Determination of Trace Element Levels in Natural Fresh Water by Inductively Coupled Plasma Mass Spectrometry

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DETERMINATION OF TRACE ELEMENT LEVELS IN NATURAL FRESH WATER BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Concentrations of trace elemental constituents in water draining an Eastern Ontario agriculture watershed have been determined using inductively-coupled plasma mass spectrometry. Water samples were collected in the Spring of 1991 from three locations. Unfiltered, 0.4 µm filtered as well as ultrafiltered fractions were analyzed. A total of 79 elemental isotopes ranging from ^{6}Li to ^{232}Th were utilized for analytical calibration to measure the concentrations of 38 trace and ultratrace inorganic elemental constituents. Estimates of concentrations were made for: Li, Be, B, Sc, V, Cr, Mn, Ni, Co, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Mo, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb, Th and U. Typical levels found ranged from a mean of 0.05 µg/L for the rare earth elements to 330 µg/L for Sr. For the majority of elements, no differences in concentrations were evident between sampling locations or due to filtration. Exceptions were concentrations of Li, Mn and Pb which were affected by site, and Y which seemed affected by filtration. These quantitative baseline results will form the basis for selection and utilization of specific elements as tracers for modelling of water drainage and flow patterns. This mass spectrometric technique was demonstrated to be a capable, highly detective multielement method for trace element research of natural waters.

KEY WORDS: Inductively coupled plasma mass spectrometry, trace elements, natural fresh water, Ontario agricultural watershed.

INTRODUCTION

Investigations of the impact of farm management practices on runoff from farm land, soil erosion and contamination of ground water and water supplies rely on the application of physical mathematical models. These models predict water drainage and flow patterns using experimentally-determined and calculated parameters. Chemicals artificially introduced into the natural ecosystem serve as tracers of water flow providing quantitative experimental information for use in modelling equations. Tracers reported in the literature include a wide

range of chemical types such as inorganic cations, inorganic anions, inorganic atoms or molecules among which there are both stable and radioactive isotopes, organic chemicals, and metal ion complexes. Specific examples are ^{18}O, Br^-, NO_3^- and uranine dye with inorganics, particularly Br^-, being the most commonly used[1-5].

In addition to being chemically stable in the natural environment and free from sorption by soil and water components, water tracers rely on sensitive analytical techniques for their measurement at low natural background concentrations. The advent, within the past decade, of inductively-coupled plasma mass spectrometry (ICPMS) has placed a powerful, highly detective (sensitive) multi-element technique into the repertoire of the analytical scientist. Applications of ICPMS to the solution of a variety of analytical problems, particularly environmental issues, have gained prominence[6-8]. This technique is well suited to the determination of trace and ultratrace elements in aqueous systems, and thus tracer elements which are generally diluted naturally to exceedingly low concentrations. In addition, it possesses the capability of isotopic discrimination and measurement, useful for studies involving safe, stable, non-radioactive isotopic forms of elements.

The objectives of this work were twofold. One was to characterize an agricultural watershed, selected for extensive agronomic modelling research, for a wide range of naturally-occurring background elemental constituents in the draining waters. This was an essential prerequisite to the selection of an element or elements to be introduced later for tracer purposes. The second was to investigate the applicability of the ICPMS technique as a tool for application to agricultural/environmental research.

EXPERIMENTAL

Sampling location

The site is located within the Greenbelt Experimental Farm of the Centre for Food and Animal Research, Agriculture Canada located in Nepean on the southwest outskirts of Ottawa, Ontario, Canada (Figure 1). There are four agricultural watersheds partially or completely within a total area of 800 hectares bounded by Cedarview/Greenbank, Fallowfield, Woodroffe and Knoxdale roads on the west, south, east and north, respectively, and a railway line at the southeast corner. One watershed of 140 hectares, at the southeast corner, is entirely contained within the designated area. Predominantly, the soil is a clayey marine soil classified as a Brandon series, an Orthic Humic Gleysol by the Canada Soil Survey Committee[9] and an Haplaquoll classified according to Soil Taxonomy[10] with clay to clay loam surface horizon (Ap), clay to silty clay subsoil (Bg) and angular blocky structured parent material (Cg). The entire cultivated area is tile-drained. Several streams drain the watersheds including Black Rapids Creek (site 2) and its branch (site 3). Water samples were collected from sites labelled 2, 3 and T with 2 and 3 referring to sites about 50m west of Woodroffe Road on Black Rapids Creek and its tributary, respectively, and T referring to a composite tile site (draining fields 16 and 25) situated adjacent to a farm road approximately 500m west of Woodroffe. Sites 3 and T are both within a smaller 140 hectare watershed with the tile water draining east via a concrete pipe into the tributary.
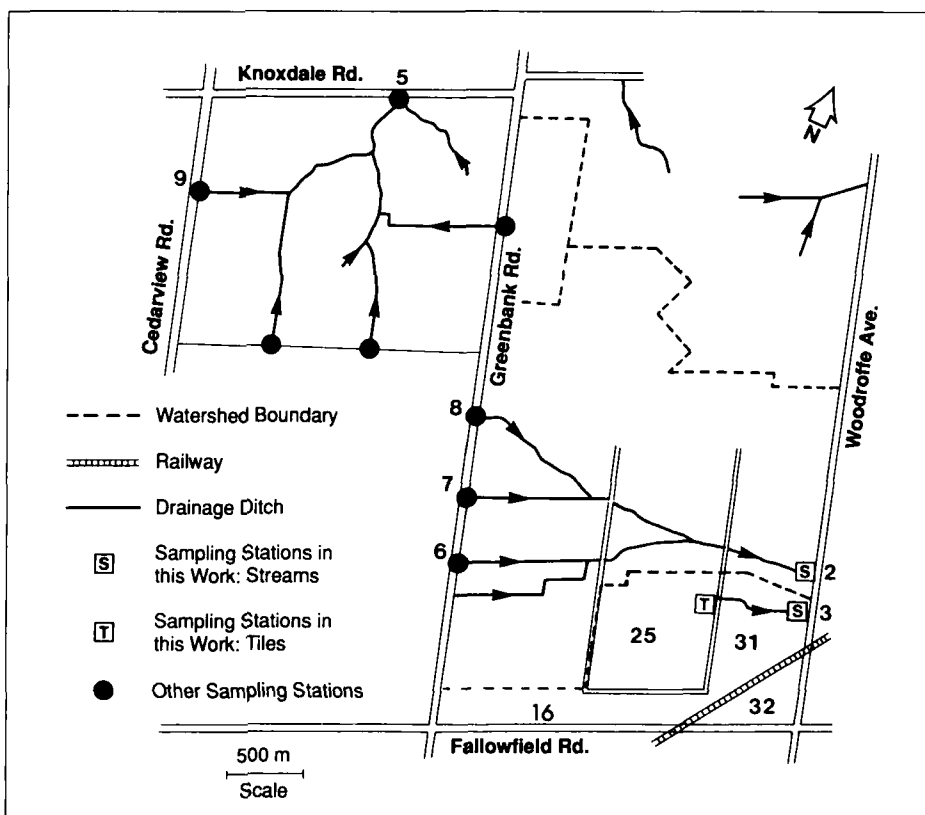
Figure 1 Site plan for watersheds and water sampling locations at the Centre for Food and Animal Research, Greenbelt Experimental Farm, Nepean, Ontario.

