

# THE DEVELOPMENT AND APPLICATION OF GEOCHEMICAL ANALYSES OF WATER

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## ABSTRACT

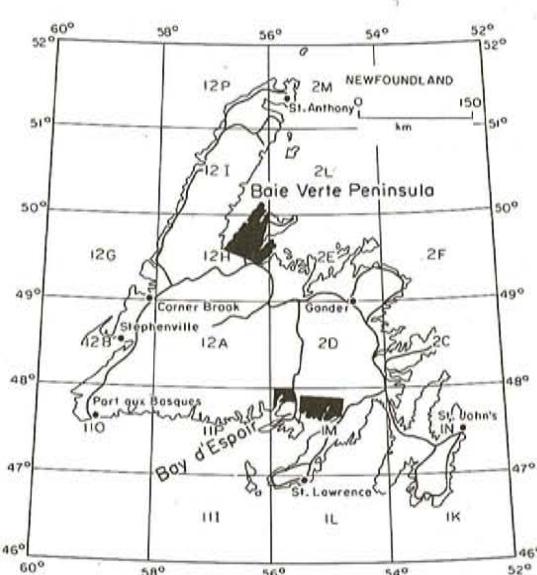
Methods of sampling, analyzing and interpreting the results of water samples from streams and lakes in Newfoundland are being developed jointly by the Geological Survey Branch and the Geological Survey of Canada. Water samples were collected from 176 sites in 1991 and have been analyzed for over 50 elements by several methods; many elements have been analyzed by two or more methods permitting determination of preferred techniques. Water data will be compared with stream sediment, overbank and lake-sediment data as appropriate. Preliminary work indicates that some water data (e.g., arsenic) give distribution patterns similar to those of lake-sediment data. Water data promise to be useful in the search for mineral resources and for assessing environmental parameters.

## INTRODUCTION

A scheme for the rapid analysis of natural fresh water samples for a wide range of elements to levels below their average abundances is being developed based on the techniques of inductively coupled plasma emission spectrometry (ICP-ES), inductively coupled plasma mass spectrometry (ICP-MS), and atomic absorption spectrophotometry (AA). The methods developed under this project, which is being conducted jointly by the Geological Survey Branch and the Geological Survey of Canada, will be used to evaluate the effectiveness of water as a sample medium for geochemical exploration. The project brings together results and techniques from several earlier projects both in Newfoundland (Christopher *et al.*, 1991) and elsewhere in Canada, and involves laboratories at the Geological Survey of Canada (AA and ICP-MS), Memorial University of Newfoundland (ICP-MS) and the Geological Survey Branch (ICP-ES).

## SAMPLING AND SAMPLE PREPARATION PROCEDURES

In June 1991, a water-sampling program was conducted in which 40 stream-water samples were obtained from the Baie Verte and Springdale peninsulas and the St. Alban's area, and 136 lake-water samples were collected in the Bay d'Espoir-Fortune Bay area (Figure 1). Seven pairs of site duplicates were collected in the stream survey and 12 pairs in the lake survey. Most of the stream sites had been sampled



**Figure 1.** *Location of survey areas.*

for overbank and active sediment in 1990 and at the same time vegetation samples were collected (Dunn, 1991), thus the water data may be compared with the data from other media for effectiveness in reflecting mineralization and catchment basin geology. The stream-sediment data have strong geochemical relief in base metals, arsenic, antimony and gold. The areas of lake-water sampling were selected in

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the expectation, based on data from reconnaissance lake-sediment surveys, that the water chemistry would show strong relief in base metals, arsenic, antimony, and rare-earth elements.

Stream and lake water were collected by immersing a 250 ml nalgene bottle beneath the surface. Lakes were sampled in their centres using a float-equipped helicopter. Streams were also sampled near their channel-centres to obtain a homogeneous sample and to avoid undue contributions from local groundwater sources.

Within 24 hours of collection and following analysis for pH and total dissolved solids, the samples were filtered through a 0.45  $\mu\text{-m}$  filter paper and acidified with 2 ml of nano-pure  $\text{HNO}_3$  to await further analyses.

#### ANALYTICAL METHODS

Table 1 summarizes the suites of elements determined thus far in the three laboratories and the methods used. The overlap in the suites will facilitate a comparison of analytical methods. Table 2 summarizes the work to be accomplished this winter (1991-1992).

The methods employed for the analysis of these waters are Direct Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Hydride Generation Inductively Coupled Plasma Mass Spectrometry (HG-ICP-MS), Ion Chromatography Inductively Coupled Plasma Mass Spectrometry (IC-ICP-MS), Inductively Coupled Plasma Emission Spectrometry (ICP-ES), Ultrasonic Nebulization Inductively Coupled Plasma Emission Spectrometry (USN-ICP-ES), Direct Flame Atomic Absorption Spectrometry (F-AA), Hydride Generation Atomic Absorption Spectrometry (HG-AA), Graphite Furnace Atomic Absorption Spectrometry (GF-AA) and Ion Selective Electrode (ISE).

Samples analyzed by direct ICP-MS underwent no additional sample preparation or preconcentration. Thirty-nine elements were measured on the acidified samples by conventional nebulization techniques (Table 1). An internal standard consisting of Sc, Y, Th, and Tb was pumped with a peristaltic pump and mixed with the sample solution before nebulization and measured by a Siex Elan ICP-MS.

The F-AA determination of Zn, Fe, and Mn was performed directly on the acidified water samples with a Perkin Elmer 3030 Spectrometer. Sodium, K, Ca and Mg were determined by AA, but the samples were made up to 0.1 percent Cs as an ionization buffer and 0.1 percent La as a releasing agent. A 10 ml portion of unacidified sample was buffered with TISAB III after which fluoride was measured by ISE.

