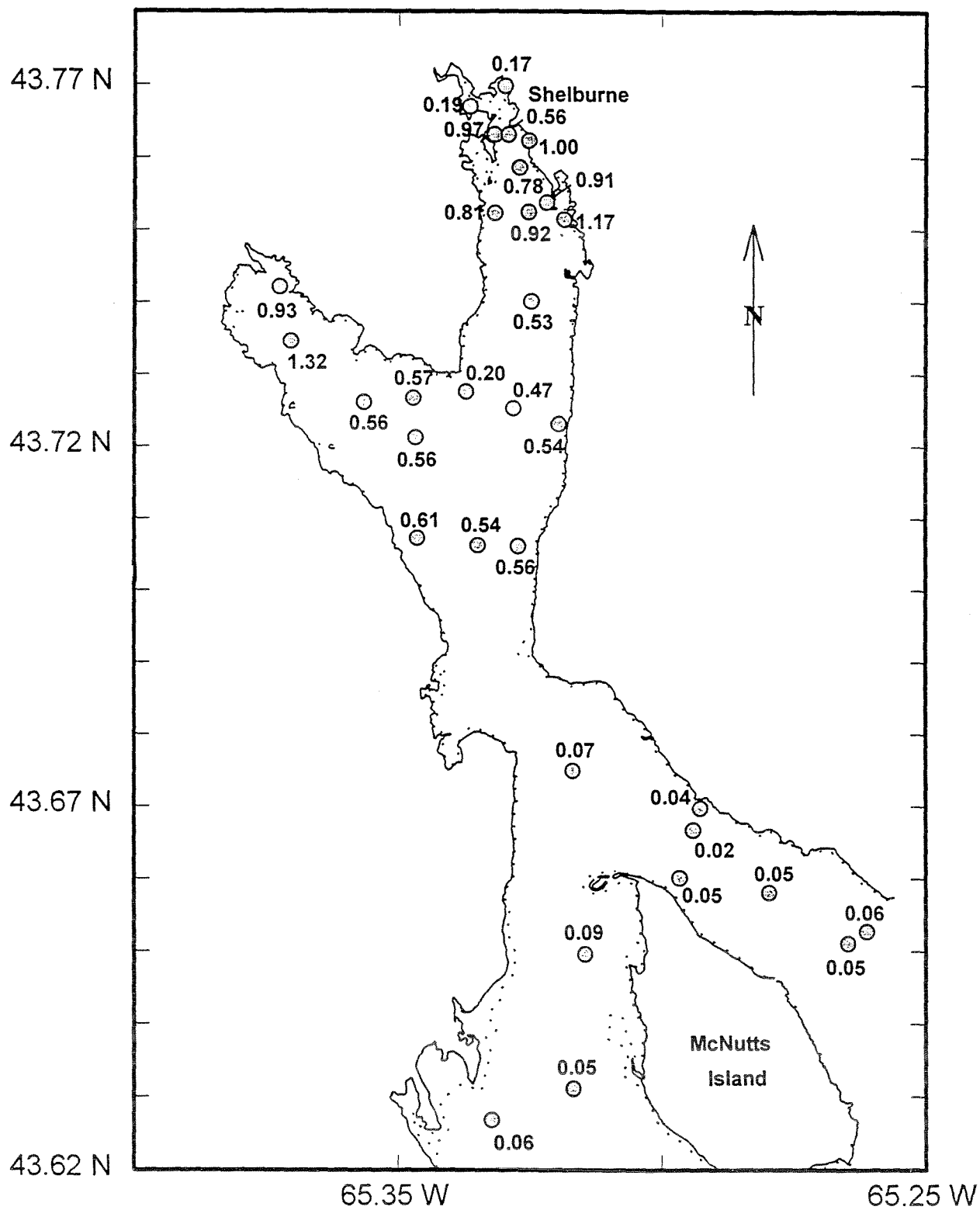**Figure 149.** Arsenic concentrations in surficial sediments
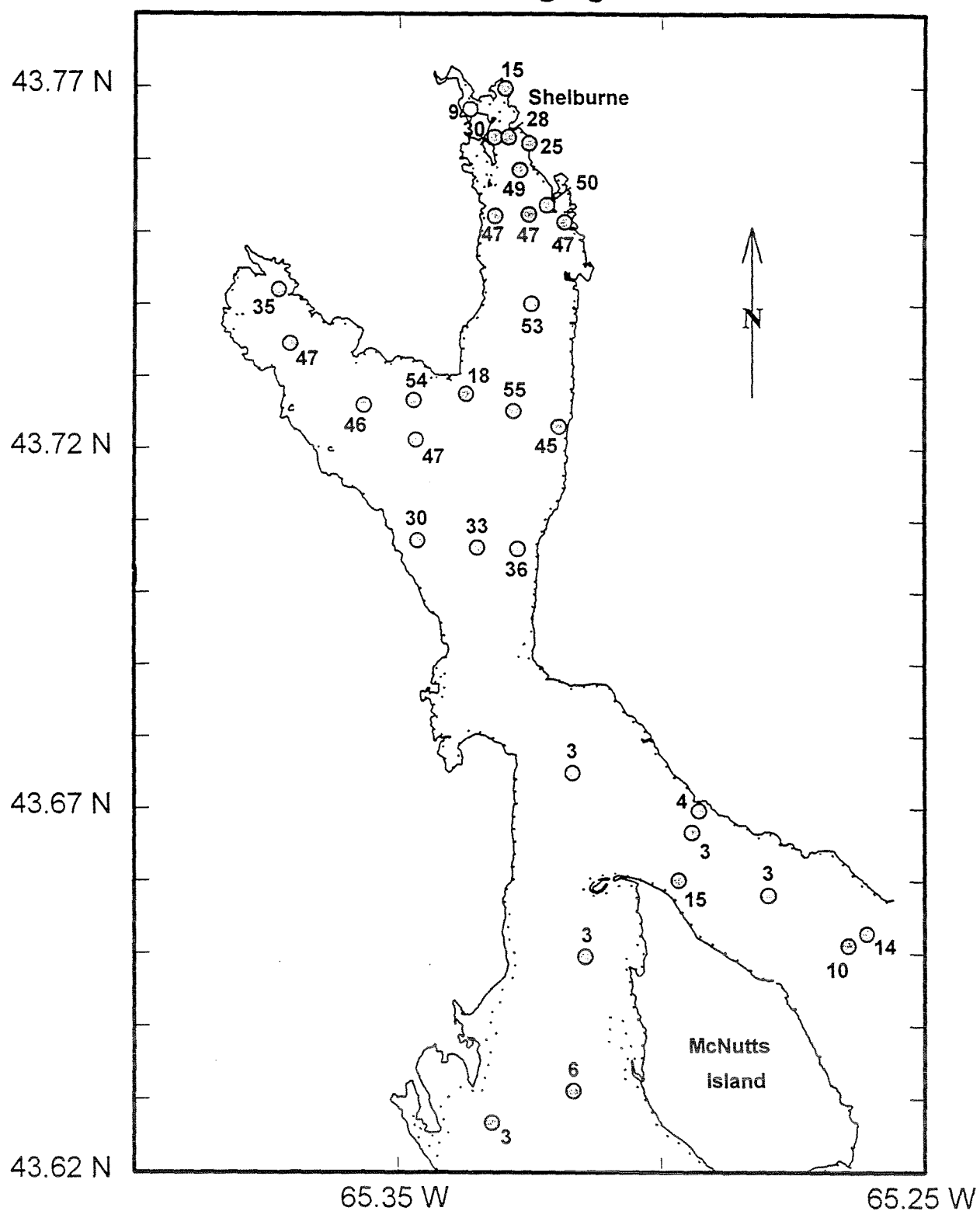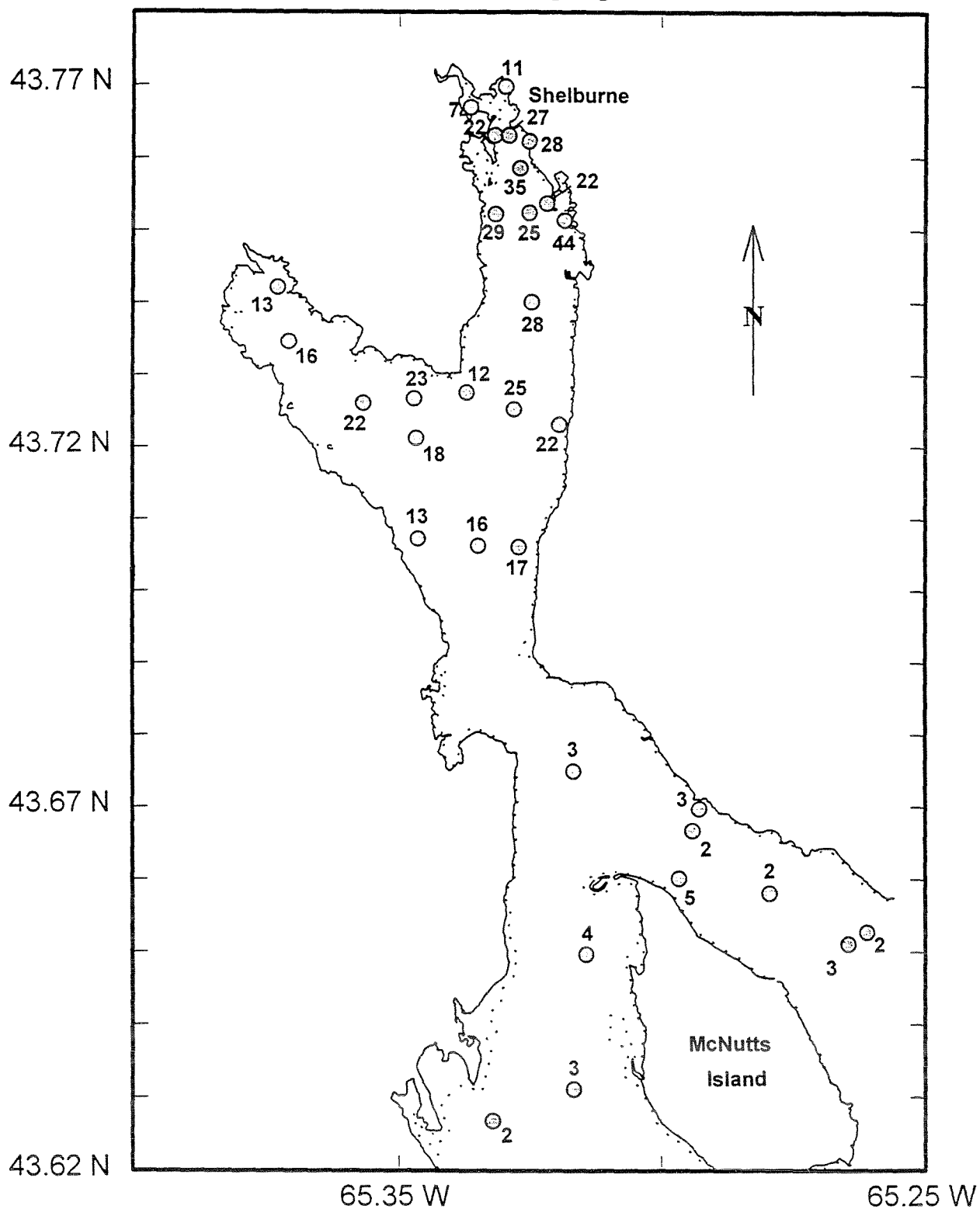
Shelburne Harbour
Cd mg/kg

0.17

Shelburne

0.19

0.56

0.97

1.00

0.78 0.91

0.81 1.17

0.92

0.93

0.53

1.32

0.57 0.20

0.47

0.56

0.54

0.56

0.61 0.54

0.56

N

0.07

0.04

0.02

0.05

0.05

0.06

0.09

0.05

43.77 N

43.72 N

43.67 N

McNutts
Island

0.05

0.06

43.62 N

65.35 W   65.25 W

Figure 150. Cadmium concentrations in surficial sediments

Shelburne Harbour
Cr mg/kg

Figure 151. Chromium concentrations in surficial sediments

Shelburne Harbour
Cu mg/kg

Figure 152. Copper concentrations in surficial sediments
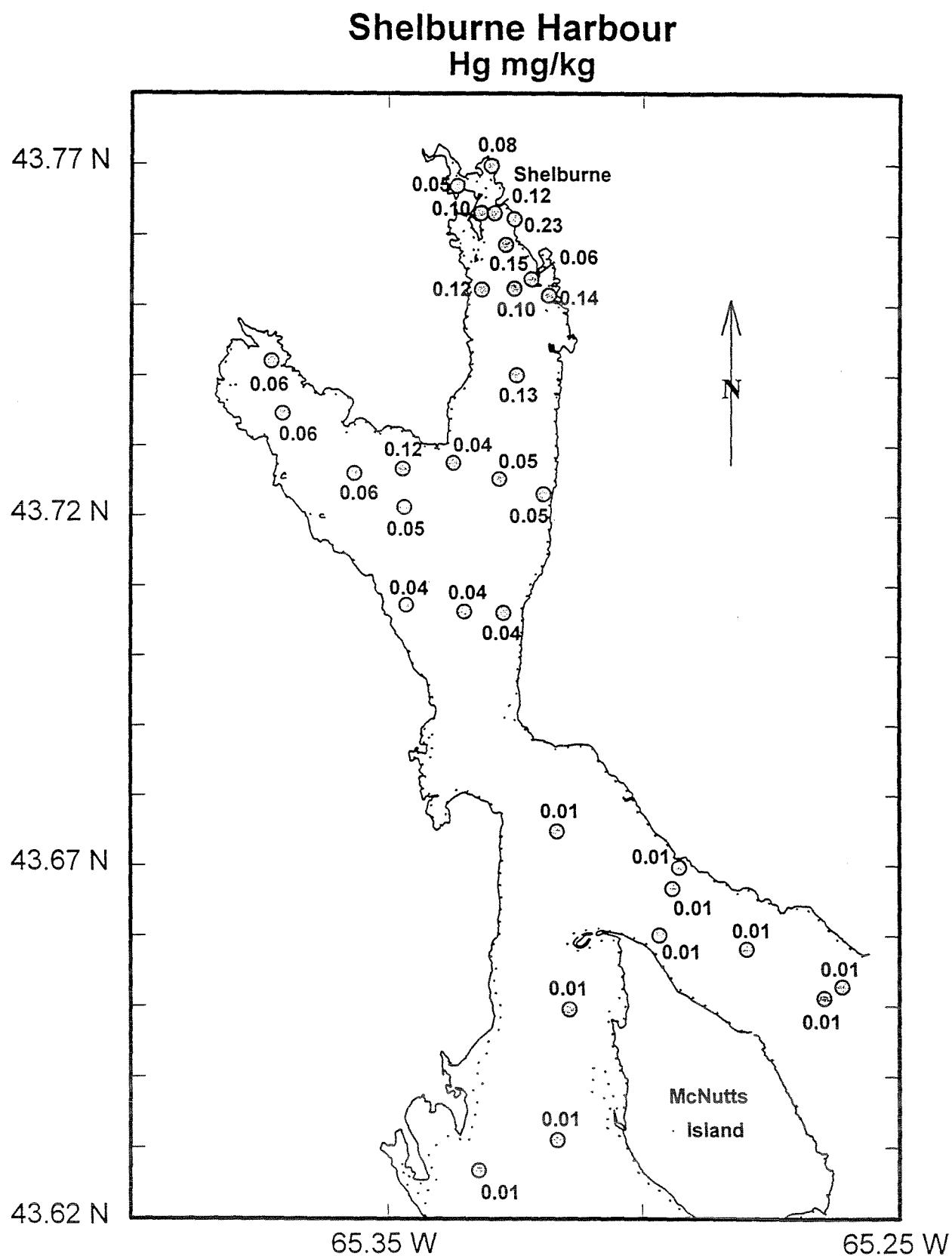
Shelburne Harbour
Hg mg/kg

Figure 153. Mercury concentrations in surficial sediments
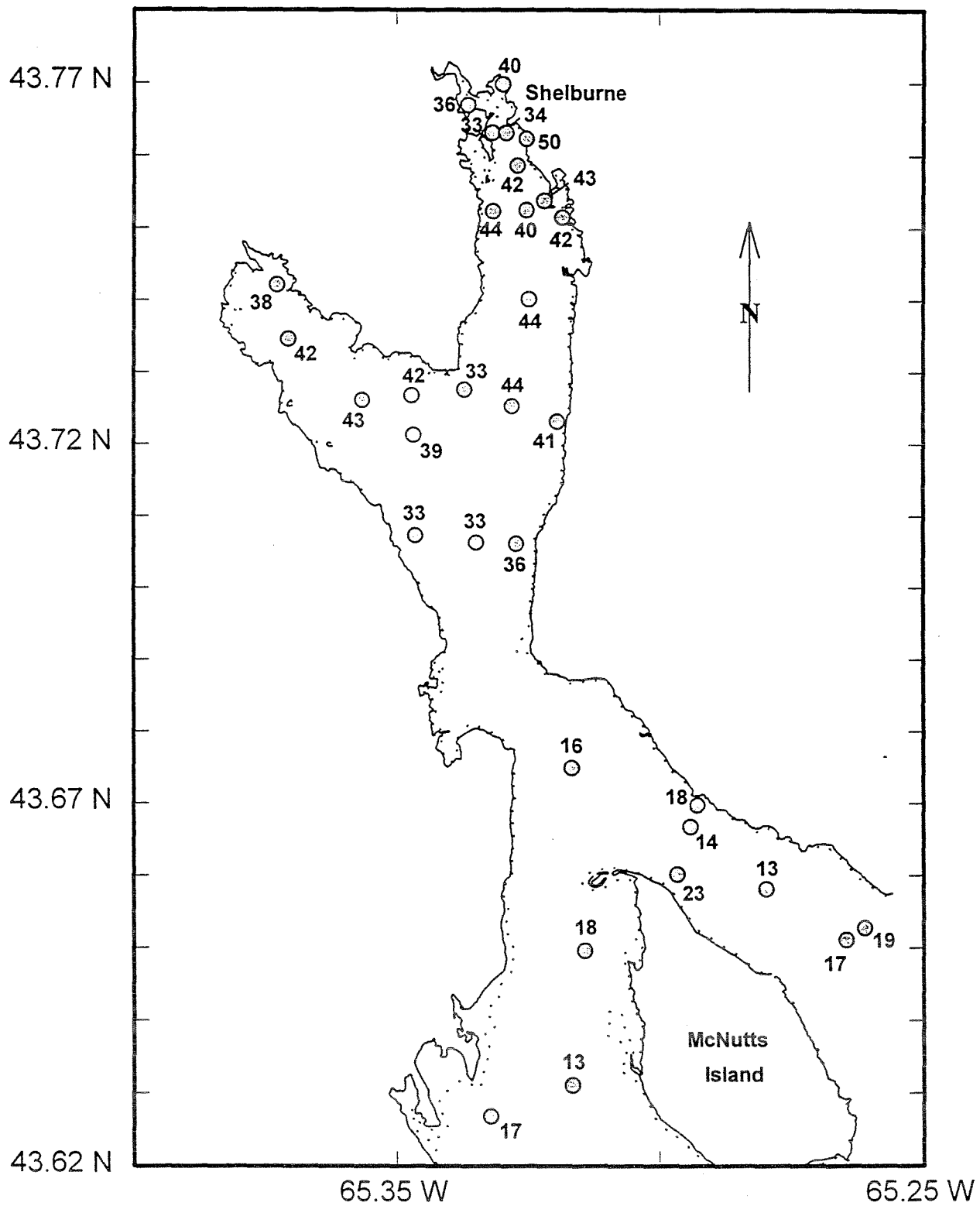
Shelburne Harbour
Li mg/kg

