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An analytical method for multi-elemental analysis in environmental matrices is proposed. Over 240 samples are analyzed for concentration and isotopic composition for 8 elements (B, Cd, Cu, Fe, Pb, Sr, Tl and Zn).

Assessment of natural variability of B, Cd, Cu, Fe, Pb, Sr, Tl and Zn concentrations and isotopic compositions in leaves, needles and mushrooms using single sample digestion and two-column matrix separation

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Abstract

An analytical procedure allowing multi-elemental analyses and isotope ratio measurements of eight of these (B, Cd, Cu, Fe, Pb, Sr, Tl and Zn) in matrices relevant for bio-monitoring using a single high-pressure acid digestion was developed. Method blanks, separation efficiency of matrix elements, repeatability and reproducibility were evaluated using sets of preparation blanks, certified reference materials and duplicate samples prepared and analyzed over a period of several months. The method was used to assess natural variability of concentrations and isotopic compositions in bio-indicators (tree leaves, needles and mushrooms, over 240 samples) collected mainly from a confined area in North-East Sweden. Ranges found from leaves and needles were compared with data obtained for limited numbers of samples collected in Spain, Italy, France, United Kingdom and Iceland.

Keywords: Isotope ratio measurements, ICP-SFMS, MC-ICP-MS; Birch leaves; Spruce needles; mushrooms; Bio-monitoring; multi-tracer studies.

1. Introduction

Isotopic information can be used to aid a wide range of scientific disciplines, including environmental geochemistry and plant sciences. Such uses include tracing metal contamination sources/pathways, studying biological processes (nutrient and anthropogenic uptakes/cycles, within plant transport mechanisms),[1] remediation and geographical provenance[2–5]. Variability in the isotopic composition of radiogenic elements, e.g. lead (Pb), strontium (Sr) and osmium (Os), has been frequently utilized in environmental studies[6–12] and application niches continue to grow. Mass-dependent fractionation of boron (B) and other light elements (carbon, oxygen and nitrogen) has now been used for provenance studies, tracing pollution sources and water mixing for decades.[2,13–15]

Enhancements in measurement precision due to developments in analytical instrumentation, e.g. the advent of multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), as well as continual refining of preparation/separation and pre-concentration methods[1] has allowed inclusion of heavier stable elements in the 'isotope toolbox' and the number of published stable isotope studies has grown exponentially in the last decade.[16] For example, in environmental studies involving bio-indicators, Pb[11,17] and Sr[18] isotopes have been relied upon for at least the past three decades, whereas Os,[19–22] Cd[23] and Tl have been relatively new additions contributing to the expanding array of investigations.

Another relatively new development is the application of multi-tracer studies,[2,24–28] as source tracing in two or three-dimensional space potentially allows distinguishing samples having overlapping isotope signatures for a single element.[16] In an exemplary study, Sherman *et al.*[24] used Pb, Sr and Hg isotopes in precipitation to identify the signature of coal combustion. $\delta^{11}B$ coupled with $^{87}Sr/^{86}Sr$ ratios have also proved to be effective in determining the origin of coal combustion residuals.[25]

Apart from anthropogenic assessment, a great deal of attention in recent studies has been given to the study of the biological processes responsible for variations in isotopic compositions in plants and animals.[27,29–35] In the plant sciences, the major focus has been on elements essential for plant growth. With the help of isotopic data, Rosner *et al.*[32] concluded that B assimilation by plants is directly influenced by the local conditions (both natural and anthropogenic). This has been further confirmed in another recent multi-isotope study where the coupling of Sr and B isotope ratios has been used to trace geographic origins of coffee beans.[2] Jouvin *et al.*[31] described two models for fractionation of the micro-nutrients Cu and Zn during uptake by plants, proposing different fractionation patterns for different uptake strategies. Uptake mechanisms for Cu, Fe and Zn by plants has been the focus of a number of studies.[29–31,36,37]

Wider applications of isotope signatures in environmental geochemistry and plant sciences are often hampered by the high cost of instrumentation, the need for often tedious, elaborative and time-consuming sample preparation and analyte separation schemes,[38,39] as well as challenges to verify the accuracy of analytical methods.[16,40–42] As a result, many studies are still based on very limited numbers of samples and often consider only a single isotope system, which may affect the transferability of any conclusion drawn. Clearly, a massive amount of isotopic information would need to be acquired for a meaningful assessment of the natural variability in various eco-systems and to identify the factors responsible for such variability. In approaching an investigation, special importance must also be given to the geographical scale of the study or else important local details may resist detection.[11] Thus the possibility to obtain isotope data for many elements coupled to concentration information in a reasonable time and without the need to use several types of instruments is of extreme value.

The aim of this work is to provide a detailed description of an analytical procedure allowing for MC-ICP-MS isotope ratio measurements of at least eight elements from a single digestion of a limited amount (approximately 0.5 g) of plant material. The analytical procedure was applied to a substantial number of leaves, needles and mushrooms (frequently used bio indicators[11,43,44]) collected from urban environments in several European countries to assess the extent of the natural variability of B, Cd, Cu, Fe, Pb, Sr, Tl and Zn isotope compositions as well as seasonal variations.

2. Experimental

2.1. Instrumentation

All isotope ratio measurements except for B in those samples with low in the analyte were performed using a NEPTUNE PLUS (Thermo Scientific, Bremen, Germany) MC-ICP-MS instrument operated with variously-configured introduction systems, including Aridus II (Teledyne CETAC Technologies, Omaha, NE, USA) and Apex (Elemental Scientific, Omaha, NE, USA) desolvating nebulizers. Cup configurations used, operating conditions and measurement parameters are given in **Table 1.**

B isotope ratio measurements in some samples and all measurements of elemental concentrations were performed by double-focusing sector field ICP-MS (ICP-SFMS;

ELEMENT XR, Thermo Scientific).[23] Methane addition to the plasma was used to decrease formation of oxide-based spectral interferences, improve sensitivity for elements with high first ionization potentials, and to minimize matrix effects.[45] Operating conditions and measurement parameters for concentration measurements were as described in a previous study.[46]

A laboratory UltraCLAVE single reaction chamber microwave digestion system (Milestone, Sovisole, Italy) was used for sample digestions.

2.2. Chemicals and reagents

Nitric acid (HNO_3) and hydrochloric acid (HCl), both from Sigma-Aldrich Chemie GmbH (Munich, Germany) and hydrogen fluoride (HF, 48%, Merck, Darmstadt, Germany) used in this work were all of analytical grade. Water used in all experimental procedures was de-ionized Milli-Q water (Millipore, Bedford, MA, USA) purified by reverse osmosis followed by ion-exchange cartridges. For dilution of sample digest aliquots intended for B isotope ratio measurements, water was further purified by sub-boiling distillation in Teflon stills (Savillex, Minnetonka, MN, USA). AG MP-1M ion-exchange resin (macroporous, 100-200 dry mesh size, 75-150 µm wet bead size, Bio-Rad Laboratories AB, Solna, Sweden) was cleaned by soaking in 0.7 M HNO_3 followed by rinsing with Milli-Q water and loading as slurry into 2 ml columns. Pre-packed 2 ml columns with Sr-Spec resin (Eichrom Technologies, IL, USA) were used as supplied.

The following chemicals were used as 'δ-zero' standards: NIST SRM 3108 Cd solution Lot 130116, NIST SRM 976 Cu standard solution, NIST SRM 951a - Boric Acid, NIST SRM 981 Common Lead, and NIST SRM 987 (NBS-987) - Strontium Carbonate (all from the National Institute of Standards and Technology, Gaithersburg, MD, USA); IRMM 3702 Zinc solution and IRMM-014 Fe metal (both from the Institute for Reference Materials and Measurements, Geel, Belgium). For Ag and Tl isotopic analyses, commercial standards (1000 mg L^{-1} mono-elemental solutions supplied by Ultra Scientific, North Kingstown, RI, USA; Ag: Lot M00474; and Tl: Lot L00709) were used as 'δ-zero' standards.

2.3. Samples

A large part of the samples was collected in the city and suburbs of Luleå (northern Sweden), a medium-sized town (population approximately 75 000) located in the province of Norrbotten. The study area lies almost entirely on a 1.9 Ga granitic bedrock with minor metasedimentary constituent.[47] Clay and silt loam are the main soil constituents[48] even though it is important to note that some of the soil components in the urban areas can be non-native. The area surrounding the town of Luleå is heavily industrialized, with a steelworks as the dominant local industry.