Water collection and processing

Glass and plastic ware including filtration membranes were cleaned by contacting for one week with 1M reagent grade HNO_3 and thoroughly rinsing with deionized water. Containers for sampling and storage of water samples were left filled with deionized water until required in the field. They were typically 1L white, linear polyethylene (LPE) bottles with polypropylene (PP) screw closures without liners, providing for leak-proof sealing (Nalge Co., Rochester NY). For collection of field water, a bottle was secured with elastic rope to the blade of a hockey stick, and following rinsing with the water to be sampled, a full bottle of water (ca 1030 mL) was collected and capped for transport to the laboratory. All three sites were sampled on 1991 March 26; additional samples were taken from site 3 on 1991 May 22. In March, all sites had briskly flowing, fairly clear water with stream widths of 2 and 3m at sites 2 and 3, respectively; conditions at site 3 were similar in May but with somewhat reduced water flow. Both centre and near-shore locations of sites 2 and 3 were sampled in March. Collection of water from the tile site T was aimed at getting a composite sample from the pool formed by tile drainage from two fields 16 and 25. A total of 26 1L samples were collected (site 2–6 bottles in March, site 3–4 units in March, 10 units in May, site T–6

units in March). In addition, six (4 in March and 2 in May) 1L samples of deionized water were prepared for laboratory processing simultaneously with natural water samples to serve as procedural reagent blanks. Five of the natural waters and two deionized waters were subjected to filtration (0.4 µm) and four natural waters were ultrafiltered.

All samples were preserved and/or filtered immediately upon return to the laboratory. Preservation was accomplished with 2 mL of 1+1 HNO_3 per L, added after filtration or ultrafiltration when such treatment was applied. Unacidified samples were vacuum filtered through 0.4 µm 47 mm diameter Nuclepore membrane filters (no. N040) supported on a Sartorius polycarbonate SM 16510 filter holder. Ultrafiltration of unacidified samples was by argon pressure through Amicon Corporation diaflo ultrafilters PM10 (passing molecules with molecular weight less than 10000) and YM2 (molecular weight cut-off 1000) supported on an Amicon model 402,400 mL stirred plexiglass cell. Suspended sediment on the Nuclepore membrane filter was determined by drying overnight at 85°C.

Several acid-preserved unfiltered, filtered and ultrafiltered natural and deionized water control samples were concentrated by sub-boiling evaporation by a factor of 20-40 usually 20 fold. Typically, 500 mL of sample was measured into a 600 mL Teflon FEP beaker and the volume was reduced by sub-boiling evaporation for *ca* 15 hr in a clean microenvironment, to approximately 15 mL, transferred to a 25 mL volumetric flask and made up to volume with water. The apparatus used for heat concentration was based on the design of Thiers[11]. Samples were placed on a tray on a large hot plate and covered with inverted 2 L pyrex beakers fitted with side arms to permit the introduction of 0.45 µm-filtered air. Heat was applied from above by 250W infra-red lamps and from below, as required, by the hot plate[12].

Standard solutions

Stock solutions of most individual elements were obtained as 1000 µg/mL (ppm) solutions generally in 2% HNO_3 (a few in 2% HCl) from High Purity Standards, Charleston, SC. Stock solutions of Cl, Br and I (1000 µg/mL) and P and S (10,000 µg/mL) in deionized water were prepared in the laboratory from pure starting materials. Composite stock solutions containing 10,000 ng/mL (ppb) of each element in 0.3M HNO_3 were prepared from the individual stocks to provide the six groups:

(A) Al, Ba, Sr
(B) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb
(C) V, Cr, Ni, Co, Cu, Zn, Ba
(D) Li, Cs, B, Be, Ga, As, Y, Cd, Pb, Th, Mn
(E) Cl, Br, I, S, P
(F) Rb, Sc, Mo, Fe, Tm, Lu

One or two serial dilutions with 0.3M HNO_3 gave calibration standard solutions of concentrations 4 to 1000 ng/mL; a standard reagent blank (0.3M HNO_3) to represent 0 ng/mL was also prepared to produce the first point in calibration.

Mass Spectrometry

A Perkin Elmer Sciex ELAN 250 inductively coupled plasma mass spectrometer (Thornhill ON, Canada) was used. Nebulizer gas flow was regulated by a mass flow controller (Matheson model 8200, Matheson Gas Products, Ottawa, ON, Canada) and solution delivery to the Meinhard concentric nebulizer was controlled at approximately 1 mL/min by a peristaltic pump (Gilson Miniplus 3, model 312, Gilson Medical Electronics Inc., Middleton, WI). A long Sciex torch supplied with the instrument was used to support the argon plasma. Typical operating conditions were as follows: rf power 1.3 kw, reflected power 5w, plasma gas flow 12 L/min, auxiliary gas flow 2 L/min, nebulizer gas flow 0.5 L/min, interface pressure 1 Torr and mass spectrometer pressure 1×10^{-5} Torr. The nickel sampler and skimmer cone orifice diameters were 1.14 and 0.89 mm, respectively. Measurements were made with mass spectrometer resolution of approximately 1.0 amu (10% of peak height) using either the sequential or multi-element mode. In both modes, three measurements per peak were made, one at the maximum and two others at ±0.1 amu of maximum; measurement time was 0.2 sec.

In a typical analysis scheme, six composite standard solutions covering the range of interest usually 4-500 or 10-1000 µg/L, including a standard reagent blank containing 0.0 µg/L of each analyte, were run to establish calibration lines.

