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Multivariate interpretation of the foliar chemical composition of Norway spruce (*Picea abies*)

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Abstract

Twenty-four chemical elements were analysed by INAA, ICP-AES and CN in needles of Norway spruce (*Picea abies* (L.) Karst.). Branches were sampled from 54 trees on eight sites in Switzerland and South Germany. From each tree, twigs were sorted into the most recent four or five age classes and their needles analysed separately. All measured concentrations could be considered as log-normally distributed and statistical analyses were, therefore, performed on logarithms. Variance components were estimated by maximum likelihood and compared between elements. Non-essential elements varied more than essential nutrients (Mn was an exception). The sites and the age of the needles were the most important sources of variance. The interaction between site and age, the individual tree, the sampled branch and the residual variance were usually much smaller sources of variance. The effects of the most significant factors – site and age – were further described by principal components and cluster analyses. Mineral elements either increased or decreased with the age of the needles according to their mobility in the phloem. Two different components were identified in the effect of the sites: a geochemical component linked to soil pH and a climate component linked to altitude, temperature and precipitation. Multivariate statistics are discussed as a tool for the interpretation of complex interaction patterns between element concentrations in plants.

Introduction

The elemental composition of plant tissues is of interest for plant physiology, plant nutrition, fertilisation, ecology and environment protection, as well as for food and forage quality. Foliage analysis is a common method for assessing the nutritional status of trees (Fiedler et al., 1973; Linder, 1995; Zöttl, 1990), while soil analyses are often hindered by the heterogeneity of forest soils (Hüttl, 1991). The importance of nutrients for plant growth led to the definition of optimal foliage concentrations for many species (Bergmann, 1992). Tree foliage is also regarded as a good bioindicator of the environment (Evers, 1986). Contents in nutrients, as well as in non-essential elements, are therefore used in the assessment of air and soil pollution (Landolt et al., 1989). Environmental and nutritional considerations are often linked, for example in the deposition of atmospheric nitrogen or in the depletion of base cations due to acid depositions. The relations between nutrition, pollution and tree vitality thus received much attention in the last two decades (Cape et al., 1990; Flückiger and Braun, 1995; Hüttl, 1991).

In soils and plants, chemical elements are not independent of each other. Pairwise interactions have for example been summarised by Robson and Pitman (1983). In the same way, the Diagnosis and Recommendation Integrated System (DRIS), proposed by Beaufils (1973) and often used in agriculture, attempts to describe the nutritional status of plants by indices based on dual concentration ratios. Since the works of Ingestad (see Ingestad, 1987), concentration ratios are also used in forestry, especially those between nitrogen and the other nutrients (Linder, 1995).

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Table 1. Main characteristics of the sites

Site and region	Altitude (m)	Average temperature (°C)	Average precipitation (mm a^{-1})	Soil type (FAO classification)	pH/$CaCl_2$ (rooting zone)	Geological substratum
Alptal (SZ), Swiss Prealps	1170	5.4	2200	humic gleysol (humus types: anmoor and mor)	4.0	flysch (rich in clay and limestone)
Auenstein (AG), Swiss Plateau	440	9.9	1100	gleyic cambisol	3.6	limestone, partly covered by moraine
Chanéaz (VD), Swiss Plateau	800	7.4	1000	gleyic luvisol	3.5	moraine
Grossalp (GR), Swiss Alps	1640	1.9	1600	eutric cambisol (humus type: moder)	5.3	limestone moraine
Regelsberg (SG), Swiss Prealps	980	6.3	1600	gleyic cambisol	7.6	freshwater molasse and limestone marnes
Sardona (SG), Swiss Alps	1760	1.2	2200	orthic podsol	3.3	flysch (poor in base cations)
Schluchsee, Black Forest, Germany	1200	4.0	1900	orthic podsol	3.6	granite (very poor in base cations)
Villingen, Black Forest, Germany	900	5.5	1000	dystric cambisol	3.2	red beds (poor in base cations)

A further step in studying interactions between elements is to use multivariate statistical methods, for example on data from different plant species. This approach was used by Garten (1978) to arrange elements according to their physiological functions. This author also applied the concept of ecological niche to the nutritional requirements of species as represented by their principal components. Another multivariate approach has been proposed by Parent and Dafir (1992) who use a specific transformation to obtain so-called 'raw-centred logratios' before subjecting compositional data to principal component analysis. Multivariate statistics has also found applications in the recognition of pollution patterns by analyses of mosses (Percy and Borland, 1985) or tree needles (Landolt et al., 1989; Mankovska and Steinnes, 1997). Because they provide a comprehensive view of complex interactions, these methods appear most useful when the number of analysed elements is large and when pollution sources are easily identifiable (short-range pollution). On a broader scale, however, climate, soils and air pollution are interacting and are therefore difficult to separate in their effects. There is thus a need for the description of 'normal patterns' (as they arise from the interaction of climatic and edaphic factors) and of possible deviations from this normality. This is the aim of the present paper, which reports on a multivariate analysis of 24 chemical elements measured simultaneously in tree needle samples.