Hydride generation methods required sample pretreatment to obtain the desired oxidation state of the elements in solution. Arsenic was measured by HG-AA. Sample pretreatment for this method involved taking 2.5 ml

of sample, 0.5 ml of 12 M HCl and 50 micro-litres of a mixture of 2.5 percent KI and 2.5 percent ascorbic acid. The samples were left for several hours to allow reduction of As (V) to As (III). The volatile hydride  $\text{AsH}_3$  (arsine) was formed with the addition of  $\text{NaBH}_4$  in a flow-injection system wherein the gases evolved were swept into the a heated quartz tube that was placed in the light-path of a Perkin-Elmer 5000 AA upon which As was measured.

Bismuth, Sb, Se and Te were determined by HG-ICP-MS. An aliquot of sample was pre-reduced overnight with the addition of 0.01 percent KI to reduce Bi (V) and Sb (V) to (III). A second aliquot of sample solution was boiled for thirty minutes in 4M HCl to reduce Se (VI) and Te (VI) to (IV). These elements were then measured by HG-ICP-MS at masses  $^{78}\text{Se}$ ,  $^{121}\text{Sb}$ ,  $^{130}\text{Te}$  and  $^{209}\text{Bi}$  using a GSC-designed hydride generation system and a Perkin-Elmer/Siex Elan 250 ICP-MS.

Rare-earth elements (REEs) are being analyzed by IC-ICP-MS at the GSC. The REEs are present in natural waters at concentrations below detection limits of even the mostly highly sensitive techniques. Research at the GSC has resulted in the ability to measure these elements in the ppt (ng/L) range using ICP-MS after 10-fold preconcentration. A chelating column, the MetPac CC-1 from Dionex Corporation, serves to concentrate and separate the REEs from the alkali and alkaline-earth elements prior to analysis and remove these possible interferences. Although this step requires about 25 minutes, it is completely automated and a batch of samples can be processed overnight without operator attendance. The resin employed is a highly cross-linked, macroporous polystyrene-divinylbenzene containing the iminodiacetate functional group, similar to Chelex-100 but without the undesirable properties of shrinking or swelling. The sample is buffered to a pH of 5.5 and a 50 ml volume pumped through the column. After washing with ammonium acetate, the REEs are eluted with 2M  $\text{HNO}_3$  to a final volume of 5.0 ml. This solution is then nebulized into the ICP-MS for determination of the REEs. Corrections are made for the spectral interferences of the oxides of the light REEs on the isotopes of the heavy REEs. Recoveries for all the REEs are about  $95 \pm 2$  percent and calibration is performed using solutions carried through the preconcentration.

Separate unacidified one-litre samples were collected in polyethylene bottles for Au analysis (selected sites). Any Au adsorbed on to the walls of the containers was leached off by the addition of 10 ml of 5 percent  $\text{Br}_2\text{-HCl}$  per litre of sample. After 48 hours of contact time, the sample was transferred to a beaker and evaporated to dryness. The Au was redissolved in 7 ml of 0.5 percent  $\text{Br}_2\text{-HBr}$ . Seven ml of water were added and the Au was extracted into MIBK (methyl isobutyl ketone). Any Fe present was back extracted into 0.1M HBr and the solvent layer analyzed by graphite furnace AA, as described in Hall *et al.* (1986).

The samples have been analyzed by Inductively Coupled Plasma Emission Spectrometry (ICP-ES) using an ARL 3520 Sequential Spectrometer for the elements listed in Table 1.

**Table 1.** Analyses performed to date by participating laboratory. (NDME—Newfoundland Department of Mines and Energy; USN—ultrasonic nebulizer; MUN/CERR—Memorial University / Centre for Earth Resources Research; GSC—Geological Survey of Canada; HG—hydride generation; ISE—ion-selective electrode; HG-AA—hydride generation atomic absorption spectrophotometry; F—flame)

NDME Laboratory			MUN/CERR			GSC Laboratory				
ICP-ES	USN-ICP-ES		ICP-MS			HG-ICP-MS	ISE	HG-AA	F-AA	GF-AA
Si	Li	Cr	Li	Br	Se	F	As	Na		Au
Ca	Be	Mn	Be	Se	Te			K		
Mg	B	Co	B	Rb	Bi			Ca		
Na	Al	Ni	Mg	Sr	Sb			Mg		
K	P	Cu	Al	Mo				Mn		
S	Fe	Zn	Si	Ag				Fe		
Fe	Sr	Y	P	Cd				Zn		
Mn	Ba	Mo	S	Sn						
	Ti		Cl	Sb						
			Ca	I						
			Ti	Cs						
			V	Ba						
			Cr	La						
			Mn	Ce						
			Fe	Hg						
			Co	Tl						
			Ni	Pb						
			Cu	Bi						
			Zn	U						
			As							

