

GEOCHEMICAL MAPPING IN NEWFOUNDLAND AND LABRADOR: ITS ROLE IN ESTABLISHING GEOCHEMICAL BASELINES FOR THE MEASUREMENT OF ENVIRONMENTAL CHANGE

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ABSTRACT

First-pass geochemical mapping of Newfoundland and Labrador was completed in 1987. For these geochemical surveys, organic sediment was collected from more than 40,000 lakes and the results used to promote mineral development by stimulating and focusing mineral exploration. These regional geochemical data are receiving increasing attention for the definition of geochemical baselines against which chemical change in the environment may be measured. To determine the natural geochemical background effectively for environmental purposes, it is necessary to demonstrate that the sample medium employed meets the following criteria: first, it is not already widely contaminated; second, that it reflects reliably the natural fluctuations in this background caused by geological variation; and thirdly, that it records environmental change where it has occurred.

Studies are in progress to evaluate organic lake sediment as sampled in the regional surveys against these criteria. The variation of trace-element levels in lake-sediment cores has been investigated in south-central Newfoundland to compare stratigraphic variance with spatial variance between lakes over geochemically contrasted geological units. Element-speciation studies employing partial and total digestions of the sediments indicate how trace elements are partitioned and hence their geochemical mobility and potential bio-availability. To determine the geochemical effects of urbanization, a lake-sediment survey was conducted of the St. John's metropolitan area.

From the results available, it is clear that lake sediment is a very appropriate medium for establishing geochemical baselines. In relatively pristine regions, the lake cores show that stratigraphic variation of trace-element concentrations in the upper metre of sediment, which are due to local environmental fluctuations over time, are generally quite minor and much smaller than geochemical variation between lakes due to the primary geochemical composition of the local bedrock. Significant proportions of a wide range of elements (i.e., Cu, Ni, Co, Zn, Y, Dy, La, Cd, Ce, Pb, Mn, V, Fe, Cr, Mo, Ba and Li) are held in the readily acid-leachable organic and amorphous oxide phases of the sediments, indicating their potential bio-availability under acid conditions. Finally, lake sediment from the St. John's region shows the effects of urbanization in a number of ways. This is most dramatically indicated by the increase in heavy metals such as Pb, which is from 5 to 10 times higher in lakes from the urban core than the normal upper limit of its natural background for the area.

INTRODUCTION

Man-made chemical changes to the environment are superimposed on a variable natural geochemical background where trace-element abundances range over several orders of magnitude. Since the chemical composition of the earth's surface directly affects the biosphere, a reliable overview of the natural variation in the geochemical background is essential in order to identify, measure and place into perspective the extent of man-made environmental changes. These changes may be local (e.g., the point discharge of pollutants to the environment or the modification of the

natural geochemical background through activities such as construction), or widespread (e.g., airborne deposition of pollutants like acid rain).

The geochemical background at the earth's surface is determined by geology. The levels of the major elements (Si, Al, Fe, Mg, Ca, Na, and K) and their spatial variation can be estimated to a first approximation from geological and soil maps that are widely available. However, such maps offer very little information on the abundances of trace elements currently regarded either as essential to many forms of life (i.e., Cl, Co, Cu, F, I, Mn, Mo, P, S, Se, V and Zn) or as

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toxic (i.e., As, Be, Cd, Hg, Ni, Pb, Sb, Tl and U). Abundance levels for these important trace elements and their spatial variations can only be provided by appropriately designed geochemical surveys.

Regional geochemical mapping in Newfoundland and most of Labrador is based on the composition of 'grab' samples of the upper 20 to 100 cm of organic sediment collected from about 40,000 lakes (Figure 1). The program commenced in 1973 following orientation studies that showed empirically that geochemical surveys of the Recent, organic, lake sediment was a cost-effective and rapid approach to mineral-resource appraisal and for focusing and stimulating mineral exploration in this province. Indeed, geochemical mapping using organic lake sediment has been widely and successfully applied in northern countries such as Canada (Friske and Hornbrook, 1991) and Finland (Tenhola, 1991), but studies to elucidate the geochemical processes that contribute to the success of the method have been relatively few (cf. Coker *et al.*, 1979).

Lake sediments reflect not only the spatial geochemical variations at the geosphere-biosphere interface but also, in many cases, they contain an historical record of the Holocene Epoch. Mineralogical and chemical changes may be preserved as a chemical stratigraphy (Engstrom and Wright, 1984). The bulk of an organic lake sediment is composed typically of indeterminate organic matter and fine-grained, inorganic material that is difficult to identify mineralogically. Chemical analysis provides the most practical way of quantifying compositional variation.

Chemical variation in a lake over time may be due to several factors that operate more or less contemporaneously. These factors include the intensity of erosion in the catchment, biological activity in the lake and variations in the groundwater regime. In addition, human activities may influence the chemistry of the upper sections of lake-sediment cores. The chemical record may be complex because of these manifold factors, and is best resolved with reference to other stratigraphic information from pollen assemblages, which provide information on climatic changes and anthropogenic activity, and diatom assemblages that reflect changes in lake-water alkalinity and salinity.

Chemical stratigraphy in lake sediment has been studied mainly to detect and characterize anthropogenic change around known sources of pollution such as mines (Qvarfort, 1983), smelters (Fortescue, 1986), and towns (Rogers and Ogden, 1991; Rogers *et al.*, 1991), as well as the effects of changes in land use (Burden *et al.*, 1986). These studies typically examine a few lakes in considerable detail with little reference to geologically determined geochemical variation. On the other hand, regional geochemical surveys for mineral-resource appraisal usually ignore or at least fail to quantify the nature and extent of anthropogenic changes that may mask the natural patterns of interest. A comparison of the upper 14 cm of lake sediment with sediment from below 20 cm was made from a collection of several hundred short cores from the Herman Lake map area north of Lake Superior in Ontario

(Fortescue and Vida, 1991). The lower samples were deposited below the 'Ambrosia rise' (the layer at which a sharp increase in the proportion of pollen from ragweed occurs, which indicates the initial, widespread clearing of the forest in this area between 1880 and 1900), so by comparing the two sample sets, the nature and amount of environmental change in this century can be assessed. Increased Sb and As values in the post-Ambrosia sediments were noted in a fallout zone downwind from a sintering plant that has operated for over 50 years in Wawa, 20 km southwest of the study area. An area-wide increase in Pb values was also observed that showed no apparent relationship to the sintering plant fallout, whereas other elements such as Cu and Mn showed no overall difference between the two layers.

The study by Fortescue and Vida (1991) clearly indicates that an understanding of both spatial and temporal variations in the geochemistry of lake sediment is necessary to interpret the results of the existing regional geochemical database for the province from either an environmental or geological perspective. Two important questions are: 1) how variable are trace-element levels with depth in a typical lake-sediment profile and how does this stratigraphic variability compare with trace-element variability between lakes; and, 2) how sensitive are the 'grab' samples in detecting chemical changes due to human activities: can minor disturbances be safely ignored, and will major changes be detected?

To answer these questions, two studies have been conducted: the first (by Sheila Vardy) involved the collection and analysis of lake-sediment cores from five lakes in south-central Newfoundland from which the characteristics of chemical stratigraphy could be determined in regions little disturbed by human activity, and in the second (by Terry Christopher), 'grab' samples of organic lake sediment were collected throughout the St. John's urban area and environs to measure the effects of urban development.

METHODS

Lake-Sediment Cores

Sediment cores from five lakes in south-central Newfoundland (Figure 2) were collected in July 1989 (Vardy, 1990) primarily to study the history of deglaciation and the subsequent development of vegetation. Secondary objectives, and the aspects discussed here, were to study the chemical stratigraphy of the cores, both in relation to climatic change and the consequent changes in vegetation, and to determine the degree of variability in the upper 100 cm of sediment from which the 'grab' samples were obtained in the regional surveys. Although the main consideration in site selection was based on dating the deglaciation history, the north-south transect (Figure 2) crosses the main geological (and geochemical) trends at about 45°, so that significant differences in the levels of several trace elements were anticipated.