The sets of biological samples collected during 2013-2015 from from approximately 50 individual locations included common birch (*Betula pubescens*) leaves, Norway spruce (*Picea abies*) needles and fruit bodies of edible mushrooms (*Boletus edulis, Leccinum scabrum, Leccinum versipelle, Leccinum aurantiacum* and *Suillus variegatus*). At a few locations leaves of oak (*Quercus*), aspen (*Populus tremula*) and rowan (*Sorbus aucuparia*) were also sampled. The amounts of material from each sampling location (corresponding to approximately 0.5-1.5 g dry weight per matrix) consisted of 10-50 leaves (depending on growth stage) collected from different branches/trees, needles from the last year grown on parts of lower branches and mushrooms collected under sampled trees (where available).

Sampling was performed either at the beginning of the growing season (May-early June, birch leaves only) or just before senescence (early September), though in the majority of locations samples were taken from different trees in spring and autumn. All samples were collected wearing powder-free laboratory gloves into Zip-Lock plastic bags marked with geographic coordinates, type of sample and collection date. Sampling locations were chosen on the base of a sampling grid of 1 km^2 mesh size, covering a total area of ca. 200 km^2. Sampling height was limited to roughly 2.5 m from the ground for all leaves and needles samples.

Samples from other geographic locations - Genoa (Italy), suburbs of Barcelona (Spain), city of Reykjavik and location Þórsmörk (Iceland), city of Paris (France) and suburbs of Birmingham (United Kingdom) – were collected during autumn 2014 and spring 2015 though in significantly lesser numbers. When no birch or spruce trees were found (Italy and Spain), leaves and needles of other tree species, oak (*Quercus*), olive (*Olea europaea*), and pine (*Pinus sylvestris*), were collected.

For verifying the method, a set of certified reference materials (CRMs) has been included and processed in parallel to "natural samples" throughout the entire procedure (digestion, separation and analysis): ERM BB186 Pig kidney (Institute for Reference Materials and Measurements), TORT-1 Lobster hepatopancreas and NASS-4 Open ocean water (National Research Council of Canada, Ottawa, Canada), NIST SRM 1547 Peach leaves (National Institute of Standards and Technology) and NJV 94-5 Wood fuel (Swedish University of Agricultural Sciences, Sweden), providing representative variability in concentrations of analytes and ranges of isotope compositions (**Table 2**). Note that none of the materials mentioned above has a certified isotopic composition.

2.4. Sample preparation

All sample manipulations were performed in clean laboratory areas (Class 10000) by personal wearing clean room gear and following all general precautions to reduce contaminations.[49] All laboratory ware coming into contact with samples/sample digests was soaked in 0.7 M HNO_3 (>24 h at room temperature) and rinsed with MQ water prior use.

Mushrooms were mechanically cleaned from external exogenous material and divided into approximately 1 cm^3 pieces using a ceramic knife on a Teflon plate. Samples were then dried at 50°C to constant weight, homogenized by crushing in plastic bags and stored air-tight packed at room temperature.

2.4.1. Sample digestion

About 0.5 g of dried material from each sample bag was accurately weighed into a 12 mL Teflon vial before addition of 5 mL 14 M HNO_3. After the initial oxidation of organic matter subsided, vials were gently agitated and solid material adhering to the walls was washed down by an additional 1 mL of HNO_3. Vials (up to 40 per batch) were placed into a carousel with numbered slots, which was then loaded into the Teflon-coated UltraCLAVE reaction chamber containing a de-ionized water-H_2O_2 mixture (10:1 v/v). The chamber was pressurized with compressed argon and the pre-programmed digestion cycle (30-min ramp to 220°C following by 20 min holding time at that temperature) was initiated. Total processing time, including cooling and subsequent transfer and dilution of sample digests to a final volume of 10 mL into storage polypropylene tubes, was approximately three hours per digestion batch.

In some samples, minor quantities of white precipitates of siliceous material were formed.

Rapid dissolution of the precipitate was achieved after addition of 30 µL 16 M HF and manual agitation for a few minutes. Sets of method blanks and CRMs were prepared with each batch of samples.

As for any of the wide variety of methods used for the preparation of biological matrices for subsequent ICP-SFMS analysis in the laboratory, e.g. ashing, hot-block and microwave digestions, high pressure ashing,[10,50,51] digestion using the UltraCLAVE has its merits and limitations. The former include complete oxidation of carbonaceous material thus ensuring negligible effects of undigested organics on the subsequent separation procedure, applicability to all matrixes tested in this study, ease of sample handling/loading (limited material manipulation and thus lowered risk of contamination), and relatively high throughput. The major limiting factor is the amount of material that can be digested in a 12-mL vessel (approximately 0.5 g dried material), which may require processing parallel digestions for samples low in some analytes, though this approach was not required in the present work.

Aliquots of digests were diluted 50-fold with 1.4 M HNO_3, providing total digestion factor of approximately 1000 v/m, and analyzed by ICP-SFMS using a combination of internal standardization and external calibration.[50] Portions of diluted digests remaining after this analysis (approximately 6 ml) were used for B isotope ratio measurements either directly or after additional dilution. The rest of the original sample digest was evaporated to dryness in a 25 mL Teflon beaker at 95°C on a ceramic-top hot-plate, followed by dissolution in 4 mL of 9.6 M HCl, thus being ready for subsequent purification.

2.4.2. Analyte purification

Briefly, after loading evaporated sample digests taken up in 4 mL of 9.6 M HCl onto AG MP-1M resin-containing columns and rinsing out matrix elements with the same acid, Cu, Fe, Zn, Cd + Tl and Hg are quantitatively eluted from the resin using first HCl of decreasing molarities and then a mixture of 6 M HNO_3 containing traces of HF. In contrast to matrix separation in geological/industrial materials, there is no risk of overloading the resin capacity with any of the analytes and therefore the entire digest volume can be used. Comparing to a Cd separation procedure,[23] sample loading in more concentrated HCl allows separation of Cu, Fe and Zn using the same column, while neither Ag nor Pb are efficiently retained by the resin. Sample load and matrix wash fractions (collected into 25 mL Teflon beaker) contained >99.5% of initial Sr and >85% of initial Pb. After evaporation and re-dissolution in 4 mL of 7 M HNO_3, Sr and Pb were separated using Sr-specific columns, by selective elution with 0.05 M HNO_3 and 0.1 M ethylenediaminetetraacetic acid (EDTA), respectively. Sample load and matrix wash fractions from this column contain >95% of the original Ag and can be used for purification of this element by loading in 4 mL of 2 M HCl onto AG MP-1M resin-containing columns and eluting with 14 M HNO_3.[23] All columns can be re-used several times, although the efficiency of matrix separation gradually deteriorates after 5-6 cycles with matrix/Cu and Zn/Cd cut-off affected most. It should be noted that approximately 0.1% of the initial Sr and 0.2-0.4% of the initial Pb remain on Sr-specific columns and therefore may affect subsequent separations for samples with much lower analyte concentrations or grossly different isotopic compositions.

All separated analyte fractions except those for Sr and Hg were evaporated to dryness and dissolved in 2-10 mL of 0.3 M HNO_3. (An aliquot of 14 M HNO_3 was pipetted directly onto the solid residue as a first step, allowed to react for 15-25 min, and then diluted appropriately by addition of MQ water.) 0.1 mL aliquots of separates were diluted 50-fold with 1.4 M HNO_3 and analyzed by ICP-SFMS (same approach as for sample digests). This provides: (I)

information on analyte contents needed to prepare concentration- and acid strength-matched solutions for isotope ratio measurements; (II) direct assessment of analyte recovery; (III) control over separation efficiency from matrix elements; and (IV) a test for the presence of potentially spectrally-interfering elements either from the sample matrix or from handling contamination.

The absence of artificially introduced fractionation during separation/evaporation and analysis stages was tested by separating mixture of 'δ-zero' standards with concentrations typical for birch leaves.

2.4.3. Isotope ratio measurements and data evaluation

As pre-analysis of purified fractions by ICP-SFMS provided proof of the absence of notable concentrations of elements forming isobaric interferences with analyte isotopes (e.g. Cr or Pd), no Faraday cup was used to monitor these interferences on-line (**Table 1**). At least 1.5 h instrumental heating-up and stabilization time with plasma on was allowed before starting the optimization of operation parameters and mass-calibration.

For B, MC-ICP-MS measurements were performed on unseparated digests which can be diluted to provide at least 20 µg L^{-1} concentrations in measurement solution yielding >1 V intensity for ^{11}B. Profound B memory effects in introduction system were minimised by using low volume spray chamber, diluting all samples, standards and blanks in 1.4 M HNO_3, employing higher sample uptake rates and increasing the washing time between samples and standards to 200 s. This ensures that the instrumental ^{11}B blank is below 0.02 V before measurement of the next solution is started.