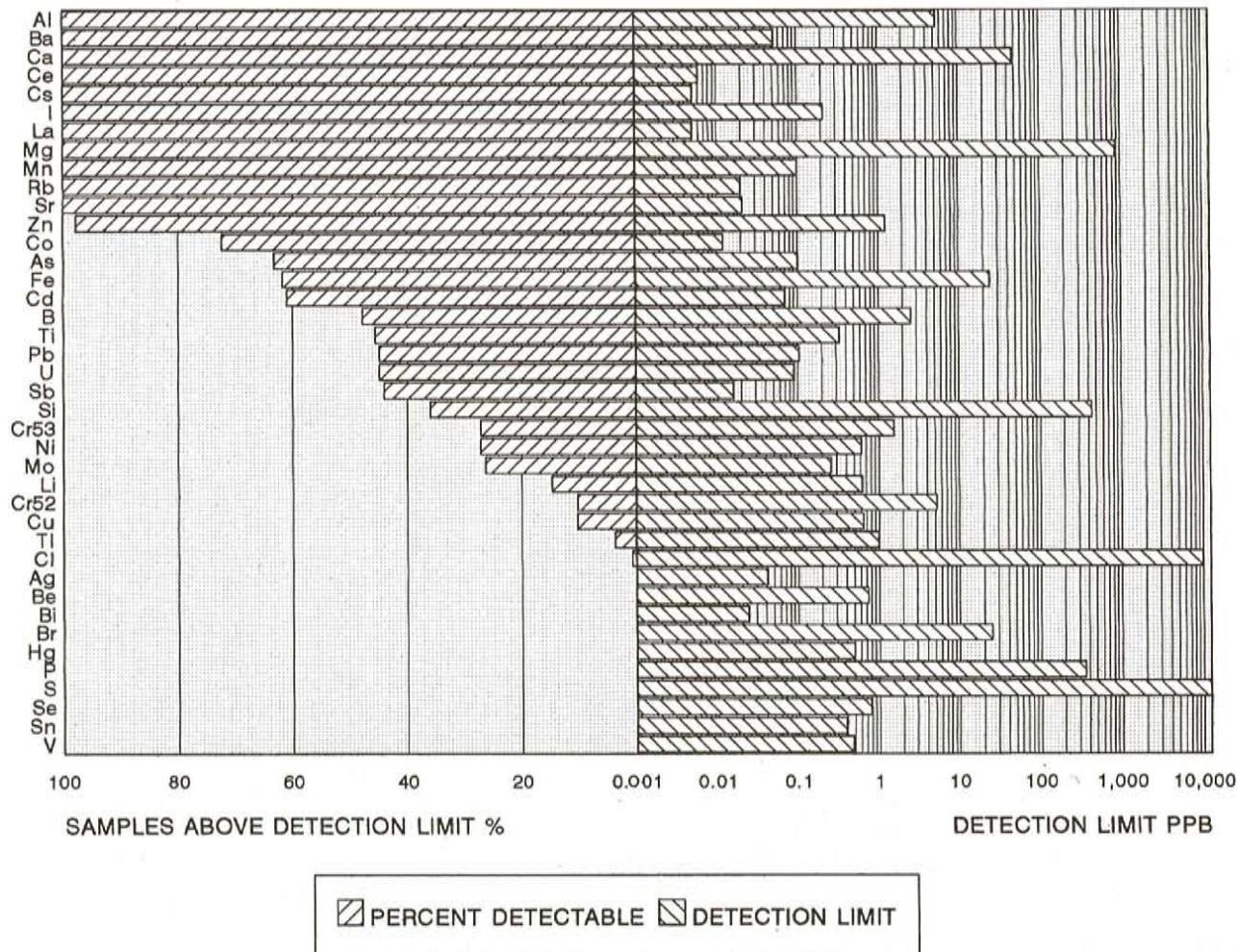
**Table 2.** Analyses to be performed during winter of 1991-92

NDME Laboratory		GSC Laboratory		
ICP-ES	ICP-hydride generation	IC-ICP-MS	IC	UV/Conductivity
C	As, Se, Sn, Sb, Te Hg, Pb, Bi	REEs (i.e., La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) Y Mn Co Ni Cu Zn Cd In Pb	SO <sub>4</sub> <sup>2-</sup> PO <sub>4</sub> <sup>2-</sup> Cl <sup>-</sup> Br <sup>-</sup> NO <sub>3</sub> <sup>-</sup>	Organic C

IC—ion chromatography; UV—ultraviolet

## ICP-MS DIRECT

## ELEMENT



**Figure 2.** Summary of percentages of samples with detectable concentrations and detection limits for ICP-MS direct analyses.

Determination of elements by Ultrasonic Nebulization Inductively Coupled Plasma Emission Spectrometry (USN-ICP-ES) and by Hydride Generation Inductively Coupled Plasma Emission Spectrometry (HG-ICP-ES) are being analyzed at the time of writing at the Geological Survey Branch Laboratory.

The ICP-ES and USN-ICP-ES do not require any sample pretreatment, but USN-ICP-ES provides a five- to ten-fold improvement in detection limits for most elements compared with direct ICP-ES. This improvement is accomplished by desolvation of the sample matrix before introduction to the ICP plasma, which effectively provides a preconcentration of the sample. The development work for HG-ICP-ES methods will be carried out this winter (1991-1992) at the Geological Survey Branch Laboratory. The major objective

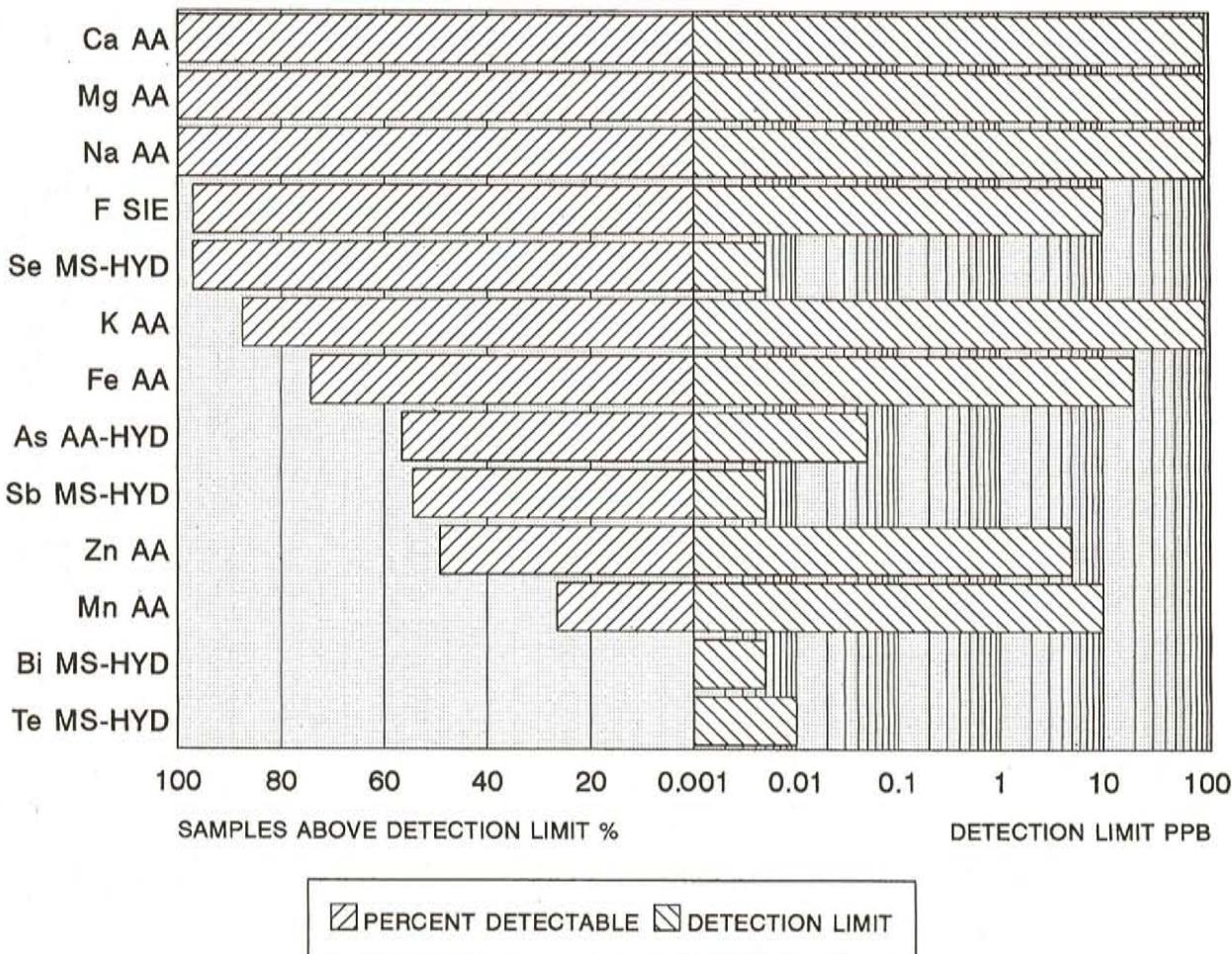
will be to provide a suite of elements that can be routinely determined in water samples at the Geological Survey Branch, Department of Mines and Energy, for applications in exploration and environmental geochemistry.