Material and methods

Sites and sampling

Eight sites with adult Norway spruce trees (*Picea*

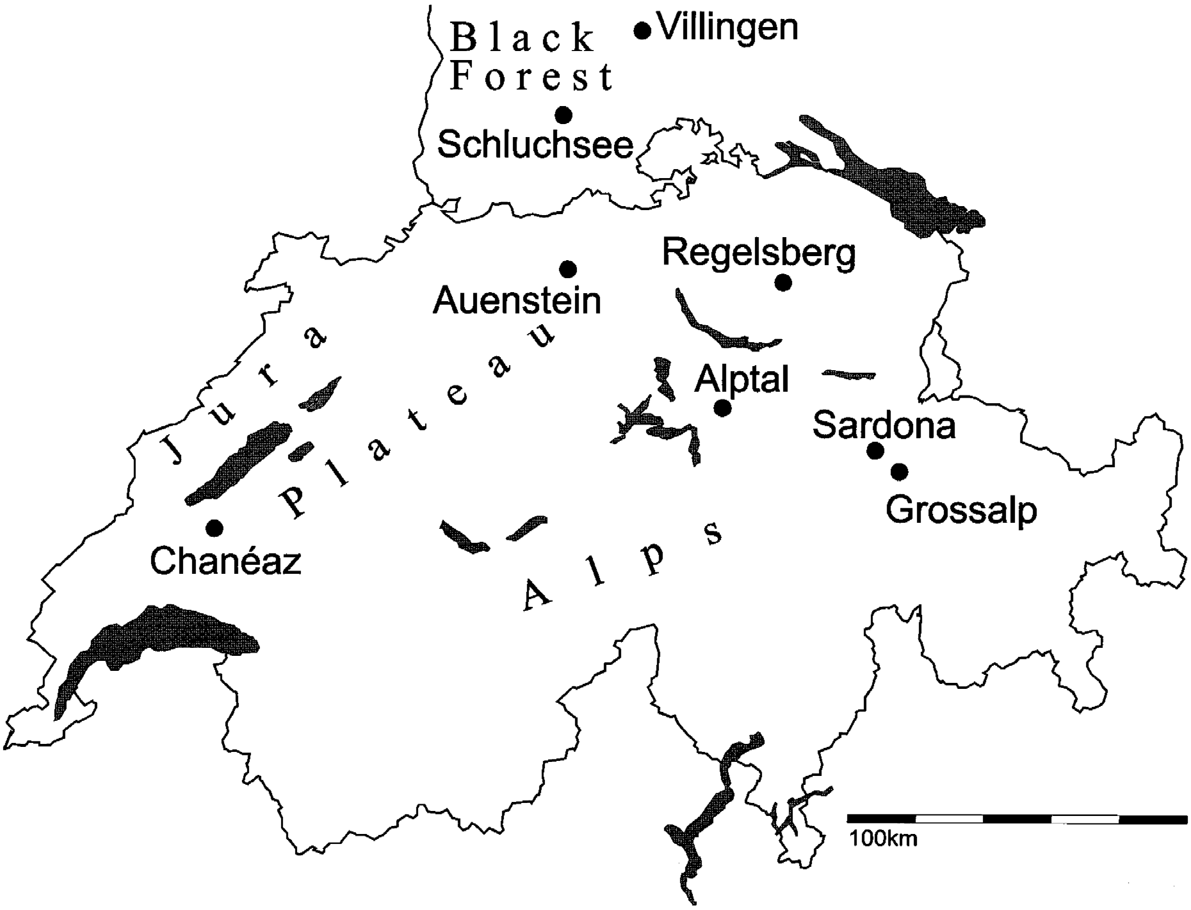

Figure 1. Location of the study sites in Switzerland and Southwest Germany.

abies (L.) Karst.) were chosen in Switzerland and southern Germany in order to represent a large variation of geological bases and soils (Table 1, Figure 1). All sites are remote from major sources of air pollution, except for Auenstein which lies in the more densely populated and industrialised Swiss Plateau (Landolt et al., 1989). The deposition of marine aerosols is low on all sites (distance to sea >500 km in the main wind directions).

Samples were taken at the end of autumn or during the winter, as this was shown to be the time with the lowest variations in element concentrations (Wyttenbach and Tobler, 1988). Branches were cut from the upper third of the crown of 5–9 dominant or co-dominant trees per site (54 trees in total). At one site (Alptal), two branches were harvested from the same whirl and handled separately. Branches were divided into twigs of the youngest four or five age classes.

Analyses

The twigs and the attached needles were washed with tetrahydrofurane/toluol. This was necessary in order to remove the outer wax layer of the needles and thus obtain intrinsic (biologically active) concentrations (Wyttenbach and Tobler, 1998). Thorough washing is an essential step in the analysis of elements having low concentrations in needles compared to soil dust and other aerosols adhering to or embedded in the wax (Na, Sc, La, Cr, Fe, Al, As, Sb, Br). After drying at 65 °C, the needles were separated from the twigs and ground in a coffee grinder. Blanks were run by substituting sugar for the needles, and they revealed no detectable traces originating from grinding.

Analyses were performed separately by tree and by needle age. Instrumental neutron activation analysis (INAA) (Wyttenbach et al., 1990), induced coupled plasma atomic emission spectrometry (ICP-AES, for Mg, Ca, Sr, Ba and P) and combustion/chromatography (C+N analyser) were used. The quality of the analyses was checked by repeated measurements and by comparison with certified standards (Wyttenbach et al., 1990). The reproducibility was always within 5% and/or negligible (<0.1%) compared to the range measured; the accuracy was better then ±10% for all elements measured.

Most plant-essential mineral elements were analysed (macro-elements: N, P, K, Ca, Mg and micro-elements: Mn, Fe, Cu, Zn, Cl) along with non-essential elements (Na, Rb, Cs, Sr, Ba, Sc, La, Cr, Co, Al, Si, As, Sb, Br). The obtained data matrix contained 238 analyses of the 24 elements. Due to different analytical problems, including the discontinued availability of the nuclear reactor used for INAA, 442 out of the 5712 values were missing. Part of these data have already been presented in articles dealing with different elements or groups of elements (Wyttenbach et al., 1994, 1995a,b, 1996, 1997; Wyttenbach and Tobler, 1999). The present paper therefore focuses entirely on comparisons and interactions between all elements.