For the remaining elements, separated fractions were diluted to equal concentration levels; because of limited analyte content in some biological samples, several fixed measurement concentrations were used with minimum requirements listed in **Table2**. A set of bracketing standards matching samples in terms of analyte and internal standard concentrations as well as acid strength was prepared for each isotope system. High degrees of concentration matching between samples and bracketing standards (better than ±10%) are needed for accurate measurements of Cd, Ag, Cu and Zn. Measuring samples against standards with halved or doubled analyte concentrations will result in up to 0.3‰ errors. The matching tolerance for Sr, Pb, Tl and Fe isotope ratio measurements is significantly broader, where up to ±30% concentration difference between samples and standards will not affect results notably.

The best signal stability and in-run precision in isotope ratios is obtained with an introduction system consisting of a self-aspirating PFA nebulizer with approximately 0.05 mL min^{-1} sample uptake, cyclonic/Scott double spray chamber arrangement and H-skimmer cone. Sample throughput can be increased by almost 40% by increasing the sample uptake four-fold using a peristaltic pump (due to much shorter solution-in, signal stabilization and wash-out times) with less pronounced matrix effects as an extra benefit. However this option requires replacing PFA with Micromist (Glass Expansion Ltd, West Melbourne, Australia) nebulizer. For ultra-trace elements, the intensity provided by such a configuration is insufficient and the use of desolvating nebulizers and the X-skimmer cone is mandatory for Cd, Ag, Pb and Tl in the majority of samples, providing, depending on analyte, seven- to 25-fold intensity gains. Intensity can be increased even further (by a factor of 3-4) by increasing the sample uptake of desolvating nebulizers to 0.15-0.20 mL min^{-1}, though this results in increasingly unstable and 'spiky' signals. Even with 0.05 mL min^{-1} sample uptake typical in-run precision is almost three times poorer than with the standard introduction system configuration.

The use of Aridus was found to be unsuitable for Hg isotope ratio measurements because Hg

vapour is lost from the system while passing the desolvating membrane. As it was impossible to pre-concentrate Hg by evaporation of the purified fraction (again because of analyte losses) and the need to further dilute 7 M HNO_3 matrix of this fraction prior to analysis, even the use of the APEX did not allow reliable Hg isotope ratio measurements in samples collected for this study. Though other means of Hg introduction to MC-ICP-MS have been suggested (e.g. cold vapour and purge-and-trap[52–54]), these were not tested here and plans to measure Hg isotopes were abandoned.

For samples with B concentrations <20 µg g^{-1}, isotope ratio measurements were performed by ICP-SFMS using the same configuration of introduction system as for MC-ICP-MS and paying special attention to avoid tailing from Ar^{4+} spectral interference appearing on the low-mass side of the ^{10}B isotope in the 5% acquisition window. Though the in-run precision of single collector instrumentation is inferior to that of MC-ICP-MS by a factor of 5-10, it nevertheless allows isotope ratio measurements at much lower B concentrations in measurement solutions. B isotope ratio measurements in NIST 1547 and NASS-4 CRMs were performed during every measurement sequence, with results from both techniques agreeing to within measurement uncertainty. Additionally, Sr and Pb isotope ratio measurements in samples low in analytes (<10 µg g^{-1} and <0.5 µg g^{-1}, respectively) were repeated by ICP-SFMS using solution remaining from MC-ICP-MS measurement sessions and an introduction system consisting of a self-aspirating PFA nebulizer, a cyclonic/Scott double spray chamber arrangement and an H-skimmer cone.

Three sample solutions were analyzed between two standards. Two consecutive measurements were performed for each solution in the sequence. The MC-ICP-MS software option of excluding pass, run and block outliers was deactivated as it was found that the presence of some outliers actually improves the correlation between instrumental mass bias levels for analyte and internal standard isotope ratios.

Data evaluation, including correction for blanks, spectral interferences and instrumental mass bias, was performed off-line using commercially available spreadsheet software. Instrumental mass bias was corrected in a two-step procedure using first exponential correction by internal standardization using an algorithm proposed by Baxter *et al.*[55] followed by standard-sample bracketing (SSB). Mean ratios from two consecutive measurements of the first and the third samples in each analytical block (standard 1–sample 1–sample 2–sample 3–standard 2) were calculated against ratios for standards 1 and 2, respectively. For the second sample, mean ratios from the bracketing standards were used assuming linear changes in instrumental mass bias persisting after internal standard correction. Results from two consecutive measurements of each sample allow calculation of mean δ-values and respective standard deviations for all isotope ratios that are less affected by variations caused by imperfect amplifier gain calibration.

For Ag, B, Cd, Cu, Fe and Zn δ-values were calculated using the general formula widely adopted in isotopic studies:

$$\delta^{x/y}M = \left[\frac{(^{x}M/^{y}M)_{sample}}{(^{x}M/^{y}M)_{\delta_0\ \mathrm{standard}}} - 1\right] * 1000$$

where ^{x}M and ^{y}M correspond to the two different isotopes of the element of interest, the $(^{x}M/^{y}M)_{sample}$ value refers to the measured ratio and $(^{x}M/^{y}M)_{\delta_0 standard}$ is the isotope ratio of the bracketing standard used as delta-zero. When the δ-value refers to a ratio of a heavier to a

lighter isotope, a positive δ-value corresponds to an enrichment in the heavier isotope compared to the standard. Calculated δ-values for different Cd, Fe and Zn isotope ratios in each sample were normalized by respective mass difference providing an additional aid to check for internal consistency of isotope data.[23]

Further details on isotope ratio measurement, data processing and corrections can be found in previous studies.[23,40,56,57]

3. Results and discussion

3.1. Performance of separation procedure

Wider use of isotope ratio measurements by MC-ICP-MS, especially in multi-tracer studies, has resulted in the development of numerous matrix separation/analyte pre-concentration schemes evaluated for various elements and sample types. The complexity of the schemes varies from the very simple, i.e. a single pass through a commercially-available pre-packed column containing a specific ion-exchanger (e.g. Sr[58], U, Th[59,60]), to the very time-consuming and elaborate, consisting of several different purification steps (e.g. Cd, Mo[38,39,61]). As the number of steps increases, so do the risks associated with potential sample contamination and/or artificially induced isotope fractionation. Application of published procedures to new types of samples often requires re-validation because the sample matrix, the concentrations of analyte and interfering elements, as well as the particulars of the sample digestion approach may severely affect separation performance.

The analyte purification scheme used in this study is an amalgamation of several published separation procedures merged to maximize separation efficiency and reduce procedural time, while ensuring high analyte recoveries and low contamination levels. Based on published isolation procedures for Cu, Fe and Zn,[62–64] Cd,[7,23] as well as Sr and Pb,[5,65] introduction of a few prudent modifications extended the number of elements isolated from the single sample digest. Volumes needed at each step were obtained through replicate calibration of columns by collecting sample load, matrix wash and all elution fractions with 1 mL resolution before analysis by ICP-SFMS to obtain detailed elution profiles for all elements present in these samples. A flow chart depicting all steps of the purification procedure is shown in **Fig. 1.**

Average method blanks for the entire procedure, assessed by applying all preparation and separation steps to set of reagent blanks handled as samples, are listed in **Table 2**. In spite of extensive sample handling, method blanks, with few exceptions, correspond to <2% contribution to concentrations found in samples containing the minimum analyte content required for isotope ratio measurements (**Table 3**) and therefore have negligible effect on measured ratios. Analyte recovery was above 95% from the majority of samples and CRMs separated during this study with the sole exception of Pb (above 85%). Though the lower recovery of the latter element implies a risk for artificially-introduced mass-dependent fractionation, the bias introduced can be tolerated given the range of radiogenic Pb ratios found. Samples with recoveries below these thresholds were either re-prepared and re-analyzed (when amount of sample collected was sufficient) or results for affected analytes were excluded from the following evaluations.

3.2. Precision

Instrumental repeatability was estimated as twice the standard deviation (SD) of duplicate consecutive measurements of a single sample preparation. The mean instrumental repeatability for isotopic measurements, averaged over all samples (n>240) was as a rule

<0.05‰ (**Table 2**). Slightly poorer repeatability for Pb ratios is due to the high proportion of samples in the datasets containing too little Pb for optimum MC-ICP-MS measurement. B repeatability represents both MC-ICP-MS (approximately 2/3 of all results) and ICP-SFMS data. These figures are by a factor of 2-2.5 times better than instrumental, between-block SDs of individual measurements due to the fact that the contribution from imperfect amplifier gain calibration has been cancelled out.