## RESULTS

For the elements analyzed, there is a wide range in the observed detection limits and the percentages of samples having detectable concentrations. Detection limits range from 0.005 ppb (cesium) by ICP-MS to 10,000 ppb (sulphur), also by ICP-MS. The detection limit for S is much lower, however, by ICP-ES. Several elements have no detectable concentrations in any of the samples whereas 13 elements were detected in all samples. These observations are quantified graphically in Figures 2 and 3.

## OTHER METHODS

## ELEMENT / METHOD



**Figure 3.** Summary of percentages of samples with detectable concentrations and detection limits for analytical methods other than ICP-MS direct analyses.

## Comparison of Methods

Several elements were analyzed by two methods. The detection limits and percentage of samples analyzed with detectable concentrations for nine elements are plotted in Figure 4. Results of two methods of analysis can also be compared by reference to Figures 5 and 6, in which data from 18 pairs of site duplicates are shown in scatterplots. For Ca and Mg, the two methods, AA and ICP-MS, give excellent and comparable results. All samples have detectable concentrations and the correlation coefficients of 18 pairs of site duplicates exceed 0.99 (Figure 6).

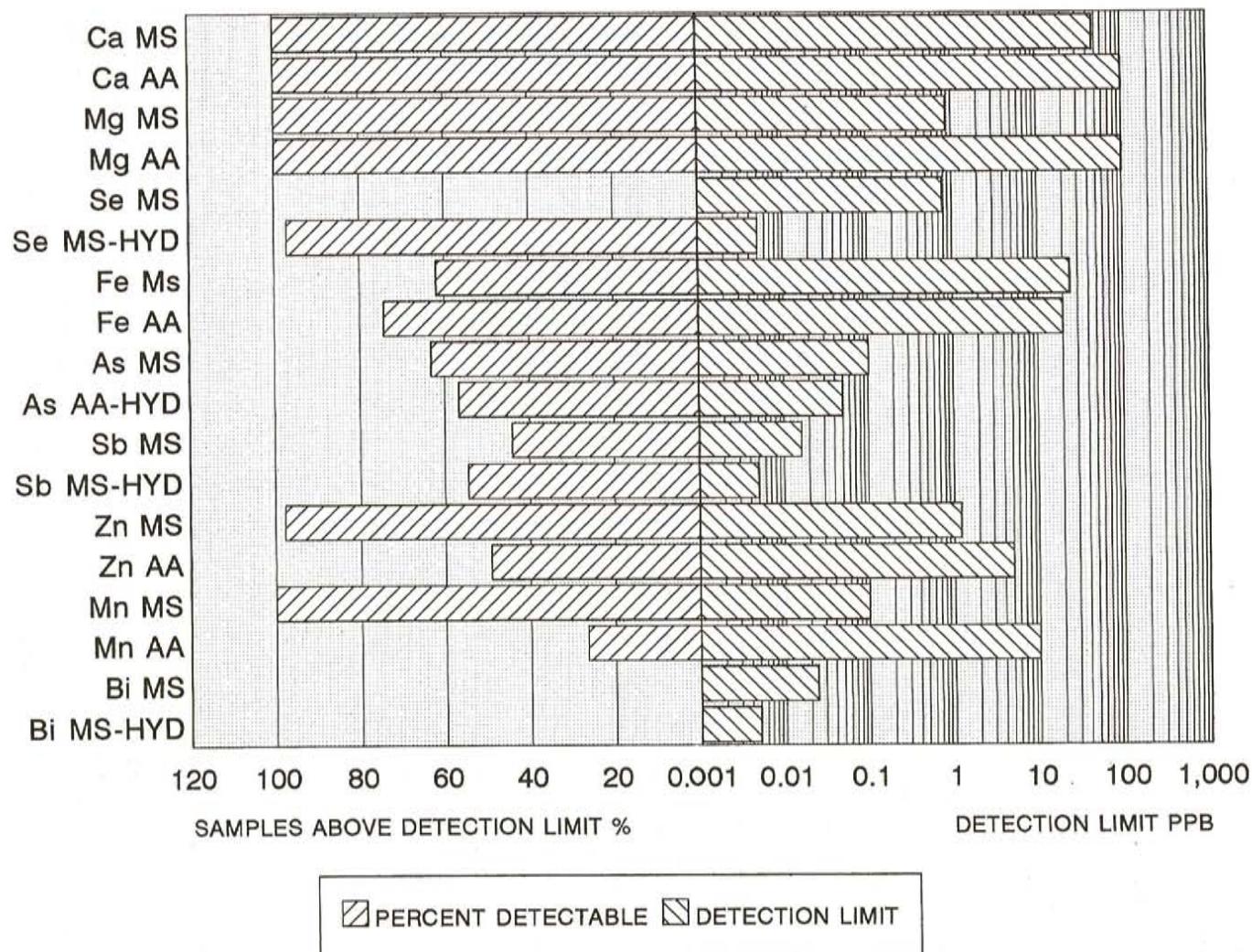
Analyses of iron (Fe) by AA appear preferable to the results by ICP-MS (Figure 4). Not only do more samples have detectable Fe in the AA method but the correlation coefficient