Statistics

According to the distribution of the data, all the measured concentrations were transformed to their logarithms prior to statistical computations. It will be shown that the assumption of log-normal distributions was reasonable.

Analyses of variance were used to identify which factors affect the different elemental concentrations. The site, the tree within a site and the age of the needles were considered in the following linear model:

$$\log(\text{concentration}) = \alpha_{\text{site}} + \beta_{\text{tree (site)}} + \gamma_{\text{age class}} + \varepsilon_{\text{residues}} \quad (1)$$

The corresponding analyses of variance were calculated considering the factor γ as fixed and the other ones as random. The interaction between age classes and sites was also tested in an extended model:

$$\log(\text{concentration}) = \alpha_{\text{site}} + \beta_{\text{tree (site)}} + \gamma_{\text{age class}} + \delta_{\text{site} * \text{age class}} + \varepsilon'_{\text{residues}} \quad (2)$$

The importance of the variance components was quantified by the method of the maximum likelihood. The variance associated with the branches was estimated from the pairwise branch sampling at Alptal.

Interactions between elements were assessed by principal component analyses. Groups of correlated elements were extracted from a cluster analysis performed according to average distances. The distance d between pairs of chemical elements was calculated as a function of their coefficient of correlation r:

$$d = \sqrt{\frac{1-r}{2}} \quad (3)$$

Our results were then compared to the procedure proposed by Parent and Dafir (1992). In their Compositional Nutrient Diagnosis (CND), these authors also use a principal component analysis, but after a different transformation. From the concentrations, they calculate ‘raw-centred logratios’:

$$z_i = \log(x_i/g(x)) \quad (4)$$

where x_i is the concentration of the ith element, g(x) the geometric mean of all concentrations and z_i is the transformed variable. They also consider that the sum of all element concentrations must be 1. To calculate g(x), all non-determined elements are therefore represented by a ‘filling-up value’ (1 minus all measured concentrations). As a result, the obtained values of z_i sum up to zero for any analysed sample.

Finally, in order to better explain the observed patterns, the concentrations were corrected for known effects prior to new multivariate computations. In a first case, effects of sites and trees were removed, and in a second case the effects of age classes. Derived variables were denoted N and S, respectively:

$$N = \log(\text{concentration}) - \alpha_{\text{site}} - \beta_{\text{tree (site)}} = \gamma_{\text{age class}} + \varepsilon_{\text{residues}} \quad (5)$$

$$S = \log(\text{concentration}) - \gamma_{\text{age class}} = \alpha_{\text{site}} + \beta_{\text{tree (site)}} + \varepsilon_{\text{residues}} \quad (6)$$

Results

Factors affecting the mineral composition of needles

Average nitrogen concentrations in current-year needles were below the published ‘optimal’ values (Bergmann, 1992; Linder, 1995; Zöttl, 1990) on half of our sites (Regelsberg 11.9 mg g^{-1} and the alpine sites Alptal 8.9, Sardona 11.1 and Grossalp 12.3 mg g^{-1}). Further limitations occurred for P (0.82 mg g^{-1}) and Cu (1.6 μg g^{-1}) at Alptal; K (3.5 mg g^{-1}) and Mg (0.70 mg g^{-1}) at Chanéaz and Mn (33 μg g^{-1})

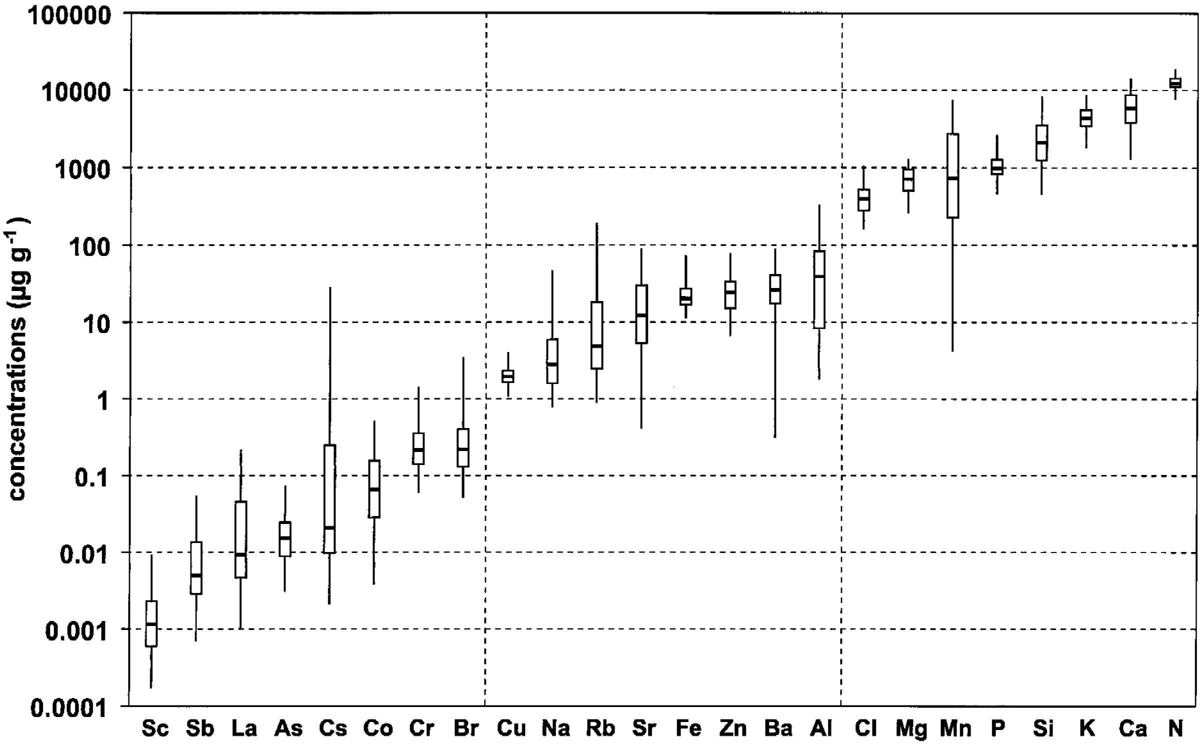

Figure 2. Quartiles of concentrations in mineral elements in 1–5 year old needles from 54 Norway spruce trees on eight sites.