For accurate assessment of the overall reproducibility of the entire method, duplicate digestions and separations were performed for 14 samples analyzed during different analytical sessions conducted by various operators. Data for the four CRMs that were a part of each analytical batch can also be used for this purpose. Results are summarized in **Table 2** and demonstrate generally that reproducibility values are two- to five-fold poorer than those of repeatability, reflecting cumulative effects arising from minor differences in the efficiency of separation, blanks, spectral interferences and mass-bias corrections, instrumental mass calibration stability and the quality of instrument optimization. This reproducibility provides a more realistic assessment of the developed methods ability to detect minor variations in isotope compositions than repeatability. It should be stressed though that reproducibility figures presented in **Table 3** are valid for sample types analyzed in this study and may not be applicable to other matrices with higher (or lower) concentrations of analytes and interfering elements.

One observation made during the precision assessment for Cd isotope ratio measurements deserves special note. It was found that agreement between duplicates analyzed using Aridus was significantly inferior to that obtained with the standard sample introduction system. In extreme cases δ^{114}Cd between-run variations exceeded 0.3‰, even when the same separated digest fractions were re-analyzed. In order to investigate the reason for poor precision, a comprehensive set of experiments was performed by measuring Cd isotopes in standard solutions: (I) with variable acid strength; (II) at different plasma sampling depth; (III) with variable sample flow rate; and (IV) with variable dry gas (Ar) flow through the Aridus desolvating membrane. It was found that changes in instrumental mass bias for Cd caused by the aforementioned variations were adequately corrected using Ag for internal standardization in tests (I), (II) and (III), while even minor changes in Ar flow through the desolvating membrane resulted in severe uncorrected effects, pointing to decoupling of the mass-bias correlation between Cd and Ag. Most probably, this is due to partial Cd losses through the membrane that could be explained by the evaporation/sublimation of Cd from cadmium nitrates $Cd(NO_3)_2 \cdot XH_2O$ in the Aridus because the desolvating module reaches temperatures above the $Cd(NO_3)_2 \cdot XH_2O$ boiling point.[66] The effect would result in preferential losses of lighter Cd isotopomers that have higher degrees of volatilization and diffusion rates through the membrane. A combination of these effects would be expected to lead to an isotope shift towards higher apparent δ^{114}Cd as the flow of drying gas through the membrane increases, which was indeed observed in the test. To avoid this undesirable effect, the Apex desolvating nebulizer was used for all subsequent Cd isotope ratio measurements, with desolvation occurring by passing through a cooled condenser rather than a heated membrane.

3.3. Accuracy

The accuracy of concentration determinations by ICP-SFMS was verified by analyses of various CRMs (**Table 2**). For the majority of analytes, recovery is within the 90%-110% range.

Though a set of in-house isotope standards (seawater CRM for B, isotope standard solutions, commercial mono-element standards or dissolved pure salts/metals with isotope composition different from respective δ-zero standards for the rest of analytes) was analyzed in every measurement session, such quality controls only apply to the instrumental stage and are thus unsuitable for assessment of the overall accuracy of the method. An absence of measurable fractionation in δ-zero standards passed through the separation procedure assures sufficiently good analyte recoveries, but as these standards are both matrix- and interfering element-free, they are not the perfect solution to quality assurance either. As to the best of our knowledge no matrix-matched CRMs with certified isotopic compositions for the elements encompassed by this study are available, the only means to evaluate method accuracy is to compare data obtained in our study (**Tables 2 and 3**) with previously published for similar matrices, where such exist. Though only two of four CRMs used were of plant origin, the inclusion of IRMM-BB186 and NRCC TORT-1 provided heavy isotope extremes for Cu and Zn, respectively.

Roux *et al.*[67] have reported δ^{11}B of (40.12 ± 0.21)‰ in NIST 1547 using purification of B by cation exchange chromatography and micro-sublimation followed by MC-ICP-MS measurements, identical within uncertainties to our result. Isotopically heavy Cu in animal kidney has been explained by fractionation during breakdown of ascorbate into oxalate.[68] Marechal *et al.*[69] have reported δ^{66}Zn of +0.51‰ in NRCC TORT-2 (Lobster hepatopancreas) and Balter *et al.*[70] lighter Zn isotope composition in sheep kidney compared to other organs. Cd and Zn isotope data for IRMM-BB186 and NRCC TORT-1 agree well with our previously published results[23] confirming if not high accuracy but at least good reproducibility for datasets generated in large analytical campaigns two years apart. Measured δ-values for different Cd, Fe and Zn isotope ratios normalized by respective mass differences agree well (correlation coefficient >0.98) for samples with analyte contents above the minimum required concentrations.

For some of the samples, B, Pb and Sr isotope ratios were measured by both MC-ICP-MS and ICP-SFMS. Sr and Pb datasets obtained by these techniques are compared in **Fig. 2** demonstrating very satisfactory agreement.

3.4. Throughput

Given a batch size of 36 samples plus two preparation blanks and two CRMs (as limited by the maximum of 40 digestion vessels positions in the UltraCLAVE), unrestricted availability of hot plate(s) for evaporation of digests and purified fractions (performed mostly overnight), and simultaneous access to ICP-SFMS and MC-ICP-MS, the entire procedure from sample weighing to data evaluation can be done by two chemists in approximately two weeks. This is approximately three-fold more time-consuming than complete isotopic analysis of a single element (e.g. Cd), but because many operations in the procedure can be performed in parallel, this is significantly more time-effective (and less sample consuming) compared to using individual preparation/separation schemes for all eight elements.

3.5. Variations in concentrations and isotopic compositions in leaves, needles and mushrooms

Element content and isotope composition in leaves can (and does) reflect different accumulation pathways from a variety of natural and anthropogenic sources. Variations in the same depend upon the type of tree (different accumulation mechanisms, nutrition supply strategies, leave morphology), age/size, tree location (on continental as well as local scales; soil type and composition, sub-soil geology, proximity to local contamination sources, etc.),

location of leaves on tree (height, orientation of branches), sampling period, weather preceding sampling occasion, etc.[23,44,71] The ability to detect such variability will entirely depend on the 'resolution' (overall reproducibility) of the analytical procedure used and data in **Table 3** demonstrate the extent of such effects.

A statistical summary of concentrations and isotope data for the majority of samples analyzed in the course of this study is presented in **Table 3.** Data for oak, aspen and rowan leaves, as well as for pine needles collected in Luleå are omitted as there were less than five samples in each category, and because the results for these samples fall into ranges found for birch leaves or spruce needles from the same collection period.

In the electronic supplementary information (ESI) data for four similarly-sized birch trees sampled annually for three years are discussed in more detail. The key finding from the latter dataset is that the individual trees, growing within a radius of 100 m, exhibit significant spatial and temporal variations in concentrations and isotopic compositions. This strongly suggests that the elemental and isotopic signatures of deciduous plants are as unique as the trees themselves and bear little connection to events on a regional scale.

3.5.1. Boron

B concentrations vary from sub-μg g^{-1} levels in mushrooms to over 50 μg g^{-1} in leaves. Leaves and needles from Luleå have lower B content compared to samples from other locations and there is a pronounced increase in leave's B concentrations throughout the growing season. Except for mushrooms, all other matrices are enriched in the heavy B isotope with needles having heavier B than leaves from the same location. Leaves from Luleå have significantly lighter B isotope composition than leaves from France, Italy and Spain, but are still heavier than the average crust (δ^{11}B ‰ ≈ –7‰[72]), with a clear temporal pattern from spring to fall. The entire span of observed δ^{11}B-values is 52‰ (ranging from –12‰ to +40‰) which agrees well with the isotopic range of B in plant tissues reported by Rosner *et al.*[32]

3.5.2. Cadmium

Cd concentrations increase in the order needles – leaves – mushrooms. The lowest mean Cd concentrations were found in leaves from Birmingham and Barcelona, while the highest were observed in leaves from Genoa and Paris. The latter also exhibit the widest range of concentrations covering 2-3 orders of magnitude, probably reflecting differences in accumulation between different tree species since not exclusively birch leaves were sampled and these locations. Cd concentrations in birch leaves are highest in spring, decreasing approximately two-fold during the growing season due to dilution with organic material. Cd in birch leaves from Sweden, Iceland and UK is significantly isotopically heavier than in leaves from France, Italy and Spain, and falls into the same range as reported for birch leaves analyzed during a previous study.[23] Wei *et al.*[38] have reported a δ^{114}Cd range from –0.39‰ to –0.08‰ for biomass collected from four plant species (*Solanum nigrum, Ricinus communis, Cyperus alternifolius* and *Pteris vittata*) from China, similar to that found for leaves from Barcelona. Needles have distinctly lighter isotopic composition than leaves from the same location. The total span of observed δ^{114}Cd is approximately 1.4‰ (–0.42‰ to +0.96‰).