The cores were collected in duplicate from each lake using a Livingstone corer having a 5 cm internal diameter,

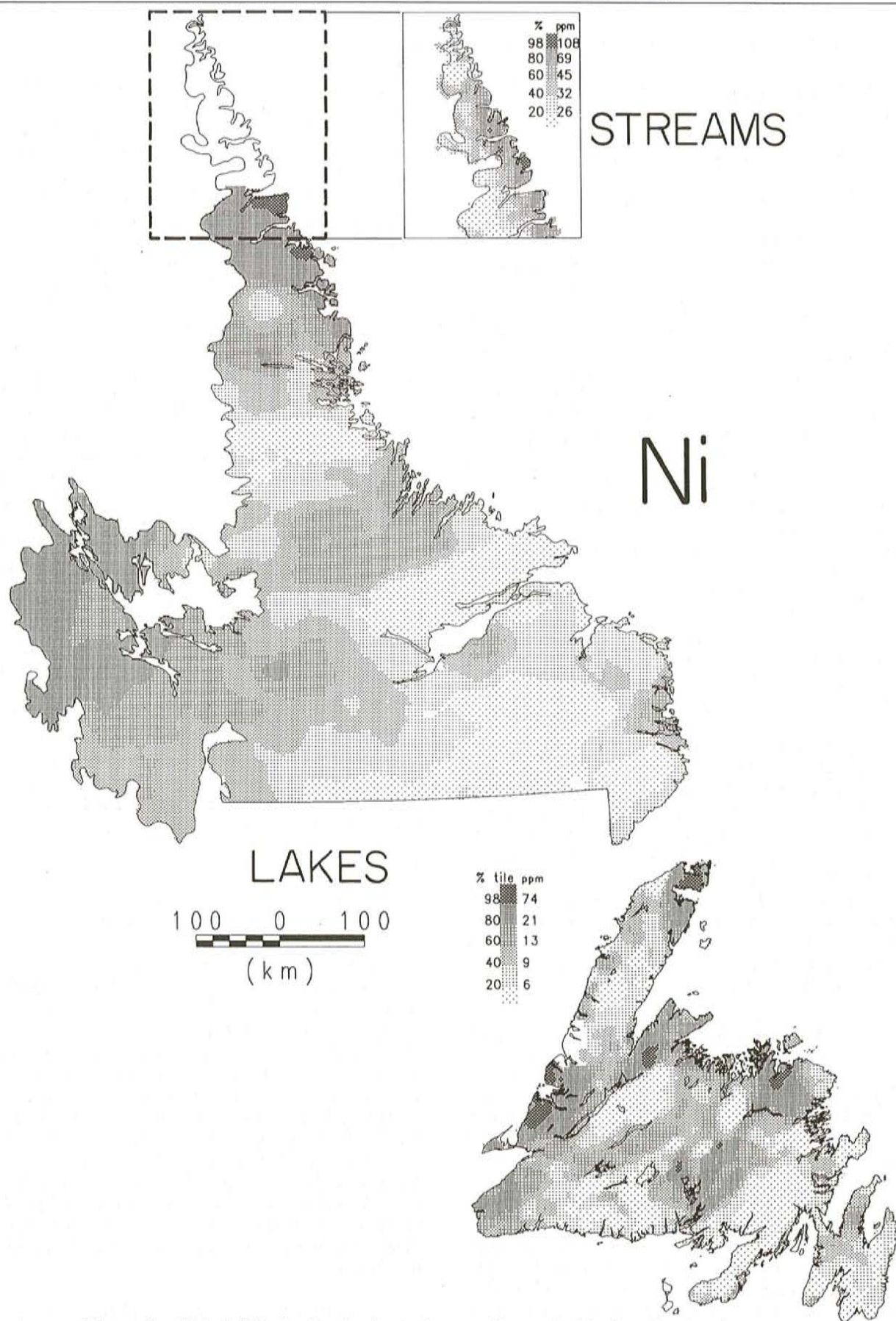


Figure 1. Nickel (Ni) distribution in drainage sediments in Newfoundland and Labrador.

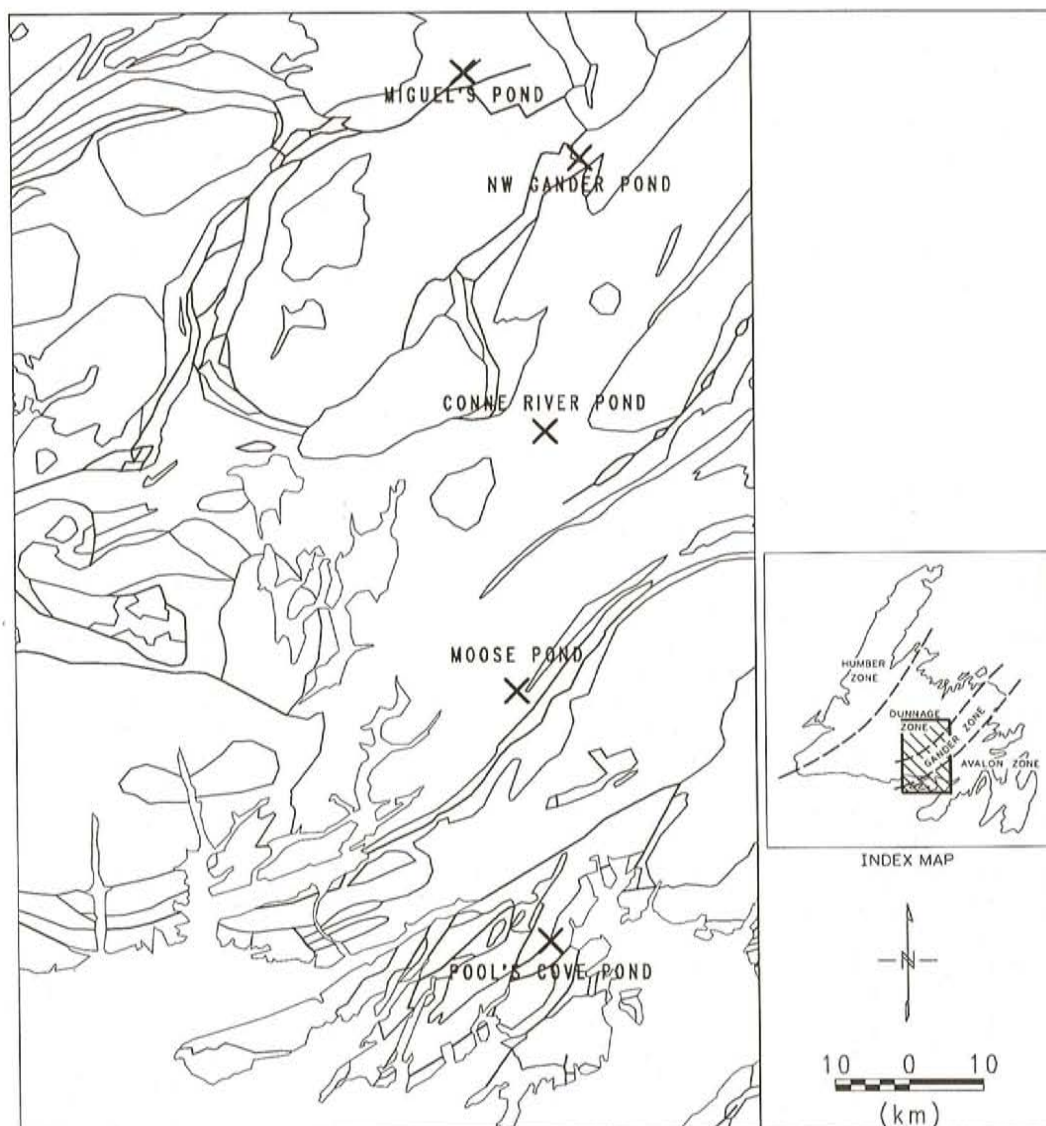


Figure 2. The location of lakes from which sediment cores were collected in south-central Newfoundland; geological contacts from Colman-Sadd *et al.* (1990).

and one of each pair was reserved exclusively for geochemical analysis. They were sampled at 5 cm intervals (except for the Pools Cove Pond core where, because of lack of material, the sampling interval was 25 cm). The samples were oven dried at 40°C, disaggregated in a porcelain mortar and pestle and passed through a 0.18 mm screen. Blind duplicate samples were introduced at this stage at a frequency of one pair in 20 samples to check analytical precision.