at Regelsberg. None of these deficiencies led to visible symptoms. Other concentrations of N, P, K, Ca, Mg, Zn and Cu were within their optimal ranges. At Villingen, Ca and Mg (2.1 and 0.8 mg g^{-1}) may be considered as deficient, depending on the reference chosen. Concentrations of Mn were above the optimal range on several sites: Sardona (600 $\mu g\ g^{-1}$), Villingen (1200 $\mu g\ g^{-1}$), Auenstein (1900 $\mu g\ g^{-1}$) and Chanéaz (2500 $\mu g\ g^{-1}$).

Together, the measured elemental concentrations covered eight orders of magnitude, from less than 1 part per billion to more than 1% (Figure 2). Most elements showed a range covering more than one order of magnitude. Their distribution was obviously not normal but rather log-normal.

The model including the factors site, tree and age (Equation 1) gave coefficients of determination between 0.85 and 0.997 for all 24 elements. The effect of the age classes was found to differ between sites for several elements (Zn, Ca, Cr, Fe, Na, Mg). After including the interaction δ (Equation 2), all coefficients of determination were above 0.9. The distribution of the residues was checked graphically. No obvious deviation from normality was found. The skewness and kurtosis were between -2 and +2 for all elements. This is a further indication of validity of the model and justifies the initial logarithmisation of the data.

The variance components estimated by the maximum likelihood are presented in Figure 3. Because they are based on logarithms, these components can be compared over all measured elements, regardless of their concentration level. All macro-elements had small variances; their geometric standard deviation was between 1.2 (N) and 1.8 (Ca). Sites accounted for about half of the variances. The micro-elements Cu, Fe, Zn and Cl also had small variances, whereas Mn exhibited an exceptionally high one. All non-essential elements were subject to important variances; geometric standard deviations ranged from 1.9 (Cr) to an extreme value of 16 (Cs). In most cases, differences between sites accounted for the largest part of the variance. The elements Sc, La, Si and Sb showed a high variance linked to needle age classes. This reflected their strong accumulation in ageing needles. The halides Cl and Br had a special pattern: they varied much more between individual spruce trees than between locations. From the data of Alptal, branches appeared to be very weak sources of variance for all elements studied.

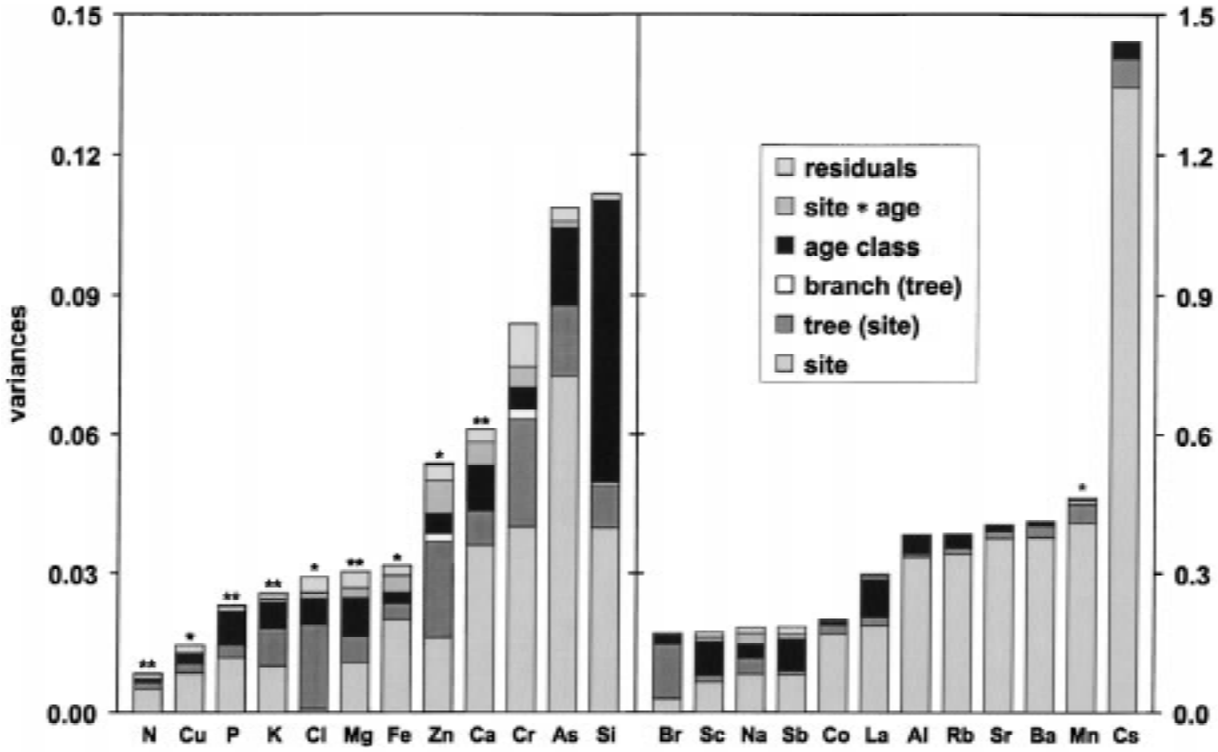

Figure 3. Variances of concentration logarithms with their components estimated by maximum likelihood; stars denote essential *micro- and **macro-elements; note the different scales between the first half (left axis) and the second half (right axis) of the elements.