3.5.3. Copper

The Cu concentration pattern in different matrices follows that for Cd, increasing in the order needles – leaves – mushrooms. As for Cd, highest levels are found in young leaves, followed by sharp decreases by a factor of 2-3 as leaves grow. Concentration ranges for Cu in birch leaves collected from different locations and at same growing stage are very similar. Light mean Cu isotopic composition was typical for all types of matrices tested in this study with the lightest Cu found in needles and mushrooms from Luleå. The measured δ^{65}Cu varies from –2.30‰ to +0.41‰ with relatively consistent spans of 0.6‰ to 1.4‰ found for birch leaves from individual locations.

3.5.3. Iron

Mean Fe concentrations vary from approximately 100 µg g^{-1} in Parisian leaves to over 750 µg g^{-1} in leaves from Iceland. Concentrations as high as almost 0.4% were found in *Suillus variegatus* mushrooms. In contrast to temporal regularities in Cu and Cd concentrations, the Fe content of birch leaves increases from spring to fall. The mean δ^{56}Fe is negative for all groups of samples except needles from Paris, confirming earlier findings,[34,73] with very little variations for birch leaves from Luleå, Paris and Birmingham. As for Cu isotopes, the lightest Fe was found in needles and mushrooms from Luleå. The total span in observed δ^{56}Fe is approximately 1.6‰ (–1.32‰ to +0.26‰). Light Fe isotope composition in plants was previously reported in a number of publications[34,73–75] with observed δ^{56}Fe ranges in leaves from –1.3‰ to +0.09‰.

3.5.4. Lead

Variability in mean Pb concentrations is amongst the highest of the elements studied, spanning from 73 ng g^{-1} in leaves from Iceland to over 2800 µg g^{-1} in Spanish leaves. The average concentration of Pb in birch leaves from Luleå increases more than three-fold during the growing season, confirming earlier data.[23] Reimann *et al.*[76] reported median Pb concentrations of 590 ng g^{-1} in birch leaves and 250 ng g^{-1} in spruce needles collected from 40 sites along a 120 km transect cutting through the city of Oslo, Norway, thus approximately double that observed from the results of the fall sampling in Luleå.

Although the extensive variations observed for ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb ratios (from 2.344 to 2.489 or 5.9% and from 1.126 to 1.259 or 11.3%, respectively) encompass the majority of all ratios reported for biological samples from Europe[11,12,76], ranges for each individual matrix, location and sampling occasion are significantly narrower. The RSD for mean ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb ratios for all sample groups is 0.48% and 0.74%, respectively. In birch leaves from the same location (Luleå) the range of measured Pb isotope ratios decreases considerably from spring to fall sampling.

3.5.5. Strontium

Mushrooms have lowest Sr concentrations (sub- to low µg g^{-1} range) while 40- to 300-fold higher levels are typical for the rest of matrices with samples from Paris (both needles and leaves) having the highest Sr contents.

There are minor differences in mean ^{87}Sr/^{86}Sr ratios between different matrices from the same location, becoming more radiogenic in the order: leaves from Iceland (0.707), leaves and needles from Paris (0.708), leaves from Genoa, Barcelona and Birmingham (0.710) and all

samples collected in Luleå (0.729 – 0.735). The ratios reflect the ages of the underlying bedrock at each location, with the oldest being found in the Luleå area ranging from 1.8 to 2.8 Ga.[77] Except for the latter location, ranges of $^{87}Sr/^{86}Sr$ ratios observed elsewhere overlap significantly, potentially complicating the use of this isotope system for confirmation of plant material geographical origin.[3,4,18] Very radiogenic mean $^{87}Sr/^{86}Sr$ ratios found in Luleå samples agree well with figures published by Åberg *et al.*[78] for plant samples collected from the central part of Sweden. Except for the Luleå location where wide ranges of observed $^{87}Sr/^{86}Sr$ ratios can be caused by heterogeneity of the $^{87}Sr/^{86}Sr$ in the granitic bedrocks,[79] variations in Sr ratios in plant samples from the same group are seldom > 0.3% RSD.

As the use of Zr for mass-bias correction[80] allows for assessment of mass-dependent fractionation of the $^{88}Sr/^{86}Sr$ ratio, it can be stated that none of the samples shows fractionation outside the –0.04‰ to +0.04‰ range. Therefore, $^{88}Sr/^{86}Sr$ ratios can safely be used for mass bias correction of $^{87}Sr/^{86}Sr$ ratios in plant samples, providing identical results to Zr corrected data (**Fig. 3)** with considerably less effort.

3.5.6. Thallium

Tl was present in all matrices tested in the low ng g^{-1} range, with the lowest extreme being found for birch leaves from Iceland and UK, and the highest for spruce needles and mushrooms from Luleå. From >240 samples, only approximately 40 had sufficient Tl content for MC-ICP-MS isotope ratio measurements, and meaningful statistics could only be derived for two matrices (**Table 3**). Needles and mushrooms from the Luleå location have Tl isotope compositions enriched in the lighter isotope with a total range in observed $\delta^{205}Tl$ values of 0.8‰ (–0.62‰ to +0.18‰). Kersten *et al.*[81] recently reported a narrow $\delta^{205}Tl$ range in green cabbage (*Brassica oleracea*) from China of –0.54‰ to –0.25‰.

3.5.7. Zinc

Mean Zn concentrations vary from 50 µg g^{-1} in leaves from Barcelona to >300 µg g^{-1} in birch leaves from Iceland and Luleå (fall sampling). Needles contain significantly lower Zn levels than leaves and mushrooms from the same locations, and Zn concentrations increase through the growing season. The mean $\delta^{66}Zn$ for the majority of matrices falls into a relatively narrow range around zero (–0.23‰ to +0.20‰), while significantly heavier Zn isotopic compositions are found in mushrooms. Viers *et al.*[35] reported a range in $\delta^{66}Zn$ from –0.50‰ to +0.08‰ in larch (*Larix gmelinii*) needles (n=12) from Central Siberia, which is approximately half of that found for spruce needles from Luleå. The total spread in observed $\delta^{66}Zn$ values is approximately 2.2‰ (–0.95‰ to +1.21‰).

3.5.8. Silver and mercury

Ag was present in the low ng g^{-1} range in almost all matrices tested, although mushrooms could exhibit concentrations in some species of *Boletus edulis* as high as 9 µg g^{-1}. Consequently Ag isotope ratios were only determined in the latter matrix with slightly negative mean $\delta^{109}Ag$ and relatively low variability (total range –0.31‰ to +0.07‰). Temporal changes in Ag birch leave concentrations resemble those for Cd and Cu, being highest in young leaves. The opposite temporal trend was found for Hg with concentrations increasing three- to four-fold between May and September.

4. Conclusions

The analytical protocol tested in this study has proved to be suitable for isotope ratio measurements of at least eight elements in birch, needle and mushroom samples. Digestion using the UltraCLAVE device provides complete oxidation of organic material, while two-column separation ensures low blank levels, efficient separation of matrix elements, sufficiently high analyte recoveries and relatively high sample throughput.

It was shown that losses of Cd may occur in membrane desolvation systems, which may result in poor precision. Therefore, utilization of an Apex desolvation system can be a better alternative than the frequently-used Aridus[82,83] for Cd isotope ratio measurements.

Regular use of duplicate sample preparations and analyses performed in different batches or measurement sessions is a must for overall reproducibility assessment. The use of synthetic, matrix-free isotope standards or replicate analyses within the same measurement session results in artificially optimistic estimates of precision.

The absence of commercially-available CRMs with certified isotopic compositions continues to hamper straightforward accuracy assessment. In contrast to the geological field, there are still only a very few published datasets containing information on the isotopic composition of CRMs of biological origin. There is thus a growing need for inter-laboratory exercises, preferably using commercially-available CRMs representing various matrices, to fill this gap and ensure data transferability until appropriate CRMs become available.

In general the proposed method represents a starting point for further development in the direction of multi-tracer studies. With some relatively modest modifications, the list of separated elements can be extended to include Ca, Mg and Ga. Vapor-phase introduction of Hg can overcome insufficient sensitivity of current system. The possibility to obtain precious information on several isotope systems from a single sample will aid the interpretation of natural processes and enable more reliable pollution source attribution.