Intensity-concentration graphs were fitted with linear least square fits by the Sciex software. A set of six water samples (either concentrated or 'as sampled') together with a standard reagent blank and a standard solution to serve as monitors of instrument performance during measurement, were run and elemental concentrations, corrected for any isobaric isotopic (elemental) interferences, were obtained. A second and third set of sample solutions were similarly processed before the spectrometer was recalibrated with standards and subsequent samples run. Procedural reagent blanks were included as samples and concentrations therein were used to make off-line corrections to sample concentrations. Further manipulations and calculations were performed off-line. Isotopes used for calibration and quantitative calculations of elemental concentrations were: ^{6}Li, ^{7}Li, ^{9}Be, ^{10}B, ^{11}B, ^{27}Al, ^{31}P, ^{32}S, ^{34}S, ^{35}Cl, ^{37}Cl, ^{45}Sc, ^{51}V, ^{52}Cr, ^{53}Cr, ^{54}Fe, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{58}Ni, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{64}Zn, ^{65}Cu, ^{66}Zn, ^{68}Zn, ^{69}Ga, ^{71}Ga, ^{75}As, ^{79}Br, ^{81}Br, ^{85}Rb, ^{86}Sr, ^{87}Rb, ^{88}Sr, ^{89}Y, ^{92}Mo, ^{94}Mo, ^{95}Mo, ^{96}Mo, ^{97}Mo, ^{98}Mo, ^{100}Mo, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd, ^{127}I, ^{133}Cs, ^{136}Ba, ^{137}Ba, ^{138}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{142}Nd, ^{144}Nd, ^{151}Eu, ^{152}Sm, ^{153}Eu, ^{154}Sm, ^{156}Gd, ^{158}Gd, ^{159}Tb, ^{160}Gd, ^{161}Dy, ^{162}Dy, ^{163}Dy, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{167}Er, ^{168}Er, ^{169}Tm, ^{170}Er, ^{172}Yb, ^{173}Yb, ^{174}Yb, ^{175}Lu, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th. Levels of ^{238}U were estimated by reference to intensities of nearby ^{232}Th.

RESULTS AND DISCUSSION

An extensive set of analytical concentration results was obtained for 38 elements utilizing 79 of the 86 isotopes listed above. Under the experimental conditions used, six isotopes, ^{27}Al, ^{31}P, ^{32}S, ^{34}S, ^{35}Cl, and ^{37}Cl were either obscured or gave flat (no slope) calibration lines due to intense background from water, plasma gases and entrained air. As uranium was not available as a calibrant in standard solutions, concentration estimates of ^{238}U were made from ^{238}U/^{232}Th ion intensity ratios and the calibration data for Th. Close proximity of these

isotope masses permitted a semi-quantitative estimate of U concentration. Concentration results were available for a variety of samples including shore-and centre-collected samples, unfiltered, filtered and ultrafiltered samples, unprocessed (1x, as collected) and concentrated (20x, 40x) samples, and collections from two time periods, March 26 and May 22, 1991.

Replicate mass spectrometric analyses of each of these solutions yielded means and standard deviations permitting statistical intercomparisons of data for the same isotope to identify significant differences and allow for stepwise pooling of comparable data to result in a more compact database. Firstly, all data for shore and centre collections from sites 2 and 3 were compared for agreement visually and by quantitative application of the paired t-test. Virtually all agreed, so shore and centre data were combined. Inspection was then made of unfiltered, 0.4 μm-filtered and ultrafiltered results for 20- or 40-fold concentrated samples and data were pooled as permitted; all 20- and 40-fold concentrated data were also combined. Pooling of 1x unfiltered and filtered results, where available, which had larger uncertainties than those for concentrated samples was done by reference to the behaviour of the more precise concentrated materials. Comparisons of the unfiltered and filtered pooled data were then made among the three sampling sites and data pooled as determined comparable. Data for the March and May collections were compared for similarity and pooled where possible. Finally, determinations of elemental concentrations deduced from independent measurements using different isotopes were either averaged over the isotopes, or judicious selection of results was made considering some of the possible polyatomic ion isobaric interferences. Typically, for a given element, isotopes with the lower relative signal intensities and calculated concentrations were selected as giving best estimates of elemental concentrations.

These intercomparisons and pooling of data yielded a strong assembly of analytical concentration results (Table 1) depicting typical concentrations in water draining the watershed. Mean concentrations ± one standard error are given for the elements listed in increasing order of atomic mass, each summarizing the results of 16–210 determinations (replicate measurements, different isotopes), reflecting typically analyses of 10 different samples. All results discussed are those from 20–40 (typically 20) fold concentrated waters.

For the mean concentration data in Table 1, it was found that no statistically significant differences occurred in the various comparisons described above. Where significant differences did occur (Li, Mn, Y and Pb), concentrations are presented as a range encompassing results for the different conditions, to be discussed further. Also included in the table for comparison are median and ranges of concentrations reported in the literature for freshwater throughout the world.

For the 38 elements determined, mean concentrations found in this work ranged from approximately 0.05 μg/l for the rare earth elements to 330 μg/L for Sr. Values found for water in this watershed agree well with medians and ranges reported by Bowen[13] for freshwater throughout the world; no comparisons can be made for Y, Pr, Gd, Ho, Er and Tm for which no values are reported in the literature. Twenty-six of the 32 elements which can be compared with the literature fall within literature ranges. Excellent agreement of experimental means with literature median concentrations is evident for B, Cr, Cu, Br, Rb, Mo, Nd and Sm. Particularly impressive agreement is seen for Cr, Cu and Mo with measured mean concentrations of 1.1 ± 0.8, 3 ± 2 and 0.56 ± 0.01 μg/L and literature reported medians of 1, 3 and 0.5 μg/L respectively.

Table 1 Estimates of elemental concentrations, μg/L, in water from an Ottawa area agricultural watershed determined by ICPMS[a].

