Electronic Supplementary Information for

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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Long-term variability in elemental concentrations and isotope ratios in birch leaves

Factors known to affect the concentrations and isotopic compositions of elements present in foliar material broadly comprise species, age, location, soil characteristics, climate and proximity to sources of contamination, as discussed in section 3.5 of the main article. **Table S1** provides both concentration and isotope data for leaves collected during the last week of May in three consecutive years, from four individual birch trees (of approximately the same size with stem diameter near ground of 30-35 cm) growing in close proximity (within 100 m) to each other at a sampling point situated approximately 5 km North-East of Luleå city center. On the basis of this experimental design it was assumed that the majority of the aforementioned sources of variation would be the same for all trees, and therefore the results for the three sampling campaigns were expected to agree within measurement uncertainty. However, this was clearly not the case for the majority of the elements studied (**Table S1**).

B concentrations are similar for all trees and show a reproducible trend of decreasing concentrations from 2013 to 2015. δ^{11}B is the same, within the long-term reproducibility of the analytical method, for three of the trees while significantly higher in one (birch B). No between-year significant variations in B isotope composition in leaves from the same tree were noted. Cd concentrations differ between individual birches with no clear between-year pattern. On the other hand, δ^{114}Cd clearly shifts towards lighter isotopic composition between 2013 and 2015. The Cd isotopic composition of one tree (birch D) is significantly heavier than in the others. During the same period, Cu concentrations tend to increase while δ^{65}Cu (and δ^{56}Fe) became less negative. Fe concentrations, however, decrease similarly to those of B.

Pb concentrations exhibit the largest between-year differences, decreasing from 2013 to 2015 almost three-fold (Birches A and B, **Table S1**) while ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb ratios increase. Ranges of Pb isotope ratios in leaves from the same vicinity are actually wider than those reported for birch leaves from 40 sampling locations in Oslo (2.421–2.451 ^{208}Pb/^{206}Pb and 1.153–1.188 for ^{206}Pb/^{207}Pb[1]).

Sr concentrations differ by a factor of 2–3 in foliage from different trees and for some birches exhibit almost two-fold between-year variability. Foliar Sr isotopic composition becomes less radiogenic with between-year variability for a single tree as high as 0.6%. Temporal variations in birch leave Zn concentrations follow the same pattern as that described for B, Fe, Pb and Sr, while δ^{66}Zn in all four trees became significantly more negative over the duration of the study.

This experiment was initially planned to provide an assessment of long-term reproducibility including contributions from the sampling process. Since findings demonstrating the existence of significant between-year differences in foliage from the same trees were highly unexpected, very thorough control of all method stages and re-analyses of all samples collected from a single birch were performed. No analytical errors could be detected. Profound changes in anthropogenic foliar uptake on both local and regional scales, for example due to annual differences in predominant wind directions during the exposure period though not unthinkable, can hardly explain the variability for elements such as Cu, Fe, Sr or Zn.

In the search for potential explanations, it was established that there were very significant differences in May weather during the study period. May 2013 was uncharacteristically hot with May 30 actually being the warmest day of the year reaching 27^{o}C with the historical average for the day being only 14^{o}C. The average daytime temperature reached 10^{o}C as early as the first week of the month, whereas May 2015 was unusually cold with the average daytime temperature approaching, but not reaching 10^{o}C only at the end of the month.[2] Therefore, though collected on almost the same annual date, birch leaves from 2013 represent a distinctly different growing stage than those from 2015. Firstly, there was an offset of at least two weeks in the appearance of the first leaves between these two years. Secondly, the frozen soil depth, which limits nutrient uptake from deep soil horizons through the root system, rhizosphere activity[3] and affects sub-surface water drainage, was much shallower in 2013 than in 2015 when collection occurred. The direction of trends observed between 2013 and 2015 data (**Table S1**) resembles that for seasonal changes noted for the entire set of birch results (two first columns in **Table S1**), given that leaves collected in 2013 represent later stages of the growth cycle. These results indicate isotopic differences between source pools supplying elements to birch leaves during the first 2-4 weeks of growth (soil solution, sap stored in stem, aerial sources) and changes in fractionation effects occurring during either uptake through the root system or element translocation between different tree compartments.