of site-duplicate pairs by AA is 0.99 compared to 0.48 by ICP-MS (Figure 5).

Both methods of analysis (ICP-MS and AA-hydride) for arsenic (As) give good and comparable results. The ICP-MS data seem slightly preferable as the correlation coefficient for site-duplicate pairs is stronger, 0.998 compared with 0.989 for AA-hydride; however, the hydride method has a marginally lower detection limit.

Analysis of antimony (Sb) is better by MS-hydride than by ICP-MS. The lower detection limit by the hydride method gives considerably more samples with detectable concentrations. The correlation coefficient for Sb in the site duplicates is lower by the hydride method (0.77) than by ICP-MS (0.94) due to the inclusion of a single 'flyer' in the data.

## METHOD COMPARISON



**Figure 4.** Comparison of percentages of samples with detectable concentrations and of detection limits for elements analyzed by two methods.

If this is removed, the remaining pairs have a correlation coefficient of 0.98.

The results for zinc (Zn) by ICP-MS and by AA differ markedly and neither dataset is satisfactory. Although the ICP-MS method apparently offers a lower detection limit and has more samples with detectable Zn, there is no correlation between analyses of site-duplicate pairs. The correlation coefficient for the ICP-MS data is -0.02 whereas for the AA data, it is 0.62. However, the stronger coefficient for the AA data is due almost entirely to one sample pair with high Zn in both analyses.

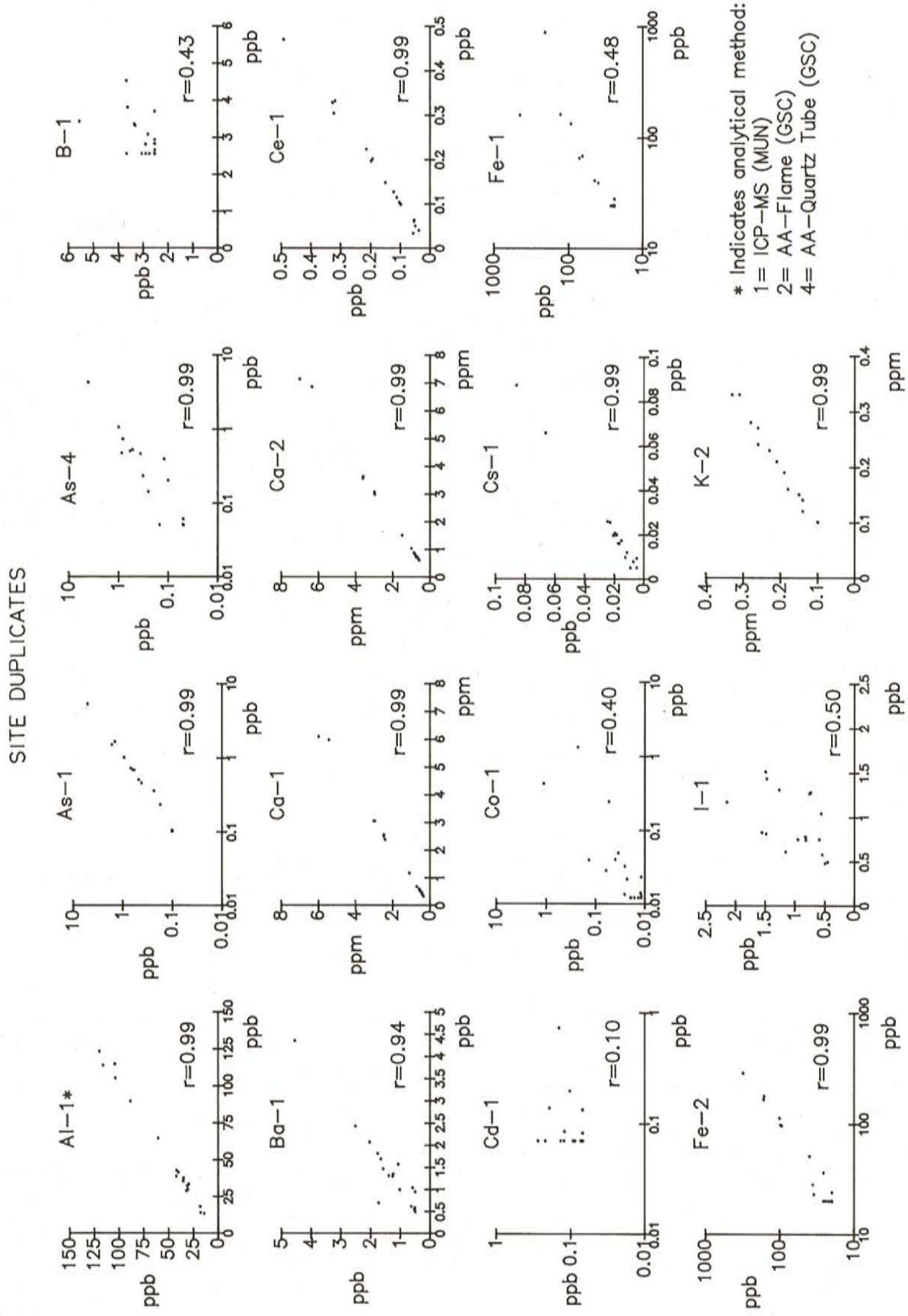
Manganese (Mn) was analyzed by ICP-MS and by F-AA. The former method gives much more useful data because of its significantly lower detection limit. The reproducibility of analyses is very good by both methods with correlation

coefficients of 0.92 and 0.99 for site-duplicate pairs by ICP-MS and F-AA, respectively.