The dried (but unashed) sample material was used for analysis. Loss on ignition (LOI, a measure of organic content) was determined at 1000°C. The major elements (expressed as the oxides SiO₂, Al₂O₃, Fe₂O₃ (total Fe), MgO, CaO, K₂O, Na₂O, P₂O₅, TiO₂ and MnO), together with Ba, Cr, and Zr were determined by inductively coupled emission spectrometer (ICP-ES) following a lithium metaborate fusion (Wagenbauer *et al.*, 1983). Instrumental neutron activation

analysis (INAA), was used to measure total concentrations of As, Au, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Mo, Na, Ni, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, W, Yb and Zn. A combination of ICP-ES and atomic absorption spectrophotometry (AAS) was employed to determine total levels of Ba, Be, Cd, Ce, Co, Cr, Cu, Dy, Fe, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sc, Y, Zn and Zr following an HF-HClO₄-HCl digestion. The multi-element suites result in some data redundancy; there are three sets of results for Ba, Cr and Fe, and two for Ce, Co, La, Mo, Na, Ni, Rb, Sc, Zn and Zr. In most cases, there was a good correlation between results from the different methods, although for Ba, Cr, Ni, Zn and Zr the ICP-ES and AAS determinations were preferred because of the higher detection limits for these elements by INAA.

In addition, a 30 percent H₂O₂-0.3M HCl digestion was used to extract elements held by organic matter and

amorphous oxides (Engstrom and Wright, 1984), and the filtered extract was analysed by a combination of ICP-ES and AAS for Ba, Be, Cd, Ce, Co, Cr, Cu, Dy, Fe, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sc, Y, Zn and Zr. The solid residue was digested in 0.2 M NaOH to dissolve biogenic (diatomaceous) silica (Engstrom and Wright, 1984), and this was determined by ICP-ES.

St. John's Urban Area Lake-Sediment Study

The method of sample collection in this study (Christopher, 1991) was the same as that used in the province-wide regional surveys in which 'grab' samples from the upper metre of organic lake sediment from the central, deeper basins of the lakes were obtained with a tubular steel gravity corer. A core 6 cm in diameter and 20 to 30 cm in length comprises a typical sample. As the sampler was allowed to free-fall from the water surface, the depth of penetration varied depending on the water depth and consistency of the sediment, and was observed to vary from as little as 20 cm to as much as 100 cm. Organic lake sediment was collected from most lakes within a 320 km² area that included the urban core and suburbs (Figure 3). Duplicate samples were taken from 52 of the 60 sample sites to allow sampling variance to be well characterized. The sediments were oven-dried at 40°C, mechanically crushed and sieved to <0.18 mm to remove any coarse debris and homogenize the material. The dried (but unashed) sediments were analyzed for 47 elements (total content): As, Au, Br, Co, Cs, Eu, Fe, Hf, La, Lu, Mo, Na, Sb, Se, Sm, Ta, Tb, Th, U, W and Yb by INAA, and Al, Ba, Be, Bi, Ca, Ce, Cr, Cu, Dy, Ga, K, Li, Mg, Mn, Nb, Ni, P, Pb, Rb, Sc, Sr, Ti, V, Y, Zn and Zr by a combination of ICP-ES and AAS, following an HF-HClO₄-HCl digestion. Organic carbon content was estimated from loss on ignition at 500°C and, in addition, the National Geochemical Reconnaissance (NGR) *aqua-regia* digestion (4M HNO₃-1 M HCl) was used to determine acid-soluble levels of Ag, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn by AAS (Friske and Hornbrook, 1991). Comparison of the total and *aqua-regia* extractable values showed the latter to be very nearly total for this whole suite of elements. These analytical methods are the same as those employed in the regional surveys.

Comparison of Analytical Methods

The methods used for total-element analysis in the lake-core study and the St. John's and regional surveys are directly comparable. Two different partial analytical methods were used and the 'efficiency' of these extractions was estimated by comparing the median values of the partial and total digestions for each element and their degree of correlation on a sample-by-sample basis (Table 1).

Considering first the H₂O₂-HCl partial digestion, most elements show a significant correlation between total and partial data (Table 1), which indicates that they are present mainly in the organic or amorphous oxide phases that are leachable in dilute acid. In general, those elements where the H₂O₂-HCl digestion is closest to total show the greatest correlation between partial and total data. Exceptions are Cd,

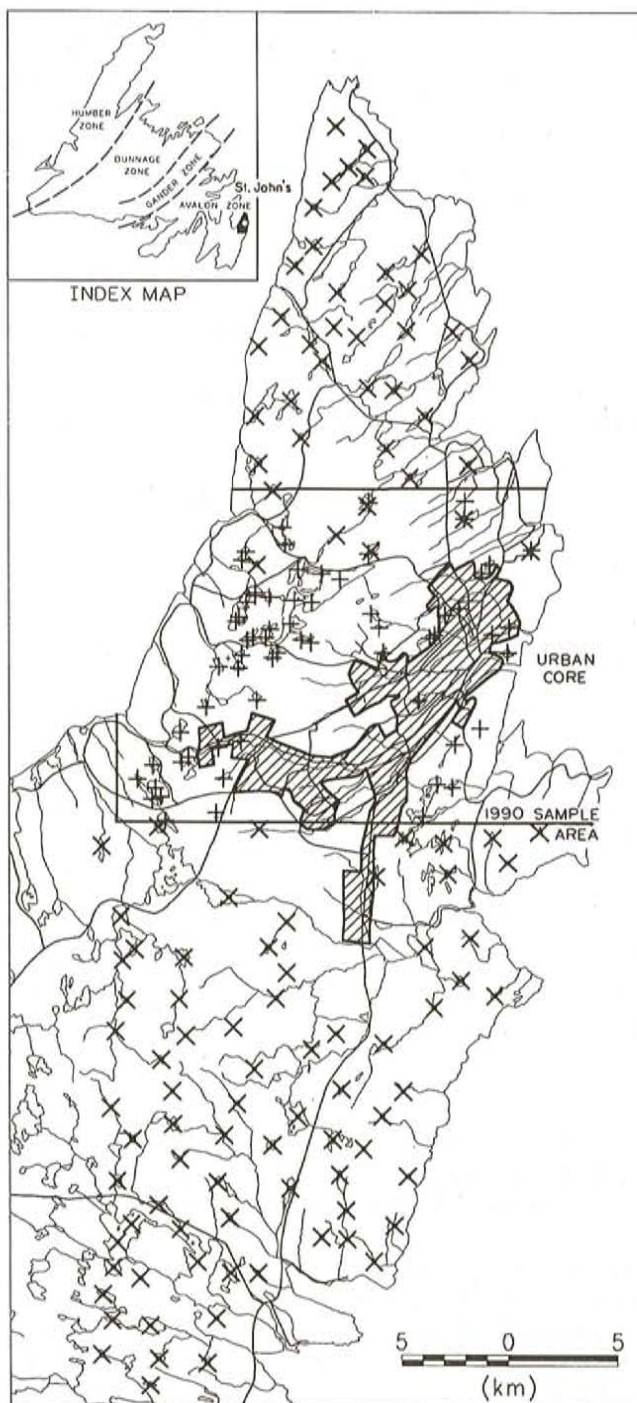


Figure 3. The location of lakes sampled in the St. John's urban area (+ symbols) in relation to the province-wide lake-sediment sample sites (X symbols).