Multivariate analyses

For the analysis of principal components, we used the correlation matrix between logarithms of concentrations. A computation based on the covariance matrix would have exaggerated the importance of variables with high variances (in our case non-essential elements, as compared to essential ones). First components PC1 and PC2 are presented in Figure 4. Principal components can be scaled as desired. Here, rather than standardising them, we chose to scale them according to their eigenvalue. Their variances are, therefore, proportional to the part of the total variance they account for (31 and 25%, respectively).

Elements with a typically high availability in alkaline soils (Ca, Sr, Ba, Mg, Zn) are on the right-hand side. On the opposite side are elements like Fe and Al which have a higher solubility in acidic soils. PC1 can, therefore, be considered as expressing soil characteristics linked to its pH value. The second component is also easily interpretable: minerals accumulating from year to year have positive loadings, while elements with decreasing contents have negative ones. PC2 is thus linked to the age of the needles. The cluster analysis based on average distances (Equation 3) takes the sign of the correlation coefficients into account. This was found to be a decisive advantage over the more common clustering based on the maximisation of between-cluster variance, which would aggregate variables with high negative correlations. Clusters of elements with distances below 0.6 are circled in Figure 4 and further links are indicated for $0.6 < d < 0.67$ (these distances were chosen arbitrarily in order to facilitate the interpretation).

Comparison of data transformations

The calculation of logratios according to Parent and Dafir (1992) (Equation 4) is relatively easy to apply on a few major nutrients. With more elements, however, the number of samples with at least one missing value tends to increase, especially when considering elements near the analytical determination limit or when comparing results from different laboratories. The consequence is that any missing concentration makes the transformation impossible for the whole sample. Since we still wanted to compare raw-centred logratios to our data set of simple logarithms, we

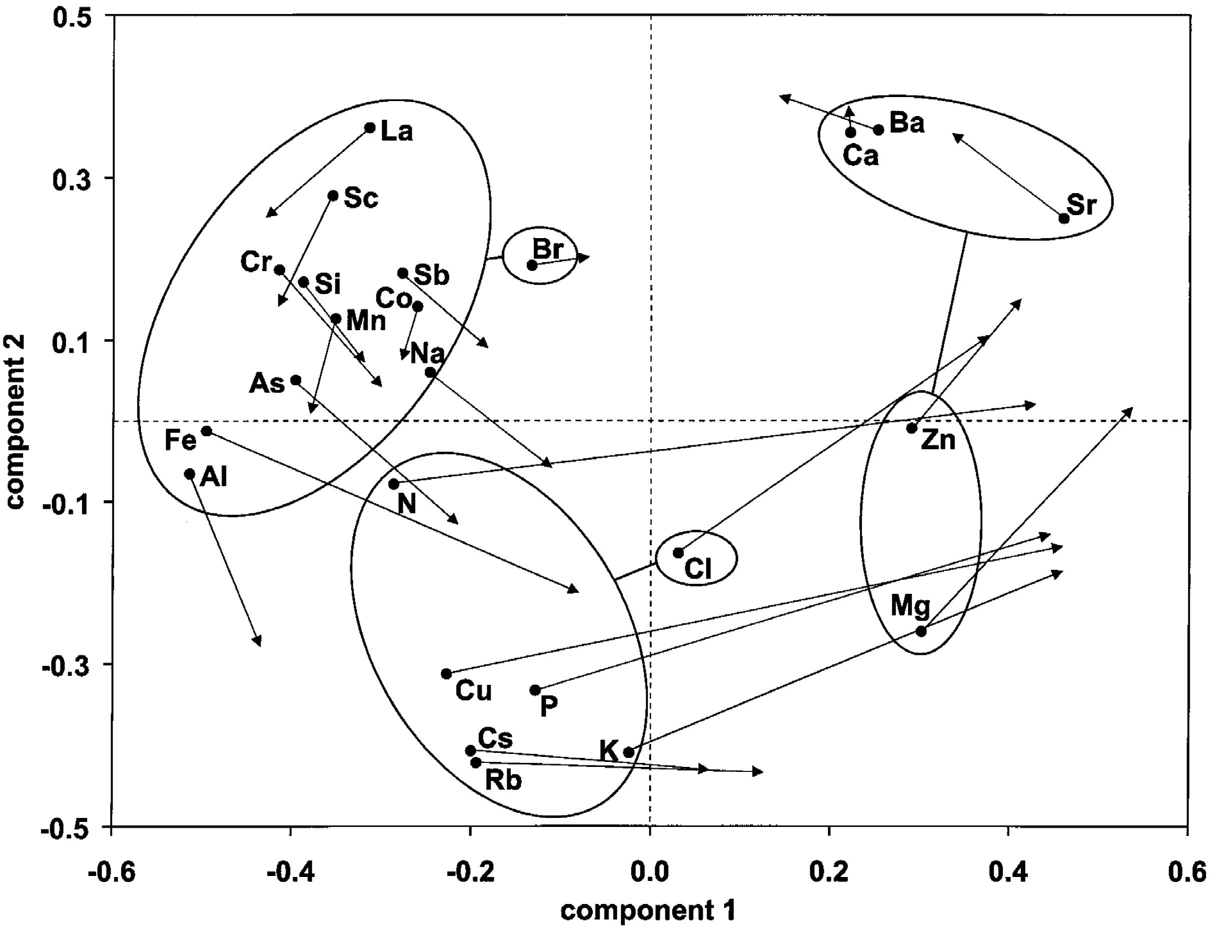

Figure 4. First two principal components and variable clusters derived from the logarithms of the concentrations; arrows indicate element positions in the analysis based on logratios.

calculated *g(x)* by replacing missing data with their predicted values according to Equation 1. In the transformed data matrix, however, the corresponding cells were left empty.