Element[b]	Concentration ± standard error this work[c]		Reported in the Literature for freshwater[d]	
			Median	Range
Li	4.8 - 7.6	(56)[e]	2	0.07 - 40
Be	0.05 ± 0.04	(54)	0.3	0.01 - 1
B	9.3 ± 0.8	(103)	15	7 - 500
Sc	3.7 ± 0.1	(30)	0.01	0.004 - 0.04
V	7 ± 2	(45)	0.5	0.01 - 20
Cr	1.1 ± 0.8	(45)	1	0.1 - 6
Mn	6 - 46	(27)[e]	8	0.02 - 130
Ni	3 ± 2	(45)	0.5	0.02 - 27
Co	2 ± 1	(45)	0.2	0.04 - 8
Cu	3 ± 2	(48)	3	0.2 - 30
Zn	4.1 ± 0.4	(45)	15	0.2 - 100
Ga	1 ± 1	(58)	0.09	-
As	2.8 ± 0.6	(48)	0.5	0.2 - 230
Br	9.0 ± 0.4	(68)	14	0.05 - 55
Rb	0.6 ± 0.5	(30)	1	0.6 - 9
Sr	334 ± 6	(16)	70	3 - 1000
Y	0.1 - 0.7	(63)[e]	-	-
Mo	0.56 ± 0.01	(210)	0.5	0.03 - 10
I	0.0 ± 0.1	(33)	2	0.5 - 7
Cs	0.1 ± 0.1	(59)	0.02	0.005 - 1
Ba	48 ± 26	(126)	10	3 - 150
La	0.3 ± 0.2	(28)	0.1	0.05 - 0.8
Ce	1.4 ± 0.2	(31)	0.2	0.1 - 0.2
Pr	0.8 ± 0.6	(31)	-	-
Nd	0.3 ± 0.2	(60)	0.15	0.06 - 0.25
Sm	0.2 ± 0.1	(30)	0.06	0.01 - 0.12
Eu	0.1 ± 0.1	(60)	0.006	0.002 - 0.009
Gd	0.11 ± 0.05	(30)	-	-
Tb	0.06 ± 0.02	(30)	0.003	0.001 - 0.005
Dy	0.08 ± 0.01	(120)	-	0.005
Ho	0.03 ± 0.01	(30)	-	-
Er	0.06 ± 0.01	(120)	-	-
Tm	0.00 ± 0.01	(29)	-	-
Yb	0.04 ± 0.03	(90)	0.01	0.005 - 0.2
Lu	0.04 ± 0.02	(30)	0.003	0.002 - 0.005
Pb	0.2 - 0.5	(52)[e]	3	0.06 - 120
Th	0.0 ± 0.1	(58)	0.03	0.007 - 0.1
U	5 ± 1	(48)	0.4	0.002 - 5

[a] Typical first estimates of concentrations averaged over two sampling times March and May 1991, 3 sites and filtered and unfiltered samples unless otherwise noted (e)

[b] Listed in order of increasing mass.

[c] The number in parentheses is the number of analytical determinations made including use of different isotopes. Concentrations are based on selected isotopes or means over 2 or more isotopes and reflect typically about 10 collections from the field.

[d] Literature values are from the compilation of Bowen[13].

[e] Ranges of concentrations are reported for elements which exhibited significant dependences on collection sites or filtration treatment detailed in Table 2.

Concentrations of four elements, Be, Zn, Pb and Th, agree at the low end of the literature range, whereas 14 elements, Li, V, Mn, Ni, Co, Ga, As, Sr, Cs, Ba, La, Dy, Yb and U fall near the upper extremes of the literature ranges. Experimentally-determined concentrations of six elements, Sc, I and the rare earths Ce, Eu, Tb and Lu occur outside the literature ranges, with I lower and the rest higher than the literature values. No I $(0.0 \pm 0.1$ µg/L) was found in the Ontario water versus a range of 0.5–7 and a median of 2 µg/L reported in the literature. Sc and Ce found at 3.7 ± 0.1 and 1.4 ± 0.2 µg/L are higher than reported medians of 0.01 and 0.2 µg/L, respectively. It is difficult to say whether such differences are real considering that final concentration estimates require further interpretations and application of isobaric polyatomic ion overlaps and corrections. It is likely that some determined values are too high due to uncorrected interferences and must be treated as upper limit estimates. In spite of this, overall, values obtained in this study are in excellent agreement with other values for freshwaters giving credibility to the data.

Data for the elements Li, Mn, Pb and Y, for which statistically significant concentration differences were found among sampling sites and filtration/ultrafiltration treatments, are presented in Table 2. Concentrations of Li using either ^{6}Li or ^{7}Li for measurement of total Li did not differ between sites 3 and T but differed significantly (t test p = 0.05) between site 2 and sites (3 + T). Utilizing combinations of ^{6}Li and ^{7}Li data gives a non significant comparison but this is of no consequence as the difference is masked by analytical

Table 2   Elements exhibiting dependence on sampling sites or filtration/ultrafiltration treatment.[a]

Element	Isotope used	Concentration µg/L ± SE (n)			
		Site 2		Sites 3 + T	
Li	6	5.83 ± 0.49	(12)	9.24 ± 0.81	(16)[c]
Li	7	3.76 ± 0.29	(12)	5.89 ± 0.52	(16)[c]
Li	6 + 7	4.80 ± 1.29	(24)	7.57 ± 2.10	(32)
Mn	55	46.3 ± 9.7	(12)	5.52 ± 0.37	(15)[c]
		Site 2 + 3		Site T	
Pb	207	0.15 ± 0.01	(16)	0.47 ± 0.14	(10)[c]
Pb	208	0.17 ± 0.04	(16)	0.47 ± 0.15	(10)[c]
Pb	207 + 208	0.16 ± 0.02	(32)	0.47 ± 0.11	(20)[c]
		Unfiltered		Filtered	
Y	89	0.71 ± 0.08	(16)	0.35 ± 0.05	(14)[c]
		Unfiltered/ Filtered		Ultrafiltered	
Y[b]	89	0.49 ± 0.08	(14)	0.05 ± 0.03	(19)[c]

[a] All samples, with the exception of those on which are based the unfiltered/filtered-ultrafiltered entries for Y, are March 26, 1991 collections.
[b] May 22, 1991 collections
[c] Significantly different at p = 0.05 by paired t-test.

differences between the two isotopes. Comparison of individual isotope data is, in this case, the acceptable and preferred way to proceed. Lithium concentrations in water from sites 3 and T are greater than in site 2, the Black Rapids Creek. Differences in flow rate among the two streams and thus dilution effect or another source of the element are two possible explanations for concentration differences. It is logical for levels in sites 3 and T to be identical as the water collecting from fields 16 and 25 into the culvert T, drains into stream 3.

Concentrations of lead, on the other hand, are identical in the two stream sites 2 and 3 at 0.16 ± 0.02 µg/L but differ significantly (t test p = 0.05) from concentrations of 0.47 ± 0.11 µg/L in tile water T. This suggests a stronger source of lead in fields 16 and 25 than in the other fields and/or greater dilution by streams 2 and 3. Levels of Pb determined using either isotopes 207 or 208 gave identical results indicating no (or at least no different) interferences on each of these two masses.