where the rather low correlation is due to relatively large analytical errors at the low levels present, and Li, Fe and Mn, where the correlations are very high, but the proportion of metal extracted is small (17 to 47 percent). There was no statistical correlation between the results from the partial attack for Ga, Nb, Rb, Sc, Th or Zr and the total element values, with the partial results being much lower and showing little overall variation. For Rb, Sc and Zr, this may indicate

Table 1. Trace-element leaching tests: the efficiency of 30 percent H_2O_2 -0.3M HCl and 4M HNO_3 -1M HCl digestions on organic lake sediment relative to total (HF- HClO_4 -HCl or INAA) data. Elements are listed in decreasing order of 'extraction' as measured by the ratio of partial to total values. There was no significant fraction of Ga, Rb, Sc, Sr, Th or Zr extracted by the 30 percent H_2O_2 -0.3M HCl digestion

Element	30 percent H_2O_2 -3M HCl		4M HNO_3 -1M HCl	
	median ratio ⁰	correlation ²	median ratio ¹	correlation ²
Cu	1.00	0.97	1.00	0.99
Ni	0.98	0.98	1.00	0.96
Co	0.87	0.97	0.95	0.99
Zn	0.85	0.94	0.89	0.98
Y	0.78	0.81		
Dy	0.71	0.91		
La	0.67	0.73		
Cd	0.67	0.58		
Ce	0.56	0.75		
Pb	0.50	0.69	0.76	0.96
Mn	0.47	0.98	1.00	0.98
V	0.38	0.56		
Fe	0.34	0.93	1.00	0.99
Cr	0.30	0.67		
Mo	0.29	0.81		
Be	0.24	0.72	0.36	0.87
Ba	0.24	0.67		
Li	0.17	0.97		

¹ ratio of the median value from 'partial' digestion to the median for the 'total' digestion

² degree of linearity between 'partial' and 'total' data as expressed by the product-moment correlation coefficient.

that these elements are present mainly in the silicate phase of the sediment, which is not dissolved in the partial digestion. For Ga, Nb and Th, the data are close to the analytical detection limit and any real correlations would be obscured by analytical noise.

Data to estimate the efficiency of the NGR (4M HNO_3 -1 M HCl) digestion for lake sediment are available from the St. John's study area only for Cu, Ni, Co, Zn, Pb, Mn and Fe (Table 1). The data for Be is for samples from the Strange Lake area of Labrador (J.W. McConnell, personal communication, 1991). A rigorous comparison between the two partial digestions is not possible because different sample sets are involved, but the results do suggest that the NGR digestion is total for Cu, Ni, Mn and Fe, and nearly so for Co and Zn, and is more efficient than the 30 percent H_2O_2 -0.3 M HCl digestion for Pb and Be.

CHEMICAL STRATIGRAPHY IN LAKE SEDIMENT IN CENTRAL NEWFOUNDLAND

Geochemical profiles for As and Sb (total content) in cores from the five lakes are plotted next to the regional distribution maps in Figures 4 and 5. Although some variability of element concentrations with depth is apparent, the upper metre or so is generally quite consistent in composition and the differences in element abundances between lakes predicted by the regional survey data are reliably reproduced throughout the upper parts of the lake-sediment cores. Indeed, close correspondence between values based on single grab samples from the regional survey and the median value in the upper 120 cm of the sediment profiles is observed (Table 2) for most elements determined for the three lakes sampled in both studies (i.e., Miguel's Pond, Northwest Gander River Pond and Moose Pond). The Conne River site and Pool's Cove Pond were not sampled in the regional survey, so data from the closest sampled lake is shown in Table 2 and, as might be expected, the correspondence between interpolated regional and profile data is not as close. Considering the regional and profile data together, the areal variations in As and Sb, which are related to the regional geology, are much larger than within lake variation. The same is true for most trace elements evaluated.

The levels of H_2O_2 -HCl extractable Pb show a marked increase in the uppermost 10 to 20 cm in two of the cores (Miguel's Pond and Moose Pond) and, less obviously, in Pool's Cove Pond and the Conne River site (Figure 6). These trends appear similar to those described from lake sediment in Ontario (Fortescue and Vida, 1991). Brunskill *et al.* (1991) describe a build up of Pb in lake sediments that were deposited since 1900 from a transect in central Canada between 49°N and 82°N, in which the amount of excess Pb decreases from south to north. Brunskill *et al.* (1991) attributed this pattern to long-range atmospheric transport of pollution, which can apparently be detected thousands of kilometres from source. The data reported here should be regarded as preliminary as the particular acid extraction used is not ideal for Pb because of the low solubility of PbCl_2 . This trend is much less obvious in total Pb.

The largest variations in the concentrations of some elements are observed in the lower core sections. Core lengths recovered vary from 200 cm in Northwest Gander River Pond to 550 cm in Miguel's Pond, and in all lakes except Miguel's Pond the transition between organic sediment or gyttja and the underlying clastic sediments was penetrated (Vardy, 1990). This change in mineralogical composition is marked by large changes in the levels of LOI, biogenic silica, major elements and some trace elements. The abrupt increases in level of As, Sb and Pb at depths greater than 100 cm in Northwest Gander River Pond occur at this sediment transition. Other large changes in trace-element concentrations are present just above this transition, and may be geochemical reflections of climate change and related changes in erosional and vegetative regimes analogous to those described by Fortescue (1986) in Ontario and Rogers *et al.* (1991) in Nova Scotia. Some radio-carbon dating of samples from these transitional sections is