As shown by arrows on Figure 4, the main effect of the transformation to logratios instead of logarithms was to move elements counter-clockwise on the plane of PC1 and PC2 (now 33 and 23% of the variance, respectively). The rotation itself does not modify the interpretation of the results. Some elements, however, were moved farther than others, especially the group N, P, Cu and K. It appears also that the analysis based on logratios yields a more even distribution of the elements on the plane. This can be explained by the 'raw-centring' effect of the transformation: because the sum of z_i must be zero in each analysed sample, no factor can affect more elements positively or more elements negatively. In our case, for example, many elements are increasing with needle age and only a few are decreasing. In the logratios, however, this general effect is corrected and slightly increasing concentrations (Fe, Ba) are transformed into slightly decreasing logratios. The same is true with more elements being associated with acidic than with neutral to alkaline soils. As a result, large clusters of elements tend to break apart and intermediate elements are pushed towards smaller clusters. This forced symmetry in element clustering may thus alter the interpretation of the results.

Derived variables

The analysis of principal components based on the values corrected for tree effects (Equation 5) is presented in Figure 5. In addition to the element loadings, the scores of the age classes in PC1 and PC2 are also given as centred values of γ (according to Equa-

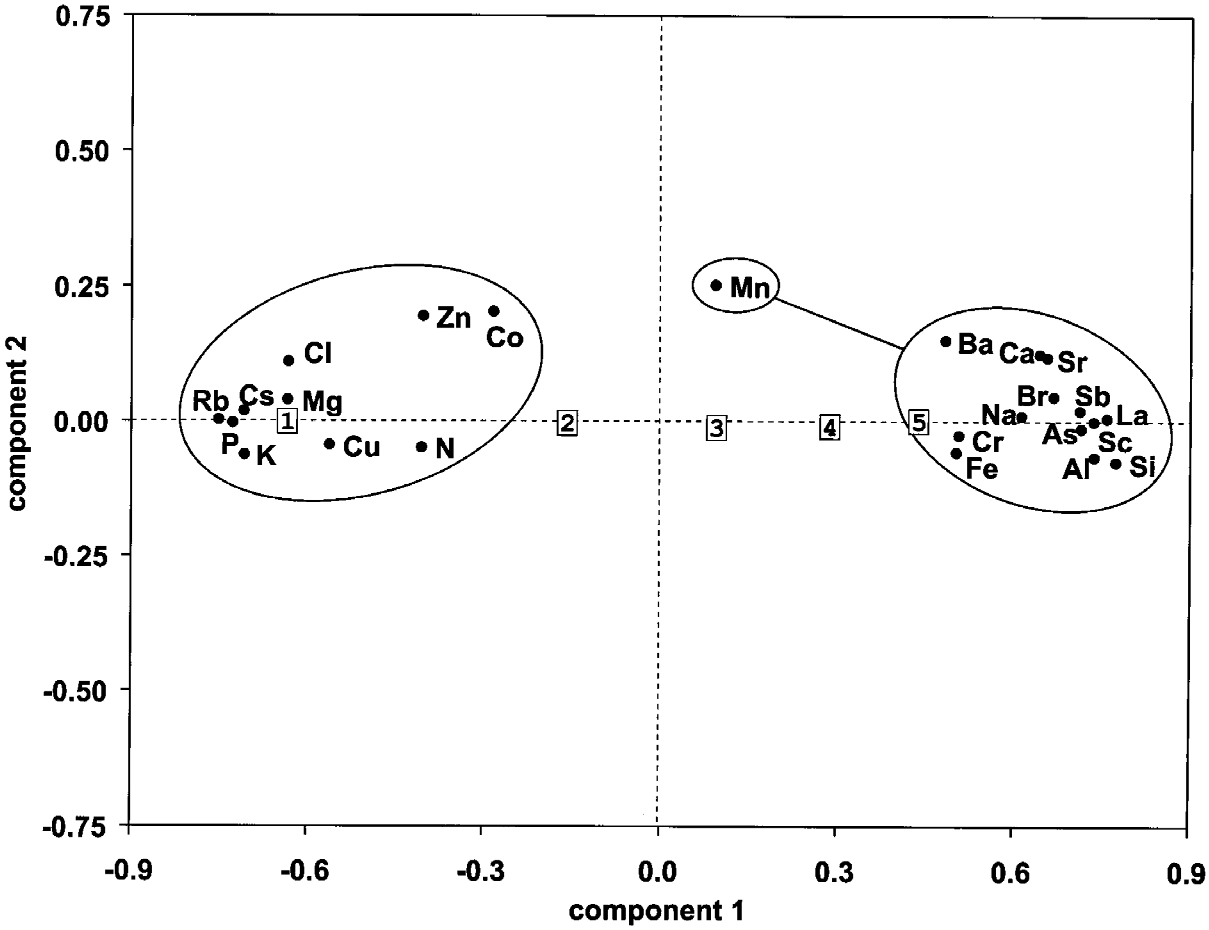

Figure 5. First two principal components and variable clusters after correcting for the effects of sites and trees; numbers indicate the position of needle age classes.

tion 1). PC1 (62% of the total variance) precisely represents the trends due to the age of the needles, to which it is correlated with a coefficient of 0.97. A variable clustering (as described above) separates chemical elements in two groups with decreasing (left) or increasing (right) concentrations. Manganese has an intermediate position as its concentration usually increases with needle age while it decreases at some sites, especially where it is present at lower levels (Wyttenbach et al., 1995a). PC2 appears to pick up these kinds of irregularities between sites, also seen for Zn and Co. The corresponding variance, however, is low (10%).