The majority of results obtained for eight isotope systems in more than 240 samples agree well with previously published data where such exists. For some bio-indicators (e.g. needles and mushrooms), our data represent the first combined characterization of B, Cd, Cu, Fe, Pb, Sr, Tl and Zn isotopic compositions. Even after removing some known variation sources such as type of bio-indicator, sampling height and sampling period, very broad ranges in isotopic compositions of many elements were found in samples collected from relatively confined geographical areas (**Table 3**) or even from within 100 m (see ESI **Table S1**), significantly exceeding method reproducibility. The observed degree of isotopic variability, irrespective if caused by natural or anthropogenic factors, may complicate such isotope applications as source tracing, geographical origin authentication, studying plant metabolism, etc., and should be carefully considered for each given study object.

Better understanding of regularities in observed isotope variability in leaves and needles would require acquiring isotope profiling of different soil compartments and soil solution as a function of soil depth – work which is currently underway.

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Table 1. MC-ICP-MS operating parameters and measurement conditions for isotope ratio measurements

RF Power: 1400-1450W
Coolant gas flow: 15 L min^{-1}. Auxiliary gas flow: 1.4 L min^{-1}. Sample gas flow: 0.9-1.25 L min^{-1}. Additional gas flow (N_2, Aridus and Apex) 0.01-0.02 L min^{-1}
Ion lens settings: Adjusted daily to obtain maximum sensitivity and signal stability
Zoom optic settings: Adjusted daily to obtain maximum resolution
Number of blocks: 9. Number of cycles per block: 5. Number of integrations: 3-5
Amplifier rotation: left

Element[a]	Configuration of introduction system	Resolution mode	Integration time (s)	Sample uptake rate (L min^{-1})	Cup configuration								
					L4	**L3**	**L2**	**L1**	**C**	**H1**	**H2**	**H3**	**H4**
Cd/Ag	Aridus/Apex desolvating systems, self-aspirating micro-concentric PFA nebulizer, X-type skimmer cone	Low	0.524	0.04-0.06	^{107}Ag	^{108}Cd (^{108}Pd)	^{109}Ag	^{110}Cd (^{110}Pd)	^{111}Cd	^{112}Cd (^{112}Sn)	^{114}Cd (^{114}Sn)	^{116}Cd (^{116}Sn)	^{117}Sn
Zn/Cu	Pumped Micromist nebulizer, double spray chamber, H-type skimmer cone	Medium	0.262	0.20-0.25	-	^{63}Cu	^{64}Zn (^{64}Ni)	^{65}Cu	^{66}Zn	^{67}Zn	^{68}Zn	^{70}Zn	-
Fe/Ni	Pumped Micromist nebulizer, double spray chamber, H-type skimmer cone	Medium	0.262	0.20-0.25	^{54}Fe (^{54}Cr)	-	^{56}Fe	^{57}Fe	-	^{60}Ni	^{61}Ni	^{62}Ni	-
Sr/Zr	Pumped Micromist nebulizer, double spray chamber, H-type skimmer cone	Low	0.262	0.20-0.25	^{82}Kr	^{83}Kr	^{84}Sr (^{84}Kr)	^{85}Rb	^{86}Sr (^{86}Kr)	^{87}Sr (^{87}Rb)	^{88}Sr	^{90}Zr	^{91}Zr
B	Pumped Micromist nebulizer, mini cyclonic spray chamber, X-type skimmer cone	Low	0.524	0.40-0.50	-	-	^{10}B	-	-	-	^{11}B	-	-
Pb/Tl	Aridus/Apex desolvating systems, self-aspirating micro-concentric PFA nebulizer, X-type skimmer cone	Low	0.524	0.04-0.06	-	^{202}Hg	^{203}Tl	^{204}Pb (^{204}Hg)	^{205}Tl	^{206}Pb	^{207}Pb	^{208}Pb	-

[a] One element is used as internal standard for the second element, except for Zr which is only used as internal standard

Table 2. Figures of merit for analytical method and results for CRMs[a]

Element	LOD (µg g^{-1})	Total procedural blank (ng)	Minimum concentration for isotope measurements (µg g^{-1})	NIST 1547 (n=16)	IRMM-BB186 (n=8)	NJV 94-5 (n=10)	NRCC-TORT-1 (n=8)
B	0.07	40	2	29.1(1.8)**29(2)**	0.58(0.12) –	5.32(0.20) –	5.21(0.27) –
Cd	0.001	0.15	0.05	0.0254(0.0011)**0.026(0.003)**	1.04(0.04)**1.09(0.05)**	0.269(0.013)**0.27(0.028)**	26.2(1.0)**26.3(8.0)**
Cu	0.01	8	2	3.45(0.16)**3.7(0.4)**	34.4(1.8)**36.5(1.8)**	2.02(0.15)**2.2(0.30)**	421(22)**439(5.0)**
Fe	0.05	450	20	209(13)**218(14)**	244(15)**255(13)**	71.8(3.7)**70(16)**	196(9)**186(5.9)**
Pb	0.002	0.25	0.025	0.795(0.066)**0.87(0.03)**	0.036(0.004)**0.040(0.005)**	0.652(0.040)**0.68(0.025)**	9.32(0.42)**10.4(1.9)**
Sr	0.02	20	2	53.5(2.5)**53(4)**	0.204(0.034) –	11.6(0.4) –	108(6)**113(4.4)**
Tl	0.0001	0.08	0.01	0.021(0.002)	0.015(0.001) –	0.166(0.006) –	0.005(0.001) –
Zn	0.1	90	5	17.2(0.8)**17.9(0.4)**	128(7)**134(5)**	37.7(1.9)**38(8.5)**	168(8)**177(5.6)**
Ag	0.0004	0.2	0.025	0.0016(0.0004)	0.0009(0.0003) –	0.020(0.002) –	6.91(0.41) –
Hg	0.001	0.05	0.5	0.034(0.003)**0.031(0.007)**	0.017(0.002)**0.023(0.011)**	0.021(0.002) –	0.309(0.013)**0.330(0.006)**

Isotopes	Mean instrumental repeatability at 2 SD level for n>240 sample duplicates (‰)	Reproducibility at 2 SD level for n>10 sample duplicates (‰)	NIST 1547 (n=16)	IRMM-BB186 (n=8)	NJV 94-5 (n=10)	NRCC-TORT-1 (n=8)
$\delta^{11}B$	1.8	2.5	40.3(2.6)	-9.1(7.2)	13.8(4.4)	26.1(4.1)
$\delta^{114}Cd$	0.047	0.158	0.068(0.148)	0.455(0.065)	-0.052(0.084)	-0.143(0.053)
$\delta^{65}Cu$	0.045	0.130	0.433(0.205)	2.669(0.245)	-0.395(0.265)	-0.083(0.097)
$\delta^{56}Fe$	0.038	0.072	-0.304(0.054)	-2.066(0.144)	-0.160(0.077)	-0.200(0.094)
$^{208}Pb/^{206}Pb$	0.079	0.330	2.482(0.010)	2.478(0.048)	2.424(0.011)	2.464(0.005)
$^{206}Pb/^{207}Pb$	0.094	0.360	1.213(0.006)	1.191(0.034)	1.159(0.007)	1.192(0.004)
$^{87}Sr/^{86}Sr$	0.036	0.210	0.71339(0.00009)	0.71003(0.00109)	0.73151(0.00013)	0.70925(0.00009)
$\delta^{205}Tl$	0.054	0.115	-0.269(0.153)	NA	-0.244(0.123)	NA
$\delta^{66}Zn$	0.032	0.084	-0.337(0.144)	-0.608(0.105)	0.075(0.101)	0.616(0.099)
$\delta^{109}Ag$	0.048	NA	NA	NA	NA	NA

[a] The uncertainty given in parentheses is either the reproducibility expressed as twice the standard deviation (SD) for n replicates performed by at least two different operators or the confidence interval for the certified value. Data for CRMs are presented in the order: experimental mean values (2 SD) certified value (95% confidence interval).