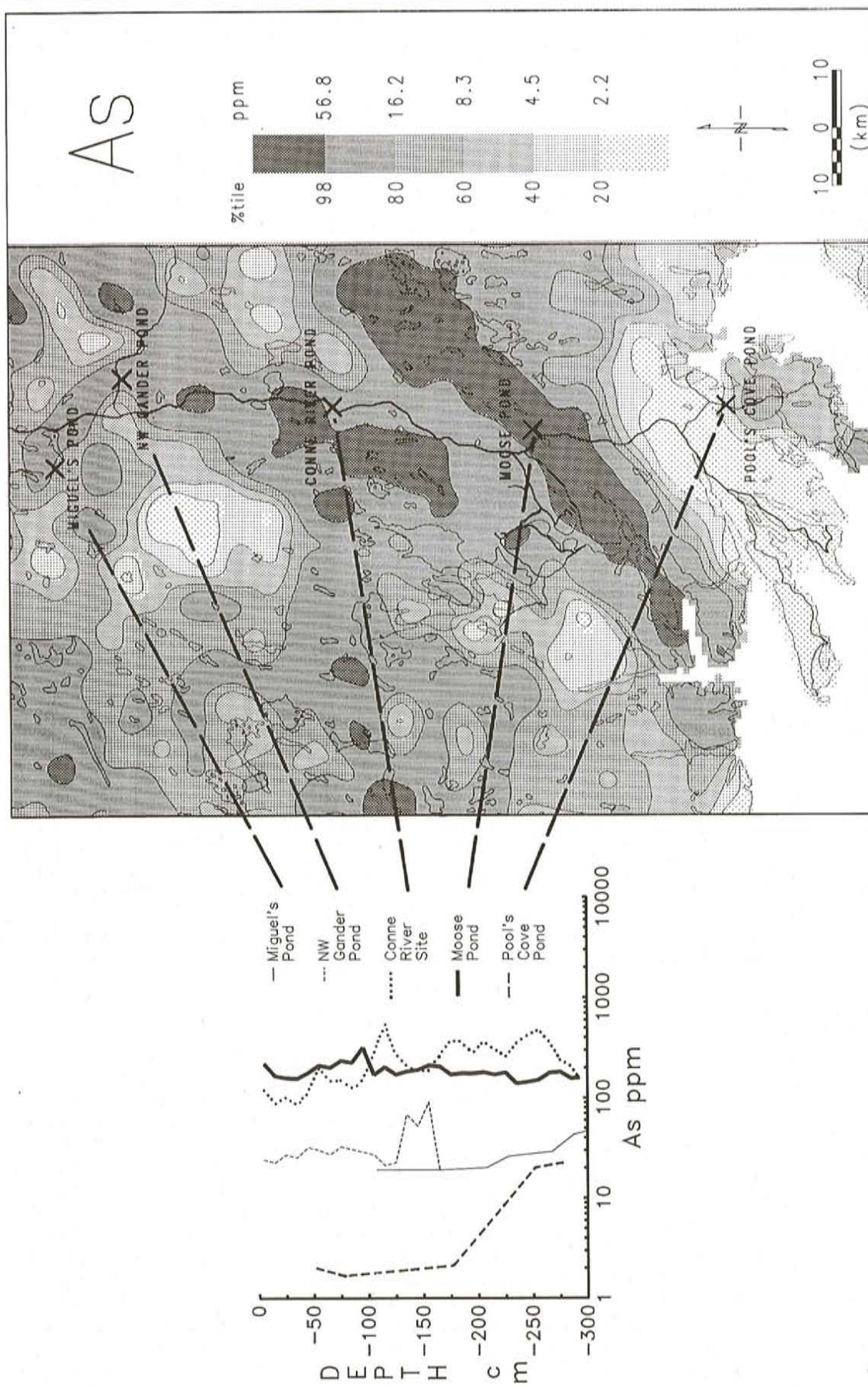


Figure 4. Arsenic (As) in lake sediment: its areal distribution (right) and (left) its distribution with sediment depth (or time).

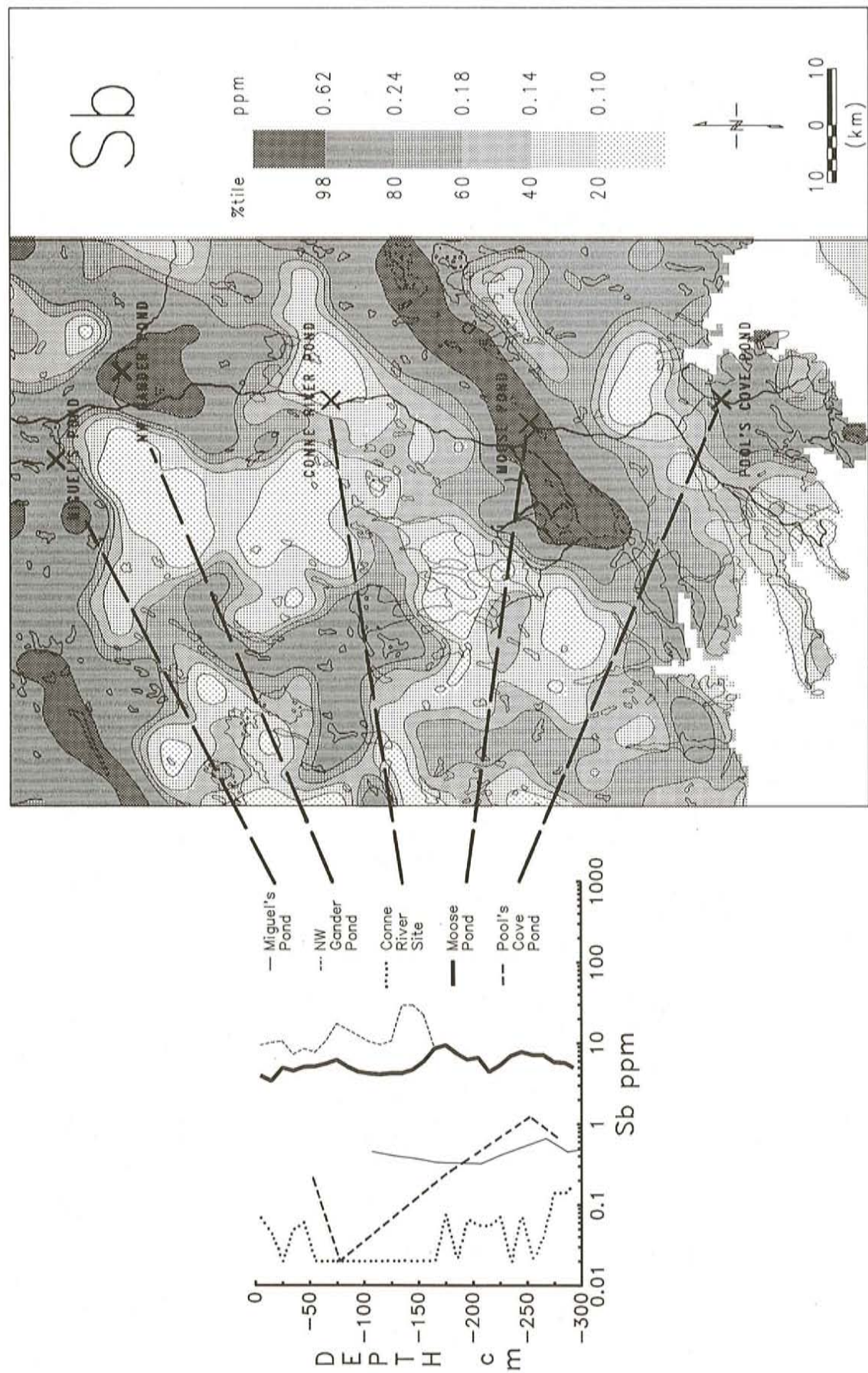


Figure 5. Antimony (Sb) in lake sediment: its areal distribution (right) and (left) its distribution with sediment depth (or time).

Table 2. Comparison of geochemical data from 'grab' samples of lake sediment collected in regional geochemical mapping with the median values from the upper 120 cm of lake-sediment cores sampled at 5 to 25 cm intervals. All data for As, Ba, Cr, Sb, U and W are total values: data for Co, Cu, Mn, Ni, Pb and Zn in 'grab' samples from the regional survey are from NGR *aqua-regia* digestions; for the cores, medians of these elements from both the H₂O₂–0.3M HCl digestion (Part. column) and total values (Tot. column) are given. Regional values are not available for the Conne River site and Pool's Cove Pond; the values in parentheses are from the nearest sampled lakes

	Miguel's Pond			NW Gander R. Pond			Moose Pond			Conne River Site			Pool's Cove Pond		
	Grab	Core		Grab	Core		Grab	Core		Grab	Core		Grab	Core	
	Part.	Tot.		Part.	Tot.		Part.	Tot.		Part.	Tot.		Part.	Tot.	
As (ppm)	29.5	—	19.0	20.2	—	23.0	145	—	198	(16.0)	—	128	(1.7)	—	2.0
Ba (ppm)	<50	—	<50	120	—	100	520	—	495	(56)	—	83	(220)	—	<50
Co (ppm)	8	6.5	9	22	18	20	42	47	58	(8.5)	13.0	13.5	(5)	3	2
Cr (ppm)	21	—	23	190	—	129	42	—	52	(<15)	—	36	(16)	—	20
Cu (ppm)	12	19	18	15	19	20	19	19	19	(9)	14	12	(17)	11	12
Mn (ppm)	693	400	300	252	200	300	3340	3400	5000	(357)	700	1300	(133)	100	100
Mo (ppm)	4	—	3	2	—	3.0	7	—	9	(2.5)	—	6.5	(6)	—	30
Ni (ppm)	32	35	40	172	184	264	36	41	49	(11.5)	21	24	(12)	4	18
Pb (ppm)	11	8	12	5	6	18	19	13	18	(2.5)	5.0	13.5	(18)	11	17
Sb (ppm)	0.24	—	0.45	7.81	—	6.2	5.23	—	4.5	(0.05)	—	<0.05	(0.22)	—	0.23
U (ppm)	2.1	—	2.4	1.2	—	1.2	2.4	—	3.0	(1.0)	—	2.1	(5.0)	—	15.0
W (ppm)	<2	—	<2	<2	—	<2	<2	—	2.2	(13.0)	—	19.0	(3.4)	—	8.0
Zn (ppm)	24	282	284	59	100	127	143	193	228	(29.5)	104	110	(29.5)	78	90

discussed by Vardy (1991), but a full interpretation of the geochemical stratigraphy will require further palynological studies. These major features of the geochemical stratigraphy are well below the sediment layer sampled in the regional surveys in this area.