Figure 154. Lithium concentrations in surficial sediments

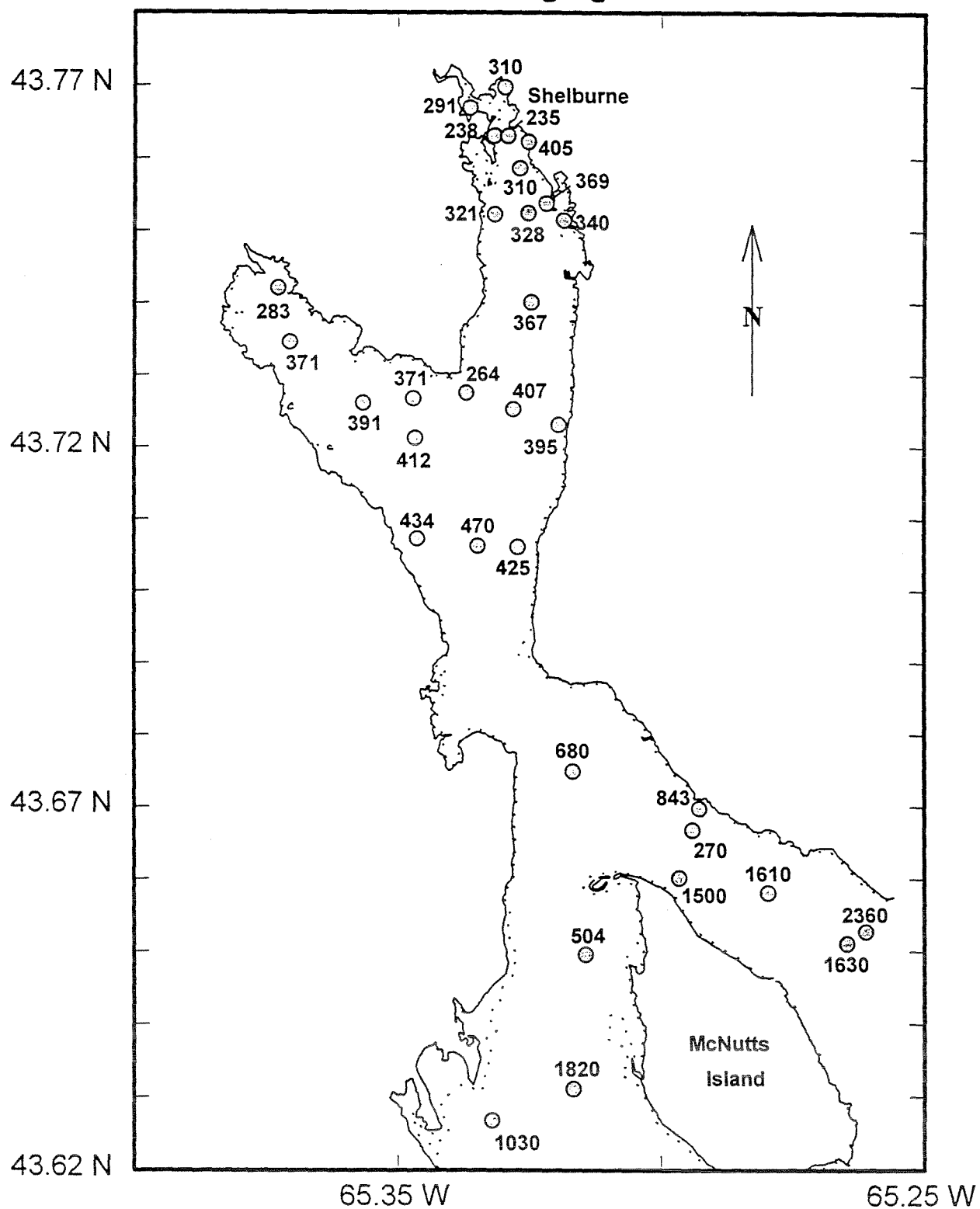# Shelburne Harbour
Mn mg/kg

Figure 155. Manganese concentrations in surficial sediments

Shelburne Harbour
Ni mg/kg

Figure 156. Nickel concentrations in surficial sediments

Shelburne Harbour
Pb mg/kg

Figure 157. Lead concentrations in surficial sediments

Shelburne Harbour
Sn mg/kg

Figure 158. Tin concentrations in surficial sediments
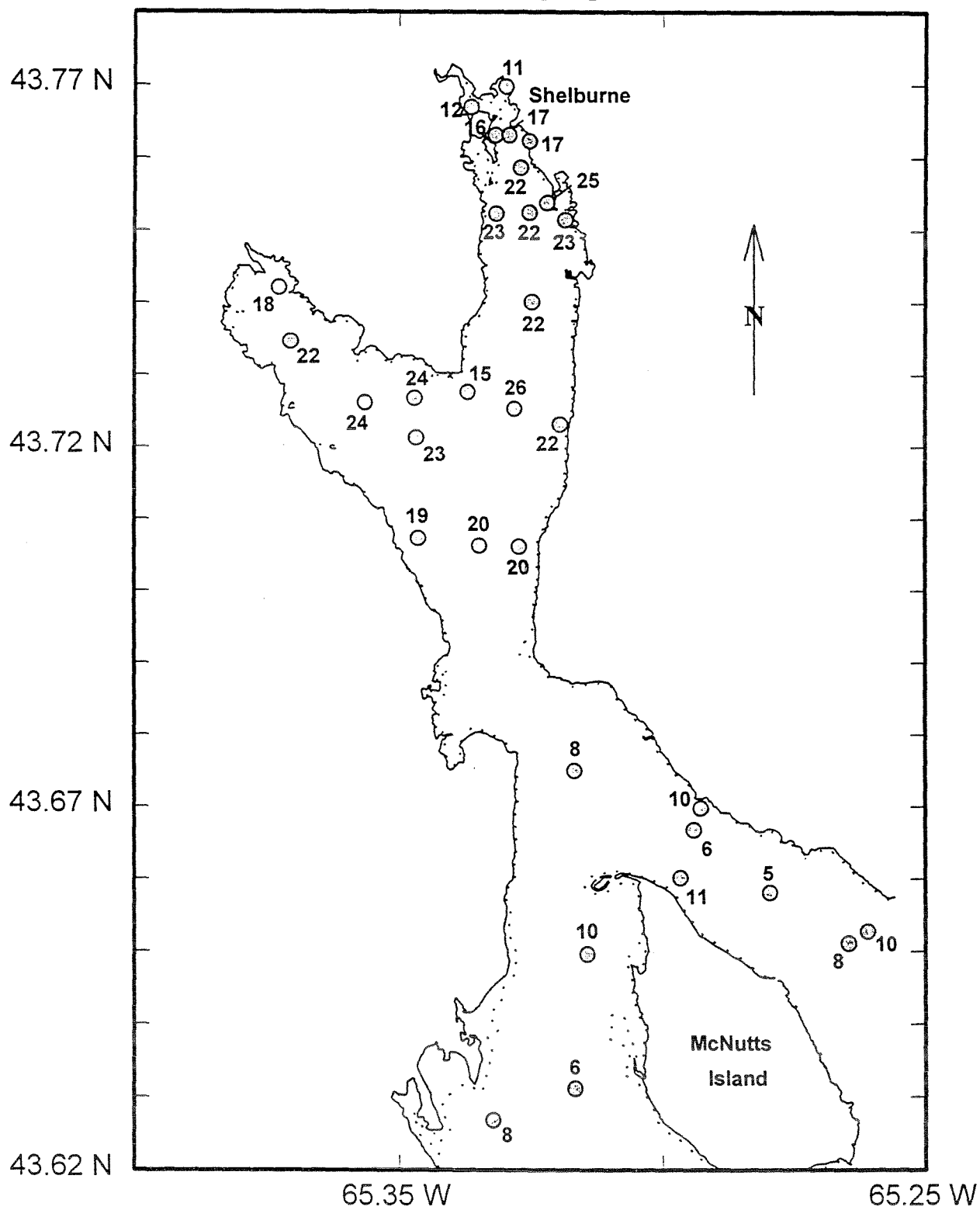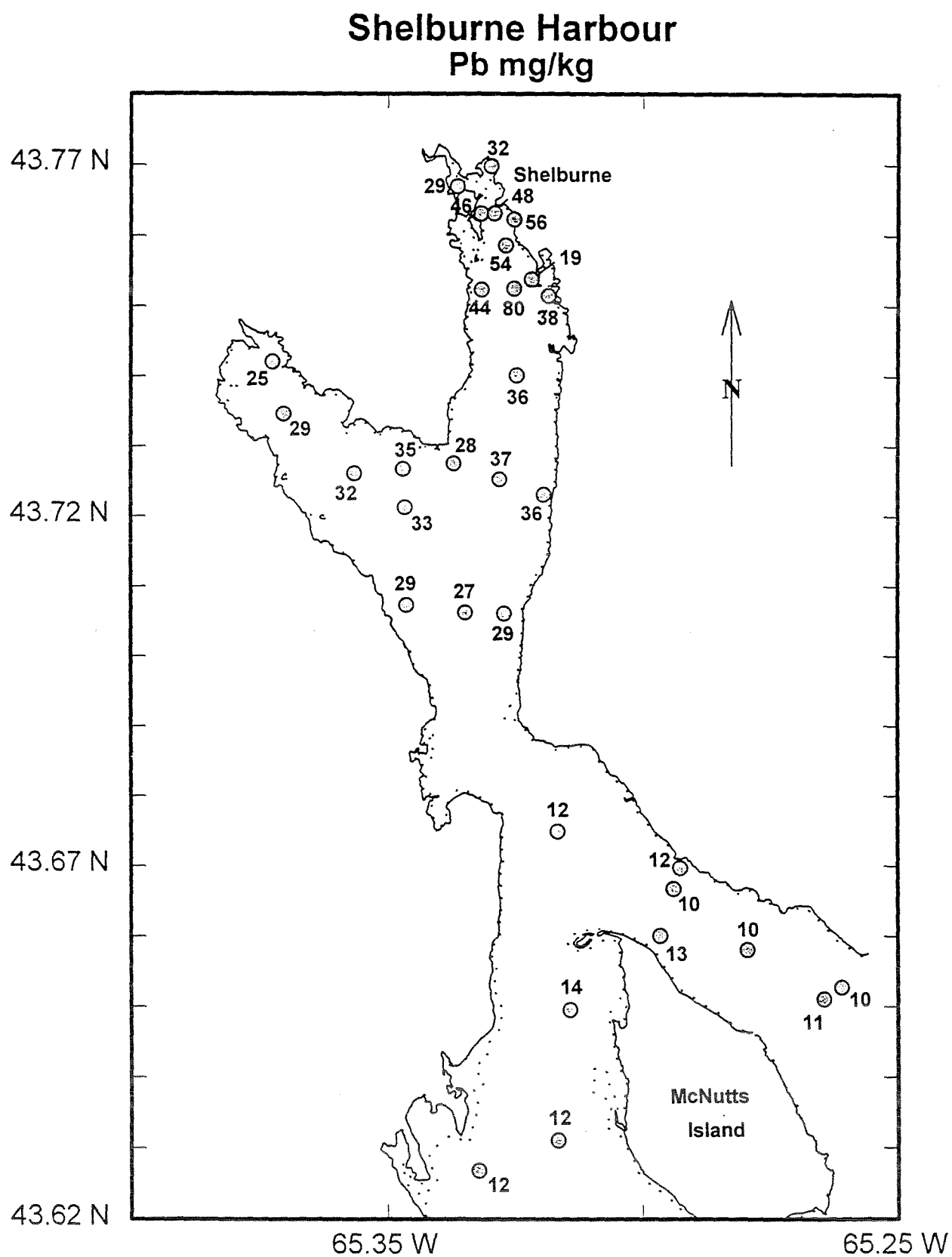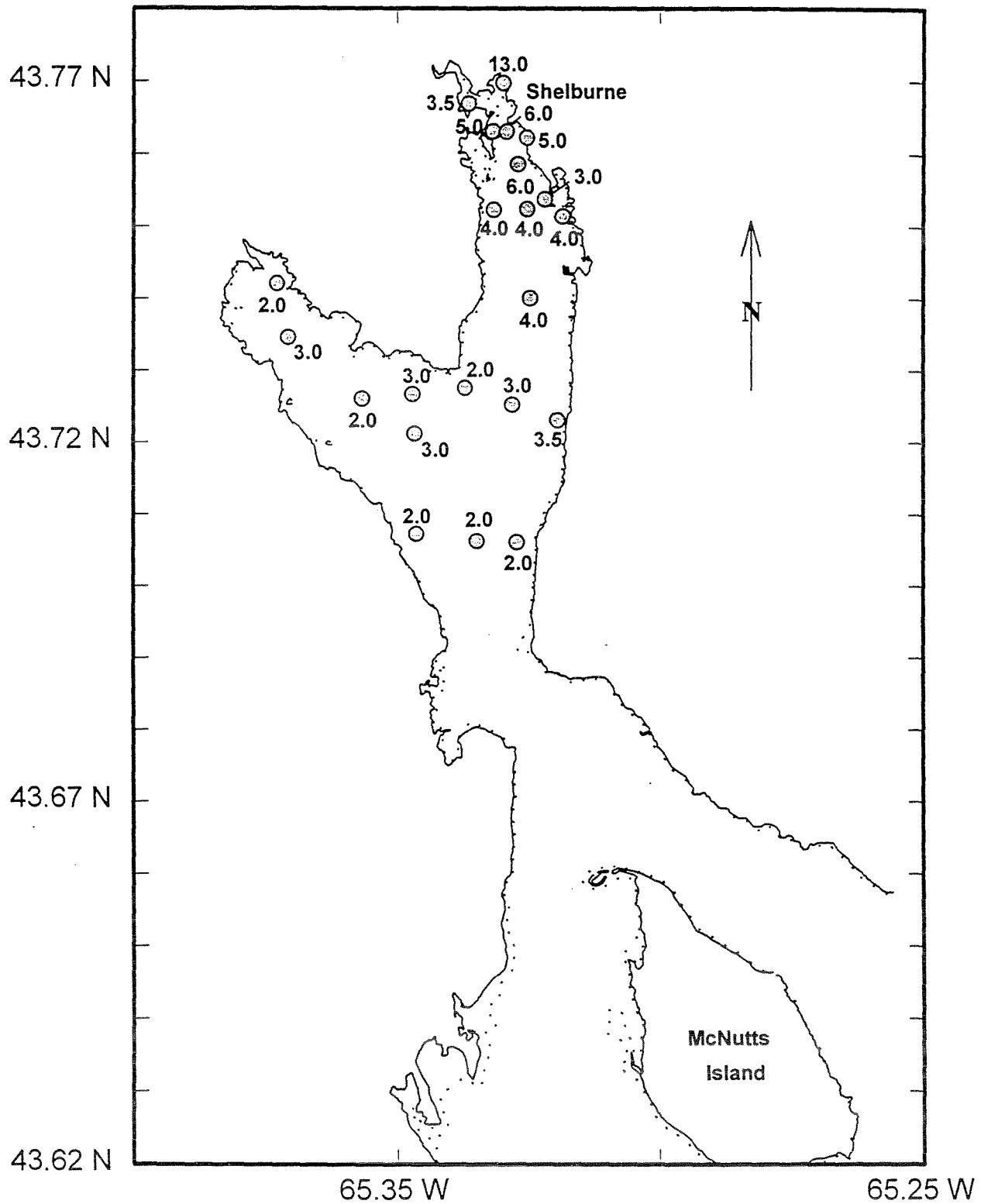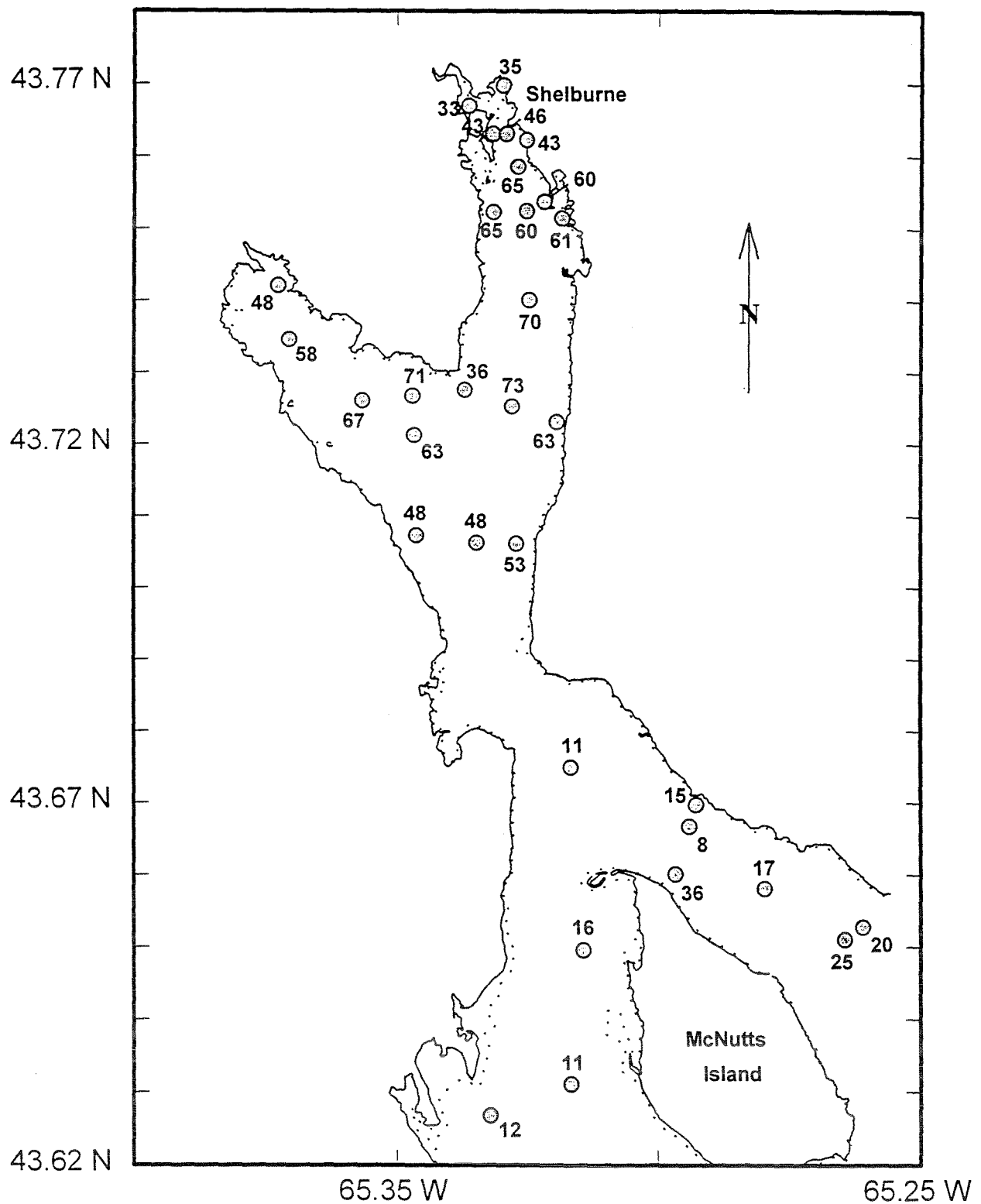
Shelburne Harbour
V mg/kg

Figure 159. Vanadium concentrations in surficial sediments
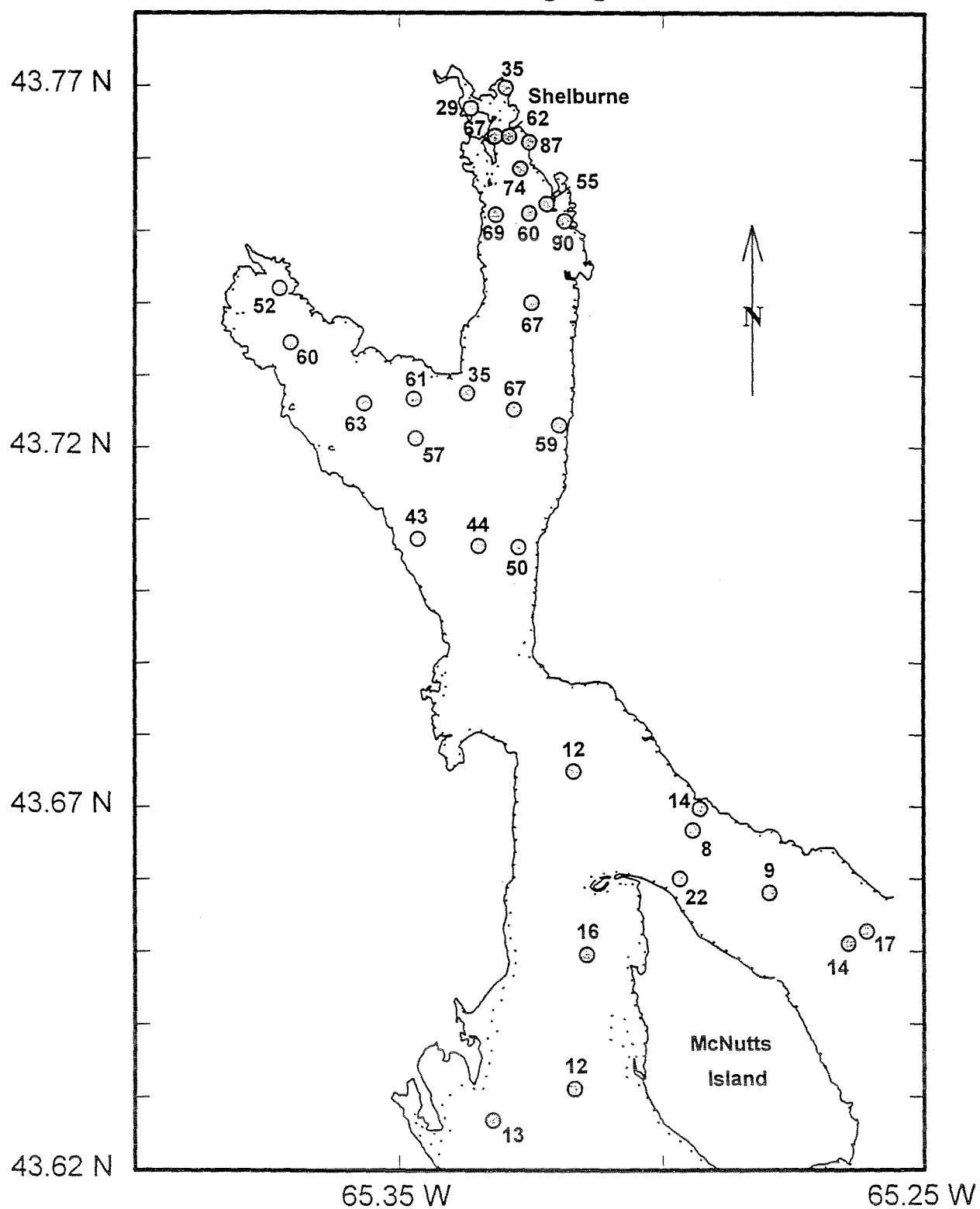
Shelburne Harbour
Zn mg/kg

Figure 160. Zinc concentrations in surficial sediments

SHIP HARBOUR

Ship Harbour occupies a long (8.3 km), narrow (0.3 km), deep (water depths up to 30 m) inlet running into the eastern shore of Nova Scotia approximately 70 km northeast of Halifax. The Harbour receives drainage from Ship Harbour River which has a drainage area of 447.7 km^2. The area is mainly wooded, with the vegetation developed on a thin mantle of glacial till underlain primarily by Devonian granites and Precambrian quartzites and slates. The village of Ship Harbour is located at the head of the inlet, and a narrow strip of cultivated land along the shores is occupied by houses and small farms. Mussel aquaculture is carried out in the inner part of the Harbour.

POTENTIAL SOURCES OF CONTAMINATION

Aside from the potential contributions of harmful substances from the local inhabitants and the mussel aquacultural activities, there are no known sources of contaminants.

RESULTS

Sediment Samples and Composition

The location of the sampling stations in Ship Harbour is shown in Figure 161. The nearshore sediments are composed of sands and muddy sands, and the deep areas are occupied by fine-grained organic-rich muds (Fig. 162). Most of the samples obtained were fine-grained muds containing 85-100% by weight <63-μm sized material. Their modal size varies from 5 to 48 μm with most of the sediments (45%) having a mode size of 5-10 μm.

Sediments in Ship Harbour fall into three distinct groups based on size distribution (Fig. 163). At the head of the Harbour, the size distributions are dominated by the steep-sloped till source material which can be seen in the size distribution for Station 3 which was sampled from an eroding bank. Station 1, located in the Ship Harbour River, has an identical slope and configuration but has been truncated at the coarse end, an indication of the maximum carrying capacity of the stream (Fig. 3). The second depositional region in Ship Harbour lies between the line of stations (Stations 5 to 7) at the head of the Harbour and the sill found near Laybolt's Island, at Stations 17 to 19. Within the region above the sill, sedimentation is dominated by floc settling, and little or no higher round sediments are present. Modal diameters are less than 20 μm, and only very minor amounts of coarser material (ca. 5%) are present. The floc portion of the sediment ranges from 40-100%, with the majority of samples having over 80% floc-derived sediment. Throughout this region, the source slope remains constant with a mean value of 0.22. The third depositional area is defined by the change in source slope and conformation and is located offshore of Stations 17 to 19. With the exception of the sediments at Station 20, the samples collected in this region have very flat source slopes, mean 0.09, and well-sorted modal peaks with the outermost stations (Stations 25 and 26) having coarse, multi-round fine sand peaks

and only very minor flat tail portions. The sediment sample collected near the shore at Station 20 has a size distribution similar to those found above the sill. This is probably due to the presence of very recently eroded material from the shoreline. The floc-settled component of the sediments further out from the sill drops significantly and ranges from 1-30%, with the highest values being found in the region of the sill. In the exposed outer reaches of the Harbour, the floc portion of the sediment falls to less than 5%. The source slopes for the floc-settled samples appear to be the result of mixing of offshore water with weathered material from the shore.

The sediment size distributions for Ship Harbour indicate that considerable trapping of fine particulate material is occurring in the central region. The lack of coarse, sorted material and the total dominance of the floc portion shows that this part of Ship Harbour is highly depositional and that the material being deposited is not subject to reworking.

Abundance and Distribution of Metals

The distribution of As, Cd, Cr, Cu, Pb, and Zn in Ship Harbour are shown in Figures 164 to 177. These figures indicate the highest concentrations of the metals occur in the inner part of the Harbour near the mouth of Ship Harbour River. The range of total metal concentrations in the sediments (n=12) are: As, 5-19 $mg \cdot kg^{-1}$; Cd, 0.17-2.2 $mg \cdot kg^{-1}$; Cr, 35-82 $mg \cdot kg^{-1}$; Cu, 13-29 $mg \cdot kg^{-1}$; Hg, 0.01-0.13 $mg \cdot kg^{-1}$; Ni, 18-34 $mg \cdot kg^{-1}$; Pb, 14-44 $mg \cdot kg^{-1}$; Sn, 1.4-3.2 $mg \cdot kg^{-1}$; V, 33-87 $mg \cdot kg^{-1}$; and Zn, 32-97 $mg \cdot kg^{-1}$ (Table 24). Most of the metals are at or near natural concentrations except for Cd, Hg, and Pb. Relatively high Cd concentrations (>0.3 $mg \cdot kg^{-1}$) occur in 92% of the samples. Of these, 63% exceed the limit for ocean dumping of 0.6 $mg \cdot kg^{-1}$ and 21% of them contain Cd concentrations >1 $mg \cdot kg^{-1}$ (Table 2). Mercury and lead concentrations also exceed their normal background levels in 17% of the samples.

Potential Bioavailability of Metals

Chemical partitioning data for the sediments are not available.

Metal Carriers and Sources

The strong negative correlation of all the metals, except As and Mn, with mode size (Table 25) indicates that the metals are concentrated in the finest sediments, i.e. concentrations increase with decreasing mode size, with the highest concentrations occurring in the sediments having a mode size between 5 and 10 μm. The positive covariance (p<0.001) of As (r=0.86), Cr (r=0.92), Cu (r=0.82), Pb (r=0.70), Sn (r= 0.97), and Zn (r=0.70) with Li (Table 23) shows that Li normalizes for the granular and mineralogical variability in the surface sediments. The proportion of the metal variability thus explained decreases in the order: Sn (94%) > Cr (86%) > As (70%) > Cu (65%) > Pb (48%) = Zn (48%) >> Hg (15%) > Cd (10%). The significant positive relationship between Cr and Al (12 samples) and the covariance of As and Cr with Li and

Fe suggests that these metals are located in the iron-rich aluminosilicates such as the ferromagnesium minerals, chlorites, and discrete chromium-bearing detrital oxide minerals such as magnetite and chromite.

Factor analyses indicate that the deposition of fine-grained Fe aluminosilicate material such as chlorite, carrying Cr, Cu, Li, Sn, and, to a lesser extent As and Pb, is the main factor (45% of the variance) controlling the deposition of these metals. Inspection of the correlation matrix (Table 24) indicates strong correlations between As, Cd, and Hg with the organic fraction (measured as loss on ignition %), indicating the association of these metals with the fine-grained organic-rich components. Factor analyses further indicate that the deposition of organic-rich fine-grained material containing Cd, Hg, and to a lesser extent As and Pb, accounts for 36% of the total variance. The significant negative covariances of Cu, Pb, and Zn with mode size, and positive covariances with loss on ignition, suggests that in addition to being structurally combined in the phyllosilicates, anomalous levels of these metals are also present along with Cd and Hg in metal-bearing iron monosulphides and/or pyrite formed *in situ* in the organic-rich, fine-grained sediments. The strong positive correlation of Cd, which is usually HOAc soluble, with loss on ignition suggests that Cd is weakly held by the fine-grained organic component. The anomalous concentrations of Cd and Hg, therefore, are most likely a consequence of biological activity and organic waste deposited in the estuary.