In the analysis based on data corrected for needle age (Equation 6), the first and second principal components (Figure 6) account for 36 and 19% of the total variance, respectively. The different sites are also plotted according to the scores based on their α factors (Equation 1). The first component has a high correlation (r=0.66) with the soil pH values. There is not much difference to the PC1 obtained from the uncorrected data and, here again, alkali-earth elements are on the right-hand side, opposite to Fe, Al and Si. The second component, however, gives new information relating to meteorological factors. It is strongly correlated with mean temperature (r=0.68) and annual precipitation (r=−0.62), both also related to the altitude of the sites. These correlations with site properties can also be plotted on the graph of principal components. New groups of elements appear in the cluster analysis: one formed by the monovalent cations and one with the monovalent anions.

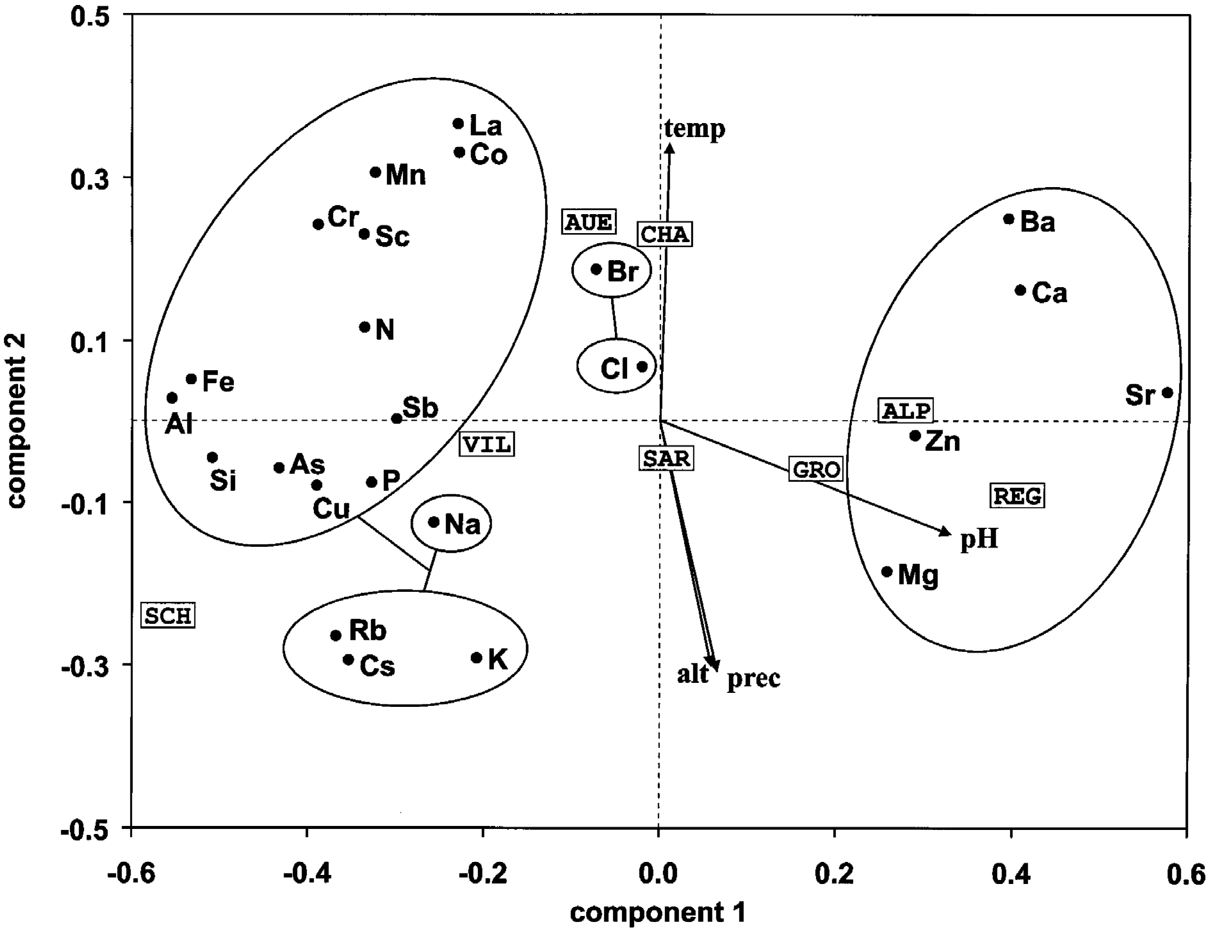

Figure 6. First two principal components and variable clusters after correcting for the effect of needle age classes; sites are indicated by their three initial letters (see Table 1) and correlations (scaled 1:2) with site properties given by arrows (abbreviations: temp=temperature, prec=precipitation and alt=altitude).

Discussion

Compared to reference values, the nutritional status at the studied sites is not optimal, especially for nitrogen concentrations. The observed ranges, however, are very representative of the situation prevailing in Switzerland (Flückiger et al., 1997; Landolt, 1997) and in the adjacent regions (Hüttl, 1991).