MAPPING GEOCHEMICAL CHANGES IN URBAN DRAINAGE SYSTEMS USING ORGANIC LAKE SEDIMENTS

Natural variations in the geochemical background for Pb are displayed in the regional lake-sediment data (Figure 7, left), which can be linked to broad-scale variations in the Pb content of bedrock, such as elevated values in belts of posttectonic granites and widespread Pb mineralization in the Cambro-Ordovician carbonate sequences of western Newfoundland. The Avalon tectono-stratigraphic zone in southeastern Newfoundland has a higher regional background for Pb than the central part of the Island (Dunnage zone), and within the northeastern part of the Avalon Peninsula the geological control of background Pb values is displayed at a more local level by elevated Pb in lake sediment over the shale-rich St. John's Group (HSJ; Figure 7, right). The highest Pb values are concentrated where the urban area overlies the St. John's Group, and there is a clear clustering of the highest values over the city core and the older suburbs. Peak values are up to 10 times higher than the natural background for the area, and above the 99th percentile for all of Newfoundland.

For Sb, lake-sediment values in the Avalon Zone are lower than in the eastern part of the Dunnage Zone, and fall between the 20 and 80th percentiles for the whole Island

(Figure 8). Within the northeast Avalon area there is a marked clustering of high Sb values in lakes in the urban core, suggesting the possibility of anthropogenic input. Peak values of over 0.6 ppm Sb in lake sediment in St. John's are above the 92nd percentile for the Island as a whole. For As, the regional picture is similar (Figure 9), with the eastern part of the Dunnage Zone showing a broad pattern of enrichment; values in lake sediment on the northeast part of the Avalon Peninsula fall in the middle of the natural range for the Island as a whole. In contrast to Sb, however, As values in lake sediments from the urban core are close to the median of 6.2 ppm for all of Newfoundland.

CONCLUSIONS

The two detailed studies discussed here provide insight into the use of the data from regional geochemical mapping in establishing reliable and relevant geochemical baselines against which environmental change can be measured and its significance assessed. The study of chemical stratigraphy confirms that, throughout most of Newfoundland and for most elements, a 'grab' sample taken from within the upper metre of the profundal lake-sediment section provides data representative of the local geochemical background. The main cause of geochemical variation is geological, and anomalies in undeveloped regions may be expected to be both reproducible, and related to real geological features such as mineralization.

The geochemical patterns in lake sediment within areas of fairly intensive and sustained development, such as in the St. John's urban region, show, however, that pollution can completely obscure natural patterns for some elements. Taken

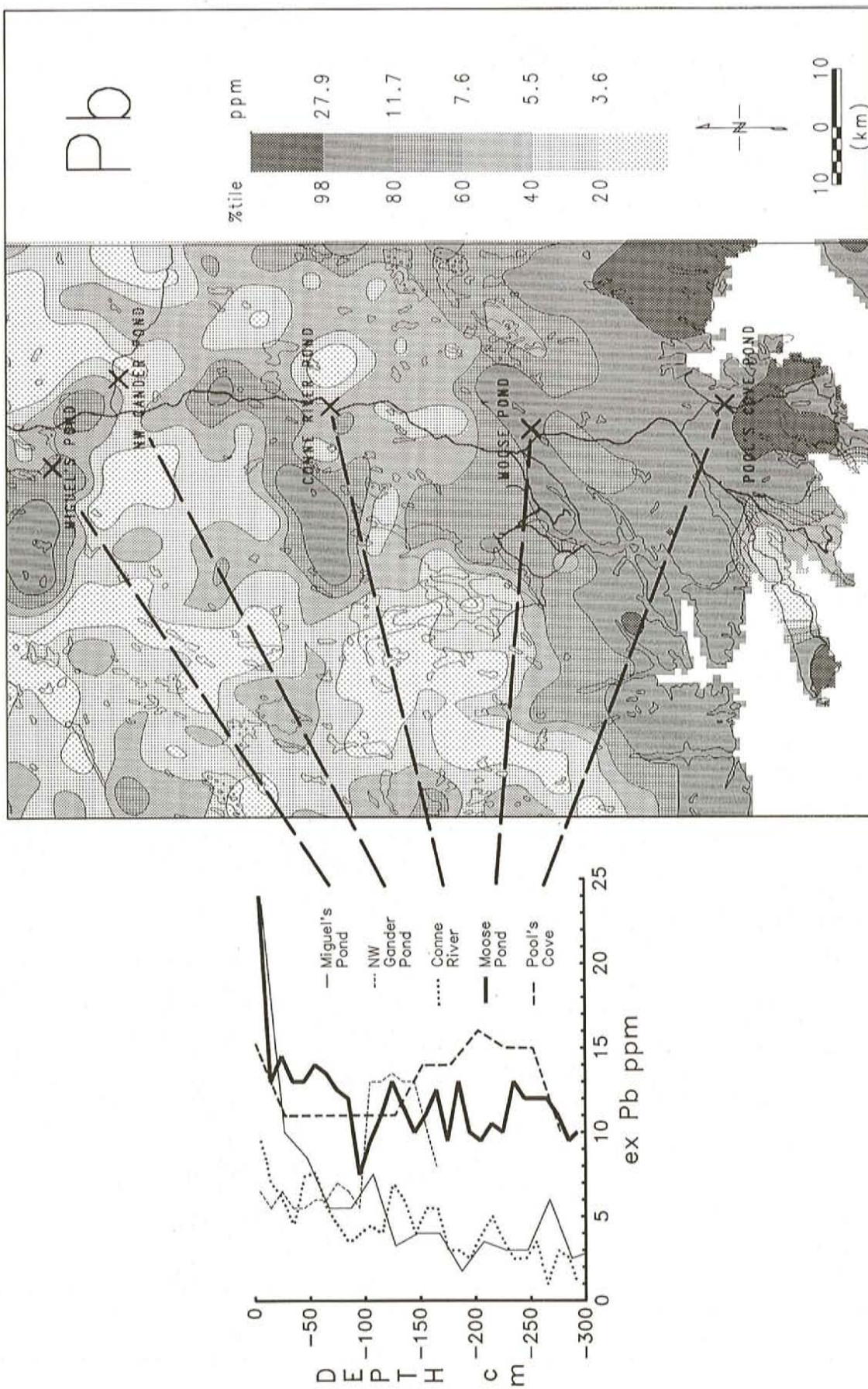


Figure 6. Lead (Pb) in lake sediment: its areal distribution (right) and (left) its distribution with sediment depth (or time).

