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Magnetic biomonitoring by moss bags for industry-derived air pollution in SW Finland

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HIGHLIGHTS

- Active magnetic monitoring by moss bags allows easy and detailed data collection.
- Exposed moss bags are enriched with low-coercivity magnetite and elements.
- Pipe emissions are not the source for the hot spot areas.
- Hot spots are due to slag processing, heavy traffic, and/or other unknown sources.

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ABSTRACT

We provide the first detailed case study using *Sphagnum papillosum* moss bags for active magnetic monitoring of airborne industrial pollution in order to evaluate the actual role of various emission sources and the competence of current environmental protection actions relative to the air quality. The origin and spatial spreading of particulate matter (PM) based on magnetic, chemical, and SEM-EDX analyses was studied around the Industrial Park in Harjavalta, SW Finland. The data was collected during two 6-month sampling periods along 8 km transects in 2010–2011. The results support our hypothesis that the main emission source of PM is not the Cu–Ni smelter's pipe as presumed in previous chemical monitorings. We argue that the hot spot area within the severe impact pollution zone is related to slag processing and/or other unidentified industrial activity. At short distances various dust-providing sources outweigh the fly-ash load from the Cu–Ni smelter's pipe. Active magnetic monitoring by moss bags will help in planning environmental actions as well as in improvement of health conditions for industrial staff and town residents living next to the Industrial Park.

1. Introduction

The main source for urban air pollution is anthropogenic processes, especially industry and heavy traffic. Increasing urbanization and the number of vehicles have recently directed research on air pollution originating from traffic rather than from industry. Tight environmental legislation and regulations, and the use of the best available technique (BAT) have decreased industrial emissions in developed countries and resulted in improved air quality on national and even continental scales (Fabian et al., 2011). Nevertheless, industry still has major local and regional impacts on environment and human health (Hansard et al., 2011) while demands for even tighter discharge or emission limits are emerging.

Traditional air pollution/quality monitoring techniques include automatic sampling stations and biomonitoring, i.e. the use of organisms and biomaterials to obtain quantitative information on the quality of the environment (Markert, 2007). Need for spatially detailed data about air pollution dispersal, particle composition, and grain size is increasing while the number of monitoring stations often becomes a limiting factor. The data collected by automatic stations is extrapolated to wide city areas as public exposure estimates (Violante et al., 2006). Since such data has high temporal resolution but poor spatial coverage (Hansard et al., 2011), local variations and other pollution sources may remain hidden. Passive biomonitoring with *in situ* mosses have weak temporal resolution but high spatial coverage which might be hindered by moss desert in heavily polluted areas. Thus, active biomonitoring with moss transplant technique is very useful and enables spatially and

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temporally accurate data (e.g. Adamo et al., 2007; Ares et al., 2012; Vasconcelos and Tavares, 1998).

During the past two decades, the methods of environmental magnetism have been successfully applied in biomonitoring of leaves, needles, lichens, and mosses (e.g. Chaparro et al., 2013; Fabian et al., 2011; Hansard et al., 2011; Lehndorff et al., 2006; Salo et al., 2012). Magnetic methods are an easy and a fast way to map or monitor spatial and temporal changes in the environment. Dusts and exhaust gases released from industry- and traffic-related combustion processes contain ferrimagnetic particles, particularly iron oxides such as magnetite or maghemite, and heavy metals. Due to the common origin, significant correlations between magnetic parameters and heavy metal concentrations have been reported in several enviromagnetic studies (e.g. Gautam et al., 2005; Petrovský et al., 2000; Yang et al., 2010).

Pleurocarpic mosses such as *Sphagnum* retain nutrients and pollutants straight from the rain and dry deposition because they lack a cuticle and root system. Ares et al. (2012) state that the genus *Sphagnum* is the most commonly used in transplant studies. Moss bags of *Sphagnum girgensohnii* and *Sphagnum papillosum* have been used in monitoring metal pollution near an industrial site in Harjavalta, Finland (Hynninen, 1986; Jussila, 2003, 2009). Vasconcelos and Tavares (1998) used bags of *Sphagnum auriculatum* in Oporto city, Portugal, and observed the highest metal uptake during the first days of exposure. Aničić et al. (2009) exposed both dry and wet bags of *S. girgensohnii* in Belgrade, Serbia. Results indicate that both exposure methods may be used for biomonitoring of air pollutants since they showed very similar trends of element accumulation. The comparison between moss bags made of *S. girgensohnii* and *Hypnum cupressiforme* in the city of Sofia, Bulgaria, resulted in the latter species being less suitable for active monitoring (Culicov and Yurukova, 2006). Adamo et al. (2007) submitted moss *H. cupressiforme* for different treatments (water washing, oven drying, HNO_3 washing, and NH_4-oxalate extraction) prior to the exposure as bags in Naples and Trieste, Italy, and concluded that the accumulation performance of devitalized moss does not significantly differ from that of a living one. They recommend to use the oven drying for moss devitalizing since it is more eco-friendly than acid washing. However, oven drying does not even out the element levels in the moss material by releasing elements bound to cation exchange sites (Ares et al., 2012).