Table 3. Statistical summary (Mean(Standard deviation)Median Min.÷Max.) for concentration and isotope data in various bio indicators[a]

Parameter	Birch leaves Luleå, May-June (n=54)	Birch leaves Luleå, September (n=58)	Spruce needles Luleå, September (n=31)	Mushrooms Luleå, September (n=30)	Leaves Genoa, May-June (n=10)	Leaves Paris, June (n=9)	Needles Paris, June (n=4)	Birch leaves Iceland, August (n=8)	Leaves Barcelona, October (n=7)	Birch leaves Birmingham, June (n=3)
B (μg g^{-1})	13(6)11 7÷40	29(15)25 7÷76	14(6)14 3÷31	1.7(1.6)1.0 0.2÷6	48(26)43 15÷88	32(10)29 18÷46	30(20)23 13÷58	50(16)44 36÷75	62(53)45 13÷160	17(8)19 8÷25
δ^{11}B (‰)	7.7(6)9.4 -4÷21	7.9(8)8.0 -7÷25	18(9)20 -2÷37	-1(10)-4 -12÷29	21(15)18 4÷40	6.4(5.5)6.0 -1÷16	25(8.6)22 18÷37	13(10)16 -6÷26	22(9)18 14÷36	16(5)16 12÷22
Cd (ng g^{-1})	380(150)330 190÷820	280(130)240 74÷630	57(43)40 13÷160	1600(1500)1100 50÷5100	490(470)420 1÷1100	560(550)330 30÷1600	60(80)30 5÷180	150(70)120 6÷180	61(59)28 6÷180	43(15)34 31÷65
δ^{114}Cd (‰)	0.42(0.21)0.44 -0.09÷0.73	0.50(0.15)0.49 0.17÷0.95	0.10(0.25)0.11 -0.42÷0.56	0.16(0.22)0.23 -0.52÷0.43	0.13(0.13)0.10 0.01÷0.49	0.09 (0.11)0.07 -0.14÷0.21	-0.15 (0.06)-0.15 -0.21÷-0.09	0.51(0.29)0.52 0.11÷0.96	-0.05 (0.14)-0.01 -0.23÷0.09	0.40 (0.33)0.25 0.18÷0.79
Cu (μg g^{-1})	10(3.4)10 4.0÷17	4.7(0.8)4.6 3.1÷6.8	3.2(0.9)3.1 2.1÷5.2	46(27)42 10÷120	16(15)13 4÷58	11(7.1)10 4.5÷28	13(9.1)12 3.3÷24	5.7(1.3)5.1 4.6÷7.9	11(9.0)6.4 3.3÷24	7.0(3.3)6.9 3.3÷11
δ^{65}Cu (‰)	-0.44(0.24)-0.42 -1.0÷-0.05	-0.55(0.27)-0.50 -1.3÷-0.09	-1.17(0.43)-1.16 -2.0÷-0.41	-1.17(0.71)-1.26 -2.3÷-0.15	-0.50(0.52)-0.59 -1.3÷-0.28	-0.26(0.22)-0.34 -0.55÷0.07	-0.24(0.34)-0.33 -0.51÷0.10	-0.30(0.41)-0.26 -0.82÷0.19	-0.14(0.50)-0.14 -1.1÷0.27	-0.28(0.27)-0.19 -0.58÷-0.06
Fe (μg g^{-1})	150(60)140 70÷360	310(210)240 110÷1500	150(110)120 40÷440	260(550)50 20÷3500	250(210)210 110÷1500	94(31)95 50÷150	440(310)420 150÷750	760(440)680 290÷1300	240(230)160 55÷750	120(50)110 77÷180
δ^{56}Fe (‰)	-0.30(0.14)-0.28 -0.58÷-0.03	-0.21(0.18)-0.20 -0.84÷0.09	-0.35(0.34)-0.27 -1.32÷0.05	-0.35(0.35)-0.35 -1.11÷0.25	-0.10(0.14)-0.13 -0.31÷0.09	-0.33(0.13)-0.30 -0.53÷-0.12	0.12(0.15)0.12 -0.05÷0.26	-0.09(0.10)-0.06 -0.31÷0.01	-0.04(0.10)-0.04 -0.17÷-0.09	-0.32(0.23)-0.26 -0.57÷-0.12
Pb (ng g^{-1})	170(130)110 60÷590	540(330)480 120÷2100	160(110)130 47÷540	190(150)130 15÷510	250(150)210 40÷480	570(300)520 340÷1400	800(1500)580 470÷2200	73(70)55 25÷240	2800(5400)750 220÷15000	290(150)260 130÷470
^{208}Pb/^{206}Pb	2.44(0.02)2.44 2.386÷2.477	2.43(0.02)2.42 2.396÷2.464	2.42(0.03)2.42 2.344÷2.472	2.44(0.02)2.43 2.405÷2.480	2.46(0.02)2.47 2.431÷2.489	2.45(0.01)2.44 2.435÷2.459	2.44(0.02)2.45 2.417÷2.466	2.45(0.02)2.46 2.423÷2.477	2.44(0.01)2.44 2.433÷2.466	2.43(0.01)2.42 2.417÷2.435
^{206}Pb/^{207}Pb	1.19(0.03)1.19 1.134÷1.252	1.17(0.02)1.17 1.126÷1.220	1.18(0.02)1.18 1.145÷1.259	1.18(0.02)1.18 1.155÷1.240	1.18(0.02)1.18 1.163÷1.210	1.18(0.01)1.18 1.164÷1.199	1.16(0.01)1.16 1.154÷1.167	1.18(0.02)1.18 1.149÷1.223	1.17(0.02)1.17 1.158÷1.218	1.16(0.01)1.17 1.154÷1.170
Sr (μg g^{-1})	29(14)26 12÷70	36(12)35 17÷70	18(16)15 2÷63	0.53(0.38)0.37 0.1÷1.8	73(38)64 29÷150	150(110)150 14÷380	110(90)90 25÷230	71(23)69 49÷110	56(60)23 11÷160	21(20)12 6÷46
^{87}Sr/^{86}Sr	0.729(0.003)0.729 0.723÷0.734	0.734(0.005)0.733 0.722÷0.748	0.735(0.007)0.733 0.724÷0.753	0.731(0.009)0.730 0.714÷0.763	0.710(0.002)0.710 0.708÷0.711	0.708(0.001)0.708 0.708÷0.711	0.708(0.001)0.708 0.708÷0.709	0.707(0.001)0.707 0.706÷0.709	0.710(0.001)0.710 0.709÷0.712	0.710(0.001)0.710 0.710÷0.711
Tl (ng g^{-1})	4.9(5.0)2.6 1÷18	7.6(6.8)6.0 2÷48	15(18)10 0.8÷90	17(17)11 2÷70	4.7(3.5)6.4 0.2÷9	3.9(2.8)3.2 0.6÷8	7.9(4.9)7.4 3÷15	1.6(1.8)0.9 0.6÷5.7	5.7(4.1)4.4 2÷14	1.5(0.9)1.0 0.9÷2.6
δ^{205}Tl (‰)	NA	NA	-0.40(0.17)-0.38 -0.62÷-0.18	-0.39(0.13)-0.40 -0.62÷-0.14	NA	NA	-0.29(0.17)-0.27 -0.49÷-0.11	NA	NA	NA
Zn (μg g^{-1})	140(70)120 35÷380	320(150)280 75÷820	52(20)51 20÷96	120(50)100 40÷240	120(130)60 10÷360	160(80)160 60÷320	64(40)50 38÷120	360(150)340 190÷570	50(40)30 12÷120	91(50)82 38÷150
δ^{66}Zn (‰)	-0.15(0.22)-0.12 -0.94÷0.13	-0.09(0.15)-0.12 -0.62÷0.24	-0.07(0.24)-0.07 -0.95÷0.47	0.53(0.35)0.55 0.02÷1.21	0.05(0.33)0.11 -0.61÷0.47	-0.23(0.20)-0.18 -0.59÷-0.01	-0.11(0.04)-0.10 -0.18÷-0.07	0.20(0.16)0.22 0.03÷-0.46	0.13(0.46)-0.22 -0.59÷-0.54	-0.15(0.06)-0.12 -0.21÷-0.10
Ag (ng g^{-1})	23(15)20 3÷54	18(36)9 2÷220	21(10)19 5÷39	3000(2300)2500 280÷9300	5.5(3.8)4.6 0.7÷11	13(3.8)12 6÷18	11(3.7)11 8÷15	3.8(1.9)3.1 2÷7	18(22)13 3÷67	8.5(0.7)8.3 7.9÷9.4
δ^{109}Ag (‰)	NA	NA	NA	-0.21(0.13)-0.20 -0.31÷-0.07	NA	NA	NA	NA	NA	NA
Hg (ng g^{-1})	3.4(1.6)3.0 0.5÷5.1	12(2.8)11 5÷20	7.1(1.7)7.1 4÷11	510(460)260 18÷1500	17(7.8)13 9÷31	17(8.4)16 6÷36	52(33)47 17÷96	8.7(1.0)8.8 7÷10	38(31)23 5÷95	9.4(6.1)5.9 5-17