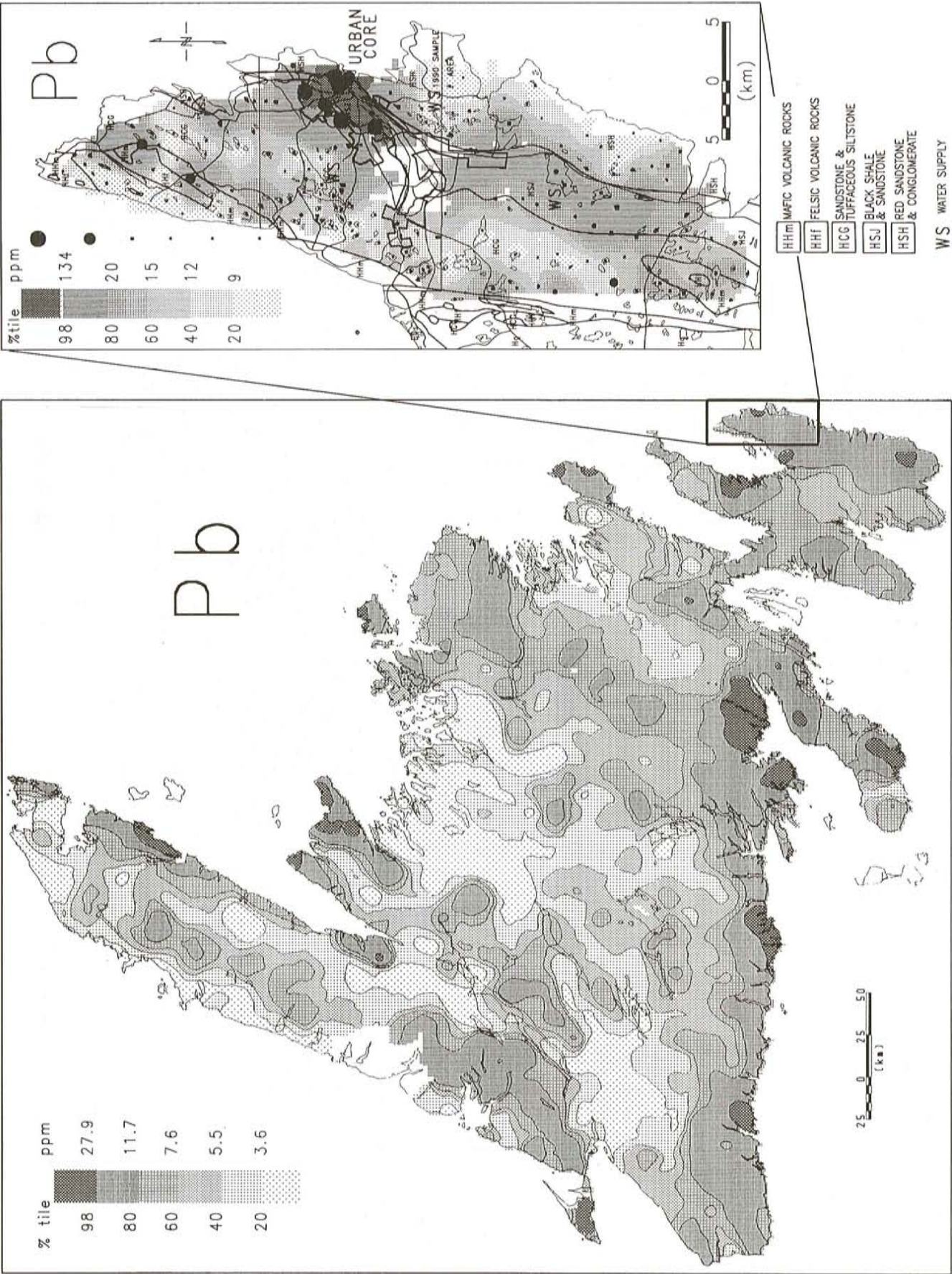


Figure 7. Regional distribution of Pb in lake sediment from 16,000 sites throughout Newfoundland (left) and, in more detail on the right, from 246 sites on the northeast Avalon Peninsula, including the St. John's urban region. Regional geology is from King (1988).

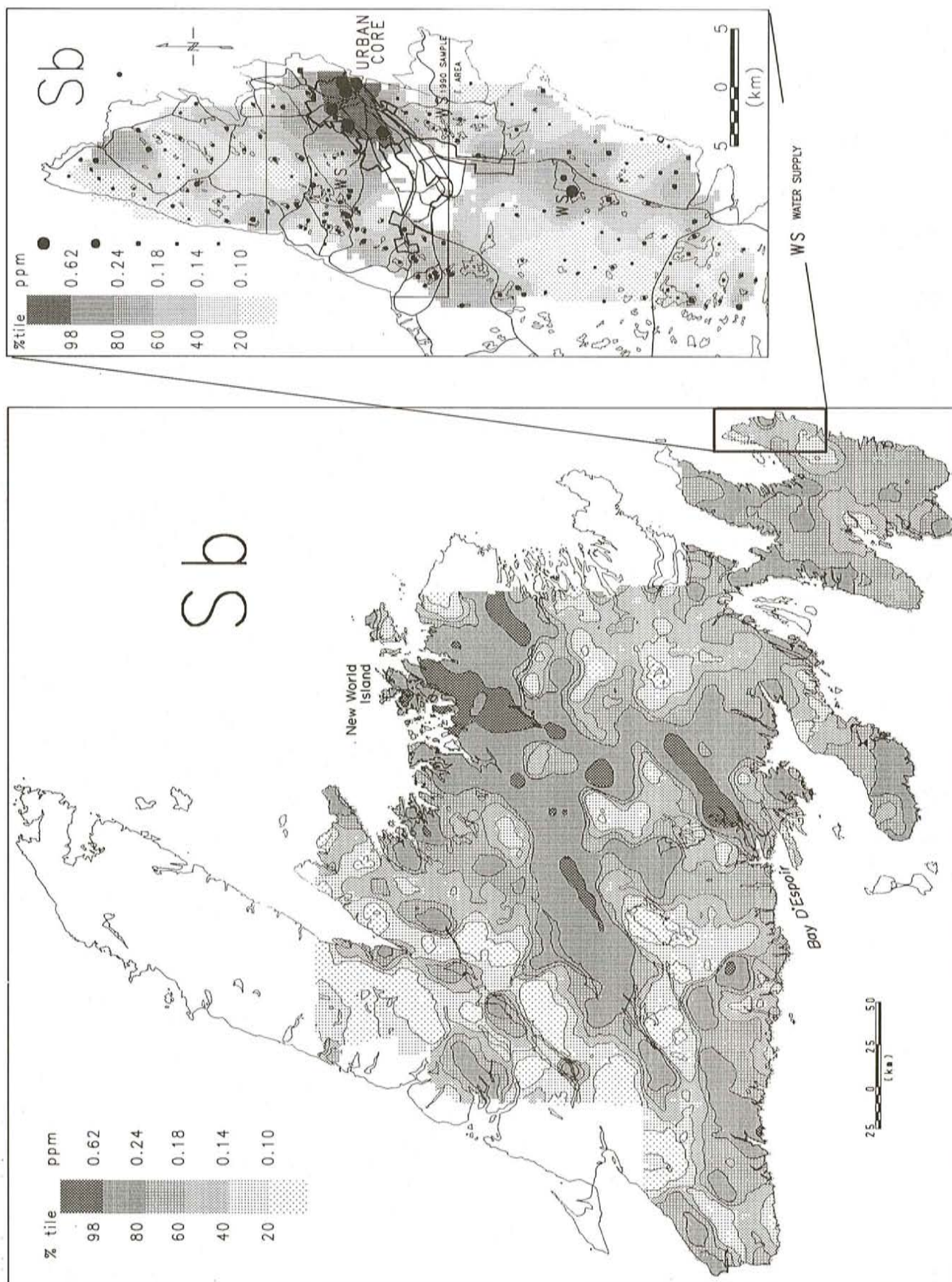


Figure 8. Regional distribution of Sb in lake sediment throughout Newfoundland (left) and, in more detail on the right, from 246 sites on the northeast Avalon Peninsula, including the St. John's urban region.

together, these results imply that for mineral exploration the sampling strategy employed in the regional surveys, both provincially and nationally, is sound and reliable except in obviously disturbed areas, where other approaches should be adopted. These might include sampling the lake sediment below the contaminated layer (Fortescue and Vida, 1991) or employing a sample medium unaffected by pollution.

The apparent enrichment in Pb in the uppermost sections of some of the cores in central Newfoundland suggests that the region may be affected by airborne pollution. More work is required to confirm these patterns, however, and to document their origin, if they are indeed real. Their restriction to the uppermost sediment layers and their relatively modest intensity suggest that they will not substantially affect the measurement of the natural Pb distribution patterns. It may be desirable, however, to discard the upper 10 to 20 cm of sediment in geochemical exploration surveys as a precautionary measure.