Table 24

Textural and metal statistics[a] for the Ship Harbour estuarine sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	24	95.5	± 4.2	85-100	LOI%	24	23.5	± 12.3	5-49
Metal					Metal				
Al%	12	4.49	± 0.68	3.30-5.90	Fe%	24	2.68 ±	0.54	1.50-3
As	12	10.8	± 4.3	5-19	Li	24	39.1 ±	6.7	23-50
Cd	24	0.81	± 0.44	0.17-2.16	Ni	12	26.9 ±	5.5	18-34
Cr	24	64.3	±13.1	35-82	Pb	24	31.6 ±	8.7	14-44
Cu	24	23.3	± 4.9	13-29	V	12	60.9 ±	17.8	33-87
Hg	24	0.06	± 0.03	0.01-0.13	Zn	24	71.0 ±	19.0	32-97
Mn%	24	0.044 ±	0.006	0.031-0.051	Sn	12	2.3 ±	0.6	1-3

[a]Concentrations in mg kg^{-1} except percent (%) for mud, LOI, Al, Fe, and Mn

Table 25

Correlation Matrix Ship Harbour

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	x	0.89	1									
Cr	0.86	0.90	x	1								
Cu	x	0.94	0.71	0.78	1							
Fe	x	0.94	x	0.86	0.92	1						
Hg	x	0.83	0.88	x	0.73	x	1					
Li	0.92	0.86	x	0.92	0.82	0.88	x	1				
Mn	x	x	x	x	x	x	-0.67	x	1			
Pb	0.91	0.87	0.71	x	0.80	0.67	0.82	0.70	x	1		
Sn	0.94	0.90	0.83	0.96	0.91	0.93	0.84	0.97	x	0.98	1	
Zn	x	0.93	0.81	0.63	0.95	0.81	0.87	0.70	x	0.89	0.86	1
mud	x	x	x	x	0.67	0.67	x	x	x	x	x	x
LOI	x	0.88	0.82	x	0.72	x	0.88	x	-0.68	0.77	0.81	0.85
mode	-0.94	-0.79	-0.68	-0.65	-0.90	-0.79	-0.79	-0.78	x	-0.86	-0.93	-0.90

n = 24

For $p \leq 0.001$ x = not significant

mud = >70% by weight material<63µm

LOI = % by weight Loss on Ignition

mode = Coulter Counter equivalent grain size

Ship Harbour
Sample Locations

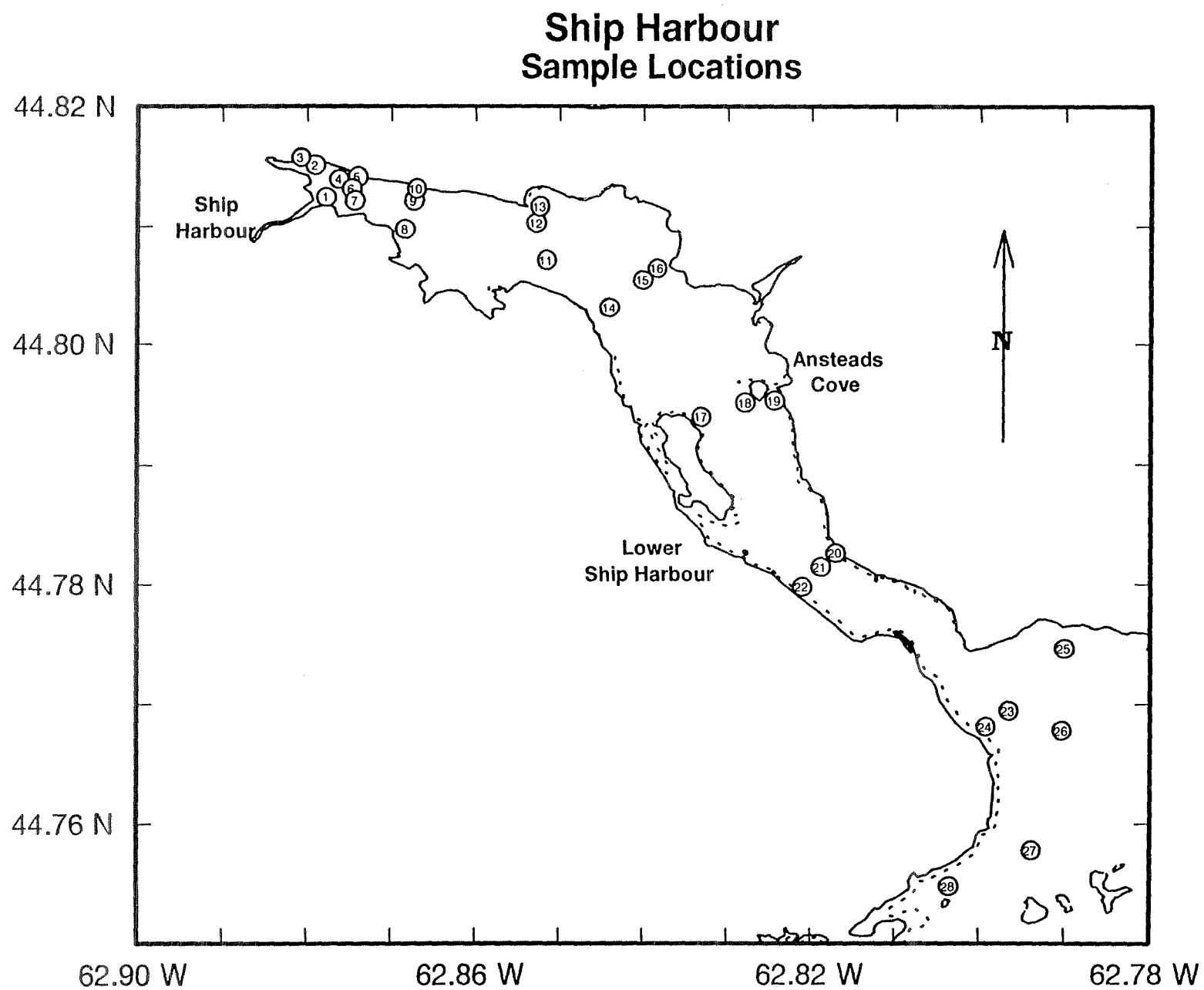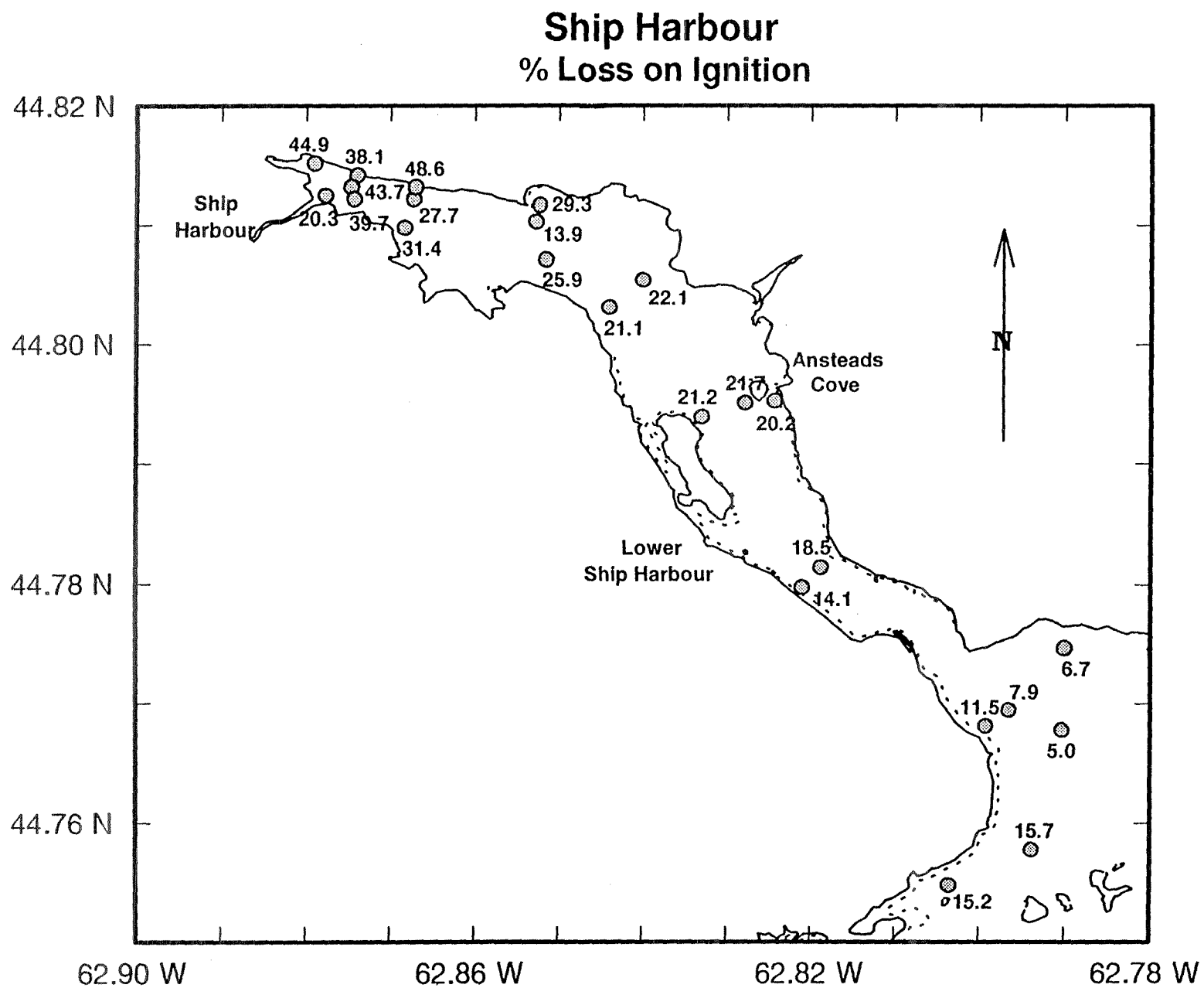Figure 161. Sample locations for Ship Harbour

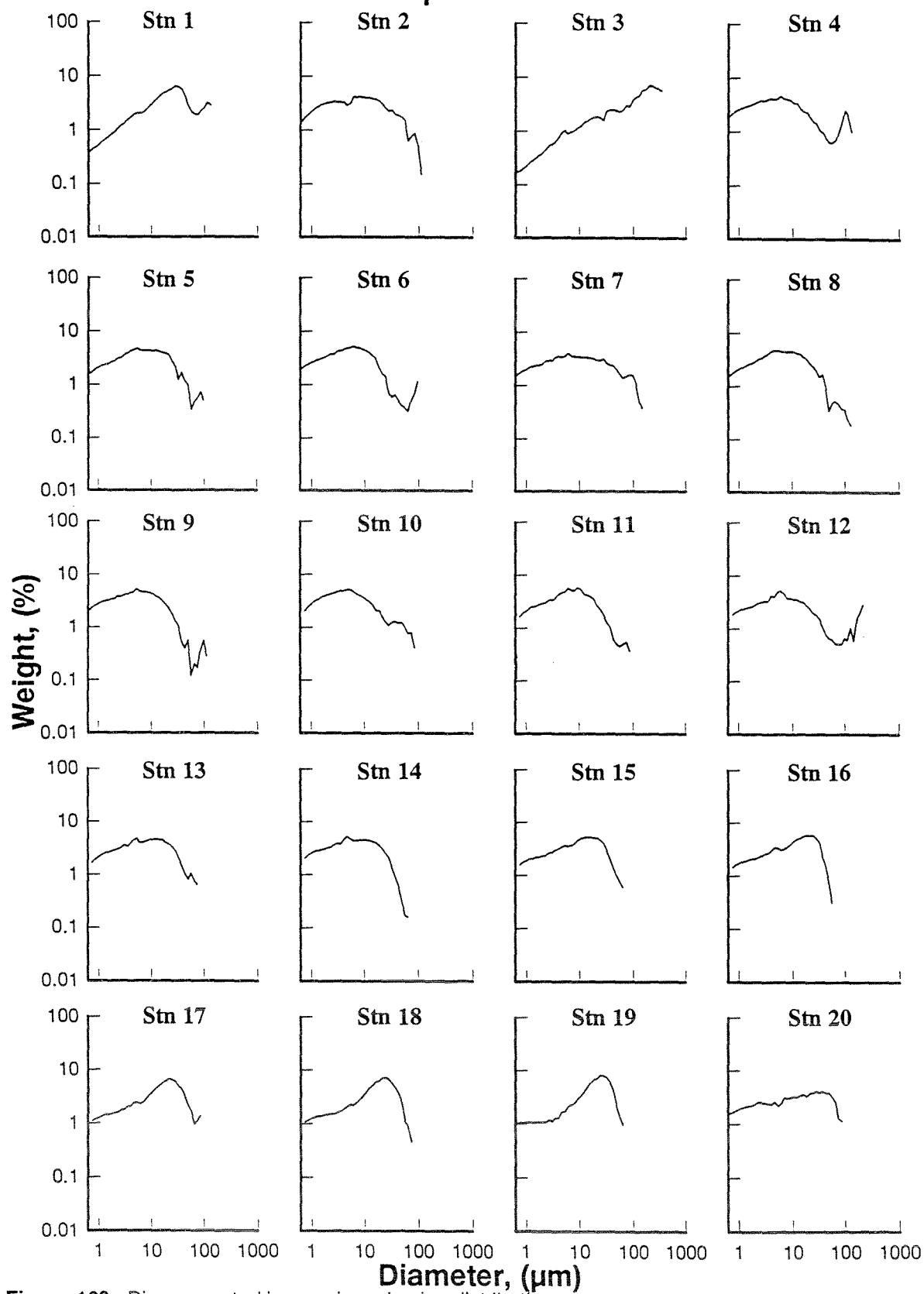Figure 162. Loss on ignition in surficial sediments

Ship Harbour

Figure 163. Disaggregated inorganic grain size distributions

Ship Harbour
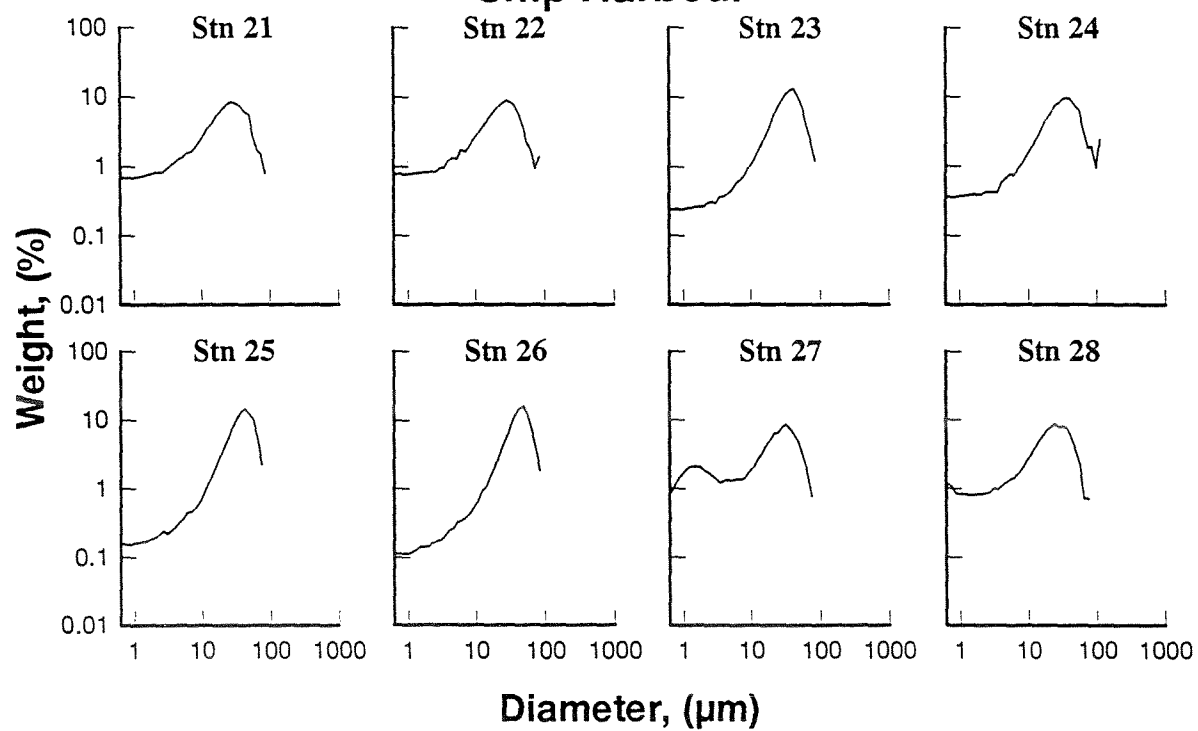

Figure 163. Disaggregated inorganic grain size distributions

Ship Harbour
Al %

Figure 164. Aluminium concentrations in surficial sediments
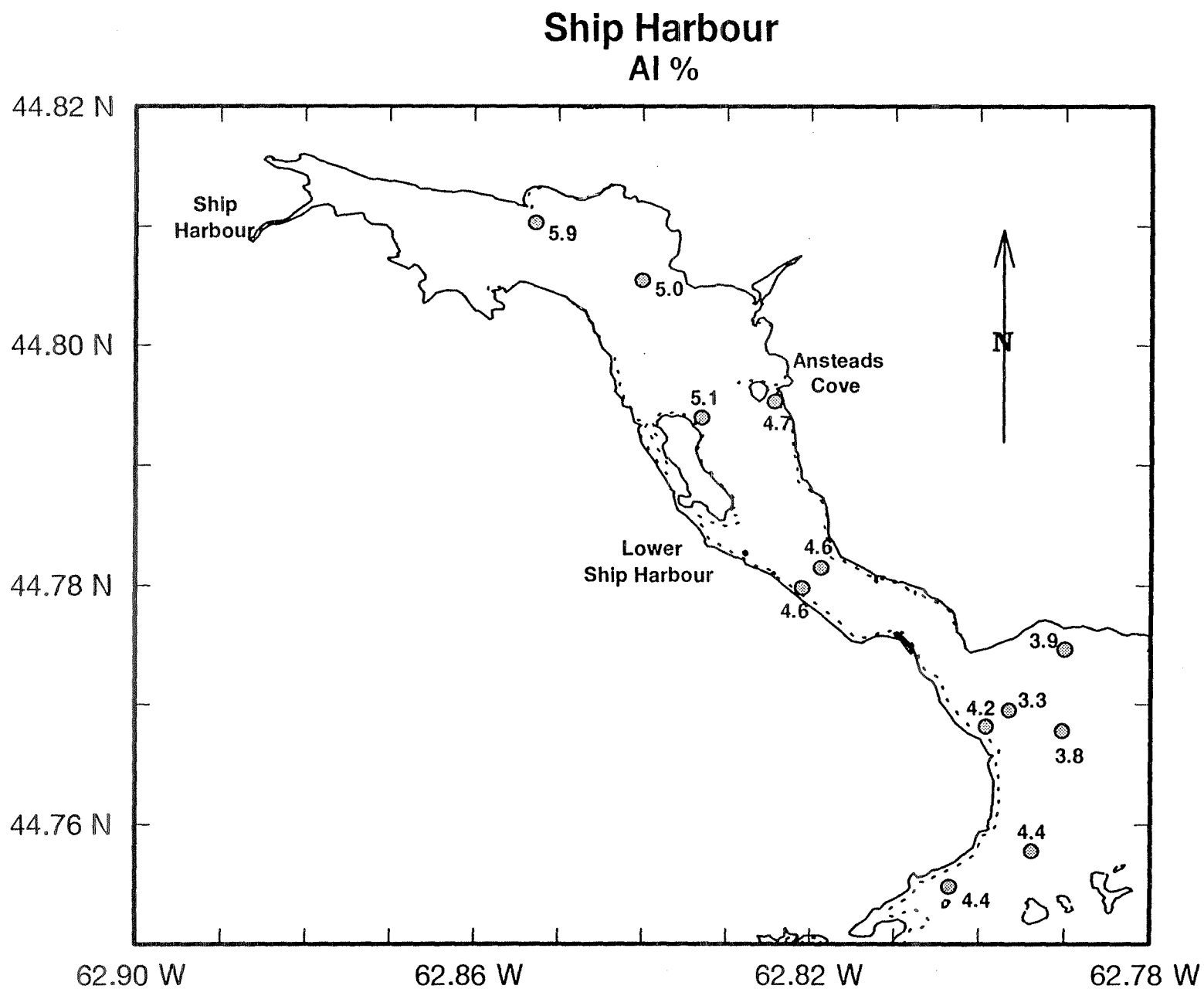
Figure 165. Iron concentrations in surficial sediments

Ship Harbour
Fe %
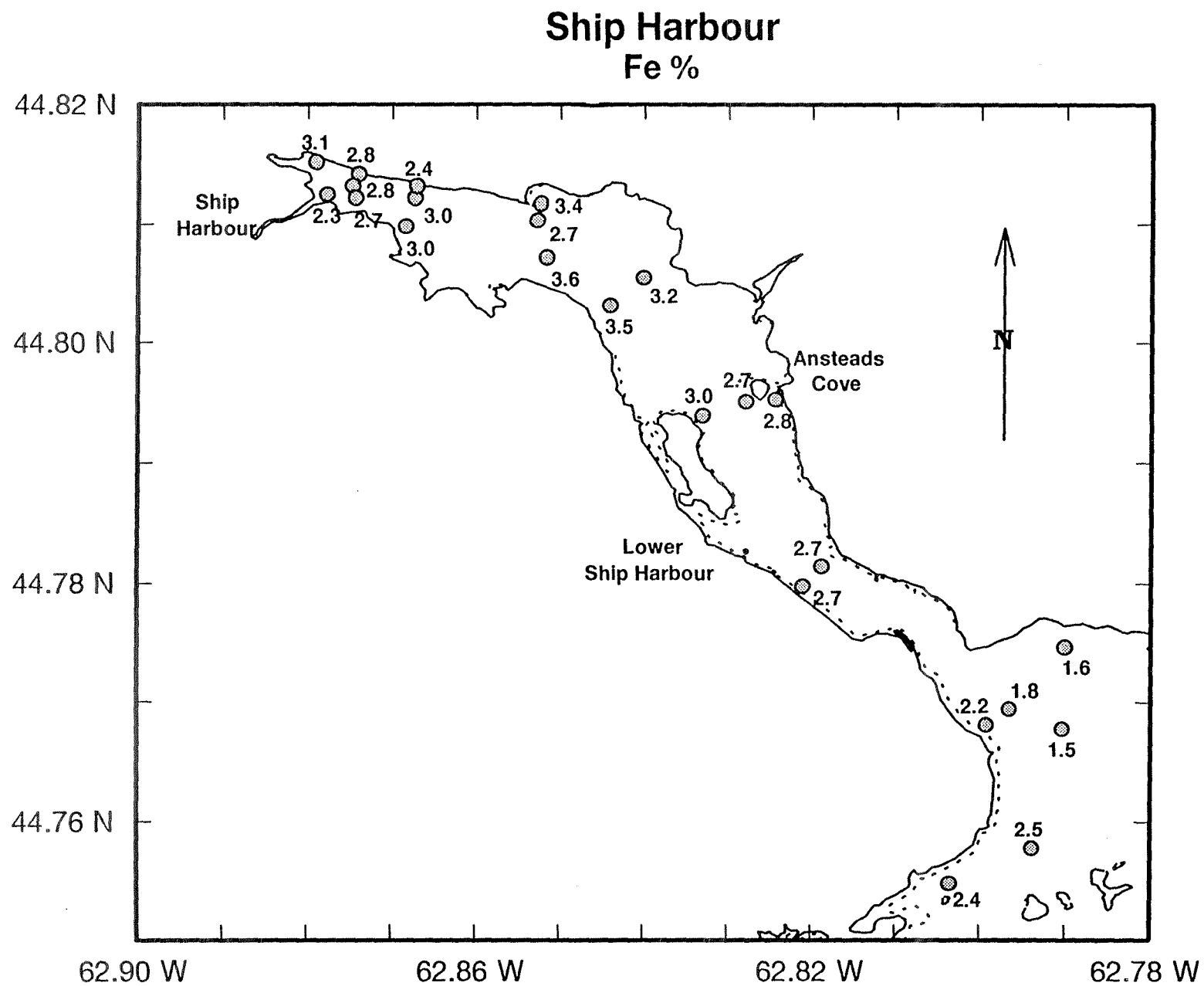
Ship Harbour
As mg/kg

Figure 166. Arsenic concentrations in surficial sediments

Ship Harbour
Cd mg/kg

Ship Harbour

2.16   1.16   1.30
0.75
0.58   1.44   1.38
1.00

0.91
0.58
0.84
0.84
0.46

Ansteads Cove

0.75   0.72
0.87

Lower Ship Harbour

0.63
0.72

0.37
0.43   0.27
0.17

0.55

0.59

N

44.82 N
44.80 N
44.78 N
44.76 N

62.90 W   62.86 W   62.82 W   62.78 W
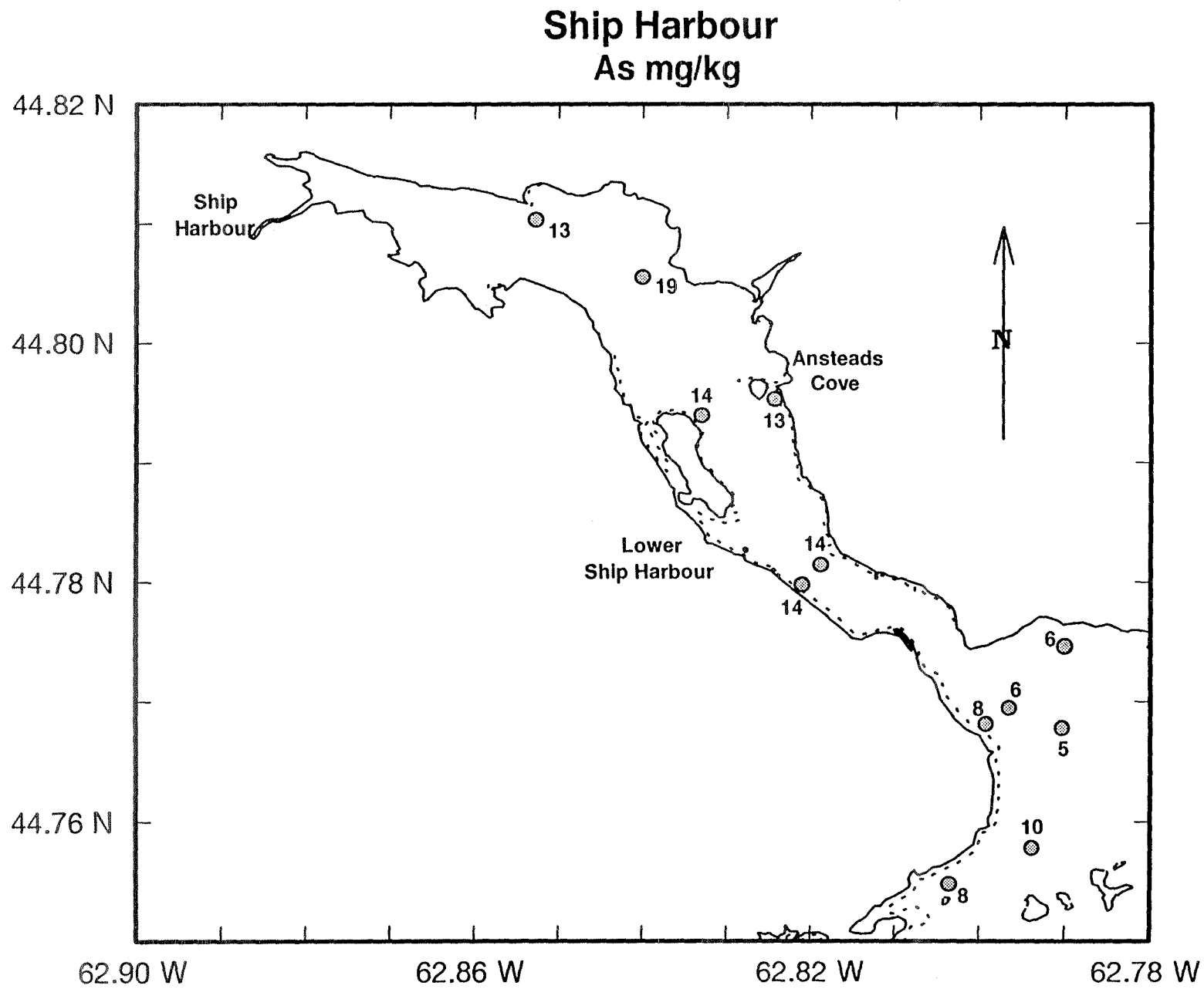
Figure 167. Cadmium concentrations in surficial sediments

