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Anthropogenic and geogenic mass input of trace elements to moss and natural surface soil in Norway

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HIGHLIGHT

- PMF determines mass input of trace elements to moss and natural surface soil.
- Major PMF factors represent air pollution Pb Mo Cd Sb As and geogenic soil Ce La Y Eu Co.
- PMF determined ratios of Y:La:Ce in soil are consistent with literature data for grazing lands.
- PCA is useful for separation of low elemental level (Eu) factors.
- PCA scores are useful to identify source areas for low elemental level factors.

GRAPHICAL ABSTRACT

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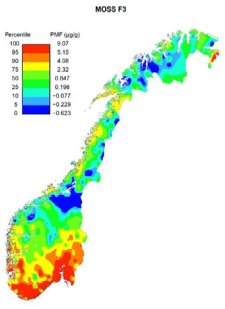
		Moss	Soil
PMF	Anthropogenic	Pb, Mo, Cd, Sb, W	Pb, As, Sb, Mo, Cd
	Geogenic	Ce, La, Y, Cr, Co	Ce, La, Y; Li; Eu
PCA	Anthropogenic	Pb, Cd, Mo, Tl, Sb, Hg	Sb, Pb, Cd, W, Tl, Mo, As, Hg; Ag
	Geogenic	Dy, Y, La, Ce, Li, Ga	La, Ce, Y, Dy; Li, Cs; Eu



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ABSTRACT

Data sets for concentrations of up to 22 elements including Pb, Cd, Ag, As, and Hg and several rare earth elements (REEs) in moss and surface soil from all over mainland Norway are analyzed by positive matrix factorization (PMF) and principal component analysis (PCA) with centered log-ratio transformation. Moss and soil samples collected in 2010 and 2005, respectively, show both a distinct long-range atmospheric transport PMF factor including a dominant Pb loading along with smaller loadings of Mo, Cd, Sb, and As, and a geogenic factor dominated by Ce, La, and Y. Other PMF factors for moss and soil are mainly anthropogenic except for two soil factors, a Cr, Co, Ce dominated factor, and an Eu factor. The source area of Eu is mainly inland consistent with its divalent oxidation state. A significant advantage of PMF factors is that their loadings are scaled according to their relative factor contributions. The PMF air pollution factor F3 in moss with average contribution of 7.11 µg/g produces an air pollution input of 5.0 µg/g which compares well with literature values for the total Pb concentration in moss for 2005 in southern Norway. PCA has the advantage that it can separate factors with very low element concentrations. To support sources of elements identified by PCA it is recommended to include calculation of factor scores to identify significant source areas.

1. Introduction

Measurement of atmospheric input of heavy metals such as Pb, Cd, Zn, and Hg and several other trace elements is important for evaluating the possibly negative impact on ecosystems and humans. Moss

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(*Hylocomium splendens*) is well suited for this because it has no root system and receives most major and trace elements from long-range atmospheric transport as well as local sources (Steinnes et al., 2011; Schaug et al., 1990). This moss species has also the advantage compared to soil that dating is easily determined from shoots which from each year of growth can be identified and selected for sampling.

Organic surface soil is another useful medium for the measurement of these elements (Nygård et al., 2012). Surface soil is generally rich in humic substances that can provide cation exchange sites for metal ions and can complex several elements highlighting its role as a sink for metals and other air pollutants. Monitoring programs for these substances have been instituted worldwide since the 1970s and especially in many European countries including Norway.

Measurement of metals in air filter samples offers an alternative method of assessing atmospheric input of a suite of metals (Amundsen et al., 1992). This method allows short-term measurements for evaluation of metal trajectories. Monitoring of selected metals and sulfur species in precipitation has occurred in Norway since around 1980 in Birkenes in southern Norway and three additional sites (Steinnes et al., 2011). However, even with the more sensitive inductively coupled plasma mass spectrometry (ICP-MS), introduced after 1990, the number of elements that can be effectively measured is less than what typically is obtained with moss or soil.

A comprehensive study in France of trace metal and rare earth element (REE) signatures showed that mosses and lichens integrated a regional atmospheric signal, including both soil derived and industrially influenced atmospheric deposition. In forested ecosystems, mosses reflect both atmospheric deposition and canopy influence (Gandois et al., 2014). Comparison between the REE distribution patterns in lichens and mosses and bedrocks in France and neighboring countries showed a regional influence from dust particles, originating from bedrock or soil weathering, that were caught by lichens and mosses. The lithological signatures were consistent over the last century (Agnan et al., 2014).

Factor analysis has been used successfully to separate geogenic and anthropogenic sources of metals in moss and other plants (Schaug et al., 1990; Nordløkken et al., 2015), in air filter samples from direct atmospheric input (Amundsen et al., 1992), and in organic surface soils (Nygård et al., 2012). In all these cases, factor analysis was carried out as principal component analysis (PCA) with zero mean and unit variance of the variables. Such an analysis treats large and small values of element concentrations similarly, but elements of the loading and score matrices can assume negative values, especially for higher order principal components, and the elements of the loading and score matrices have limited physical meaning. A robust principal factor analysis method based on centered log-ratio (CLR) transformation of the analytical data was presented by Filzmoser et al. (2009) and applied to data for trace elements in natural soils from Norway by Steinnes and Lierhagen (2017). The method has merit but is characterized by similar constraints as outlined for PCA. In order to overcome these limitations, we used here positive matrix factorization (PMF) which, to our knowledge, has not previously been used for the analysis of trace elements in moss and soil.

