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Accumulation histories of major and trace elements on pine needles in the Cologne Conurbation as function of air quality

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Abstract

For a biomonitoring study in the greater Cologne area, we analyzed the accumulation of major and trace elements on *Pinus nigra* needles. At six sites, samples were collected separately in summer and winter 2004 from five needle generations ($n = 51$). The elements Ba, Ca, Cd, Fe, Mo, Na, Pb, Sb, Ti, V, and Zr were determined by HR-ICP-MS and normalized to upper continental crust concentration using rare earth elements (REE). Inter-site variability was significantly higher than intra-site variability allowing for reliable source allocation. A systematic and steady increase in element loads with exposure was noted, with a seasonal trend superimposed on Pb, Cd, Na, and REE. Normalization onto lithogenic REE removes seasonal variability due to dust loadings. Enrichment factors for V, Fe, and Zr reveal the most pronounced summer/winter variability. The average enrichment factors were 967 for Sb, 620 for Cd, 176 for Mo, 33 for Pb and between 3 and 5 for Ba, Fe, Na, and V, wheras Ti and Zr gave enrichment factors <1. Most reliable as source indicators were REE for lithogenic dust, Sb, Fe, V for traffic, Mo and Pb for petrochemical emissions, and Cd for mining activity. Barium proved unsuitable as traffic indicator in the Cologne Conurbation area. Accumulation trends of major and trace elements on *P. nigra* needles confirm that these passive samplers are suitable for atmospheric quality analysis in areas with multiple emission sources.

Keywords: *Pinus nigra*; Biomonitoring; Atmospheric pollution; Enrichment factors; Cologne Conurbation

1. Introduction

Atmospheric pollution comprises a serious thread to human health and behaviour of atmospheric pollutants requires ongoing investigations (EC Directive, 1996; US-EPA, 2004). Processes of emission, transport and dispersal, reactivity and natural attenuation of atmospheric pollutants are investigated by laboratory experiments, modelling and study of real-world concentrations determined by active air sampling or utilization of passive samplers. Biomonitoring is a now well-established technique (Smodis et al., 2004) in atmospheric pollution studies and allows obtaining temporally and spatially highly resolved data in a time-integrative manner. We have previously studied the air quality of the Cologne Conurbation, one of the most air pollution affected regions in Germany, by biomonitoring using *Pinus nigra* needles as passive samplers for air pollutants (Lehndorff et al., 2006). One of the most important advantages

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of biomonitoring lies in the acquisition of time-integrated records of air quality, provided that the accumulation behaviour of the plant biomonitor is adequately known and understood. The accumulation of magnetic particulates in the greater Cologne Conurbation was studied by environmental magnetic techniques (Lehndorff et al., 2006), which enable the recognition of fine to ultrafine particulates. These result from high-temperature combustion processes that are of great environmental concern due to their easy respiratory uptake. The technique, however, is unsuitable for the investigation of non-magnetic particulates, which requires the analyses of a wider suite of elements in plants originating from a variety of different processes.

In general, elements in plants can be attributed to biogenic, lithogenic, and anthropogenic sources (Bargagli, 1998) and may be differentiated due to the following criteria: elements exceeding the essential element concentration in pine needles may be attributed to additional uptake via soil or bedrock enriched in certain elements or to atmospheric wet and dry deposition. Source apportionment can be achieved by analyses of element concentration in soil/bedrock and plant and calculation of enrichment factors (EFs) (Bargagli, 1998; Sardans and Penuelas, 2006). Elimination of elements associated with dust particles loosely attached to the needle surface is achieved by washing in distilled water (Migaszewski et al., 2001; Galuszka, 2005). Identification of anthropogenic versus lithogenic contributions or dust loadings is done by calculating enrichment of selected elements versus average dust composition using reference elements (Bargagli, 1998; Sardans and Penuelas, 2006). Dust composition is either determined by collection of dust particles in the study area and determination of element concentrations or by using globally averaged dust elemental composition (McLennan, 2001). A variety of source indicator elements have been identified and the preferred mode of emission from anthropogenic activities has been compiled (Pacyna and Pacyna, 2001). The knowledge that certain indicator elements are most informative for pollution studies allows a reduction in the number of critical elements to be studied.

Environmental biomonitoring frequently aims towards identification of spatial or temporal variations in critical element loads and thus requires knowledge on accumulation histories of pollutants in needles or leaves of perennial plants. Sampling of different needle cohorts and repetitive sampling over the growing season allows identifying seasonal effects, approach of equilibrium concentrations and degradation or detoxification processes. Pine needle element loadings have been studied for several needle ages and a systematic increase in element concentrations was observed for non-washed (Rautio et al., 1998; Giertych et al., 1999; Sawidis et al., 2001; Tzvetkova and Hadjiivanova, 2006) and washed samples (Migaszewski et al., 2001; Galuszka, 2005).

We here present a detailed pollutant accumulation study of *P. nigra* needles up to 5 years in age, collected separately to represent summer and winter concentrations for the environmentally relevant elements Ba, Ca, Cd, Fe, Mo, Na, Pb, Sb, Ti, V, Zr, and rare earth elements (REE). Pines were sampled at six different locations selected according to highly different emission scenarios as shown by an environmental magnetic biomonitoring survey (Lehndorff et al., 2006).

2. Locations and sampling methods

The study area of the greater Cologne Conurbation has been described in detail in a previous publication (Lehndorff et al., 2006) and thus only the most important characteristics are summarized here. The six stations selected for investigating the accumulation of major and trace elements on pine needles were chosen to represent natural background and exposition towards region-specific anthropogenic emission sources (Table 1). Sample collection procedures are specified in Lehndorff et al. (2006) and aimed towards exclusion of local point sources, differentiation between summer versus winter seasonal effects and recovery of maximum number of needle age classes (3–5). For analysis of major and trace elements, 51 samples were obtained from the six locations studied.

3. Analytical methods

Pine needle collection was performed as given in Lehndorff et al. (2006) by using a pruning shear on an extension device. Samples were stored frozen at $-15\,^{\circ}C$ until analyses. A total of >600 needle subsamples (4 per tree, 3 trees per location, ca. 9 needle cohorts, 6 locations) were used for the preparation of 51 composite samples.