Ship Harbour
Cr mg/kg
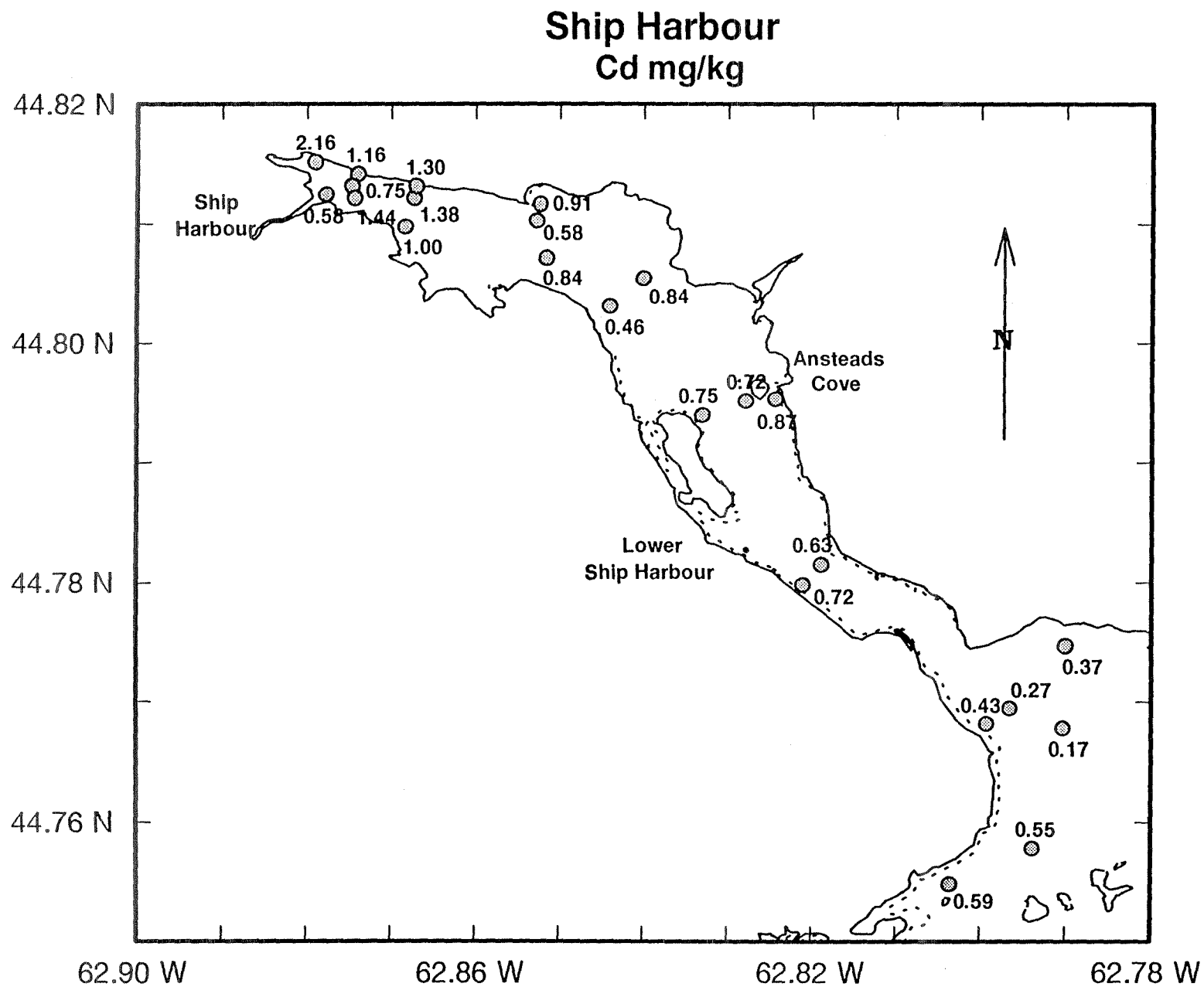
Figure 168. Chromium concentrations in surficial sediments

Ship Harbour
Cu mg/kg
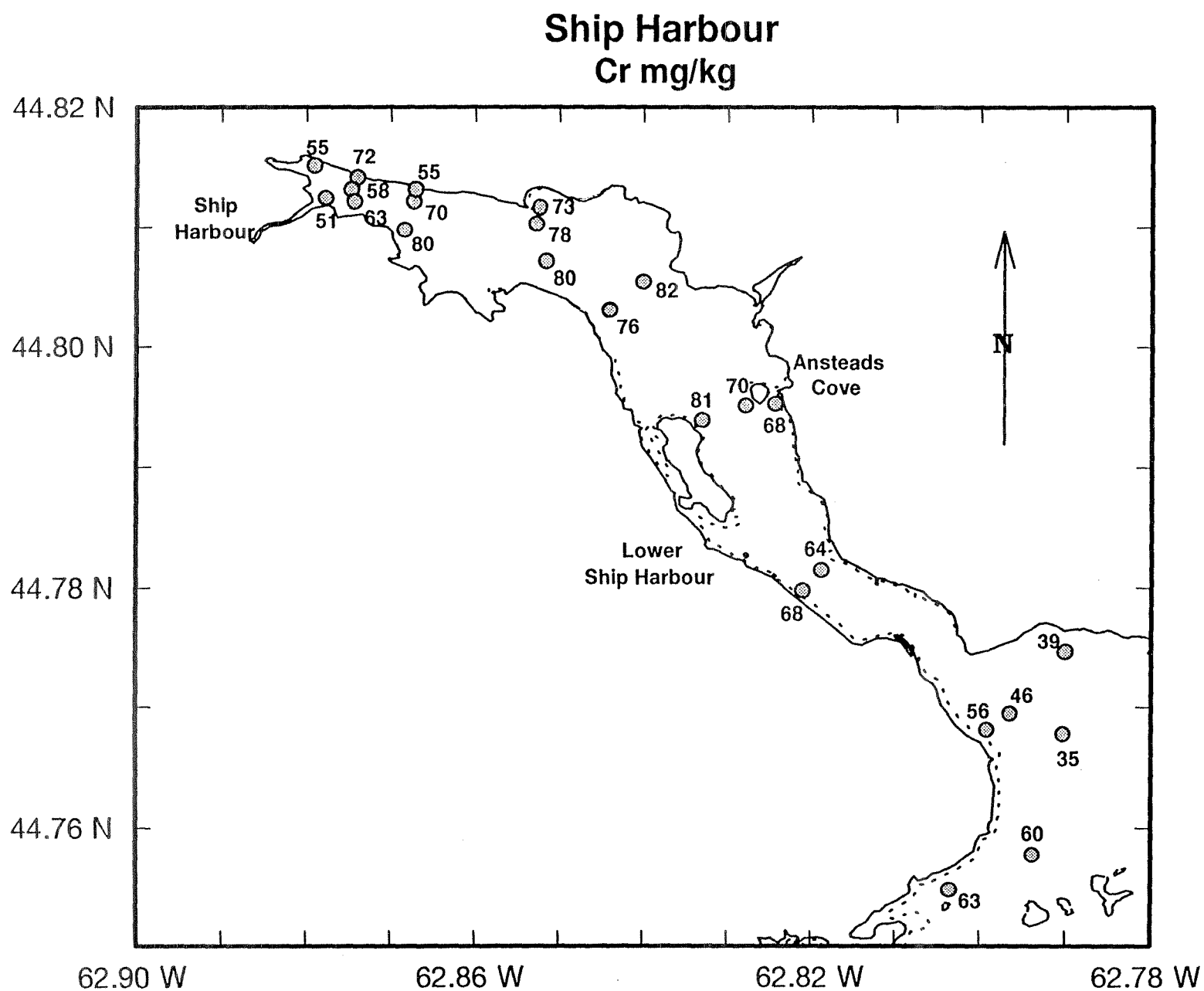
Figure 169. Copper concentrations in surficial sediments

Ship Harbour
Hg mg/kg

44.82 N

0.13 0.13
0.10
Ship
Harbour
0.09
0.06
0.05 0.11 0.11
0.05
0.07
0.06
0.07
0.06

44.80 N

Ansteads
Cove
0.05
0.07 0.04

Lower
Ship Harbour
0.04
0.04
0.06

44.78 N

0.02
0.03
0.03 0.03
0.01

44.76 N

0.05
0.05

N

62.90 W   62.86 W   62.82 W   62.78 W
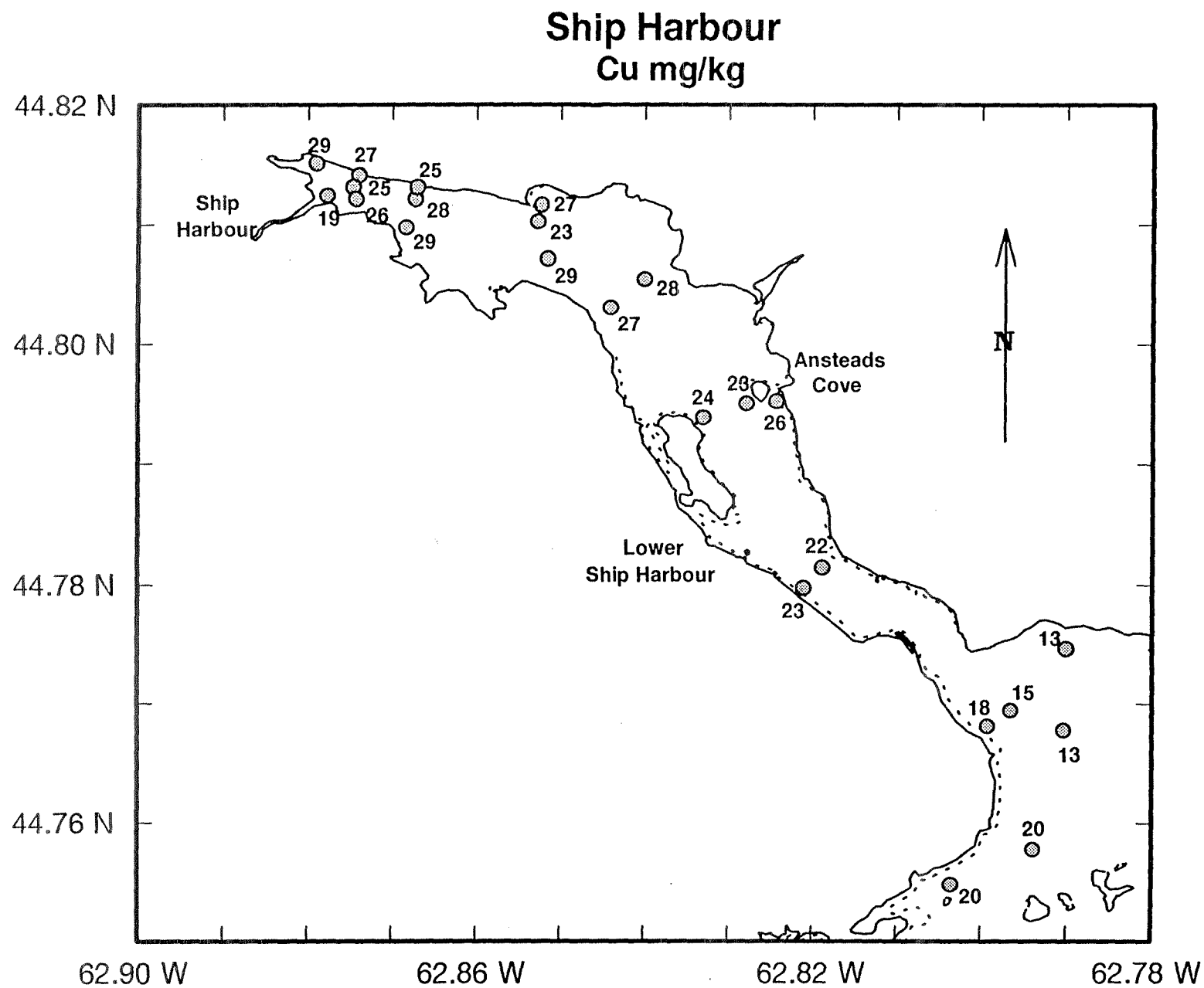
Figure 170. Mercury concentrations in surficial sediments

Ship Harbour
Li mg/kg
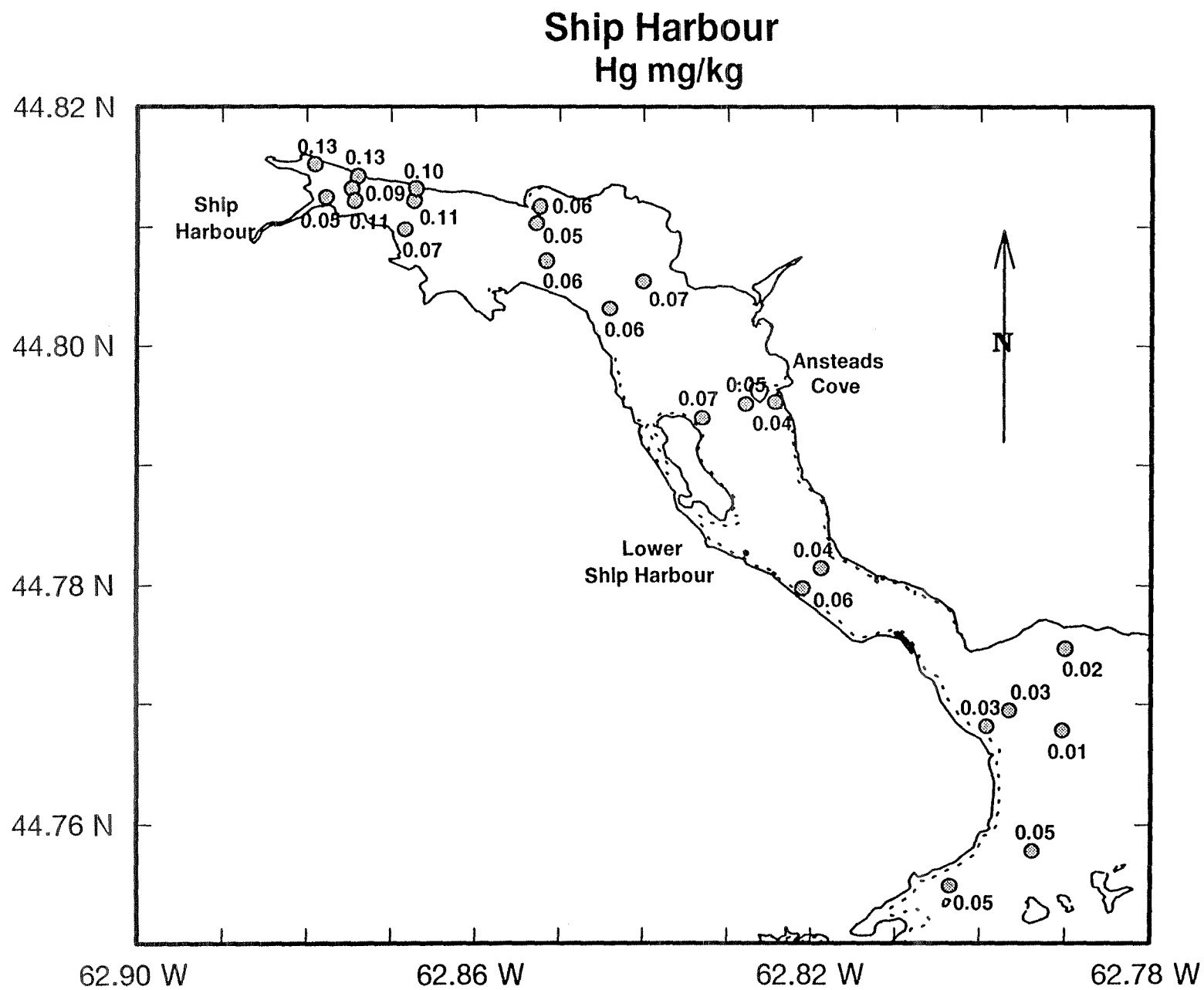
Figure 171. Lithium concentrations in surficial sediments

Ship Harbour
Mn mg/kg
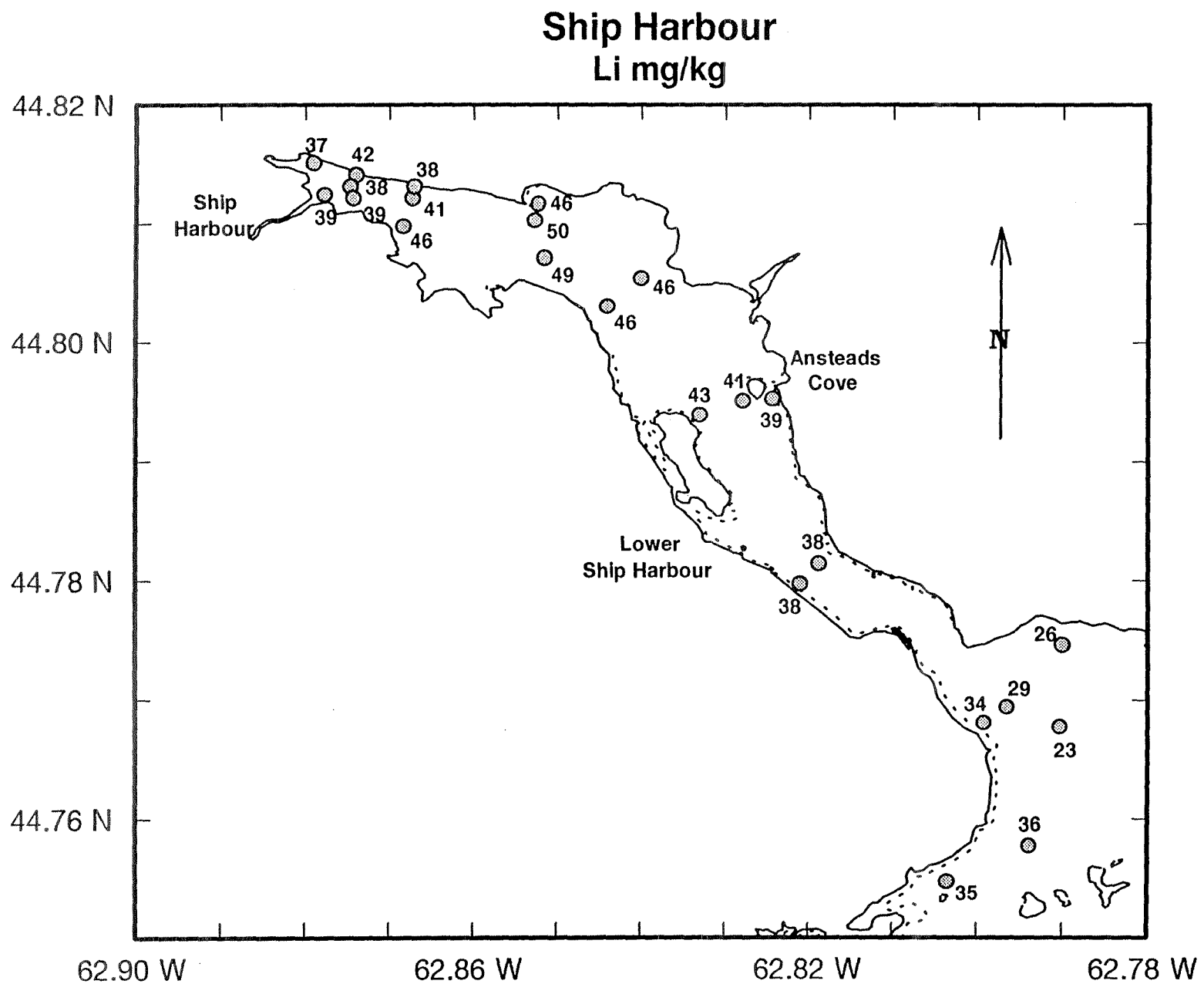
Figure 172. Manganese concentrations in surficial sediments

Ship Harbour
Ni mg/kg

44.82 N

44.80 N

44.78 N

44.76 N

62.90 W   62.86 W   62.82 W   62.78 W

Ship Harbour

Ansteads Cove

Lower Ship Harbour

N

29

33

34

31

29

32

21

18

25

18

26

27
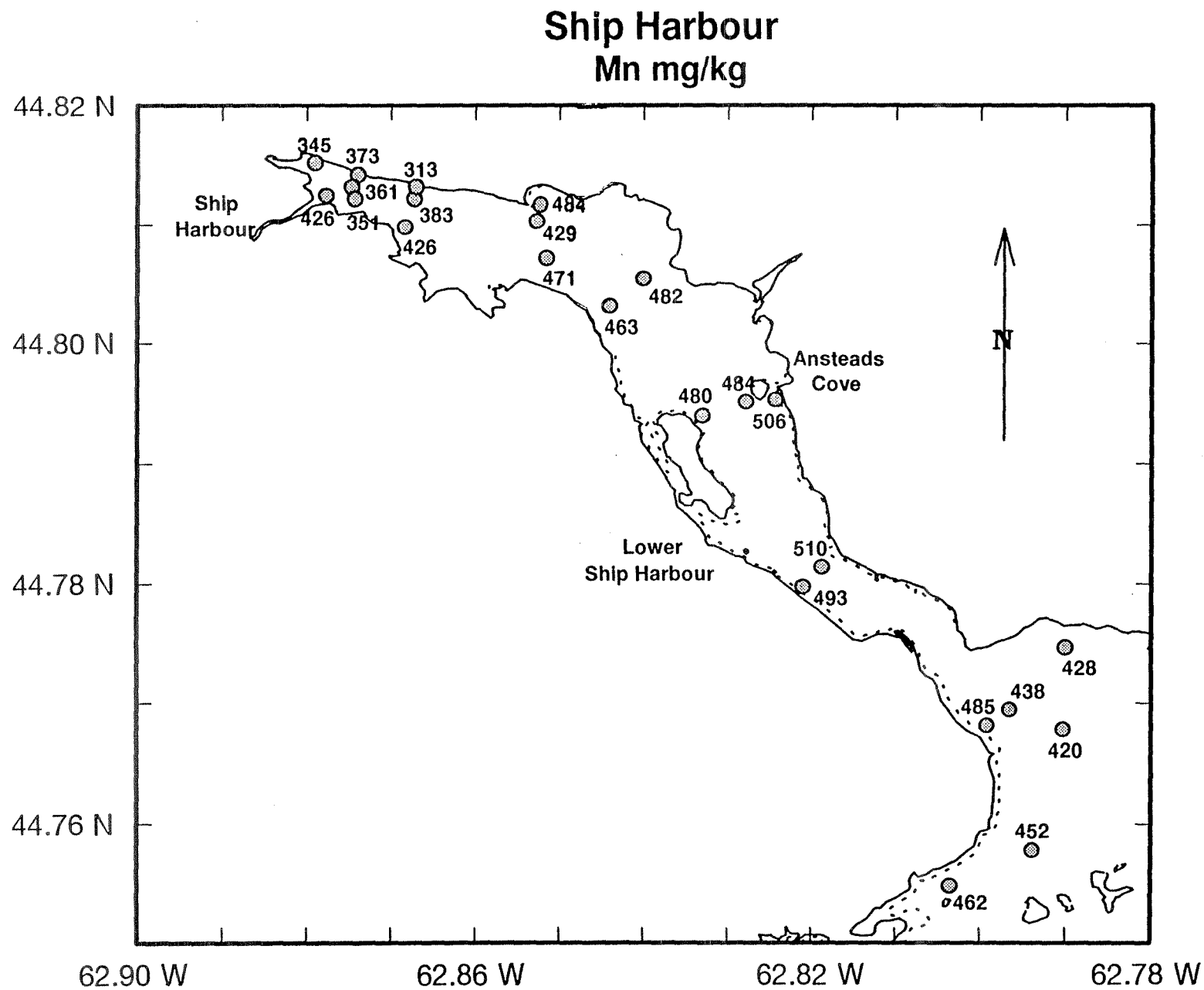
Figure 173. Nickel concentrations in surficial sediments
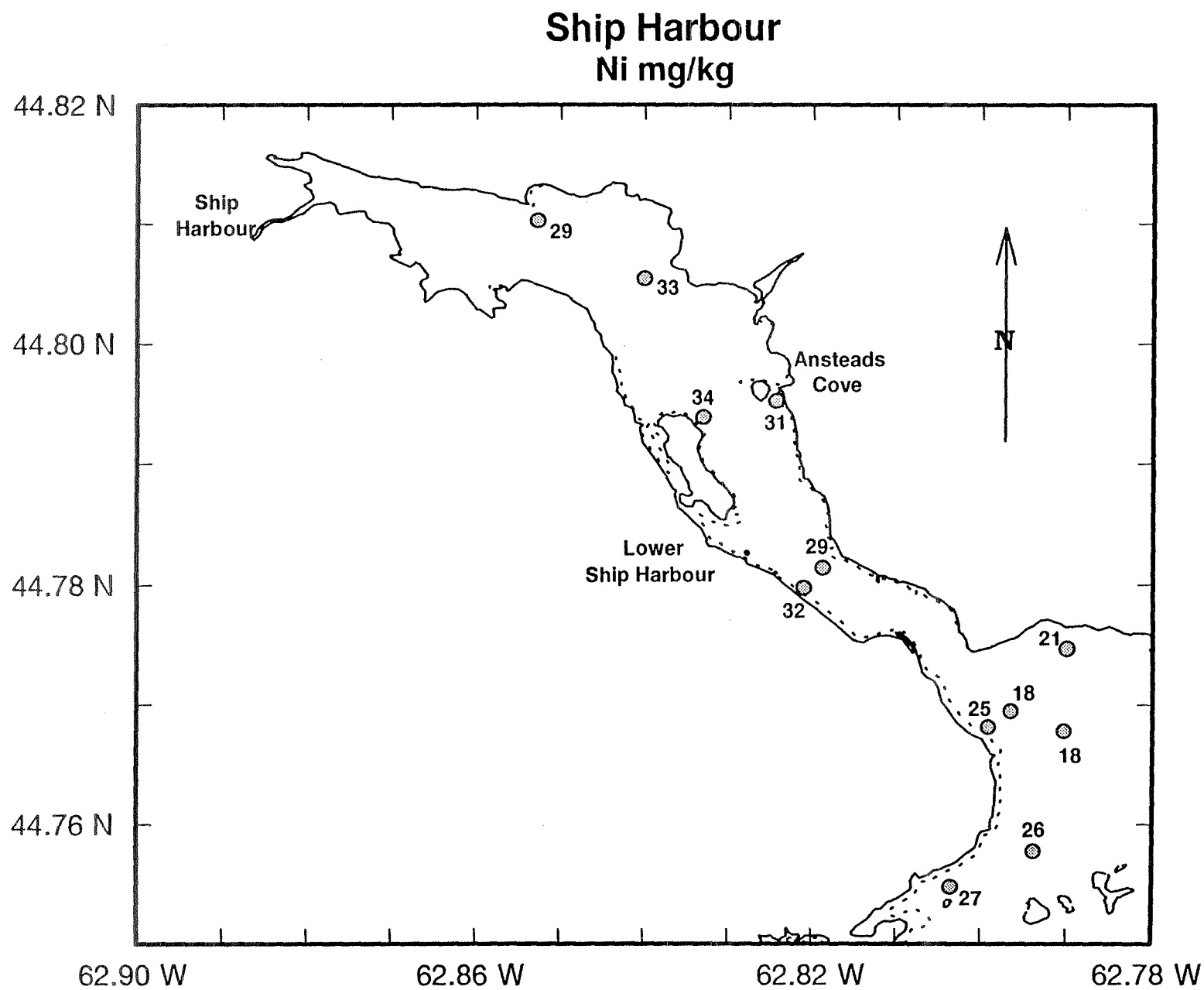
Figure 174. Lead concentrations in surficial sediments