Bismuth (Bi) has no detectable concentration in these samples by either ICP-MS or MS-hydride. For selenium (Se), only the MS-hydride method gives useful data.

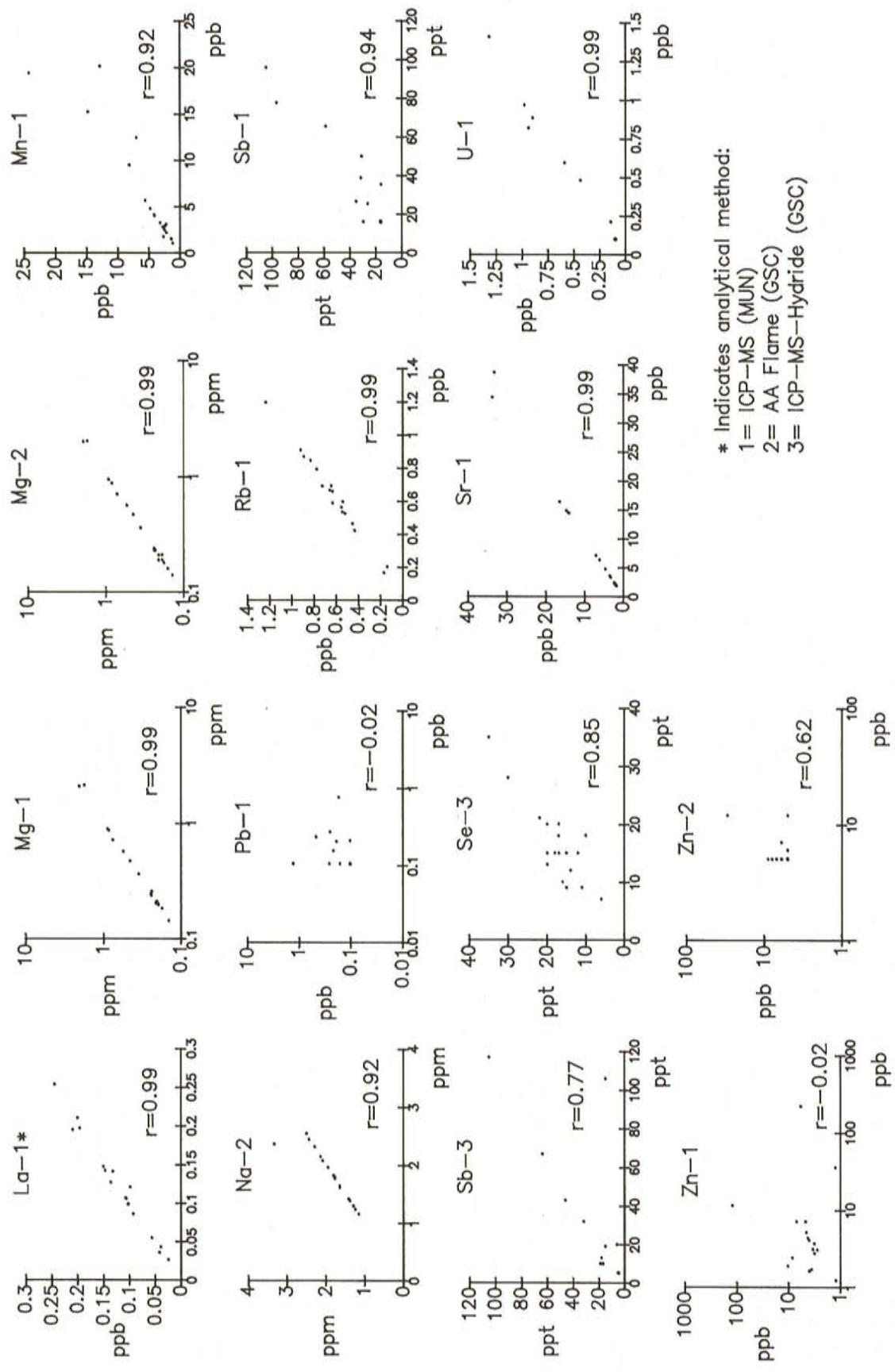
#### Reproducibility of data-analysis of site-duplicate pairs

One method of assessing the significance and variance of the analytical data is to evaluate the results of analyses of site-duplicate samples. This is done here by presenting scatterplots and Pearson correlation coefficients of data from 18 pairs of site duplicates (Figures 5 and 6). Elements included are those for which more than 40 percent of the samples analyzed by the three major methods have detectable



**Figure 5.** Scatterplots of analyses of site duplicates for aluminium, arsenic, boron, barium, calcium, cerium, cadmium, cobalt, cesium, iron, iodine, and potassium. (Note: log axes for As, Cd, Co and Fe).

## SITE DUPLICATES



\* Indicates analytical method:

1 = ICP-MS (MUN)

2 = AA Flame (GSC)

3 = ICP-MS-Hydride (GSC)

Figure 6. Scatterplots of analyses of site duplicates for lanthanum, magnesium, manganese, sodium, lead, antimony, selenium, strontium, uranium and zinc.  
(Note: log axes for Mg, Pb and Zn).

concentrations. For ICP-MS, these elements are: Al, As, B, Ba, Ca, Ce, Cd, Co, Cs, Fe, I, La, Mg, Mn, Pb, Rb, Sb, Sr, U and Zn. For AA, the elements include: Ca, Fe, K, Mg, Na and Zn. For MS-hydride the elements are Sb and Se and for AA-hydride the element is As.

The results of individual elements analyzed by two separate methods have been discussed above. Of the remaining elements, most analyses reproduce with good to excellent correlations. These include Al, Ba, Ce, Cs, K, La, Mn, Na, Rb, Se, Sr and U. Fair correlation is seen in B, Co and I. Correlation is poor for Cd.