Yttrium was the only element exhibiting dependence on filtration/ultrafiltration treatment. For March collections, unfiltered water contained 0.71 ± 0.08 µg/L, twice the concentration of 0.35 ± 0.05 µg/L in 0.4 µm filtered samples. Collections in May showed identical levels of 0.49 ± 0.08 µg/L in filtered and 0.4 µm filtered samples, but these differed from the 0.05 ± 0.03 µg/L present in ultrafiltered samples. The higher levels in unfiltered vs filtered (March) or in unfiltered/filtered vs ultrafiltered (May) waters are logical, suggesting element association with suspended sediment particles or colloidal/molecular moieties larger than 10,000 or 1000 daltons retained by ultrafiltration membranes PM10 and YM2, respectively. Suspended sediment concentrations were 3.4, 3.5 and 1.7 mg/L in water from sites 2, 3 and T, respectively in March, and 1.6 mg/L in water from site 3 in May. The relationships observed are consistent with a lower load in May. Low suspended sediment levels in these relatively clean waters are responsible for lack of visible filtration effects on elemental concentrations, even with such a highly detective analytical procedure. More effects are expected in heavier sediment-laden water[12,14]. In that study, demonstrable relationships between elemental concentrations and suspended sediment concentrations were found for water with suspended sediment concentrations up to 700 mg/L.

In an attempt to increase the detectivity of the ICPMS technique to improve measurement of elements present at low concentrations, natural water samples were concentrated typically 20-fold by heat. Table 3 presents a comparison of selected elemental concentrations determined directly on the sample and on concentrated sample solutions for identical samples collected on May 22 from site 3. Four elements, Sc, As, Cs and Pb as well as the rare earth elements (REE) were not measured by direct determination due to low levels. Of the 17 elements for which comparisons are presented, concentrations for one half agree within two standard errors. Concentrations of ^{6}Li, ^{7}Li, Mn, Co, Cu, Ga, ^{79}Br, Y and Th, determined directly or using concentrates, were identical whereas those for ^{10}B, ^{11}B, V, Cr, Ni, Zn, ^{81}Br and Mo differed. Standard errors based on similar numbers of determinations were better using the concentrates in 10 out of 17 instances (^{6}Li, ^{7}Li, ^{10}B, ^{11}B, Cr, Ga, ^{79}Br, ^{81}Br, Y, Th), close to identical in 3/17 (Mn, Zn, Mo) and worse in 4/17 cases (V, Ni, Co, Cu). Hence, as expected, precision was generally improved using concentrated water samples.

It is not unexpected to have differences occurring between measurements on directly-collected and concentrated water samples. Although better estimates are generally anticipated using concentrates in which elemental concentrations are more highly in excess of the

Table 3   Comparison of elemental concentrations determined directly in natural water samples and in concentrated solutions[a].

Element and Isotope used for calibration	Concentration µg/L ± SE	
	Directly	Concentrated sample
Li6	5.5 ± 1.4	5.8 ± 0.5
Li7	3.4 ± 0.8	3.8 ± 0.3
B10	3.0 ± 2.7	9.1 ± 1.0
B11	17.1 ± 3.0	8.9 ± 2.1
Sc45	_b	3.9 ± 0.1
V51	4.2 ± 0.1	8.8 ± 1.3
Cr52	3.5 ± 0.5	1.8 ± 0.2
Mn55	57 ± 9	46 ± 10
Ni58	2.0 ± 0.4	4.9 ± 0.9
Co59	3.0 ± 0.2	2.6 ± 0.4
Cu63	3.4 ± 0.2	4.4 ± 0.6
Zn66	6.6 ± 0.4	3.7 ± 0.5
Ga71	0.17 ± 0.29	0.15 ± 0.05
As75	_b	2.9 ± 0.3
Br79	12.0 ± 0.6	10.1 ± 0.3
Br81	17.1 ± 1.3	9.1 ± 0.5
Y89	0.3 ± 0.3	0.7 ± 0.1
Mo (92–100)	0.21 ± 0.01	0.57 ± 0.02
Cs133	_b	0.12 ± 0.05
REE	_b	0.00 ± 0.01 to 1.4 ± 0.2
Pb206	_b	0.07 ± 0.06
Pb207	_b	0.15 ± 0.01
Pb208	_b	0.17 ± 0.04
Th232	0.7 ± 0.4	0.1 ± 0.1

[a] Comparisons are for identical samples run directly and following typically 20-fold concentration; the number of determinations for each mean is typically in excess of 20.
[b] Some elements were not determined directly due to low concentrations.

respective detection limits, other factors such as increased biases from increased interferences in the concentrated solutions come into play. These biases can arise, for example, from higher concentrations of oxide and chloride molecule ions of major species overlapping isotopic masses of elements being determined.

One unique aspect inherent in atomic mass spectrometry, not available in other analytical techniques, is the possibility of determining elemental concentrations using calibration based on two or more different isotopes of the given element. This is akin to the use of different wavelengths in atomic emission spectrometry but yet significantly different in that physically different atomic species are involved in atomic mass spectrometry. Thus, as mentioned, the analytical concentration data presented here have been averaged over data obtained using calibration with two or more different isotopes of the given element when results were judged equivalent. Alternatively, results were selected from only one isotope considering some possible polyatomic ion overlaps. It should be clarified that although actual measurement of concentrations of the various isotopes is feasible, this was not done in this study. Rather, various isotopes were used for *calibration* to determine the *total* (over

all isotopes) concentration of the element. By way of example, the concentration of Zn in a sample was found to be 6.6 μg/L using naturally occurring ^{64}Zn for establishing the calibration, and 4.5 μg/L using ^{66}Zn. Both values should be theoretically identical and either one or a mean of the two, depending on precision considerations due to differences in isotopic abundances and thus signal intensities, could be used to represent the total Zn concentration.

Table 4 presents a comparison of elemental concentrations determined in a natural water sample using different isotopes for analytical calibration. Each concentration stems from about 20 separate determinations (calibration with standards and sample measurement) yielding good means with associated standard errors. Concentrations are presented for a total of 50 isotopes representing 18 elements with each determined using at least two but frequently more (up to seven for Mo) isotopes. Natural abundances are included for each isotope, indicating the percent of the element occurring in each of the isotopic species. In the majority of cases, within a given element, concentration results agree quite well, usually within the respective standard errors. This is the case for ^{6}Li ^{7}Li, ^{10}B ^{11}B, ^{64}Zn ^{66}Zn, ^{79}Br ^{81}Br,

Table 4 Comparison of elemental concentrations determined in a natural water sample using different isotopes for calibration[a].