Ship Harbour
Pb mg/kg

Ship Harbour
Sn mg/kg

44.82 N

Ship Harbour

3.2

3.0

44.80 N

Ansteads Cove

2.9

2.5

N

Lower Ship Harbour

2.4

44.78 N

2.6

1.5

1.9 1.4

1.4

44.76 N

2.3

2.0

62.90 W   62.86 W   62.82 W   62.78 W
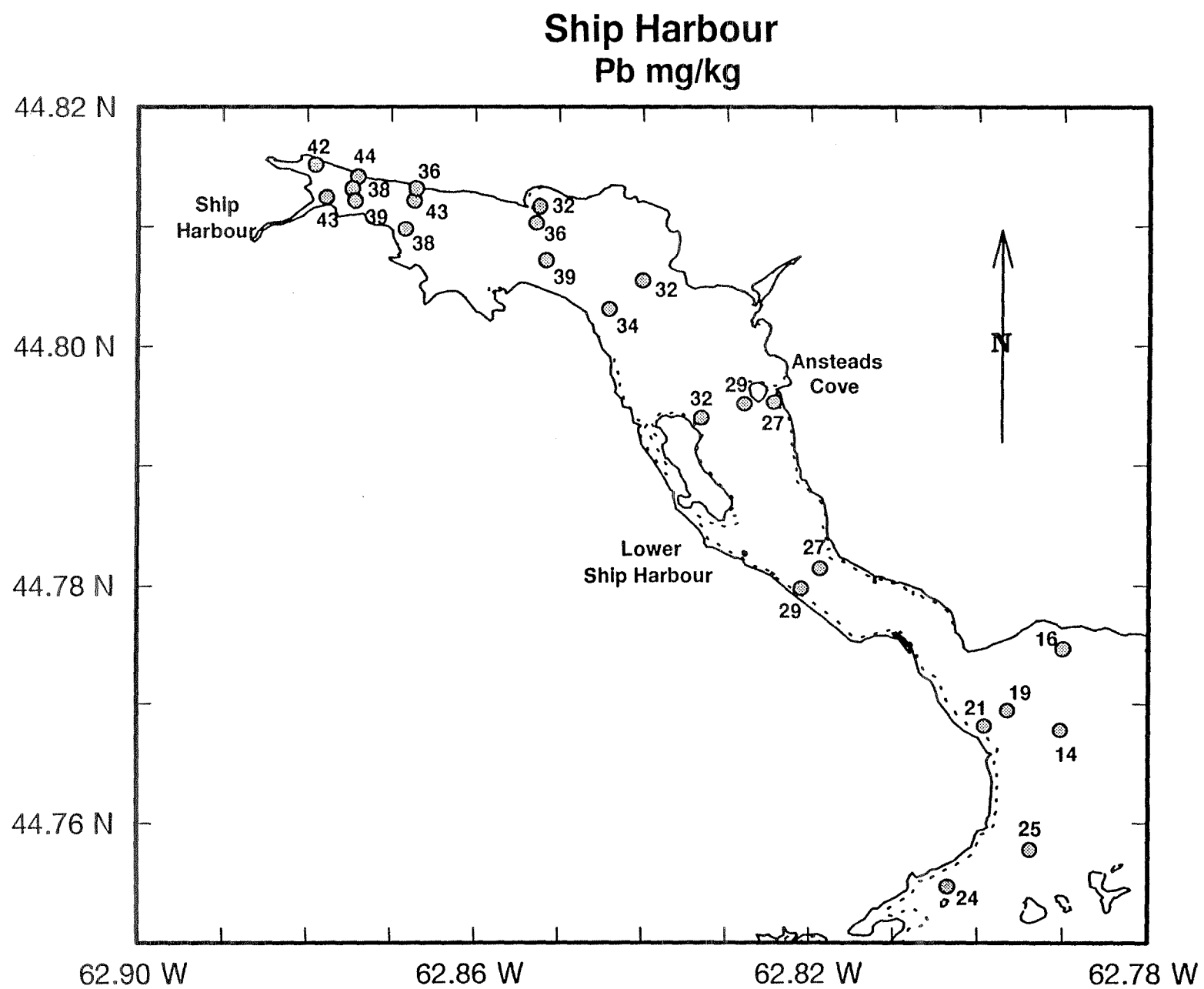
Figure 175. Tin concentrations in surficial sediments

Ship Harbour
V mg/kg
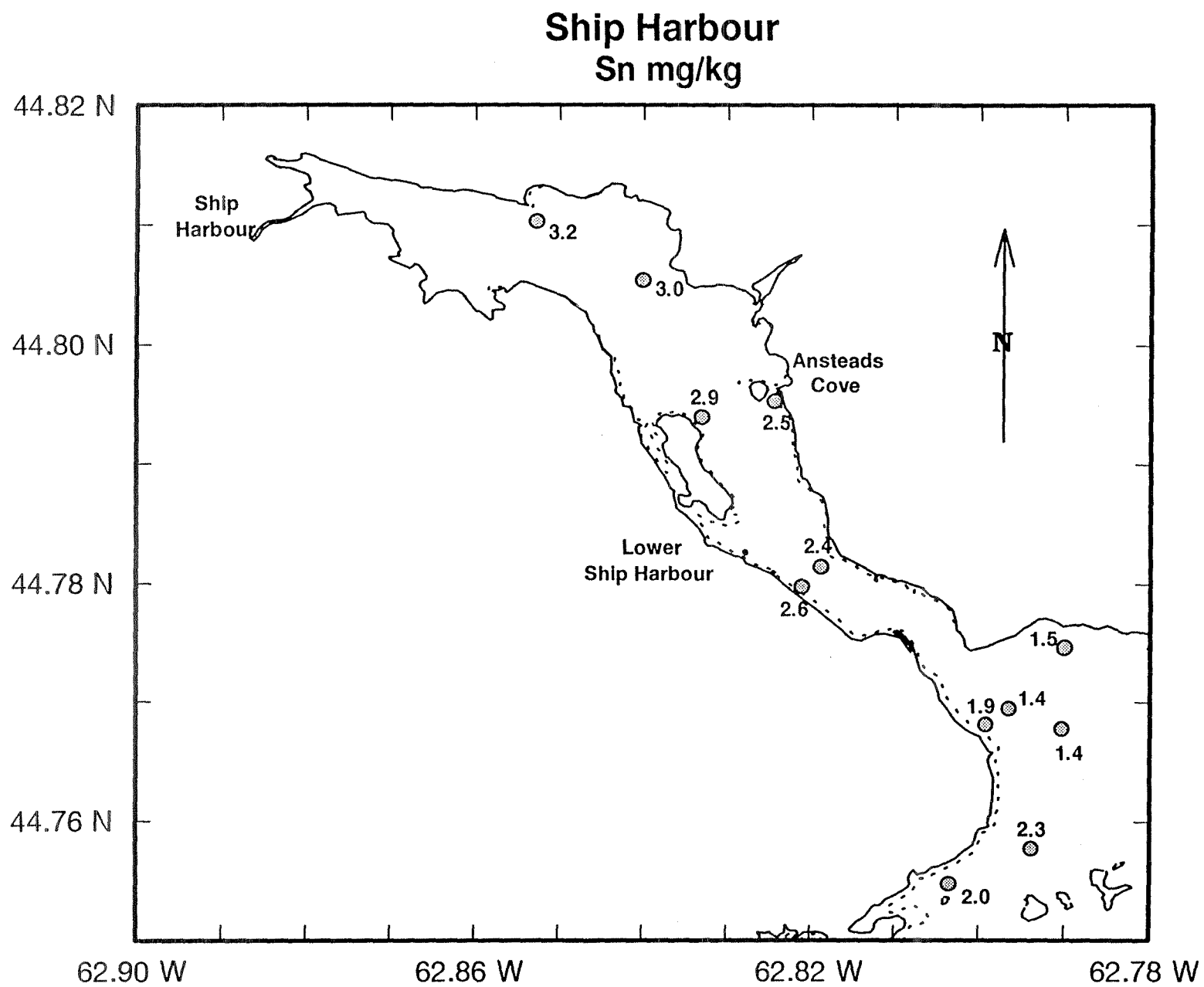
Figure 176. Vanadium concentrations in surficial sediments
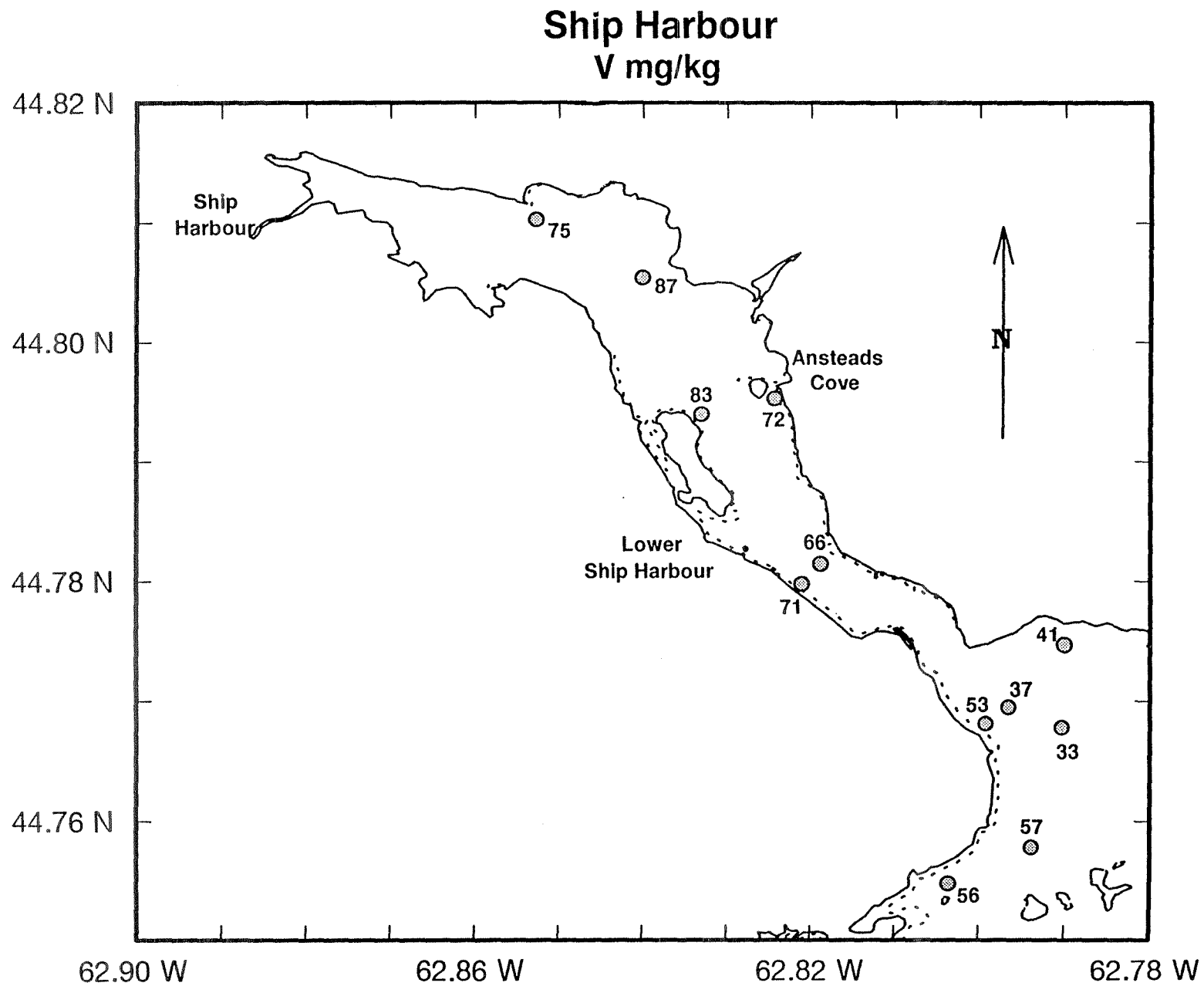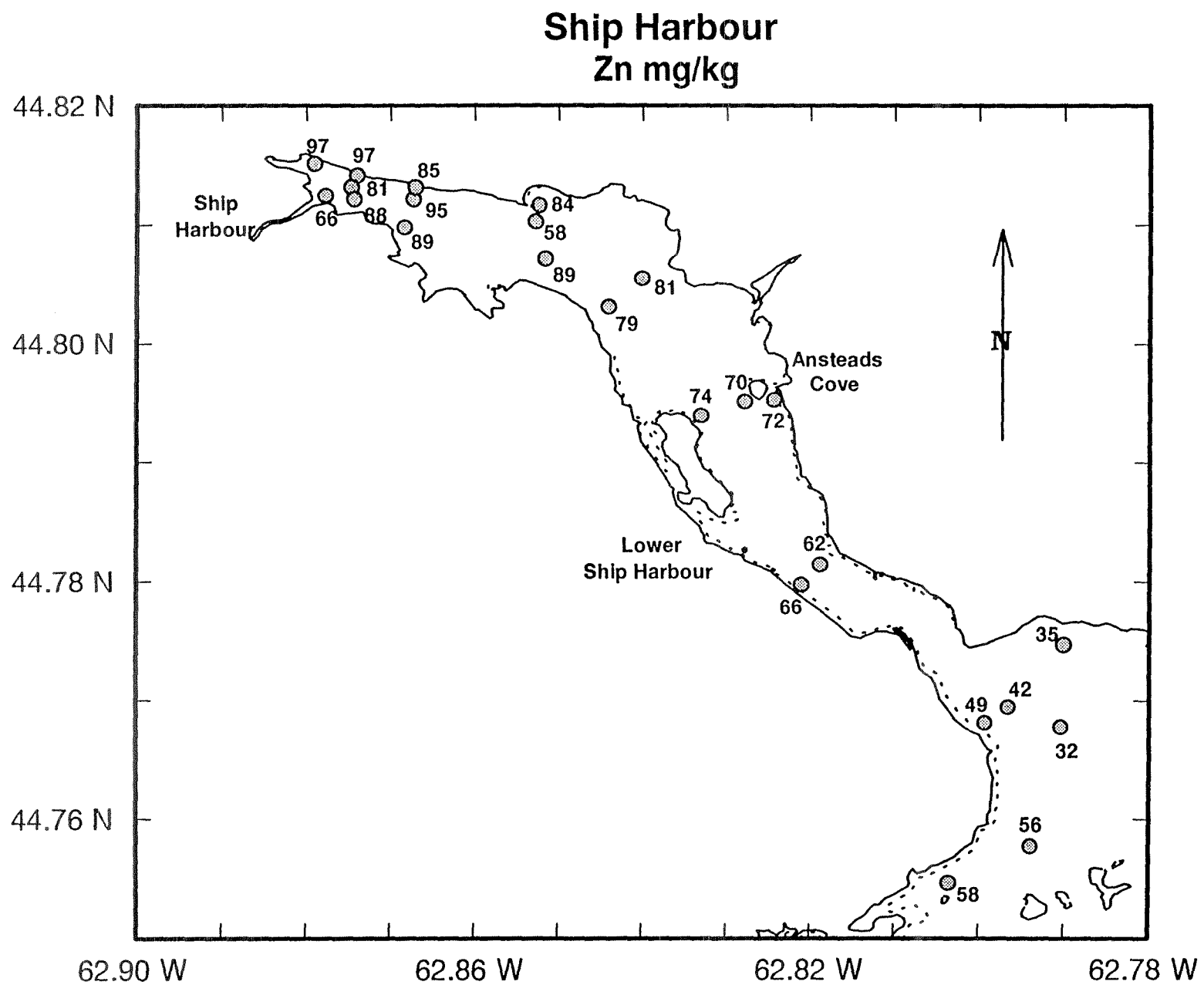
Ship Harbour
Zn mg/kg

Figure 177. Zinc concentrations in surficial sediments

ST. MARY'S ESTUARY

The estuary of the St. Mary's River is a long (16.7 km), narrow (0.1-2.4 km), shallow (water depths of 0.3 to 10 m) inlet running into the eastern shore of Nova Scotia, at the town of Sherbrooke, Guysborough County. At its head, the estuary receives drainage via the St. Mary's River from a drainage area of 1512 km^2. The drainage area is mainly wooded with the vegetation developed on a thin mantle of glacial till underlain primarily by Permo-Carboniferous sandstones and shales in its upper reaches and by Precambrian quartzites and slates in its lower reaches. A narrow fertile floodplain borders the lower reaches of the river and supports mixed farming.

POTENTIAL SOURCES OF CONTAMINATION

Aside from the potential contributions of contaminants from agricultural activities and villages along its banks and the town of Sherbrooke, the only potential source of industrial contamination is the leaching of mine wastes and tailings derived from gold mining activity in the area between 1891 and 1909 (Malcom 1912).

RESULTS

Sediment Samples and Composition

The location of the sampling stations (n=14) in the estuary is shown in Figure 178. The estuary is bordered by shallow (1 m deep) (sometimes sandy) black mud flats covered with eel grass, while the main channel and the mouth of the estuary is occupied by brownish-black sands and muddy sands containing varying amounts of organic matter (Fig. 179).

The high energy of this narrow river system can be seen in the St. Mary's samples which have modal diameters greater than 100 μm and very low concentrations of floc-settled material (Fig. 180). Source slopes at the mouth are similar to those in Country Harbour, and the size spectra show very well sorted sand peaks. Upstream, the source slope remains constant and samples collected in the river channel are also dominated by the bed load sand peak. Samples collected from the mud flats (Stations 12, 13, 17, and 18) have much greater concentrations of floc material due to trapping of fine sediment in the low-energy regions. The coarse nature of the sediments and the poorly developed tail shows that little or no fine sediment is being trapped within the channel and that the only fine sediment present is being held on the mud flats.

Abundance and Distribution of Metals

The concentrations of the metals at each sampling station (n=14) are shown in Figures 181 to 194. The range of total metal concentrations determined in the St. Mary's estuarine sediments are: As, 3-29 mg·kg^{-1}; Cd, 0.03-0.56 mg·kg^{-1}; Cr, 19-48 mg·kg^{-1}; Cu, 4-19 mg·kg^{-1}; Hg, 0.01-

0.11 mg·kg^{-1}; Ni, 7-20 mg·kg^{-1}; Pb, 6-29 mg·kg^{-1}; Sn, 1.5-2.0 mg·kg^{-1}; V, 23-70 mg·kg^{-1}; and Zn, 20-101 mg·kg^{-1} (Table 26). Most of the metals are at, or near, natural concentrations; but 8% of the samples contained >20 mg·kg^{-1} As, 4 of the 14 samples (29%) contained > 0.3 mg·kg^{-1} Cd, and 7% of the samples contained Hg and Zn at levels above normal background. The highest concentrations of these metals occur in fine-grained sediments about 5 km below the mouth of the river. The relatively high concentrations of Cd and Hg occur in these fine-grained, organic-rich sediments occupying the shallow flats adjacent to the main channel in the upper part of the estuary.

Potential Bioavailability of Metals

Chemical partitioning of three selected samples indicate that most (50-100%) of the total Cd, 4-18% of the total Cu, 20-40% of the total Pb, and 15-32% of the total Zn are potentially bioavailable.

Metal Carriers and Sources

The strong positive correlations of all the metals, excepting Mn, Pb, and Sn, with increasing mud (material <63 μm) content confirm that the metal carriers are predominantly fine-grained (Table 27). Factor analyses indicate that deposition of fine-grained inorganic and organic material is the main factor (accounting for 65% of the total variance) controlling the abundance and distribution of the metals in the sediments. The strong positive correlations of all the metals, excepting As, Cd, Hg, Sn, and Mn with increasing Li concentration, reflect the inclusion and/or association of fine-grained aluminophyllosilicate minerals such as the micas, illite, chlorite, and kaolinite (Table 25). The positive covariance (p<0.01) of Cr (r=0.82), Cu (r=0.80), Pb(r=0.87), and Zn (r=0.90) with Li shows that lithium normalizes for varying amounts of the granular and mineralogical variability of these metals in the surface sediments. The proportion of the metal variability explained by the granular variability of the phyllosilicates decreases in the order: Zn (81%) > Pb (76%) > Cr (67%) >Cu (64%) > As (60%) > Hg (57%) >> Cd (36%) > Sn (33%).

Inspection of the correlation matrix indicates strong correlations between As, Cd, and Hg with the <63-μm fraction and organic matter reflecting the association of these metals. In addition, the strong covariances of As, Cr, Cu, Hg, Pb, and Zn with Fe suggest that important carriers of As, Cu, Pb, Zn, and Hg are discrete ferriferous metallic particles. These would have been derived from the deposition of detrital iron sulphide minerals associated with gold-bearing veins or with those transported into the estuary from mine wastes and tailings derived from gold-mining activity in the area between 1891 and 1909 or the *in situ* formation of metal-bearing iron monsulphides and/or pyrite containing As, Cd, Cu, Hg, Pb, and Zn which is formed *in situ* in the organic-rich fine-grained sediments. The strong positive correlation of Cd, which is mainly HOAc soluble with organic matter, indicates that it is weakly held by the organic component. The strong association of Hg with organic matter in addition to Fe suggests that it may also be weakly retained by organic material. Anomalous Cd and the few relatively high Hg concentrations,

therefore, most likely result from the introduction of organic wastes that accumulate together with fine-grained particles in the eel grass flats adjacent to the main channel of the estuary.