The objective of this work was to investigate the merit of using positive matrix factorization to analyze trace element data from moss and soil. Although PCA, with or without CLR, is not directly comparable to PMF, it is used to contrast the two methods because it has been used extensively for similar work in the past. We expect that PMF will improve the identification and quantitative treatment of sources of trace metals. An existing large data base with 464 sampling sites distributed throughout Norway will be used for this. Guidelines and recommendations for use of PMF and PCA will be developed. The developed framework will be used to look for sources of elements that have not previously been identified. Several elements that have not been included in previous analyses (Nygård et al., 2012; Schaug et al., 1990) will be considered: W, Ga, Nb, Hg, U and the rare earth elements Dy, Eu. Of these elements, W and Eu were included recently in a soil principal factor study by Steinnes and Lierhagen (2017). Because this study was focused on trace elements, elements with high abundances such as Na, Cl, Fe, Mn, and Sr were not included in the analysis.

2. Materials and methods

2.1. Sampling and chemical analysis

Collection of 446 surface soil samples in the summer of 2005, and 447 moss samples during the summer 2010, were carried out all over mainland Norway at open air sites listed in Table S1 and Figs. S1, S2. Soil samples were obtained with a steel cylinder of 10 cm internal diameter. The uppermost 3 cm of the O horizon was taken from four sub-sites within a 5 × 5 m plot and mixed to one composite sample as described in Nygård et al. (2012). Moss samples came from the feather moss *Hylocomium splendens* (Hedw.) Schimp which is ubiquitous and grows in annual segments of which three were selected representing three years of growth (Schaug et al., 1990; Steinnes et al., 2011).

Soil samples were dried and subjected to 550 °C for 2 h for loss on ignition tests. About 0.5 g of each sample was then digested for 10 h at 180 °C in Teflon bombs using 9 mL of 14 M HNO_3. After cooling to room temperature, the samples were diluted to 50 mL with dionized water, and the clear solution was decanted off before inductively coupled plasma mass spectrometry (ICP-MS) as described in Nygård et al. (2012). Of several elements determined, 21 were selected for this work: Ag, As, Cd, Ce, Co, Cr, Cs, Dy, Eu, Ga, Hg, La, Li, Mo, Nb, Pb, Sb, Tl, U, W and Y.

The chemical analysis of moss followed similar steps. Moss samples were dried to constant weight at room temperature. Weighed plant samples of about 0.2 g were digested in concentrated nitric acid at high pressure (2 bar; $2 * 10^5$ Pa) in a microwave oven using closed digestion vessels, with gradual power rise according to a pre-set scheme. After digestion, the samples were diluted with deionized water to a final HNO_3 concentration of 0.6 M for analysis split in two. Concentrations of elements in one part were determined using high-resolution ICP-MS (Nordløkken et al., 2015). The other part of the split sample, after addition of $BrCl_2$, was analyzed for Hg by the use of cold vapor atomic fluorescence spectrometry, CV-AFS using $SnCl_2$ as a reduction agent (Steinnes et al., 2003). Several elements were determined out of which 22 were selected: Ag, As, Cd, Ce, Co, Cr, Cs, Dy, Eu, Ga, Hg, La, Li, Mo, Nb, Pb, Sb, Tl, U, W, Y and Zr.

Elements for both moss and soil were selected so as to include toxic trace metals known to impact plants and soil, for example Pb, Cd, and Hg, and the metalloid As, along with REEs that have been shown to characterize mainland Norway, especially La and Ce. Other REEs include Eu and Dy. Yttrium (Y) is considered because it is sometimes included into the REE group, and because it behaves chemically as an REE (Sadeghi et al., 2013). Zirconium was only selected in moss because it was not part of the available soil data. A few stations with several elements near the detection limit were not included reducing the total number of stations from 464 to 447 (moss) or 446 (soil).

2.2. Statistical analyses

Positive matrix factorization (Paatero and Tapper, 1994; Bzdusek, 2005; Zou et al., 2016) was used to resolve data matrices $\mathbf{X}(m \times n)$ for moss and soil, where m = number of trace elements and n = number of samples, into products of a loading or source profile matrix $\mathbf{G}(m \times f)$ where f = number of factors, and a score or contribution matrix $\mathbf{F}(f \times n)$,

$$\mathbf{X} = \mathbf{G}\,\mathbf{F} + \mathbf{E} \quad (1)$$

where $\mathbf{E}$ $(m \times n)$ is an error matrix. The data matrix $\mathbf{X}$ contains m rows of each of n element concentrations. Prior to PMF analysis, concentrations for each sample in the data matrix $\mathbf{X}$ are scaled (i.e.,