Non-essential elements were shown to vary more in their concentrations than essential nutrients do. The best example is given by potassium and its chemical homologues rubidium and caesium. As an essential element with limited availability, K is actively taken up to meet plant requirements (Mengel and Kirkby, 1987). Rb and Cs follow K in numerous physiological processes and, accordingly, show similar age patterns (Tobler et al., 1994). Their ratios to K, however, differ widely between sites and even between trees on one site (Wyttenbach et al., 1995b), indicating the absence of a specific control of Rb and Cs independent of K metabolism. Accordingly, the difference in variance between essential and non-essential elements can be considered as the result of the physiological control exerted by plants on absorption, translocation and storage of their required nutrients. Non-essential nutrients are, therefore, easier to use as bioindicators (Evers, 1986). However, because the enrichment factor (plant content/soil content) can be very different between sites (Wyttenbach et al., 1995b), caution must be used in the biomonitoring of pollutants and radioactive elements deposited on the soil.

Nutrient contents are known to change with the age of needles (e.g. Fiedler et al., 1973). Non-essential elements were also shown to undergo changes that can be well described by mathematical functions (Wyttenbach et al., 1995c). The high coefficients of determination obtained from our model (Equation 1) show that these age functions usually hold in proportion over different trees within a site and also over different sites. They can be interpreted in terms of import into and export out of the needles. Import occurs mainly through the xylem (transpiration flow) while export is practically restricted to the phloem (Mengel and Kirkby, 1987). Phloem transport enables the retranslocation from old tissues into younger ones in order to meet new nutritional requirements. Some elements, however, are poorly or not at all transported via the phloem and accumulate in the foliage. The ability of chemical elements to be retranslocated may be expressed by the concentration ratio between phloem sap and xylem sap. Ranking these mobility ratios according to values from Robson Pitman (1983) gives: P > Mg > K > Cu > Fe > Cl > Zn > Mn > Ca > Na. This is almost the same ranking as obtained from the concentration ratio between young and old needles according to our results (Equation 1 model): Mg>P>K>Cl>Cu>Zn>Mn>Fe>Ca>Na. The Spearman correlation between both rankings is 0.89 (p=0.0005). As already written by Hüttl (1991), the mobility of chemical elements in the phloem is thus a key factor governing foliar contents as they change with tissue age. The PC1 values in Figure 5 can, therefore, be considered as indicative of the elements' mobility in the phloem.

The site is the other important factor affecting the composition of needles. Correcting for needle age allowed us to get further details about this effect from the analysis of principal components (Figure 6). The soil clearly appears in the first PC. Basic cations originating from calcareous bedrocks are grouped on the right side. In alkaline to neutral soils, these elements are present in carbonated minerals. They are, therefore, always available for plants when the soil is buffered by carbonates. High scores in PC1 are therefore synonymous to carbonated bedrocks and young or developed soils with a high pH. Cations originating mainly from silicates are on the opposite side. In decarbonated soils, below pH 6.2, pH buffering is effected by silicates, exchangeable cations, aluminium hydroxides and finally iron hydroxides (Khanna and Ulrich, 1984). It is, therefore, not surprising that Si, Fe and Al are grouped together on the left-hand side: their availability is higher at low pH. A negative score in PC1 thus comes from decarbonated, developed to degraded soils, with an acidic to very acidic reaction. Further groups of elements are also indicative of similarities in soil chemistry: a group of the monovalent cations (K, Rb and Cs, also linked to Na) and a sub-group of elements associated with manganese hydroxides (Mn, Co, Sc, La and, a little further, Cr).

The second principal component in Figure 6 has been shown to be related to the altitude and to climatic factors. Precipitation usually increases with altitude while temperature decreases. These correlations explain why all three factors appear together within PC2. In spite of the correction of needle age effects, elements with increasing or decreasing concentrations have rather low or high PC2 scores, respectively. This is probably an effect of higher temperatures increasing the transpiration flow and thus the storage of immobile elements in the needles. It can further be seen that Cl and Br appear close to the origin of both first components because they have only weak correlations with other elements. This may be related to the different origin of these elements: both originate mainly from atmospheric deposition and can be taken up by the foliage (Evers, 1986; Wyttenbach et al., 1989). They are correlated with each other in sea spray (an important source, even at locations relatively remote from coasts) as well as in pollution from road traffic and industries (Wyttenbach et al., 1989). It remains unclear, however, why the concentrations in Cl and Br vary more between trees on one site than between site averages. Since the variance between branches was low, it seems unlikely that this behaviour could relate to differences in the deposition rates at the scale of the tree crowns. Since we did not include competitively suppressed tress, trees of different ages or branches from different levels, these effects can not be discussed from our data set.

Out of the complex interactions between 24 different elemental cycles, the multivariate approach used in this study extracted three main factors affecting the mineral composition of spruce needles:

1. A physiological factor: elements transported via the phloem are remobilised from older needles into younger tissues. Immobile elements, on the other hand, accumulate from year to year (Figure 5, PC1).
2. A geochemical factor: the availability of nutrients differs between sites. Geological substratum and soil pH play a major role here (Figure 6, PC1).
3. A climatic factor: temperature and precipitation change with altitude. This affects the transpiration and also the composition of needles (Figure 6, PC2).

Our approach may be very useful in comparing sites in different climates and on different soils. At higher locations, for example, it was shown that forests often exhibit nutritional shortages. In comparison with reference values, these sites are generally 'suboptimal'. This point of view, however, is misleading as it asks for a 'correction' in form of fertilisers while the trees are perhaps absolutely 'normal' for their bedrock, soil and climate. Our study sites were mostly far from pollution sources and, therefore, affected by only long-distance pollutants. The observed patterns may therefore be used as background information for surveys or experiments on more specific pollution or stress situations.

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