Table 26

Textural and metal statistics[a] for the St Marys estuarine sediments

Text	n	AVG	SD	Range	Text	n	AVG	SD	Range
Mud(%)	14	46.9	±37.0	5-98	OM(%)	10	1.57	± 1.99	0.16-6.63
Metal					Metal				
Al%	14	4.34	± 0.38	3.70-5.10	Fe%	14	1.74	± 0.59	1.00-3.00
As	13	9.1	± 7.7	3-29	Li	14	30.5	± 8.4	16-43
Cd	14	0.20	± 0.16	0.03-0.56	Ni	13	12.7	± 4.8	7-20
Cr	14	31.6	±10.6	19-48	Pb	14	14.9	± 7.0	6-29
Cu	14	9.6	± 4.1	4-19	Sn	7	1.9	± 0.2	1.5-2.0
Hg	14	0.04	± 0.03	0.01-0.11	V	13	38.4	±14.0	23-70
Mn%	14	0.043	± 0.012	0.025-0.075	Zn	14	48.6	±22.6	20-101

[a]Concentrations in mg kg^{-1} except percent(%) for mud, organic matter(OM), Al, Fe, and Mn

Table 27

Correlation Matrix St. Marys Estuary

	Al	As	Cd	Cr	Cu	Fe	Hg	Li	Mn	Pb	Sn	Zn
Al	1											
As	x	1										
Cd	x	0.90	1									
Cr	0.85	0.87	0.86	1								
Cu	x	0.88	0.82	0.89	1							
Fe	0.82	0.92	x	0.91	0.93	1						
Hg	x	0.95	0.93	0.92	0.89	0.90	1					
Li	0.85	x	x	0.82	0.80	0.90	x	1				
Mn	x	x	x	x	x	x	x	x	1			
Pb	0.77	0.86	x	0.88	0.95	0.96	0.84	0.87	x	1		
Sn	x	x	x	x	x	x	x	x	x	x	1	
Zn	0.77	0.94	0.81	0.91	0.94	0.97	0.94	0.90	x	0.95	x	1
Mud	x	0.84	0.86	0.93	0.80	0.80	0.90	x	x	x	x	0.80
OM	x	0.97	0.94	0.92	x	x	0.91	x	x	x	x	x

n = 14
For p ≤ 0.001 x = not significant
mud = >70% by weight material<63μm
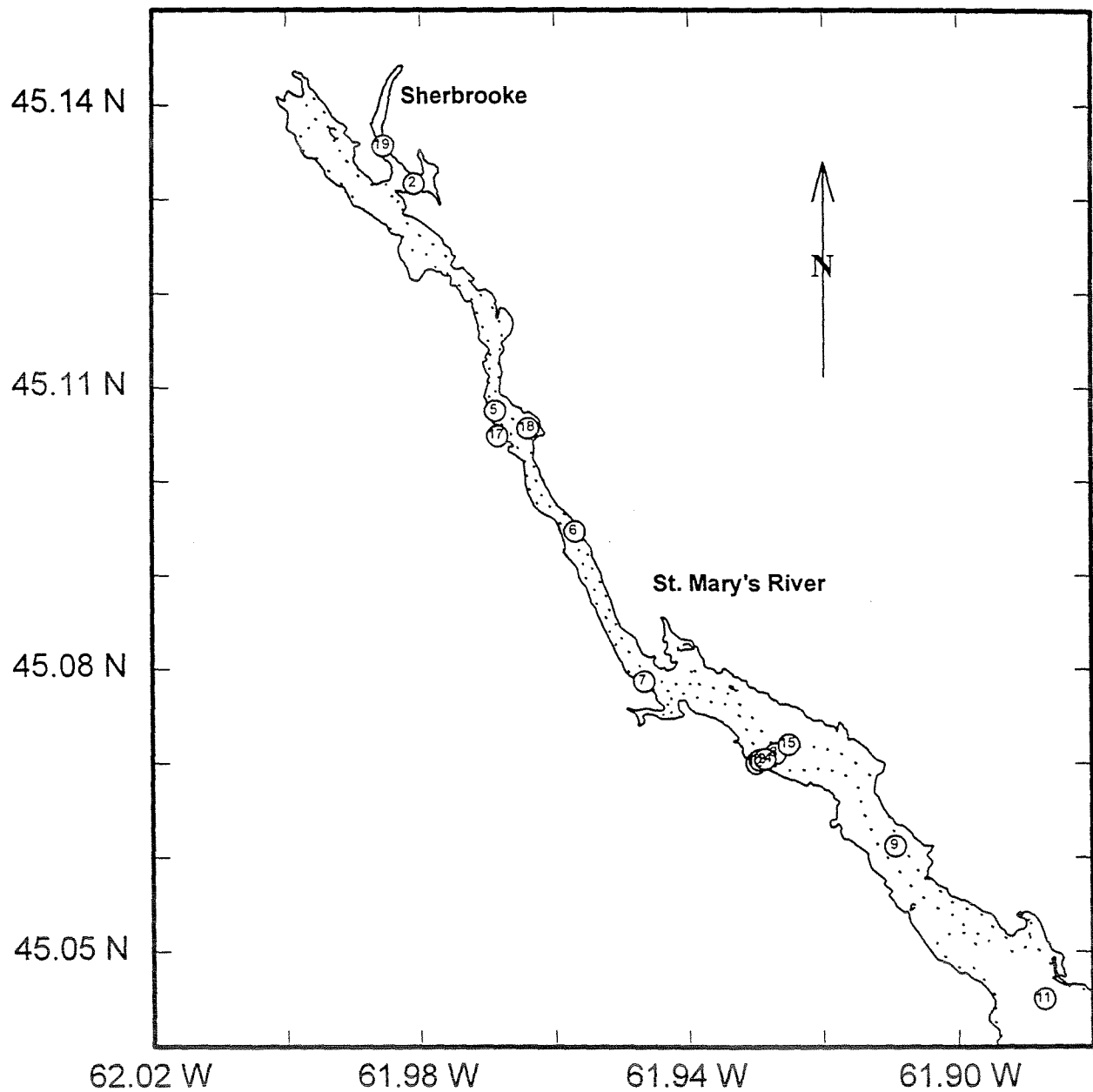OM = % by weight organic matter

St. Mary's Estuary
Sample Locations

Figure 178. Sample locations for St. Mary's Estuary

244

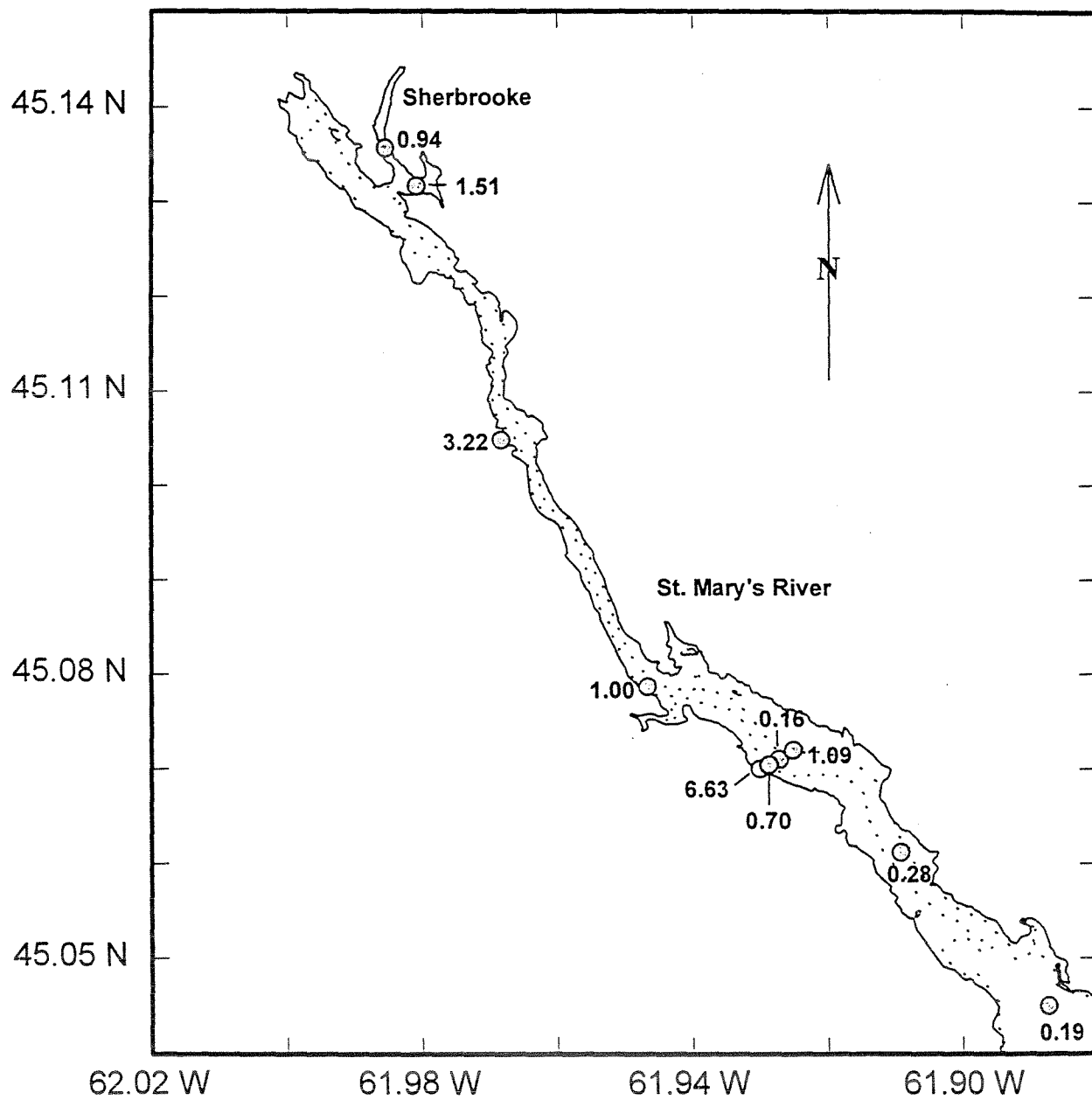# St. Mary's Estuary
% Organic Matter

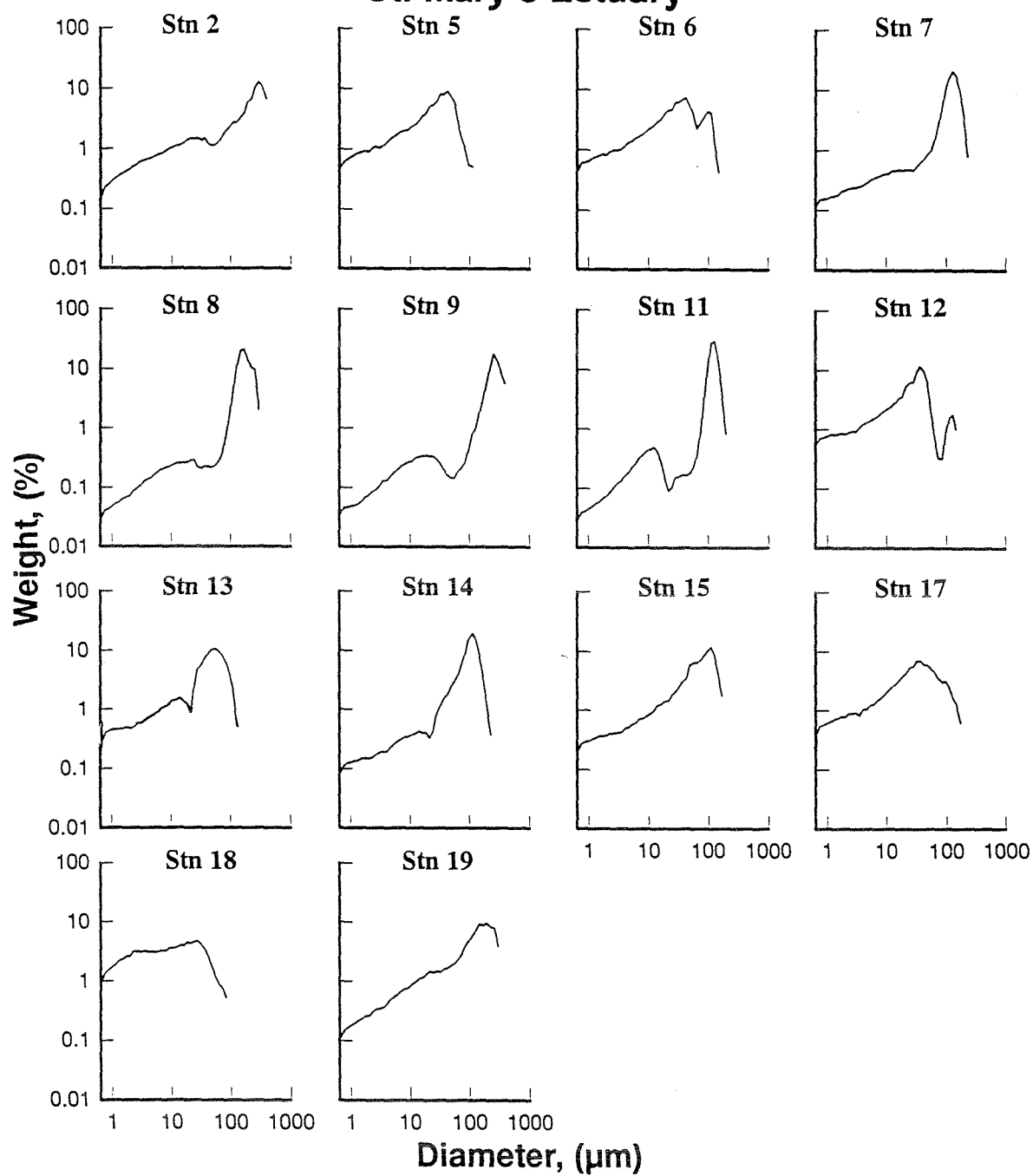**Figure 179.** Organic matter concentrations in surficial sediments

St. Mary's Estuary

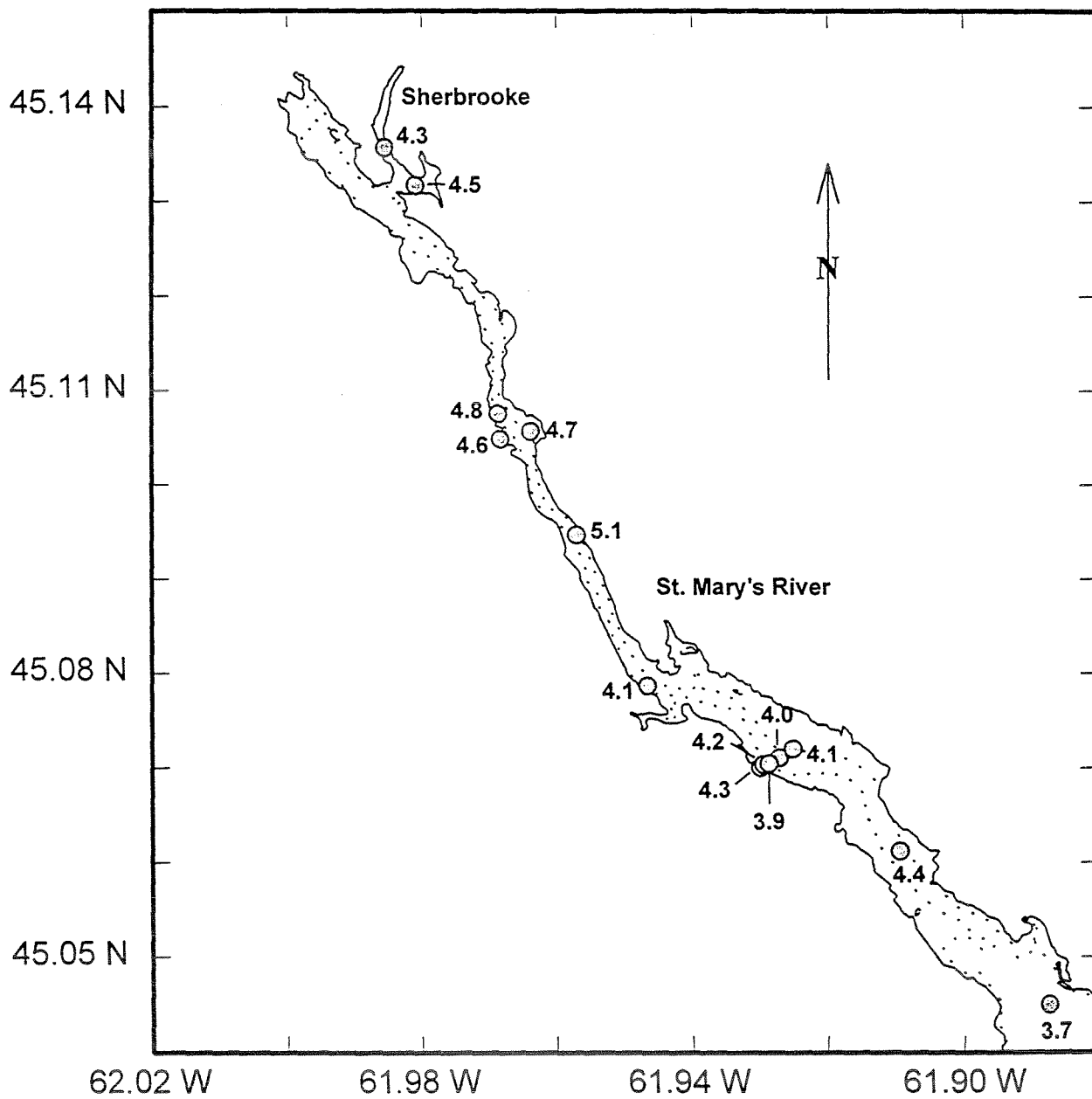**Figure 180.** Disaggregated inorganic grain size distributions

St. Mary's Estuary
Al %

Figure 181. Aluminium concentrations in surficial sediments
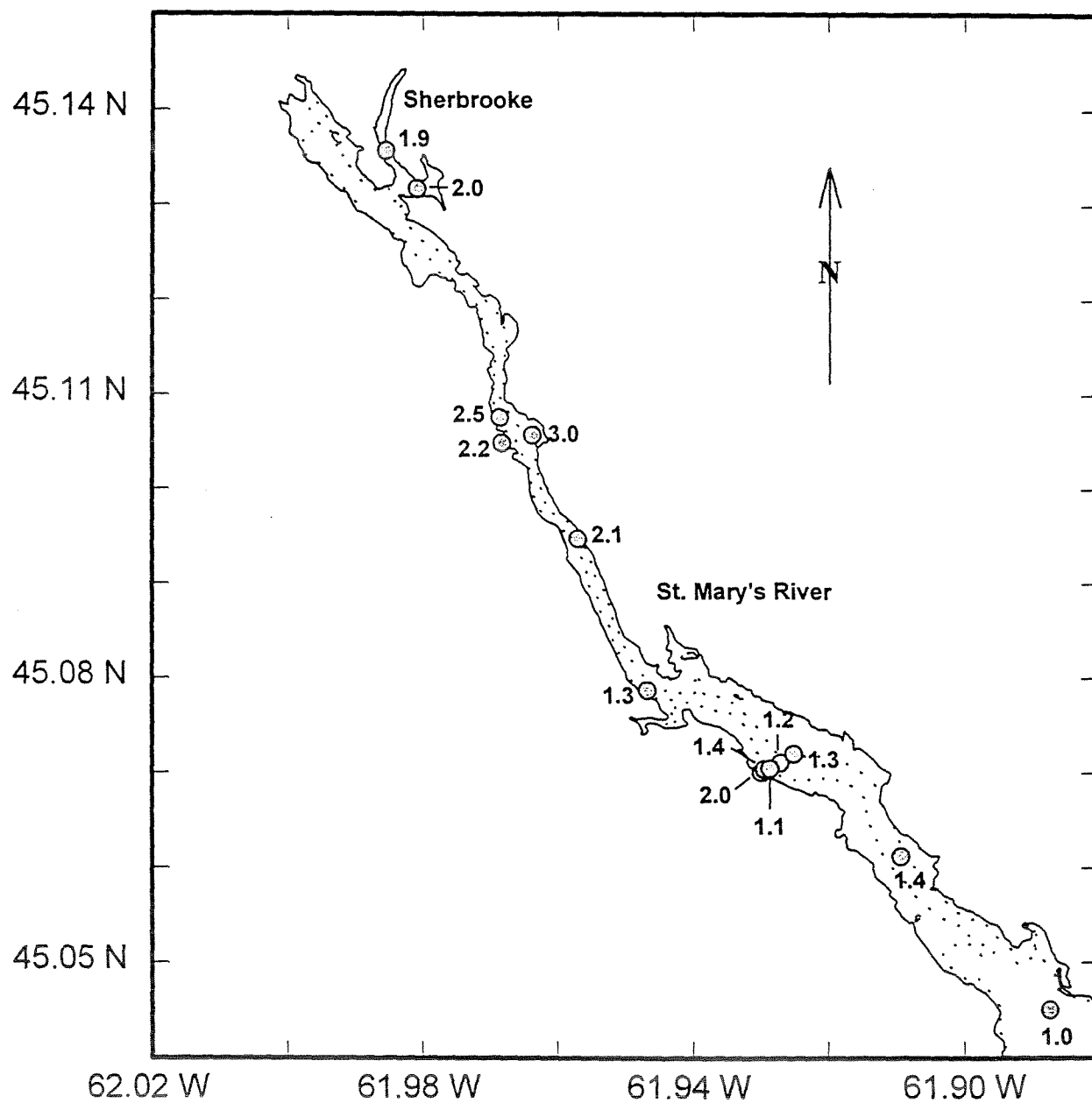
St. Mary's Estuary
Fe %