[a] Results are presented in the format: average (standard deviation) median, minimum ÷ maximum; note that n is the number of different samples of the specified material collected and averaged in each dataset

Figures

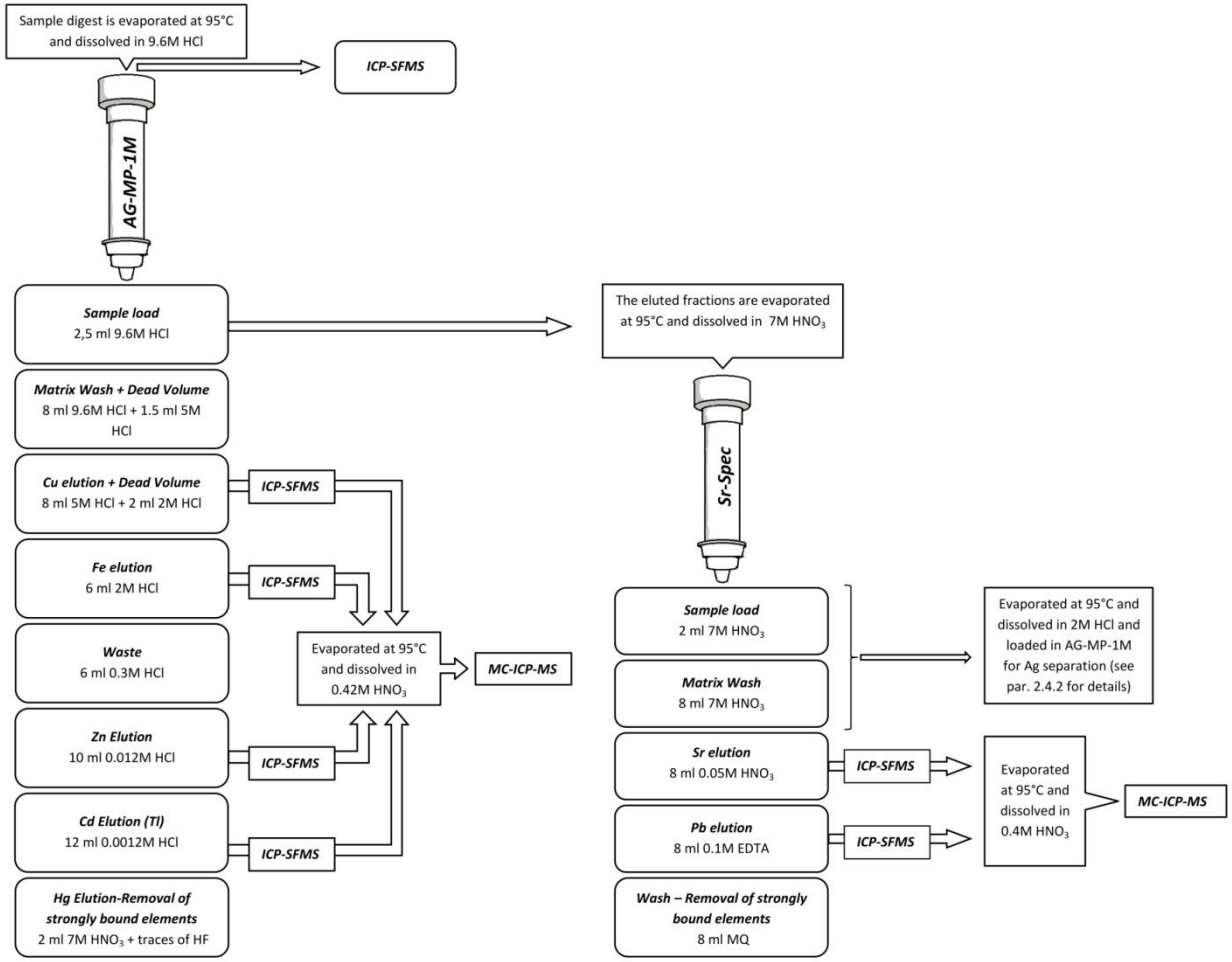

Figure 1 Flowchart of the purification procedure

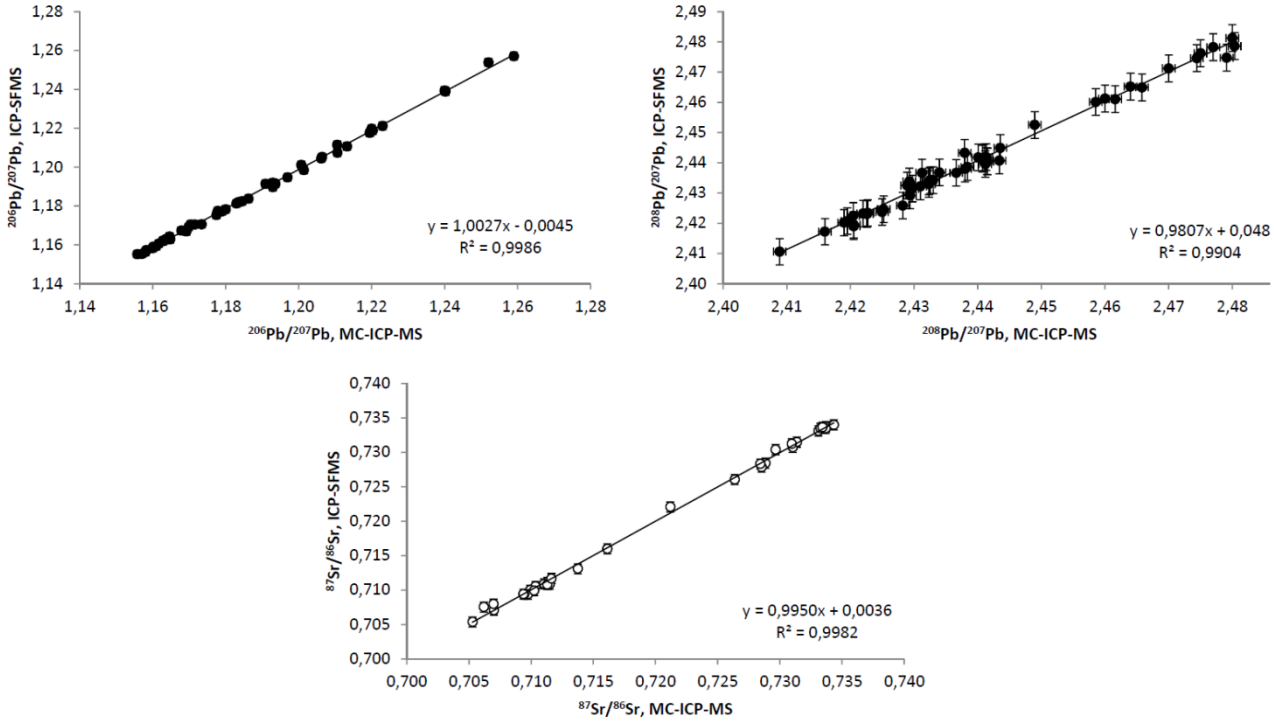

Figure 2 Comparison of Pb and Sr isotope ratios obtained in bio-indicators by ICP-SFMS and MC-ICP-MS. The ordinary linear regression equations are: (top left) y=(-0.0045 ±0.0175) + (1.0027±0.0148)x; (top right) y=(0.0480±0.0913)+(0.9807±0.0374)x; and (bottom) y=(0.0036±0.0155)+(0.9950± 0.0215)x where the uncertainties correspond to 99% confidence intervals.

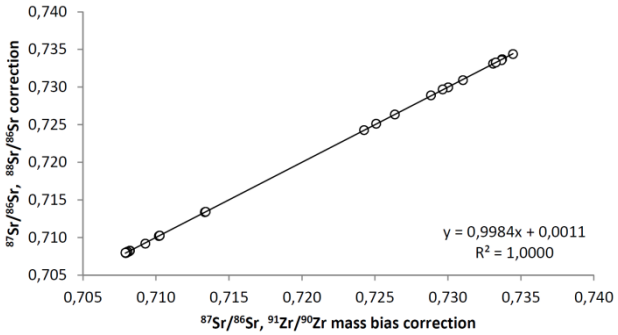

Figure 3 Comparison between two approaches for MC-CP-MS Sr mass bias correction. The ordinary linear regression equation is y=(0.0011±0.0015)+(0.9984±0.0021)x where the uncertainties correspond to 99% confidence intervals.