The REE data are given in Table 3 for five separate analyses of two control samples (waters from the Ottawa River and Meech Lake). Relative standard deviations are generally better than 10 percent, even at levels of REEs below 10 ppt. This preconcentration procedure is also effective for the first-row transition elements, Cd and Pb (Siriraks *et al.*, 1990). These results when completed will be compared to those by direct ICP-MS.

**Table 3.** Reproducibilities of REE analysis by IC-ICP-MS

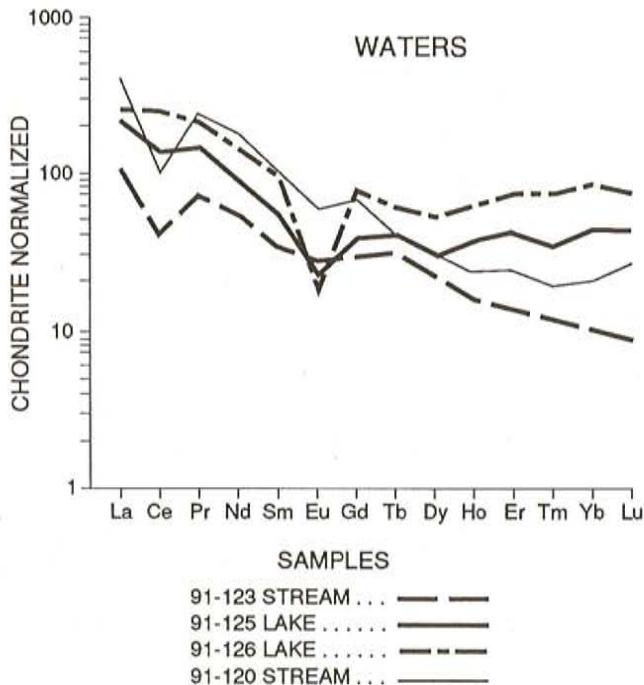
Element	Ottawa River (n=5) mean, ppt	RSD, %*	Meech Lake (n=5) mean, ppt	RSD, %
Y	141	2.2	42	2.8
La	270	2.5	33	2.3
Ce	335	1.6	42	4.0
Pr	63	2.7	7	2.4
Nd	251	3.5	29	8.4
Sm	41	5.3	5	12
Eu	9	7.3	7	4.5
Gd	31	15	5	15
Tb	4	5.7	0.7	21
Dy	20	4.5	4	10
Ho	4	3.7	1	9.2
Er	11	5.3	3	6.6
Tm	0.5	10	0.5	9.2
Yb	11	4.9	4	8.2
Lu	2	13	0.8	17

\* Relative Standard Deviation

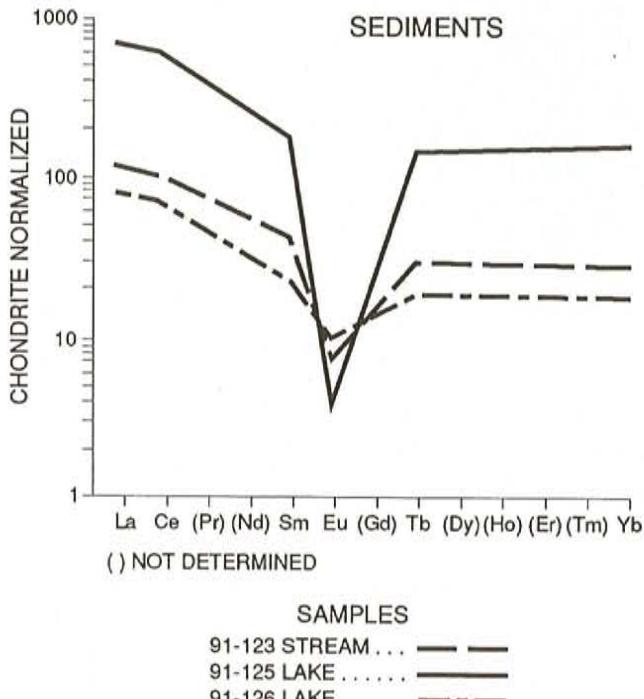
Chondrite-normalized plots (Figure 7) are shown for two stream waters and two lake waters from the Bay d'Espoir area. Note the distinct, negative, Ce anomalies for the stream waters, possibly indicating input from marine aerosols. Both lakes show sharp negative Eu anomalies. The corresponding sediment plots (Figure 8)—derived from neutron-activation analysis for La, Ce, Sm, Eu, Tb, and Yb—also feature Eu anomalies. The one for stream sediment 91-123 is much more pronounced than is observed for its water.

## APPLICATIONS

One method of portraying the distribution of elements in the physical landscape is provided by contoured data maps.



**Figure 7.** Chondrite normalized plots of REEs for stream and lake-water samples from the Bay d'Espoir area.



**Figure 8.** Chondrite normalized plots of REEs for stream and lake-sediment samples from the Bay d'Espoir area.

The distributions of arsenic in lake water and arsenic in lake sediment in the Bay d'Espoir area are illustrated in Figures 9 and 10. Sample sites are shown by '+' symbols. The lake-sediment samples were collected in 1978 (Davenport *et al.*, 1990) and were not necessarily collected from the same lakes