Figure 182. Iron concentrations in surficial sediments

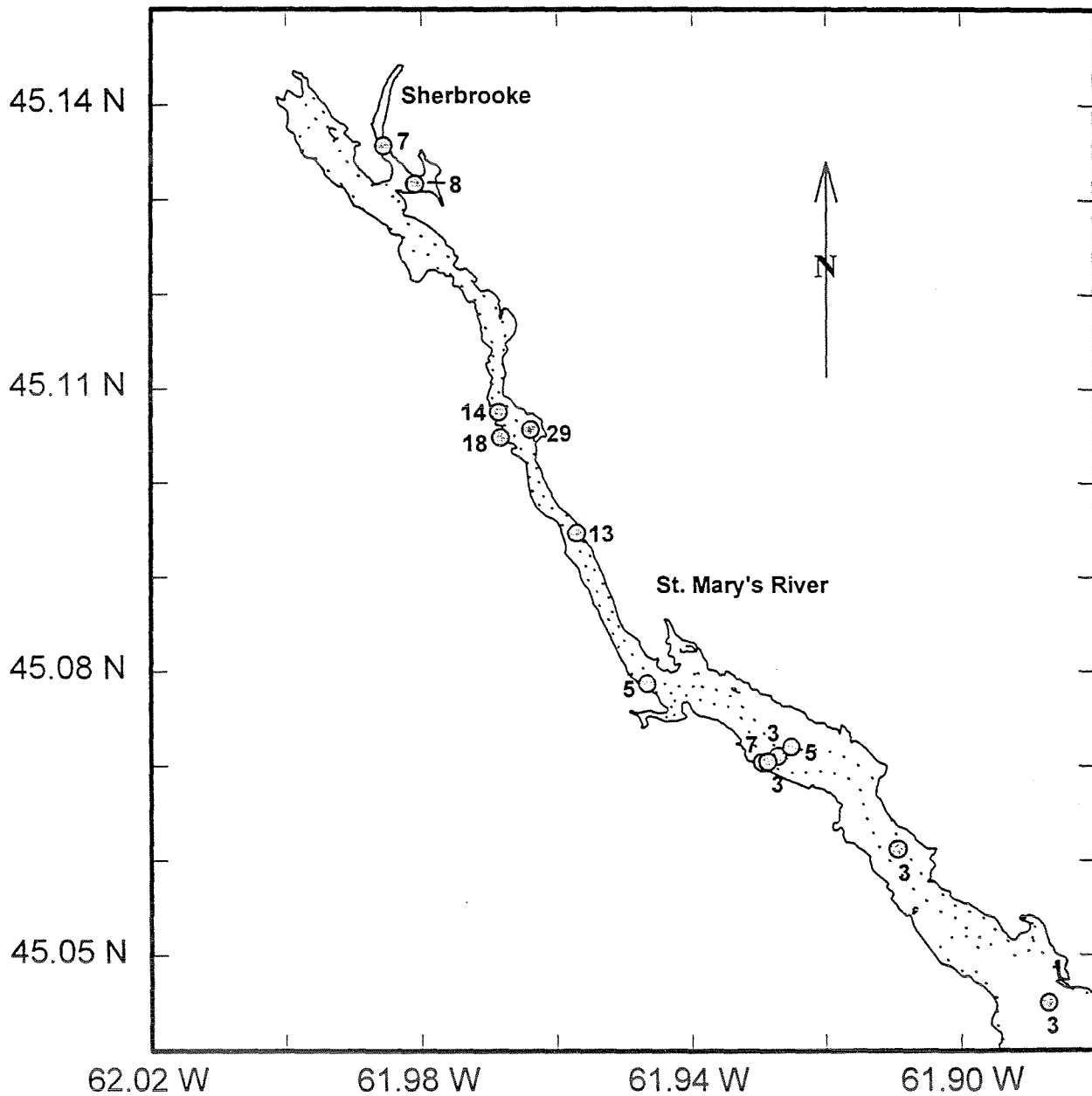# St. Mary's Estuary
As mg/kg

Figure 183. Arsenic concentrations in surficial sediments

St. Mary's Estuary
Cd mg/kg

Figure 184. Cadmium concentrations in surficial sediments

St. Mary's Estuary
Cr mg/kg

Figure 185. Chromium concentrations in surficial sediments

St. Mary's Estuary
Cu mg/kg
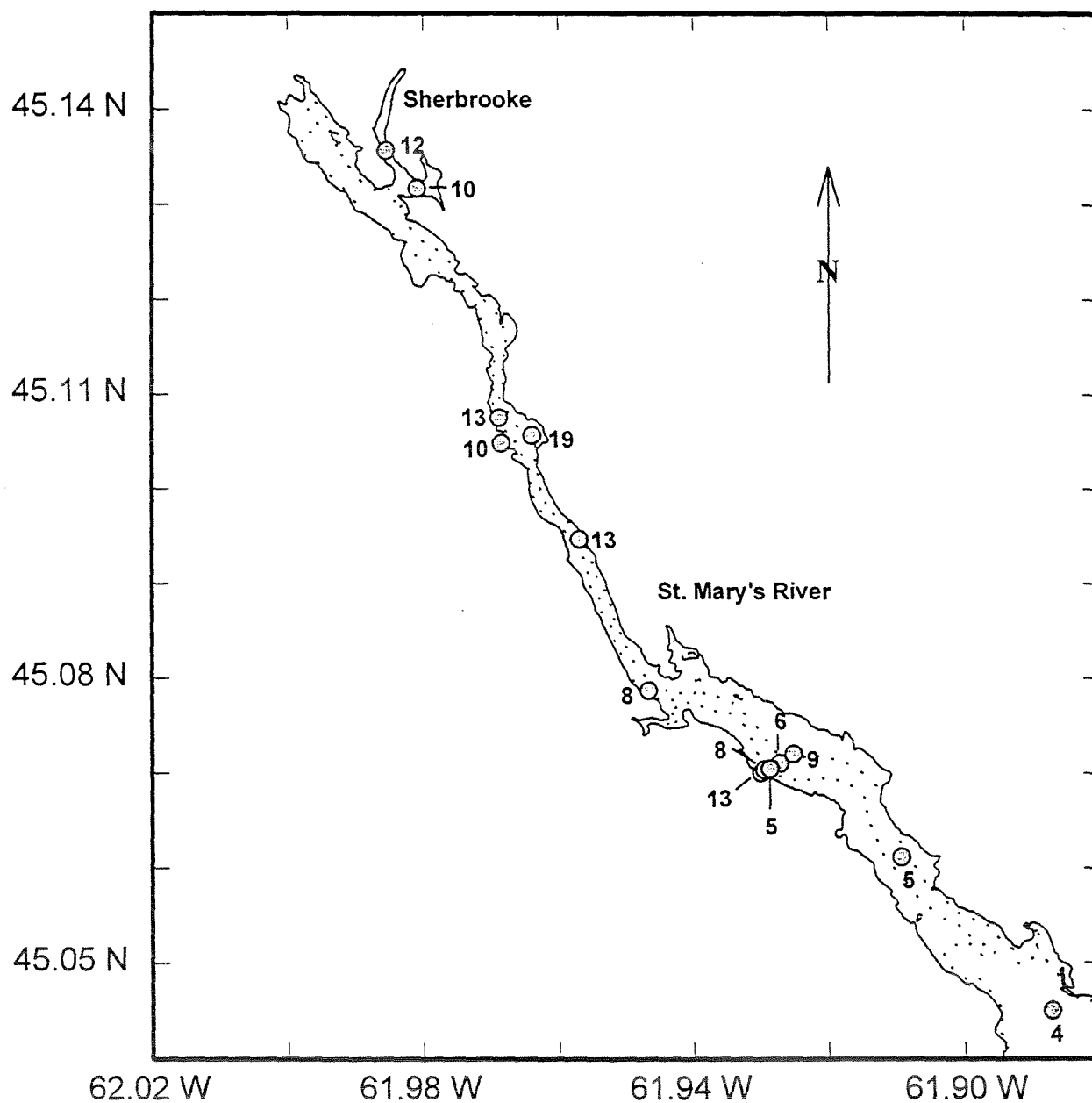
Figure 186. Copper concentrations in surficial sediments
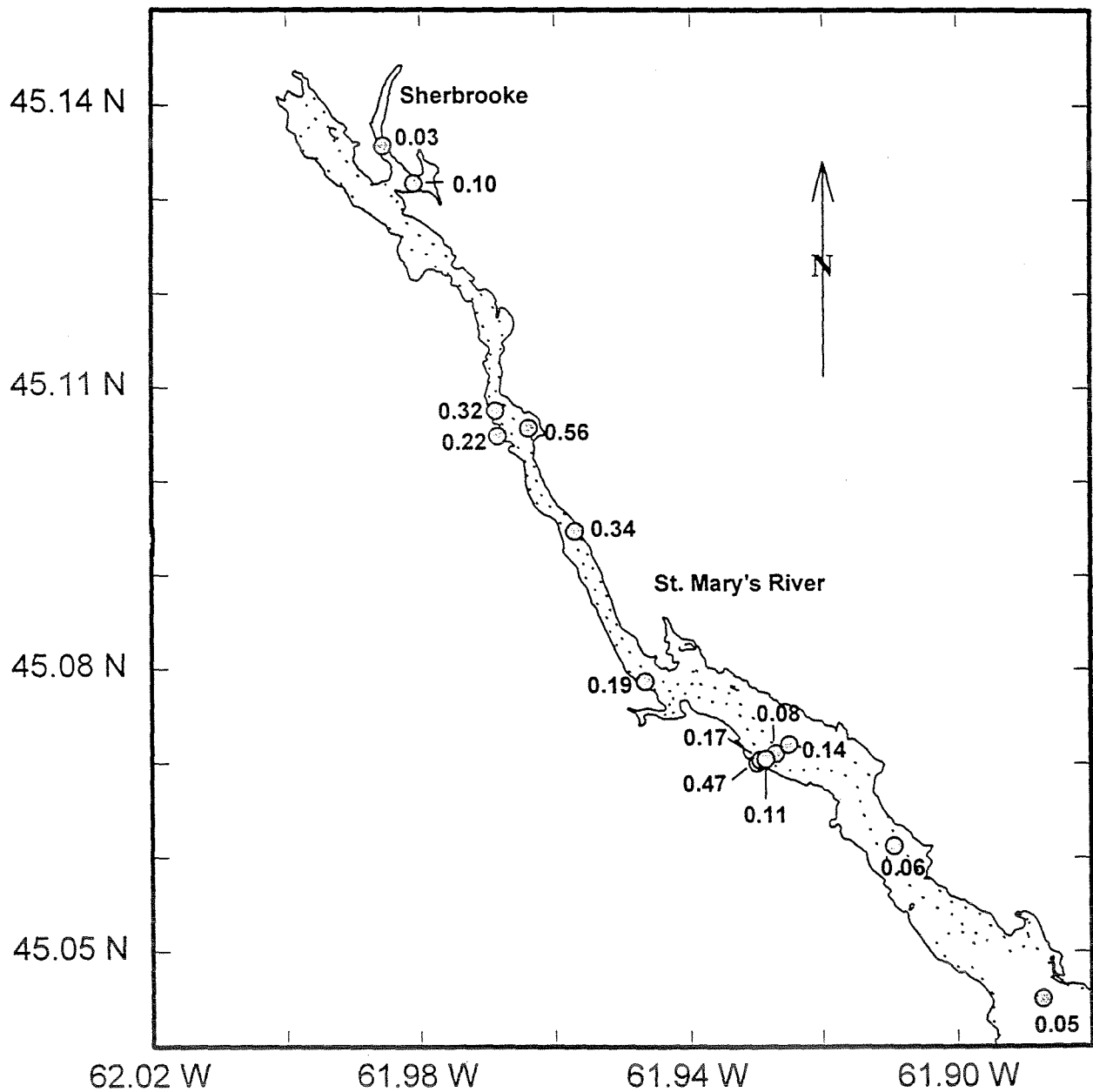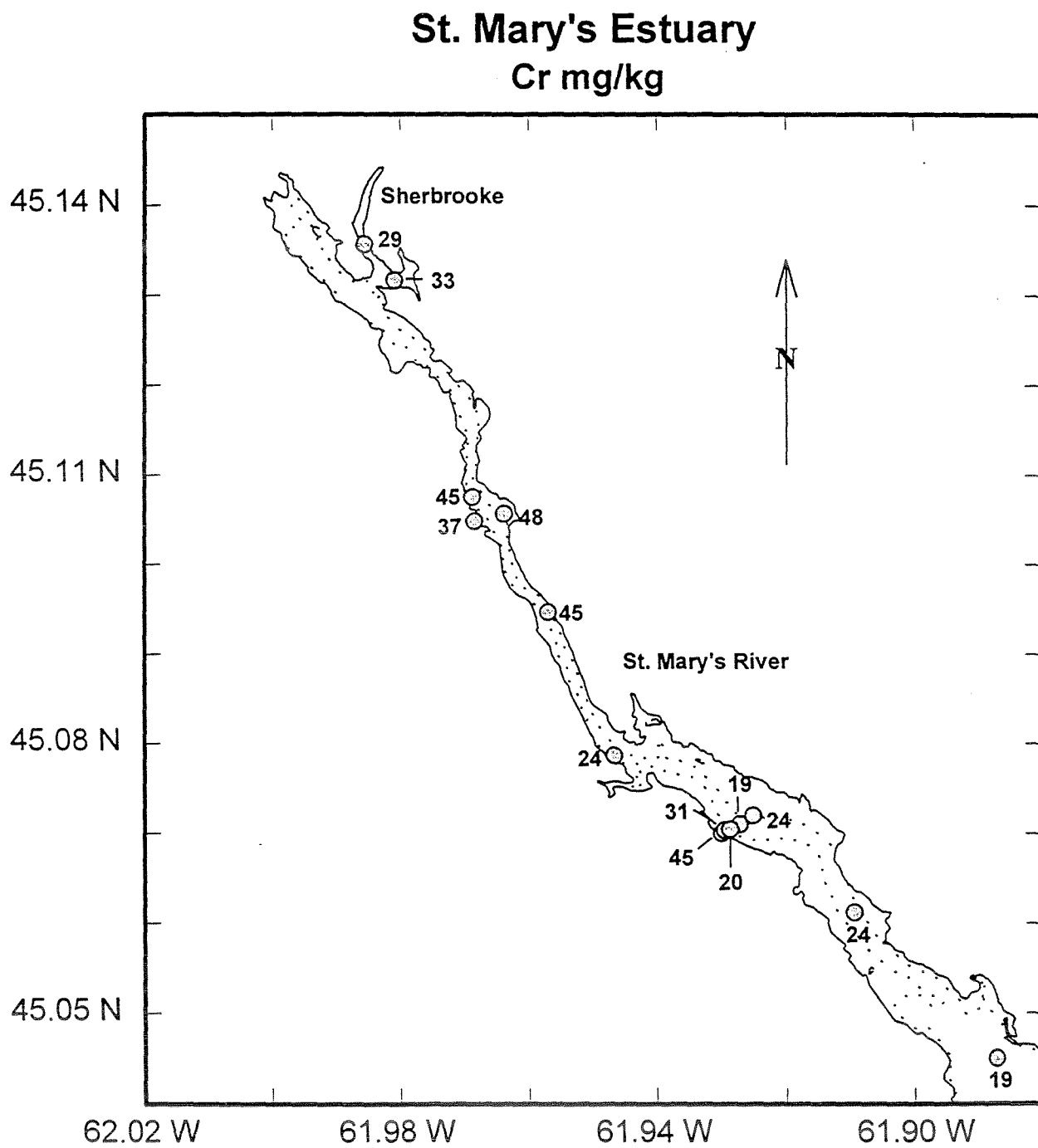
St. Mary's Estuary
Hg mg/kg

Figure 187. Mercury concentrations in surficial sediments

St. Mary's Estuary
Li mg/kg

Figure 188. Lithium concentrations in surficial sediments

St. Mary's Estuary
Mn mg/kg

Figure 189. Manganese concentrations in surficial sediments

St. Mary's Estuary
Ni mg/kg

Figure 190. Nickel concentrations in surficial sediments

St. Mary's Estuary
Pb mg/kg
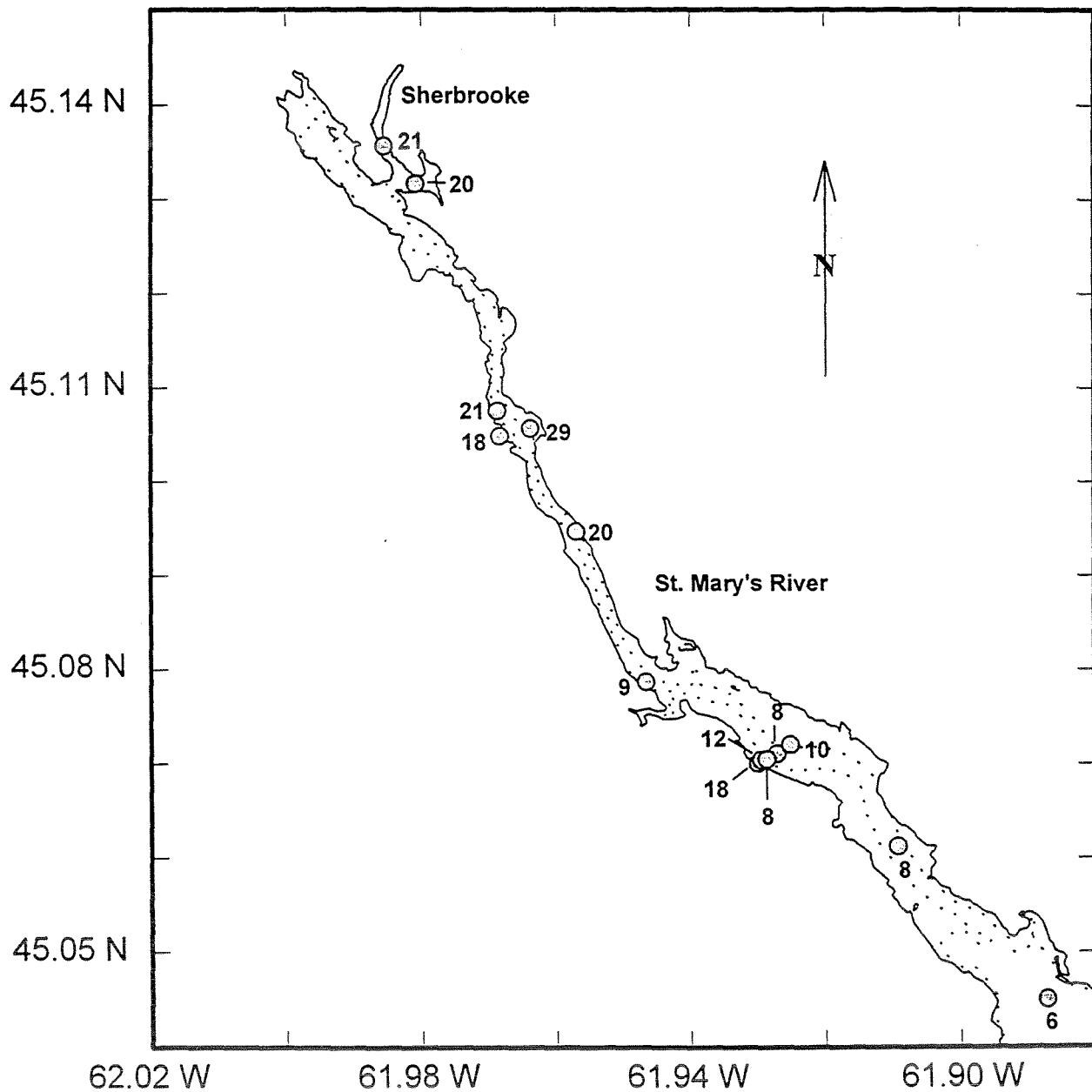
Figure 191. Lead concentrations in surficial sediments

St. Mary's Estuary
Sn mg/kg

Figure 192. Tin concentrations in surficial sediments

St. Mary's Estuary
V mg/kg

Figure 193. Vanadium concentrations in surficial sediments
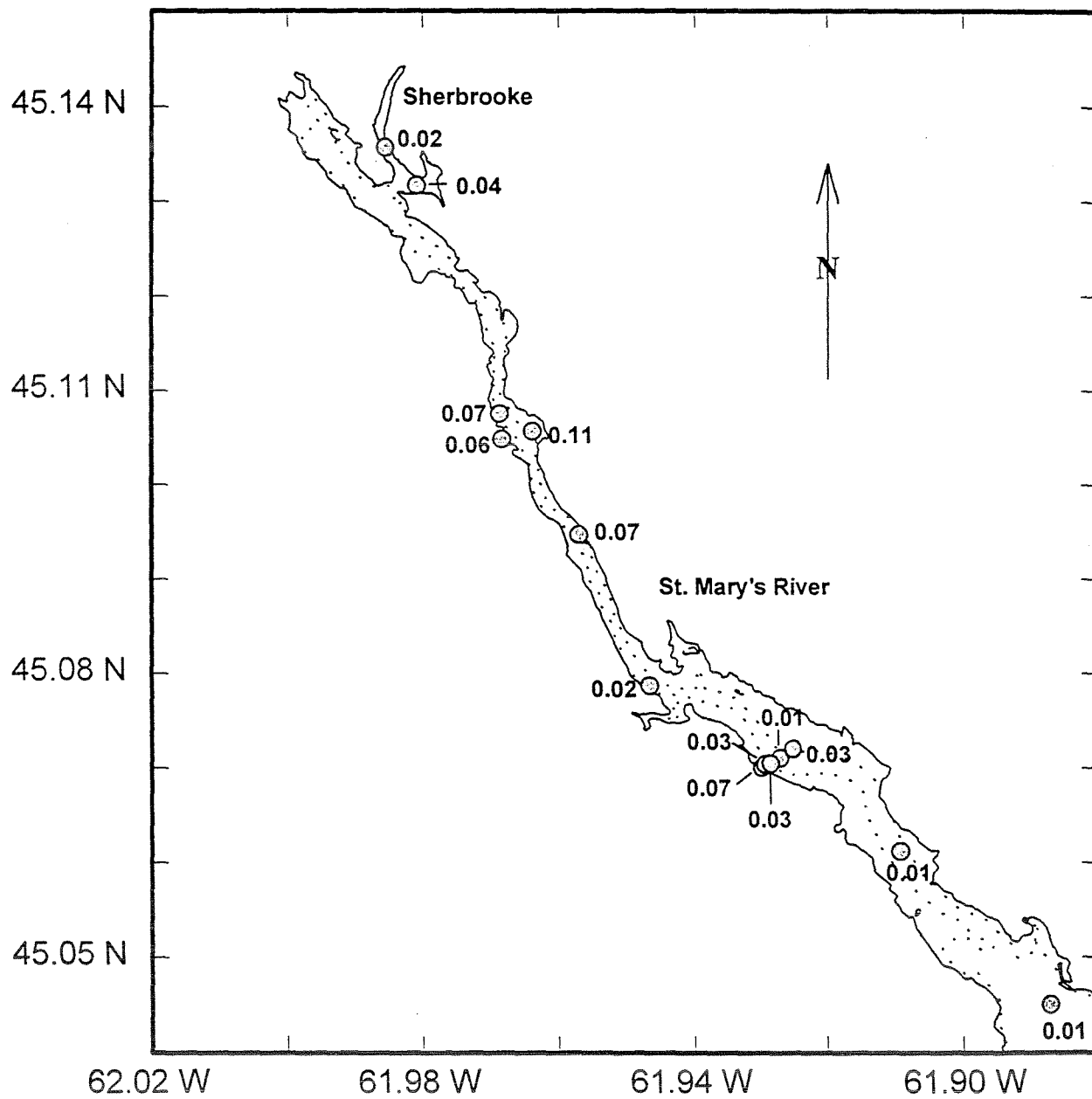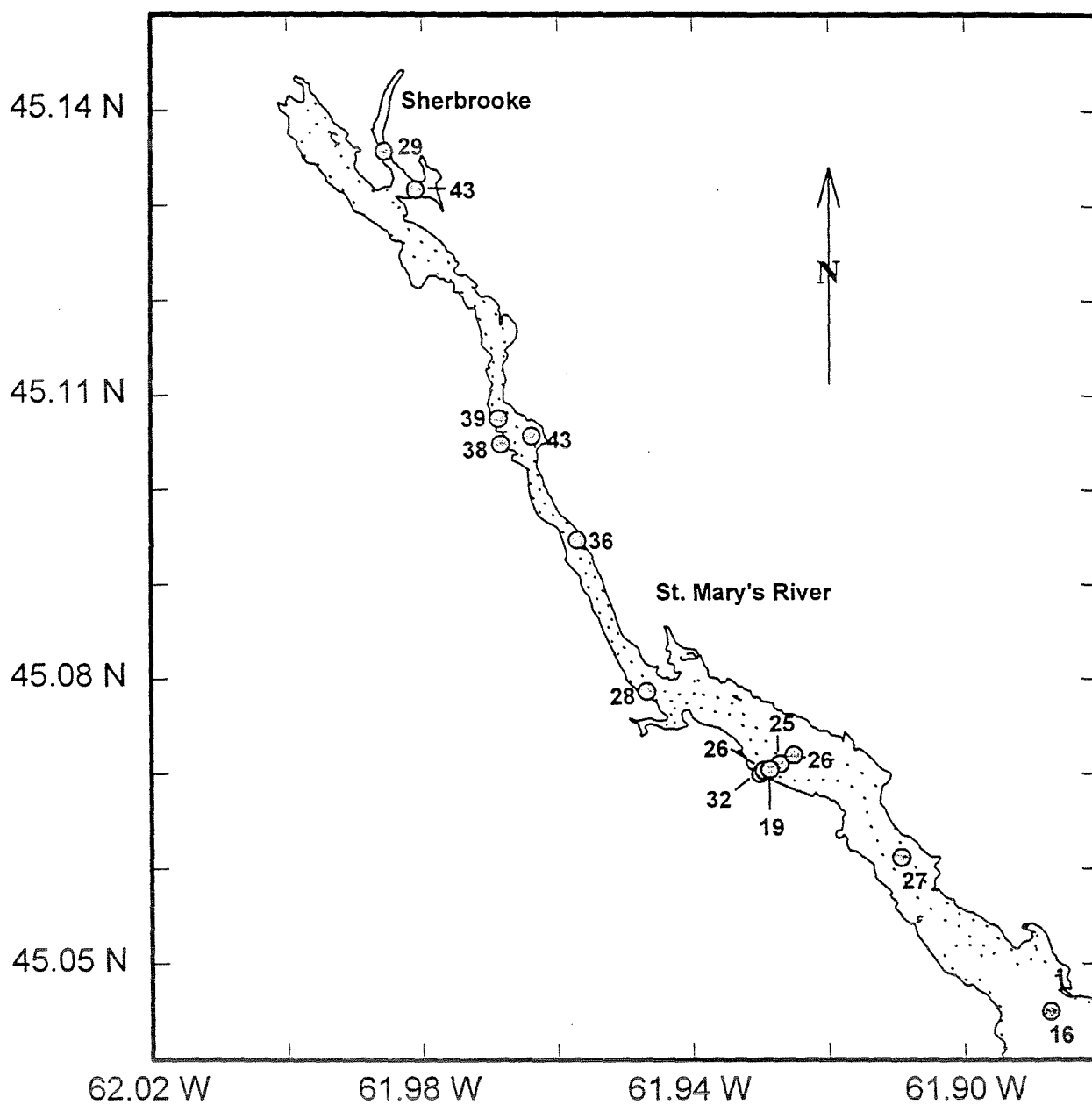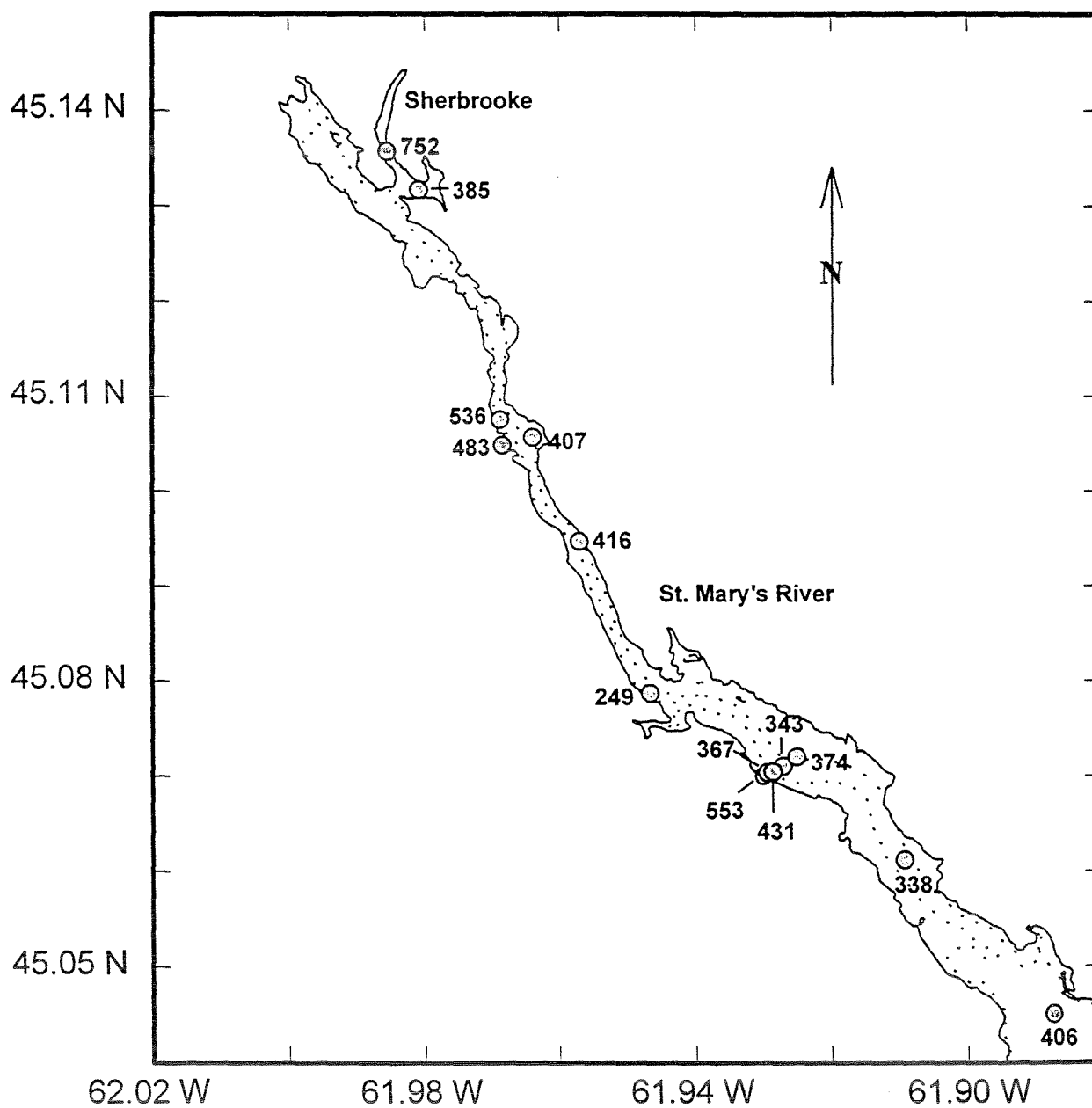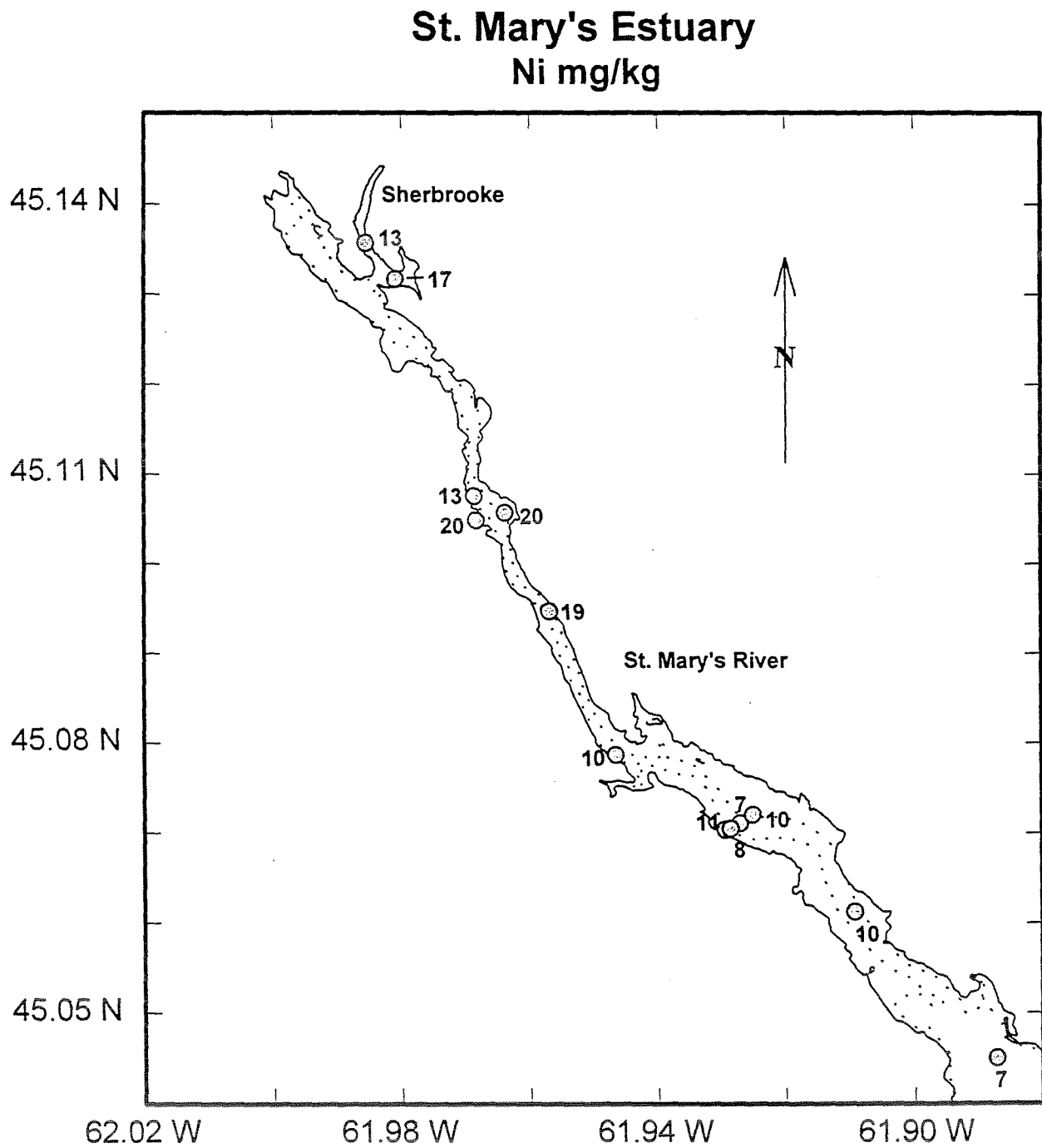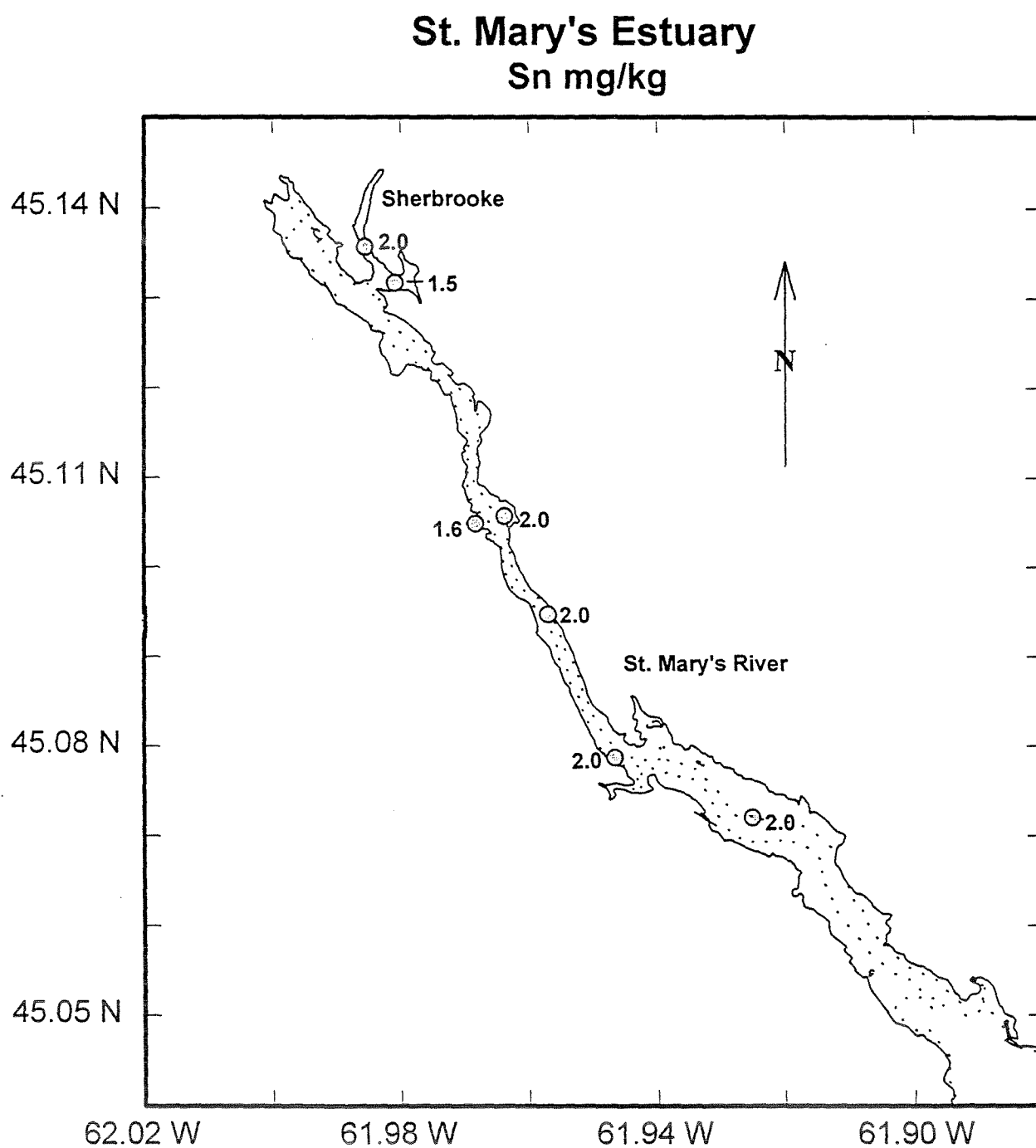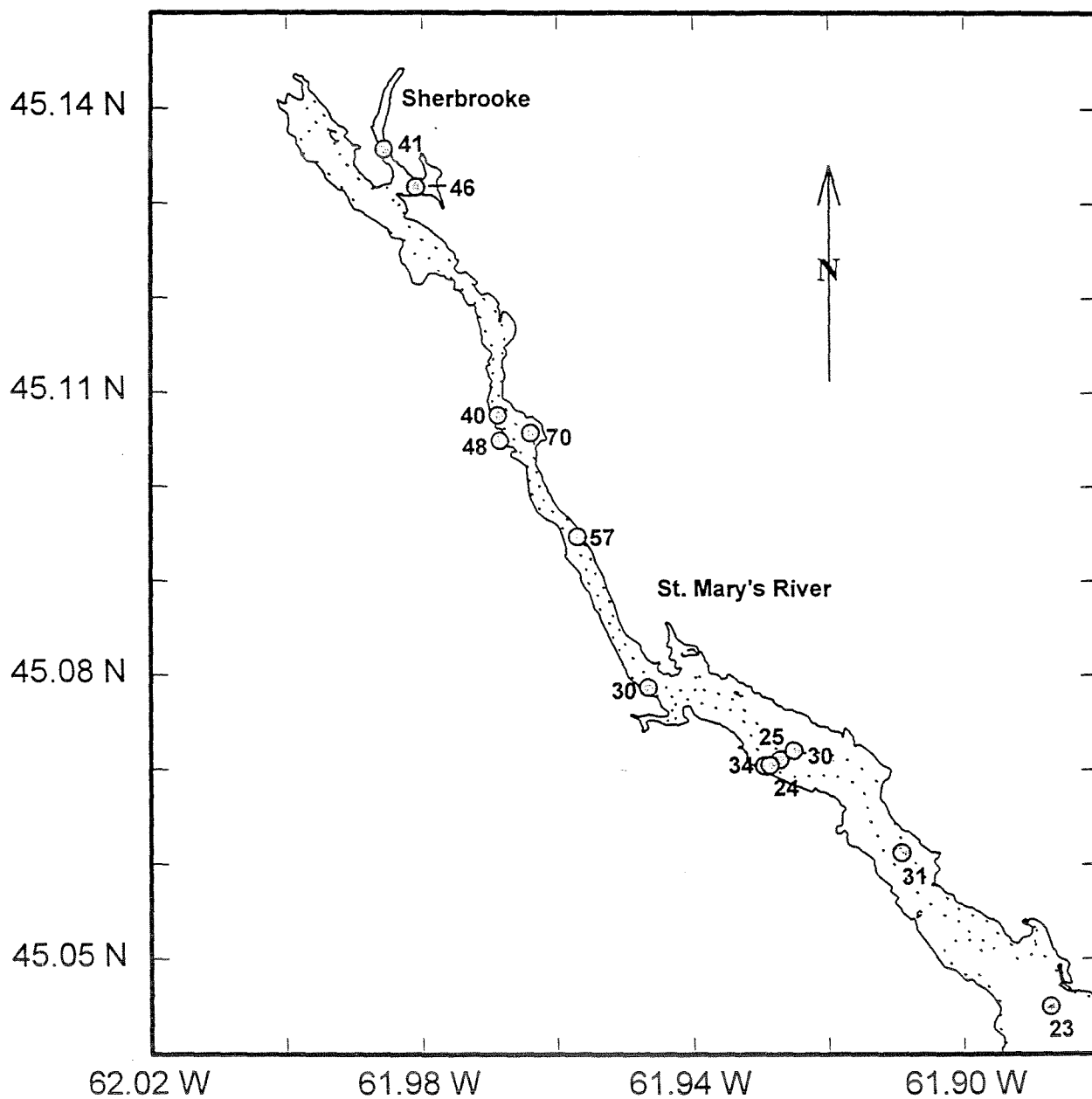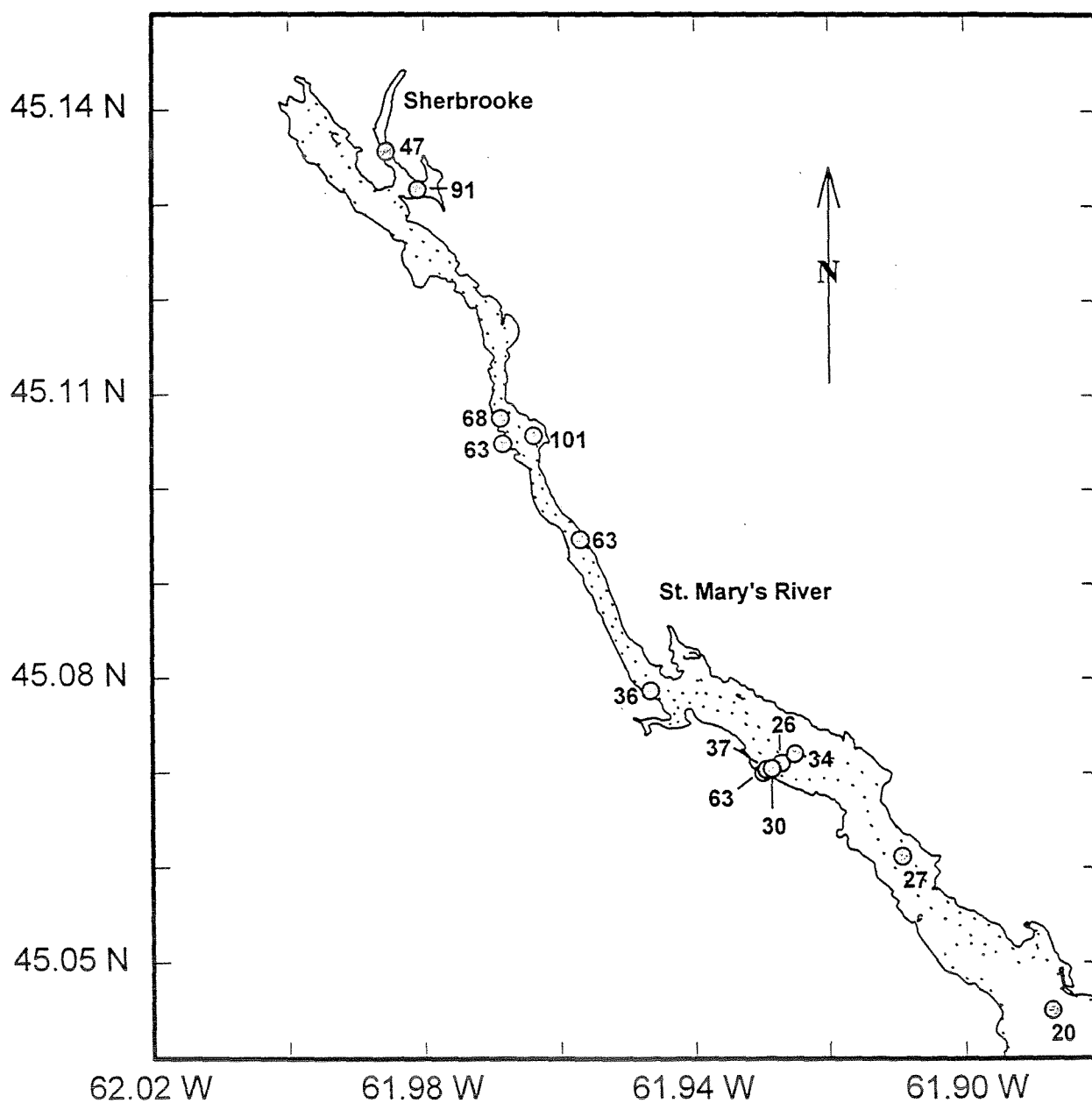
St. Mary's Estuary
Zn mg/kg