In the case of Harjavalta Industrial Park, the pollution includes various sources such as smokestack emissions, heavy industrial traffic, and unloading, transporting and storing of raw materials and wastes. Environmental protection actions, locally in Harjavalta as well as in global industry, have focused on smokestack emissions whereas the importance of other sources has been less investigated. Compared with previous monitoring studies, we provide more detailed results for the estimation/identification of smokestack emissions in order to evaluate the competence of the current environmental protection actions for improvement of the air quality. The hypothesis of our research is that nowadays the local pollution load of airborne particulate matter (PM) from the Industrial Park is mainly caused by other pollutant sources than the Cu–Ni smelter's pipe. Our aim was 1) to map the characteristics and spatial spreading of air pollutants with magnetic methods, and 2) to identify the most important industrial emission sources affecting the local air quality. In this article we report the first spatially representative detailed biomagnetic monitoring with moss bags made of *S. papillosum* over a sampling period of one year (2010–2011). The moss bag methodology used in this study as well as in previous bioindicator studies around the Industrial Park follow the Finnish standard SFS 5794.

2. Samples and measurements

2.1. Study area

The town Harjavalta (61°19′N, 22°19′E) is located in southwestern Finland (Fig. 1(A)). It has an area of 128 km^2 and about 7500 residents. Harjavalta belongs to the southern boreal coniferous zone and the Kokemäenjoki River bypass the town center in the direction of SE–NW. Industrial Park, a cluster of heavy metal and chemical industries, is located within 1 km to the SW from the center. Its primary products are copper, sulfuric acid, nickel and special chemicals, as well as fertilizers. Industrial Park is one of the largest point sources for heavy metal emissions (Salemaa et al., 2001), and one of the most intensively studied areas in Finland. Two monitoring stations survey the air quality (PM_{10} and SO_2 level) constantly at town center and residential areas. Further, ELY Centre Satakunta has obliged the industrial companies to monitor the air quality and metal emission spread in every fifth year by the bioindicator studies and moss bag technique.

The Cu–Ni smelter complex is considered as the main source of air pollution in Harjavalta. Common pollutants are sulfur dioxides, dust, and heavy metals such as Cu, Ni, Zn, Pb, As, Cd, and Hg. In 2001 and 2011, the average annual emissions of SO_2 were 3387 t and 2970 t, and of total dust 50 t and 6.8 t, respectively. Smelting produces annually over 300,000 t of Cu-slag and over 150,000 t of granulated Ni-slag which are deposited in separate heaps and eventually landscaped (ELY Centre Southwest Finland, 2009). The slag heaps are an additional source of dust emissions when they remain uncovered or the edges dry out (Nieminen et al., 2002).

2.2. Sample preparation

The moss bags were prepared after Finnish standard SFS 5794 (Finnish Standards Association, 1994), except for the longer exposure time. First, the green parts of the moss *S. papillosum* were collected from a non-polluted bog. After removing the pieces of other vegetation and litter, the moss was washed in 0.5 M HCl and rinsed with deionized H_2O to even out the element levels. Approximately 30 g of wet moss was placed in a polyamide net (with 0.64 cm^2 mesh) and closed with a cotton thread. Part of the acid-washed moss was stored as a non-exposed control sample (amount corresponding to 10 moss bags) which magnetic and chemical results were subtracted from the data.

Five moss bags were tied in trees at a height of 2.5–3 m in each sampling site. Sampling continued for one year: the first set of moss bags were placed from December 2010 to June 2011, and the second from June to December 2011. Thus, collection periods were 179–183 and 181–185 days. Six month collection periods were a compromise in order to reduce the sample amount and to test the moss bags' permanence. Further, the main interest in our study was the spatial, rather than the temporal representativeness of the data. The bags were situated along eight transects approximately at the distances of 0.5, 1, 1.5, 2, 3, 4, 6, and 8 km from the Cu–Ni smelter's pipe (Fig. 1(C)). Our transects include the previous transects used in chemical moss bag study by Jussila (2003, 2009) in 2001–2002 and 2007 and the results are comparable through monthly accumulation rates (mg kg^{-1}/month). The background level for pollutants was determined from the southern shore of Sääksjärvi Lake locating 17.5 km in NE from Harjavalta. Local circumstances such as wind conditions and tree cutting affected the moss bag permanence and sample loss. In total, 6 and 15 samples were lost in period I and II, respectively. The prevailing wind directions and the strongest winds (>4 m s^{-1}) in the study area were from S–SW–W–NW during the first period, and SE–S–SW during the second (Fig. 1(D) and (F)).