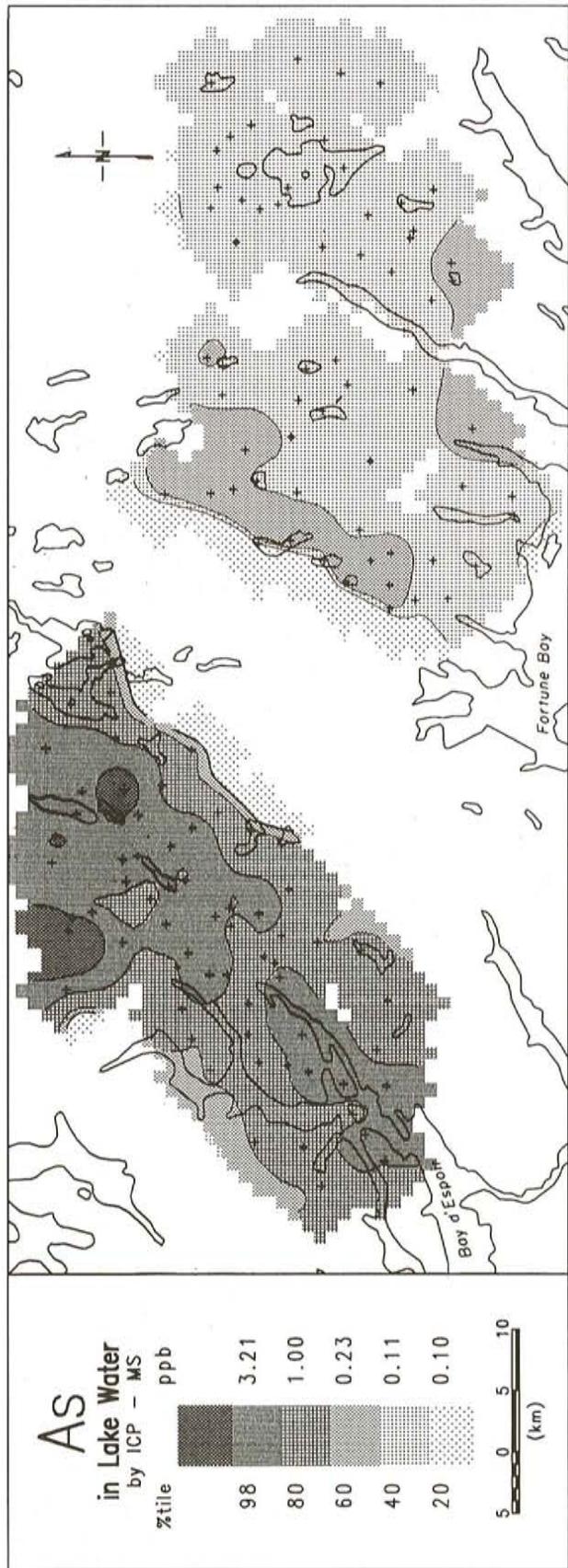


Figure 9. Map of contoured arsenic data from lake water in the Bay d'Espoir area, Newfoundland.

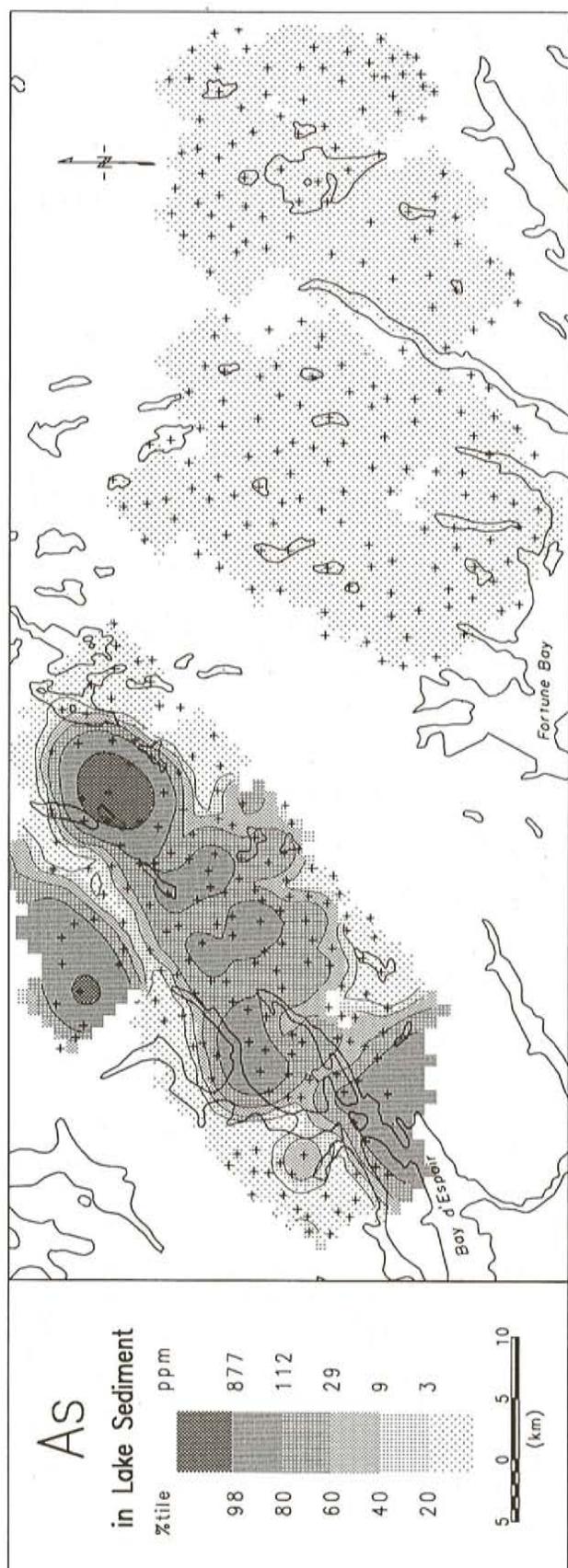


Figure 10. Map of contoured arsenic data from lake sediment in the Bay d'Espoir area, Newfoundland.

as were the water samples. The data in each set have been gridded to a 1 by 1 km grid, a process that results in some smoothing of the data. The area to the west in each figure is underlain primarily by clastic sedimentary and volcanic rocks whereas the area to the east is dominated by granitic rocks. The distribution patterns of As in the two media are seen to be broadly similar despite the samples being, in many instances, from different lakes and despite a 13-year gap between the two surveys. The analyses of As in sediment are uniformly low in the eastern area.

## CONCLUSIONS

Recently developed analytical techniques permit the determination of a wide range of elements in samples of surface waters. For many elements, the analytical detection limits are sufficiently low to determine element concentrations in most samples. Preliminary comparison of lake water and lake-sediment data from common lakes indicate that some elements can be correlated between the two media.

## ACKNOWLEDGMENTS

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