Our Zn isotope data reaffirm recently published findings[4] that the increased rooting depth and the decreased organic carbon concentration in the root uptake zone resulting from progressively thawing soil leads to heavy isotopes becoming more and more available for larch roots. This results in a shift towards heavier Zn composition in larch needles during the course of the vegetative season. Using sequential leaching of soil, Song *et al.*[5] have demonstrated that Sr in the exchangeable and carbonate fractions (bioavailable) has a lower ^{87}Sr/^{86}Sr ratio that that in the silicate fraction, consistent with a low ^{87}Sr/^{86}Sr ratio in the plant and therefore in the organic-rich topsoil horizon. This would explain the more radiogenic Sr ratios in leaves collected in 2013 **(Table S1)** as increased contributions from deeper thawed soil horizons. Variations of bioavailable Sr concentrations and ^{87}Sr/^{86}Sr with depth of root uptake were also reported by Poszwa *et al.*[6]

These results demonstrate that foliage samples provide highly spatially- and temporally-resolved snapshots of elemental and isotopic interactions with deciduous plants on the individual scale.

Table S1. Concentrations and isotopic composition of B, Cd, Cu, Fe, Pb, Sr and Zn in leaves collected from 4 individual birch trees collected last week of May 2013-2015

Birch	Sampling period	B (µg g^{-1})	δ^{11}B (‰)	Cd (ng g^{-1})	δ^{114}Cd (‰)	Cd (µg g^{-1})	δ^{65}Cu (‰)	Fe (µg g^{-1})	δ^{56}Fe (‰)	Pb (ng g^{-1})	^{208}Pb/^{206}Pb	^{206}Pb/^{207}Pb	Sr (µg g^{-1})	^{87}Sr/^{86}Sr	Zn (µg g^{-1})	δ^{66}Zn (‰)
A	May 2013	14,1	6.2	547	0.463	8.5	-0.440	171	-0.488	203	2.396	1.164	15.1	0.7310	179	-0.219
	May 2014	11.9	7.2	490	0.367	9.3	-0.502	137	-0.368	122	2.421	1.179	14.9	0.7300	169	-0.359
	May 2015	11.2	7.2	535	0.278	11.8	-0.188	125	-0.366	71	2.470	1.213	12.9	0.7276	125	-0.457
B	May 2013	16.1	9.6	395	0.402	9.7	-0.617	165	-0.457	200	2.404	1.168	53.9	0.7296	382	0.016
	May 2014	9.9	9.8	285	0.344	10.7	-0.404	137	-0.313	146	2.407	1.174	49.9	0.7270	296	-0.123
	May 2015	8.7	10.7	347	0.306	11.1	-0.301	103	-0.315	69	2.450	1.208	28.3	0.7255	137	-0.307
C	May 2013	10	5.9	444	0.411	12.1	-0.580	163	-0.482	142	2.418	1.177	43.4	0.7296	288	0.104
	May 2014	7.7	6.8	289	0.351	13.5	-0.471	114	-0.287	112	2.432	1.186	37.1	0.7269	179	-0.022
	May 2015	7.4	7.6	403	0.288	14.1	-0.308	94	-0.255	64	2.449	1.202	35.1	0.7268	144	-0.198
D	May 2013	13.4	4.9	357	0.650	9.3	-0.452	188	-0.288	104	2.425	1.182	31.8	0.7284	186	-0.112
	May 2014	10.9	6.6	223	0.621	10.0	-0.328	146	-0.264	84	2.428	1.184	28.8	0.7250	149	-0.301
	May 2015	10.5	7.1	209	0.574	11.2	-0.241	125	-0.261	71	2.458	1.205	17.7	0.7252	63	-0.405

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