Isotope and (abundance %)	Elemental Concentration ±SE μg/L	Isotope and abundance %	Elemental concentration ±SE μg/L
Li 6 (7.5)	8.7 ± 0.1	Cd 112 (24.1)	0.25 ± 0.15
Li 7 (92.5)	5.7 ± 0.1	Cd 113 (12.2)	0.23 ± 0.04
B 10 (20)	11.1 ± 2.7	Cd 114 (28.7)	-
B 11 (80)	8.1 ± 0.8	Nd 142 (27.1)	0.06 ± 0.06
Cr 52 (83.8)	0.48 ± 0.06	Nd 144 (23.8)	0.19 ± 0.02
Cr 53 (9.5)	9.14 ± 0.25	Eu 151 (47.8)	0.13 ± 0.02
Ni 58 (68.3)	1.7 ± 0.1	Eu 153 (52.2)	0.19 ± 0.01
Ni 60 (26.1)	8.1 ± 0.2	Sm 152 (26.7)	0.28 ± 0.02
Cu 63 (69.2)	1.3 ± 0.1	Sm 154 (22.7)	1.94 ± 0.04
Cu 65 (30.8)	10.9 ± 0.9	Gd 156 (20.5)	0.29 ± 0.02
Zn 64 (48.6)	6.6 ± 0.3	Gd 158 (24.8)	0.15 ± 0.02
Zn 66 (27.9)	4.5 ± 0.7	Gd 160 (21.8)	0.05 ± 0.01
Zn 68 (18.8)	0.9 ± 0.2	Dy 161 (18.9)	0.08 ± 0.01
Br 79 (50.7)	8.1 ± 0.3	Dy 162 (25.5)	0.08 ± 0.01
Br 81 (49.3)	8.8 ± 0.3	Dy 163 (24.9)	0.08 ± 0.01
Rb 85 (72.2)	0.25 ± 0.01	Dy 164 (28.2)	0.06 ± 0.01
Rb 87 (27.8)	54 ± 2	Er 166 (33.6)	0.06 ± 0.01
Mo 92 (14.8)	0.51 ± 0.01	Er 167 (22.9)	0.08 ± 0.01
Mo 94 (9.3)	0.53 ± 0.01	Er 168 (26.8)	0.06 ± 0.01
Mo 95 (15.9)	0.51 ± 0.01	Er 170 (15.0)	0.06 ± 0.01
Mo 96 (16.7)	0.58 ± 0.02	Yb 172 (21.9)	0.06 ± 0.01
Mo 97 (9.6)	0.52 ± 0.02	Yb 173 (16.2)	0.09 ± 0.01
Mo 98 (24.1)	0.50 ± 0.01	Yb 174 (31.8)	0.04 ± 0.01
Mo 100 (9.6)	0.56 ± 0.02	Pb 206 (24.1)	0.05 ± 0.02
Cd 110 (12.5)	-	Pb 207 (22.1)	0.15 ± 0.04
Cd 111 (12.8)	0.12 ± 0.04	Pb 208 (52.4)	0.22 ± 0.05

[a] Determinations (typically 20) were conducted on 20-fold concentrated water samples collected May 22, 1991 from site 3.

^{92}Mo ^{94}Mo ^{95}Mo ^{96}Mo ^{97}Mo ^{98}Mo ^{100}Mo, ^{111}Cd ^{112}Cd ^{113}Cd, ^{142}Nd ^{144}Nd, ^{151}Eu ^{153}Eu, ^{156}Gd ^{158}Gd, ^{161}D$_y$ ^{162}D$_y$ ^{163}D$_y$ ^{164}D$_y$, ^{166}Er ^{167}Er ^{168}Er ^{170}Er, ^{172}Yb ^{173}Yb ^{174}Yb, and ^{206}Pb ^{207}Pb ^{208}Pb. On the other hand, in several instances, differences are evident for ^{52}Cr ^{53}Cr, ^{58}Ni ^{60}Ni, ^{63}Cu ^{65}Cu, ^{64}Zn ^{68}Zn, ^{66}Zn ^{68}Zn, ^{85}Rb ^{87}Rb, and ^{152}Sm ^{156}Sm. Of particular mention are the good agreements for the two isotopes each of B and Br, namely ^{10}B ^{11}B, ^{79}Br ^{81}Br and the seven isotopes of Mo. Agreement of concentration results among isotopes of the same element provides for confirmation of the mass spectrometric measurement step. Disagreement signals an interference on one or more of the isotopes and dictates the need to investigate the underlying causes to select correct values.