Figure 194. Zinc concentrations in surficial sediments

ACKNOWLEDGEMENTS

REFERENCES

Ackermann, F. 1980. A procedure for correcting grain size effect in heavy metal analysis of estuarine and coastal sediments. Environ. Technol. Lett. 1: 517-527.

DeGroot, A.J., and K.H. Zschuppe. 1981. Contribution to the standardization of the methods for heavy metals in sediments. Rapp. P.-v. Réun. Cons. Int. Explor. Mer 181: 111-122.

Gibbs, R.J., M.D. Matthews, and D.A. Link. 1971. The relationship between sphere size and settling velocity. J. Sediment Petrol. 41: 7-18.

Gregory, D., B. Petrie, F. Jordan, and P. Langille. 1993. Oceanographic, geographic and hydrological parameters of Scotia-Fundy and southern Gulf of St. Lawrence inlets. Can. Tech. Rep. of Hydrogr. Ocean Sci. 143: viii + 248 p.

Hatch, W.R., and W.L. Ott. 1968. Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. Ann. Chem. 40: 2085-2087.

Hirst, D.M. 1962. The geochemistry of modern sediments from the Gulf of Paria - II. Geochim. Cosmochim. Acta 26: 1147-1187

Kranck, K. 1980. Experiments on the significance of flocculation in the settling of fine-grained sediment in still water. Can. J. Earth Sci. 17: 1517-1526.

Kranck, K. 1980. Variability of particulate matter in a small coastal inlet. Can. J. Fish. Aquat. Sci. 37(8): 1209-1215.

Kranck, K., and T.G. Milligan. 1985. Origin of grain size spectra of suspension deposited sediment. Geo. Mar. Lett. 5: 61-66.

Kranck, K. 1986. Settling behaviour of cohesive sediment, p. 151-169. In A.J. Mehta [ed.]. Estuarine Cohesive Sediment Dynamics. Springer-Verlag.

Kranck, K. 1993. Flocculation and sediment particle size. Arch. Hydrobiol. Suppl. 75: 266-309.

Loring, D.H. 1978. Geochemistry of zinc, copper, and lead in the sediments of the estuary and Gulf of St. Lawrence. Can. J. Earth Sci. 15: 757-772.

Loring, D.H. 1979. Geochemistry of cobalt, nickel, chromium, and vanadium in the sediments of the estuary and Gulf of St. Lawrence. Can. J. Earth Sci. 16: 1196-1209.

Loring, D.H. 1982. Geochemical factors controlling the accumulation and dispersal of heavy metals in the Bay of Fundy sediments. Can. J. Earth Sci. 19(5): 930-944.

Loring, D.H. 1984. Trace-metal geochemistry of sediments from Baffin Bay. Can. J. Earth Sci. 21: 1368-1378.

Loring, D.H. 1990. The Li solution - a new approach for the granulometric normalization of trace metal data. Mar. Chem. 29: 155-168.

Loring, D.H. 1991. Normalization of heavy-metal data from estuarine and coastal sediments. Int. Counc. Explor. Sea. J. Mar. Sci. 48: 101-115.

Loring, D.H., and R.T.T. Rantala. 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci. Rev. 32: 235-283.

Loring, D.H., K. Naes, S. Dahle, G.G. Matishov, and G. Illin. 1995. Arsenic, trace metals, and organic micro contaminants in sediments from the Pechora Sea, Russia. Mar. Geol: in press.

Malcolm, W. 1912. Goldfields of Nova Scotia. Dep. Mines Bull. 20-E. 330 p.

Milligan, T.G., and K. Kranck. 1992. Electroresistance particle size analyzers. In J.P.M. Syvitski [ed.]. Theory, Methods and Applications of Particle Size Analysis. Cambridge Univ. Press, N.Y.

Nota, D.J.G., and D.H. Loring. 1964. Recent depositional conditions in the St. Lawrence River and Gulf. Mar. Geol. 2: 198-235.

Rantala, R.T.T., and D.H. Loring. 1989. Teflon bomb decomposition of silicate materials in a microwave oven. Anal. Chim. 220: 263-267.

Scarratt, D. 1995. Under water survey of Lunenburg Harbour LaHave river estuary, Shelburne Harbour, Liverpool Bay and Harbour. David Scarratt & Associates, Halifax, N.S. 30 p.

Walkey, D. 1947. A critical examination of a rapid method for determining organic carbon in soil. Soil Sci. 63: 177-192.

Windom, H.L., S.T. Schropp, F.D. Calder, J.D. Ryan, R.G. Smith, Jr., L.C. Burnway, F.G. Lewis, and C.H. Rawlinson. 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern U.S. Environ. Sci. Tech. 23: 314-320.

APPENDIX I. STATISTICAL DATA[a] FOR ELEMENTS DETERMINED BY ICP-MS

	B	Ba	Co	Mo	Sr	Th	U
AB n = 21							
AVG	<5	288	8	<2	108	0.4	1.0
STD		16	1		13	0.1	0.2
CH n = 28							
AVG	6	350	7	3	136	0.5	2.0
STD	4	58	1	1	47	0.2	0.6
LA n = 35							
AVG	5	391	9	4	134	0.6	2.6
SD	8	28	3	2	14	0.1	0.8
LV n = 12							
AVG	<5	274	3	<2	125	0.6	1.0
SD		29	1		19	0.1	0.3
LU n = 14							
AVG	8	370	8	9	127	0.9	3.6
SD	11	34	2	5	14	0.2	1.2
PI n = 13							
AVG	<5	299	7	8	124	0.5	3.2
SD		84	2	6	45	0.2	2.3
PU n = 12							
AVG	<5	290	6	<2	149	0.4	1.5
SD		33	1		13	0.1	0.3
SB n = 23							
AVG	<5	287	5	3	141	0.4	2.3
SD		46	1	2	13	0.1	0.7
SH n = 12							
AVG	<5	277	7	2	111	0.5	1.8
SD		91	2	1	13	0.1	0.4
SM n = 13							
AVG	6	246	5	8[b]	95	0.3	1.8
SD	5	50	2	8	14	0.1	2.0

[a]Concentrations in mg kg^{-1}
n = number of samples
AVG = average
SD = standard deviation.
[b]average and SD of two samples
Be and Sb were determined but were below detection limits of <5 and <2 mg·kg^{-1} repectively

APPENDIX II. BACKGROUND AND CONTAMINANT LEVELS

It is necessary to establish natural background metal levels before the extent, if any, of heavy metal contamination can be estimated. Such background levels are subtracted from the total values to yield an estimate of the anthropogenic contribution. Background levels, taking their natural variability in account, can be estimated by: a) average metal concentrations of texturally equivalent sediments reported in the literature, b) direct measurements of metal concentrations in recent texturally and mineralogically equivalent sediments from a known pristine region, c) direct measurements of metal concentrations in texturally equivalent sub-surface core samples obtained from a depth below any possible contamination or biological mixing, and d) normalization procedures described in the Statistical Analyses subsection of the Materials and Methods section of this report.

Geochemical studies of pristine sedimentary environments in the Canadian and Russian Arctic (Loring 1984; Loring et al. 1995) that are comparable to those of Nova Scotian nearshore sediments indicate that muddy silicate sediments from Baffin Bay (Canadian Arctic) comprising material >70% by weight <63 μm diameter material contain 0.15 ± 0.1 mg·kg^{-1} Cd, 29 ± 8 mg·kg^{-1} Cu, 0.05 ± 0.02 mg·kg^{-1} Hg, 15 ± 5 mg·kg^{-1} Pb, and 61 ± 14 mg·kg^{-1} Zn (Loring 1984). Pechora and Kara Sea (Russian Arctic) fine-grained sediments contain 0.11 ± 0.05 mg·kg^{-1} Cd, 21 ± 2 mg·kg^{-1} Cu, 0.03 ± 0.01 mg·kg^{-1} Hg, 18 ± 2 mg·kg^{-1} Pb, 1.1 ± 0.5 mg·kg^{-1} Sn, 84 ± 9 mg·kg^{-1} Zn, and. 0.06 ± 0.03 mg·kg^{-1} Cd, 21 ± 3 mg·kg^{-1} Cu, 0.03 ± 0.012 mg·kg^{-1} Hg, 15 ± 4 mg·kg^{-1} Pb, 1.3 ± 0.6 mg·kg^{-1} Sn, and 63 ± 36 mg·kg^{-1} Zn respectively (Loring et al. 1995).

The main difficulty arises in defining the level of metal concentration that signifies that the sediments contain excessive amounts of the metals and can be more or less equally applied to embayments receiving anthropogenic inputs. Such values must be low enough to detect the initial stages of contamination but high enough to account for the natural variability. In the case of the embayments evaluated in this report it is considered, reasonably, that a contaminant may be considered to be at a significant level if it is found at concentrations about a factor of 1.5 to 2 greater than acceptable background levels for fine-grained sediments based on the results of previous studies. Because of the uncertainty of the concentrations of Sn in fine-grained sediments, a factor of 5 has been used in this report to denote a significant level of contamination. Few accurate data are also available for the As levels in fine-grained marine sediments, but fine-grained certified reference materials, such as NRCC materials BCSS-1 and MESS-1 and USGS material MAG-1 from North Atlantic coastal waters, have levels of approximately 10 mg·kg^{-1} As. Accordingly, a factor of 2 was used to define a lower limit to contaminant levels for As.

In this report, therefore, metal concentrations greater than 20 mg·kg^{-1} As, 0.3 mg·kg^{-1} Cd, 40 mg·kg^{-1} Cu, 0.1 mg·kg^{-1} Hg, 40 mg·kg^{-1} Pb, 5 mg·kg^{-1} Sn, and 150 mg·kg^{-1} Zn are used to define when metal concentrations exceed natural background levels in fine-grained sediments.

It should be noted that the term "background levels" used in this report is different from the term "baseline levels" which is used to denote contemporary values for the concentrations of metals in surface sediments.

APPENDIX III. COMPOSITION OF SOURCE MATERIALS AND ROCKS

Metal concentrations in source materials (total and <63 µm) and rocks for nearshore sediments (mg·kg^{-1} except % for Al and Fe).

Till Sources[a]:

Totals	Al	As	Cd	Cr	Cu	Fe	Li	Mn	Ni	Pb	V	Zn	mud%
PE1	4.54	11	0.08	37	24	1.98	44	768	22	15	38	50	18
PE2	5.55	29	0.10	40	16	1.91	60	1005	18	40	37	49	30
PE3	6.73	13	0.09	63	25	3.20	60	744	28	24	70	73	63
PE4	6.62	9	0.16	68	30	3.11	63	983	30	24	75	72	66
SH1	5.93	3	0.08	17	60	1.17	97	446	7	16	23	31	24
SH2	5.41	4	0.02	42	19	2.18	29	574	24	8	42	41	26
LA1	5.40	8	0.02	43	18	1.76	32	204	11	17	42	22	10
LA2	8.01	24	0.11	67	33	3.6	62	1072	28	27	80	70	49
LU1	7.43	21	0.11	64	33	3.79	60	982	36	23	86	75	57
LU2	7.73	15	0.13	87	32	3.93	62	744	34	35	93	76	50

<63um	Al	As	Cd	Cr	Cu	Fe	Li	Mn	Ni	Pb	V	Zn
PE1	7.03	33	0.15	57	56	3.94	88	2195	44	36	59	112
PE2	6.86	41	0.15	50	29	3.22	80	2010	25	85	60	80
PE3	8.74	18	0.12	70	36	4.30	81	806	43	31	98	102
PE4	8.48	15	0.15	96	30	4.15	86	1244	43	29	108	98
SH1	7.29	9	0.10	40	112	2.39	126	754	14	32	48	54
SH2	7.43	7	0.04	81	34	3.37	45	918	33	16	75	68
LA1	8.40	23	0.05	88	38	4.64	63	460	19	97	89	56
LA2	9.84	28	0.10	91	46	4.81	84	956	38	30	119	101
LU1	9.53	28	0.10	90	49	5.21	84	1093	42	28	131	104
LU2	9.93	18	0.14	116	40	5.01	85	950	46	39	131	104

Contributions of the <63 µm fraction to the total concentrations in the whole sample (mg·kg^{-1} except % for Al and Fe):

	Al	As	Cd	Cr	Cu	Fe	Li	Mn	Ni	Pb	V	Zn
PE1	1.27	6	0.03	10	10	0.71	16	395	8	6	11	20
PE2	2.06	12	0.05	15	9	0.97	24	603	8	26	26	24
PE3	5.51	11	0.08	44	23	2.71	51	508	27	20	62	64
PE4	5.60	10	0.10	63	20	2.74	57	821	28	19	71	65

SH1	1.75	2	0.02	10	27	0.57	30	181	3	8	11	13
SH2	1.93	1	0.01	21	9	0.88	12	239	9	4	20	18
LA1	0.84	2	0.01	9	4	0.46	6	46	2	10	9	6
LA2	4.82	14	0.05	45	23	2.36	41	468	19	15	58	49
LU1	5.43	16	0.06	51	28	2.97	48	623	24	16	75	59
LU2	4.97	9	0.07	58	20	2.51	43	475	23	20	66	52

Rock Sources:

Rocks[b]	Al	As	Cd	Cr	Cu	Fe	Li	Mn	Ni	Pb	V	Zn
Gran.	8.61	3	0.07	10	10	0.83	120	217	6	33	15	38
Qtz.	7.98	12	0.05	82	11	3.53	45	548	30	12	78	66
Slate1	12.3	<1	<0.01	125	2	2.12	99	437	<2	16	169	36
Slate2	13.51	13	0.19	163	11	1.86	86	180	8	37	206	43
Slate3	7.61	30	0.22	67	30	5.25	93	259	40	19	75	102

---

[a] Till sources: PE1 = till from head of Petspeswick inlet, PE2 = till from east side of Petspeswick inlet, PE3 = till from mouth of Petspeswick inlet, PE4 = till from mouth of Petspeswick inlet, SH1 = granite till from head of Ship Harbour, SH2 = quartzite till from western side of Ship Harbour, LA1 = till from western side of the LaHave estuary, LA2 = till from near Riverport on the LaHave estuary, LU1 = till from the head of Lunenburg Harbour, LU2 = till from head of Lunenburg Harbour.

[b] Rock Sources: Gran. = granite rock from head of Ship Harbour, Qtz. = quartzite from head of Petspeswick inlet, Slate1 = slate rock from LaHave River, Slate 2 = slate rock from LaHave River, Slate3 = slate rock from the LaHave River near Bridgewater.