A comparison of the weak acid digestions with the total-element determinations (Table 1) permits some preliminary conclusions about the partitioning of the elements within the different phases of the lake sediment and about element mobilities and their potential bio-availability. First, both Cu and Ni are strongly partitioned into the organic phase and are completely leached by both partial digestions (30 percent H_2O_2 –0.3 M HCl and 4M HNO_3 –1M HCl). This conclusion is supported by the generally observed correlation in the regional lake-sediment data between these two elements and organic content. Second, the greater efficiency of the NGR digestion in dissolving Mn and Fe oxides and hydroxides is probably responsible for the higher proportions of Co, Zn and Be extracted, and suggests that these oxide-hydroxide phases, together with the organic phase, contain a significant fraction of these elements. This conclusion is also in accord with observed correlations for the regional dataset as a whole. The ability of dilute, oxidizing acid digestions to leach a significant and fairly consistent proportion of the majority of elements determined suggests these elements possess a good deal of geochemical mobility in the surficial environment, and indicates that these partial digestions provide a fairly reliable measure of variations in concentration of elements potentially available to biological systems. Even elements such as Ba, Pb and Cr, normally considered immobile under normal surface conditions from thermodynamic data (Brookins, 1988), clearly have a labile fraction in lake sediment. These observations suggest that geochemical data based on dilute acid leaches of lake sediment (such as those employed in Canada's National Reconnaissance Program) can establish geochemical baselines that are very relevant to the measurement of environmental change.

The results from the St. John's area illustrate the relevance to environmental studies of the regional geochemical data based on organic lake sediment. The medium is clearly sensitive to environmental change, both natural and anthropogenic and, in order to assess the

significance of anthropogenic change, it is essential to establish the bounds of natural variation. Lakes in the oldest and most urbanized part of St. John's show considerable geochemical change with elevated levels in sediment of many metals (Ag, Au, Ba, Cd, Cr, Cs, Cu, F, Hf, Lu, Ni, Rb, Sc, Ta, Th, U, V, W, Yb and Zn) in the inner city core (Christopher, 1991), but not in all cases above geochemical background. Levels of Pb in lake sediment from the urban core are above the 99th percentile of values found in all Newfoundland; natural values at this level result from Pb-bearing mineral deposits in the catchment but no Pb mineralization is known in the St. John's area. In contrast, although Sb shows a well-defined pattern of enrichment in lakes in the urban core, this enrichment is relative to the local background only. There are extensive areas between New World Island and Bay d'Espoir (Figure 8) where Sb values in lake sediment are as high or higher; this is thought to be due to the widespread effects of major hydrothermal systems (Davenport and Nolan, 1991). As a third example, for As there is no evidence of any enrichment pattern in the urban area and, in fact, levels of As on the northeastern Avalon Peninsula are normal relative to most of Newfoundland. Potential environmental problems with Sb and As are more likely to result should construction and development occur in areas naturally enriched in these elements, as happened in Nova Scotia in the vicinity of Halifax airport (Guilcher, 1987; Worgan, 1987), rather than in the St. John's region.

Lake sediments give a geochemical signal integrated over several years of deposition that reflects the sum of human activities (farming, deforestation, construction, waste disposal, industry, etc.) as well as natural physical, chemical and biological processes operating in the catchment. Where human disturbance has been intensive and sustained over several decades the geochemical changes are obvious even in a quick reconnaissance survey in which 'grab' samples of sediment are collected. If adequate baseline data are available, this approach provides a cost-effective method of gaining an overview of the nature and location of environmental changes, which allows follow-up to be focused on the main problem areas through more careful study of geochemical stratigraphy to determine a detailed history of change (e.g., Qvarfort, 1983; Rogers *et al.*, 1991).

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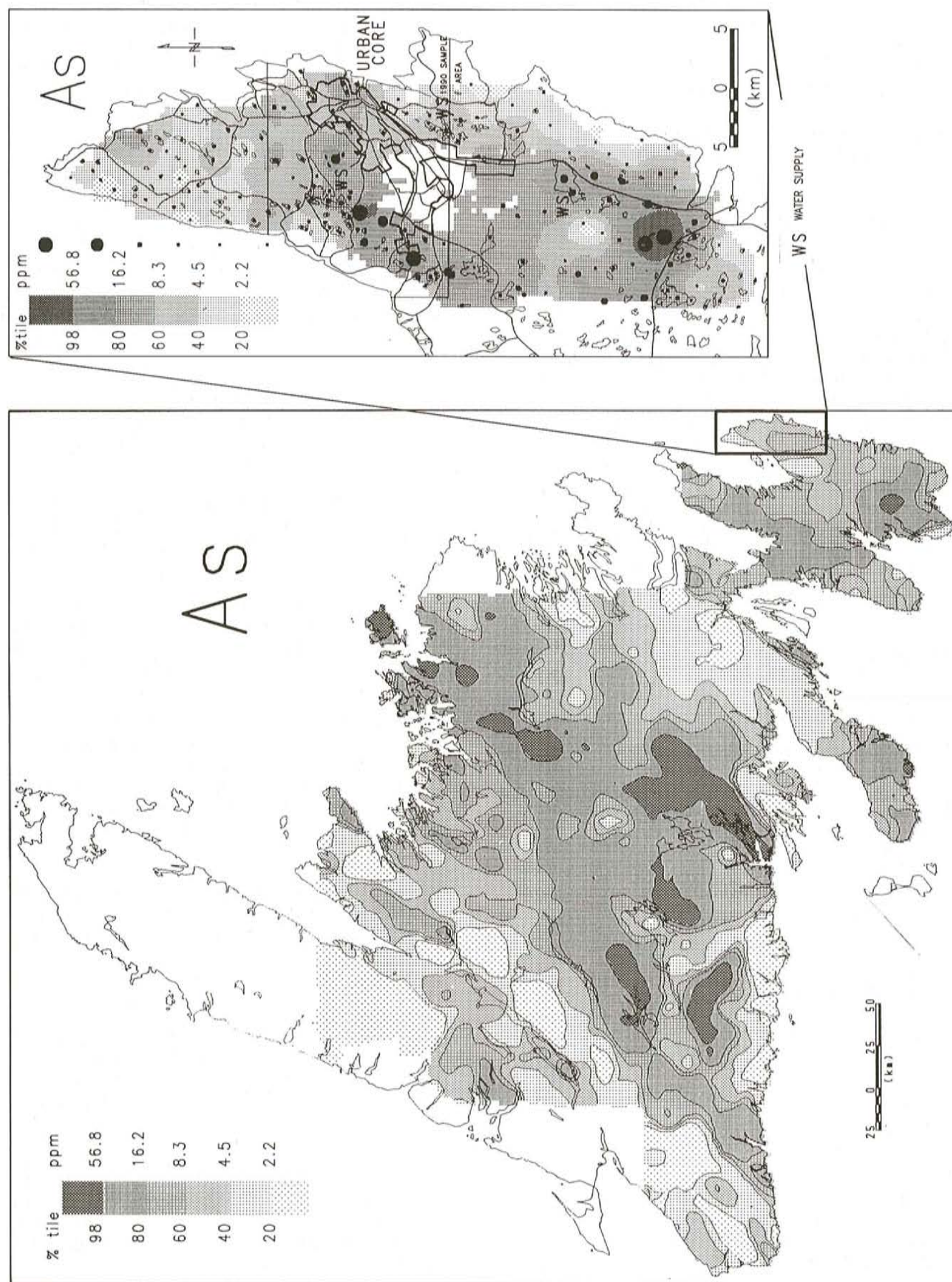


Figure 9. Regional distribution of As in lake sediment throughout Newfoundland (left) and, in more detail on the right, from 246 sites on the northeast Avalon Peninsula, including the St. John's urban region.

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