Figures 2 and 3 depict the entire elemental mass spectrum (ions/s signal intensity versus mass) of a twenty fold concentrated natural water sample covering the 4–238 amu region. Indicated thereon are all of the 86 isotopes used (or attempted) in this work to determine a wide range of elemental constituents in natural waters. Clearly visible are signals arising from ^{6}Li, ^{7}Li, ^{10}B, ^{11}B, ^{79}Br and ^{81}Br on either side of an argon dimer (^{40}Ar$_2$) peak centred at mass 80, large peaks due to strontium including ^{86}Sr and ^{88}Sr, the Mo isotopes in the 92–100 mass region, ^{127}I, large Ba signals in the 130–138 region including ^{136}Ba, ^{137}Ba and ^{138}Ba, rare earth elements at 139–175, three Pb isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb, ^{232}Th and ^{238}U as well as a small peak due to ^{235}U with a 0.72% abundance.
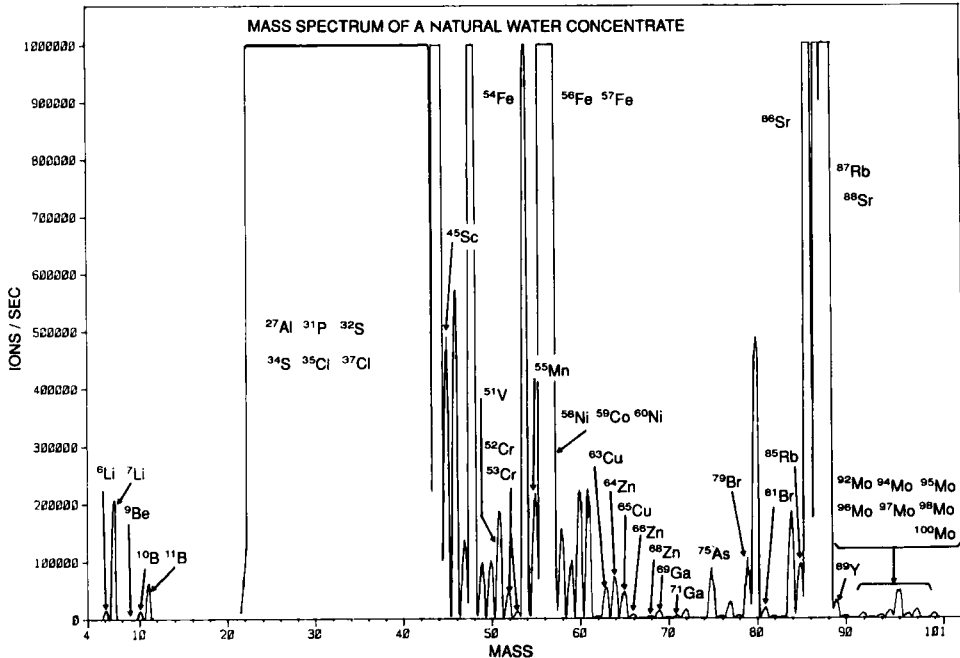
Figure 2 ICP mass spectrum of a twenty-fold concentrated fresh natural water sample covering the 4–101 atomic mass unit region. Isotopes listed are those which were used for analytical calibration in this work. Mass positions for each isotope are indicated but it should be kept in mind that isotopes of other elements as well as molecular ions can contribute to observed peaks. The 22–44 amu region, contains, in addition to the listed isotopes of interest, low mass molecular interferences such as C_2, N_2, O_2, CO, NO, CO_2, NaO, MgO, AlO arising from the plasma gas, water and other major components in the sample solution, resulting in a large signal obscuring the region and swamping any possible measurements.
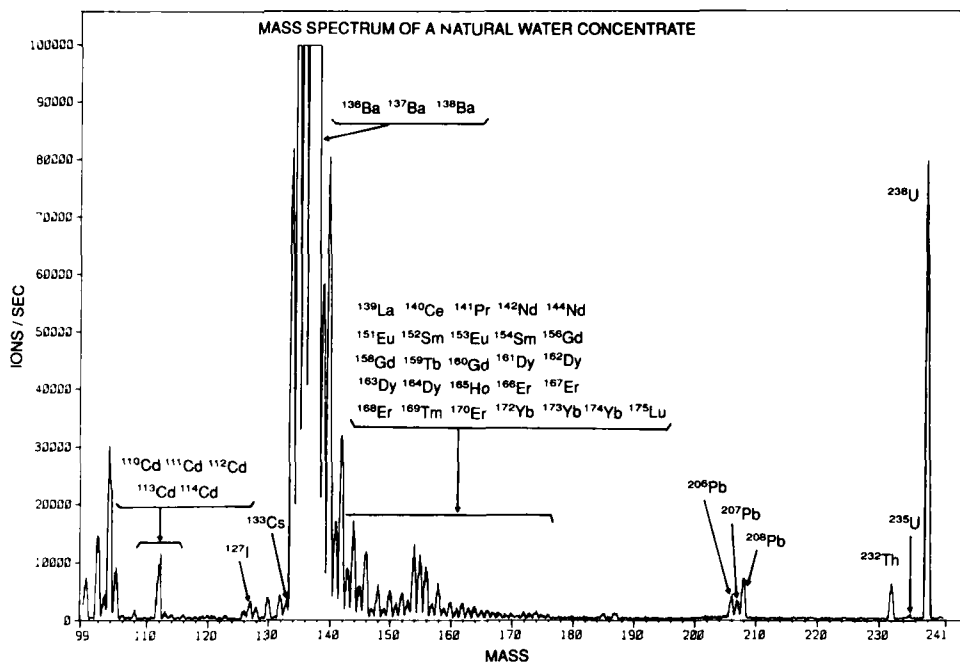
Figure 3 Continuation of the ICP mass spectrum of a twenty-fold concentrated fresh natural water sample covering the 99–238 atomic mass unit region. Refer to caption of Figure 2.

Barring the presence of other signals, each spectral peak represents one isotope whose height is proportional, to a first approximation, to its natural abundance. Hence the peak height of ⁷Li (natural abundance 92.5%) is, as expected, about 12 times the height of ⁶Li (natural abundance 7.5%). Although the structure of an inorganic atomic mass spectrum is fairly simple with a maximum of only some 200 spectral lines, there are some isotopic overlaps, and corrections are required in order to arrive at accurate concentration estimates. This is achieved by estimating the signal intensity contribution of other elements, using natural isotopic abundance data, at the mass of the element of interest and subtracting those intensities from the total signal to get the net signal due to the element of interest. These computations are automatically done by instrumental computer software. Table 5 records equations used by the SCIEX ELAN spectrometer for isotopes used in this study. Out of a total of 85 isotopes of interest in this work, corrections were applied to 27 with the remaining 58 suffering no isotopic interference. The approach can be more clearly seen by way of example using ⁹⁶Mo. Three elements occur at this mass—⁹⁶Zr, ⁹⁶Ru and ⁹⁶Mo. To conduct determinations of molybdenum using the molybdenum signal at mass 96, the observed signal must be corrected for contributions of ⁹⁶Zr and ⁹⁶Ru. Reference to isotopic abundance tables such as those published by de Bièvre and Barnes[15] shows the isotopic abundances of Zr and Ru to be: ⁹⁰Zr 51.4%, ⁹¹Zr 11.2%, ⁹²Zr 17.1%, ⁹⁴Zr 17.5%, ⁹⁶Zr 2.8% and ⁹⁶Ru 5.5%, ⁹⁸Ru 1.9%, ⁹⁹Ru 12.7%, ¹⁰⁰Ru 12.6%, ¹⁰¹Ru 17.0%, ¹⁰²Ru 31.6%, ¹⁰⁴Ru 18.7%. ⁹⁰Zr and ¹⁰¹Ru are the only species occurring at masses 90 and 101, respectively. Measuring the signal at masses 90 and 101 permits an estimation of the signals expected at mass 96 contributed by Zr (2.8/51.4) and Ru (5.5/17.0) giving the two factors in the correction equation (I(Mo96) =

Table 5 Equations utilized by Sciex software for isobaric corrections[a].

I(Fe54)	= I(54)	- 0.0284 × I(Cr52)
I(Ni58)	= I(58)	- 0.0036 × I(Fe56)
I(Zn64)	= I(64)	- 0.0412 × I(Ni60)
I(Sr86)	= I(86)	- 1.504 × I(Kr83)
I(Rb87)	= I(87)	- 0.0852 × I(Sr88)
I(Mo92)	= I(92)	- 0.3325 × I(Zr90)
I(Mo94)	= I(94)	- 0.3381 × I(Zr90)
I(Mo96)	= I(96)	- 0.0544 × I(Zr90) - 0.3228 × I(Ru101)
I(Mo98)	= I(98)	- 0.1095 × I(Ru101)
I(Mo100)	= I(100)	- 0.7393 × I(Ru101)
I(Cd110)	= I(110)	- 0.5313 × I(Pd105)
I(Cd112)	= I(112)	- 0.0396 × I(Sn118)
I(Cd114)	= I(114)	- 0.0271 × I(Sn118)
I(Ba136)	= I(136)	- 0.3355 × I(Xe129) - 0.0022 × I(Ce140)
I(Ba138)	= I(138)	- 0.0009 × I(La139) - 0.0028 × I(Ce140)
I(Nd142)	= I(142)	- 0.1251 × I(Ce140)
I(Nd144)	= I(144)	- 0.2087 × I(Sm147)
I(Sm152)	= I(152)	- 0.0131 × I(Gd157)
I(Sm154)	= I(154)	- 0.1420 × I(Gd157)
I(Gd156)	= I(156)	- 0.0021 × I(Dy163)
I(Gd158)	= I(158)	- 0.0036 × I(Dy163)
I(Gd160)	= I(160)	- 0.0919 × I(Dy163)
I(Dy162)	= I(162)	- 0.0041 × I(Er166)
I(Dy164)	= I(164)	- 0.0467 × I(Er166)
I(Er168)	= I(168)	- 0.0062 × I(Yb172)
I(Er170)	= I(170)	- 0.1389 × I(Yb172)
I(Yb174)	= I(174)	- 0.0066 × I(Hf178)

[a]I(element, mass) and I(mass) represent, respectively, ion intensity for the specific isotope and ion intensity of all atomic species with the identical mass. No isobaric corrections were applied to the remaining isotopes in this work: ^{6}Li, ^{7}Li, ^{9}Be, ^{10}B, ^{11}B, ^{27}Al, ^{31}P, ^{32}S, ^{34}S, ^{35}Cl, ^{37}Cl, ^{45}Sc, ^{51}V, ^{52}Cr, ^{53}Cr, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{68}Zn, ^{69}Ga, ^{71}Ga, ^{75}As, ^{79}Br, ^{81}Br, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{95}Mo, ^{97}Mo, ^{111}Cd, ^{113}Cd, ^{127}I, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{151}Eu, ^{153}Eu, ^{159}Tb, ^{161}Dy, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{167}Er, ^{169}Tm, ^{172}Yb, ^{173}Yb, ^{175}Lu, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th.

I(96) - 0.0544 × I(Zr90) - 0.3228 × I (Ru101)) and thus an estimate of the signal at 96 due to solely molybdenum.

Peaks other than those due to elemental isotopes are invariably present in all atomic mass spectra. These are present or arise from the argon plasma gas, entrained air, water as well as a variety of molecular ions formed from major components in the sample solution. Natural fresh waters contain significant concentrations of Na, Mg, S, Cl, Ca, Sr and Ba which in combination with abundantly present Ar, O, C and N form molecular ions. Some of these ions have molecular masses identical, within the resolution of the mass spectrometer, with some of the elemental isotopes being measured, overlap with them and thus obscure some of the isotopes of elements being determined. This manifests itself as a departure of the measured isotope ratio for a given element from the natural ratio for that element. Several elements, eg. Cr, Ni, Cu, Zn, Ga, Rb, Sm and Gd were observed to have anomalous isotopic ratios caused by interferences of suspect ions[16-18]. There are certainly others, including ^{51}V

Table 6 Estimated detection limits of the ICPMS procedure applied
to fresh natural waters in this study.

| Isotope | Detection limit $(\mu g/L)^a$ | |
	Direct	Concentrated sample
Li6	4	0.6
Li7	4	0.3
B10	53	5
B11	10	5
Sc45	-	0.1
V51	0.2	0.4
Cr52	2	0.5
Mn55	3	1
Ni58	4	0.4
Co59	0.4	0.5
Cu63	0.4	2
Zn66	2	3
Ga71	5	0.9
As75	-	2
Br79	16	0.4
Br81	22	3
Mo (92–100)	-	0.04
I127	30	2
Cs133	4	0.2
REE	-	0.03
Pb206	4	0.2
Pb207	5	0.2
Pb208	6	0.5
Th232	6	0.7

[a] Detection limits are calculated as 3 × standard deviation of typically
10 determinations (complete analytical procedure) directly on col-
lected samples or on 20-fold concentrated samples;—not determined.

and monoisotopic elements such as ^{75}As which are expected to be interfered with.

Such signals are not corrected by isobaric elemental isotopic overlap equations in the spectrometer software, necessitating other steps and corrections to reduce or eliminate molecular ion effects. In particular the 20–44 atomic mass region has severe overlaps resulting from low mass molecular interferences such as C_2, N_2, O_2, CO, NO, CO_2, NaO, MgO and AlO formed by recombination in the argon plasma as well as dominant isotopes of Ca. Smaller, subtle but nevertheless significant molecular ion overlaps also occur in the 44–140 mass region. Effects of molecular ions formed from components of the blank are easily compensated for by blank subtraction; effects arising from the sample matrix pose more difficulties, a subject explored in a subsequent publication.

Estimated detection limits of the ICPMS procedure applied to fresh natural waters in this study are summarized for a number of elements in Table 6. Detection limits are presented, on a sample basis, for the water samples as collected (direct measurement), and following 20-fold concentration. As expected, much superior (lower) detection limits were observed with concentrated samples and concentration was pursued to obtain concentrations of low level elements.

CONCLUSIONS

This work has resulted in a comprehensive elemental characterization of water in an agricultural watershed study area. It has also demonstrated the multi-element, high detectivity capability of ICPMS for agricultural/environmental research. Knowledge of background/baseline/natural concentrations of elemental constituents in this water is a necessary prerequisite to future research in progress regarding the selection of tracer ions expected to be measurable in this natural system.

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