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Monitoring of heavy metal concentrations in home outdoor air using moss bags

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The long-term spatial distribution of heavy metals, measured with moss bags, is mainly determined by proximity to bus lines.

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ABSTRACT

One monitoring station is insufficient to characterize the high spatial variation of traffic-related heavy metals within cities. We tested moss bags (*Hylocomium splendens*), deployed in a dense network, for the monitoring of metals in outdoor air and characterized metals' long-term spatial distribution and its determinants in Girona, Spain. Mosses were exposed outside 23 homes for two months; NO_2 was monitored for comparison. Metals were not highly correlated with NO_2 and showed higher spatial variation than NO_2. Regression models explained 61–85% of Cu, Cr, Mo, Pb, Sb, Sn, and Zn and 72% of NO_2 variability. Metals were strongly associated with the number of bus lines in the nearest street. Heavy metals are an alternative traffic-marker to NO_2 given their toxicological relevance, stronger association with local traffic and higher spatial variability. Monitoring heavy metals with mosses is appealing, particularly for long-term exposure assessment, as mosses can remain on site many months without maintenance.

1. Introduction

It is well known that air pollution affects human health (Dockery, 2009; Kunzli and Tager, 2005). Atmospheric particulate matter (PM) induces adverse effects on the respiratory and cardiovascular systems through various mechanisms (Nel et al., 2001; Simkhovich et al., 2008; WHO, 2006). There is emerging interest in the toxic features of ultrafine particles, as a source of highly oxidative constituents bound to their surface (de Kok et al., 2006). Several recent studies identified particle bound heavy metals as particularly relevant in causing the health effects of particles (Bell et al., 2009; Chen and Lippmann, 2009) such as induction of oxidative stress (Nel et al., 2001) and mitochondrial damage (Li et al., 2003), which ultimately lead to an increase in cardiovascular morbidity and mortality (Araujo and Nel, 2009).

Most existing studies relied on environmental concentrations of PM-constituents measured at a few locations. A primary challenge in the assessment of long-term exposure to local traffic-related pollutants – such as ultrafine particles and related constituencies – is its high spatial variation on the local scale along busy roads and street canyons, which are a typical feature of many compact

Abbreviations: ADT, average daily traffic; Al, aluminum; As, arsenic; Sb, antimony; Cd, cadmium; Cr, chromium; Cu, copper; Pb, lead; Pt, platinum; Mo, molybdenum; Sn, tin; Zn, zinc; NO_2, nitrogen dioxide; NO_x, nitrogen oxides; PM, particulate matter; $PM_{2.5}$, PM_{10}, the fraction of aerosol particles with the aerodynamic diameter less than 2.5 μm and 10 μm respectively; REGICOR, Girona Heart Register (*Registre Gironí del Cor*) Study.

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European cities (Hoek et al., 2008). Therefore, to characterize long-term exposure to these local pollutants it is not sufficient to rely on one or a few monitoring stations. The spatial contrasts of pollutants emitted by traffic can be very large within the first hundred meters of roads (Monn, 2001), reaching background levels after some 100–200 m only (Hoek et al., 2008). A dense network of long-term measurements is thus needed to capture the spatial contrasts of these contaminants (Harrison and Deacon, 1998). This has been done extensively with passive samplers using mostly NO_x and occasionally other traffic-related gases, used as markers of traffic-related pollutants. Due to the saturation of samplers, repeated deployment of passive samplers for a few (often two) weeks is needed to describe long-term average conditions. Conventional measurement of PM mass concentration or particle bound toxicants, including metals, is even more demanding and costly, and thus long-term monitoring at a high spatial resolution is prohibitive.

The purpose of our study was to characterize the long-term small-scale spatial distribution of heavy metals, using mosses as biomonitors of particle bound metals, and to identify the main determinants of the spatial distribution of these metals in Girona (Spain). We also compared the spatial distribution of heavy metals to that of nitrogen dioxide (NO_2) as commonly used markers of traffic-related local pollution.

Biomonitoring techniques, such as moss sampling, allow monitoring pollutants for long periods of time. With the active biomonitoring technique a small amount of moss is exposed in the sites of interest and analyzed subsequently (also known as “moss bag” method (Goodman and Roberts, 1971)). Accumulation of deposited particulate matter takes place on the moss for as long as it is exposed, which can be several months. These features are very appealing for the use of moss bags as long-term markers of airborne metals in epidemiologic studies investigating health effects of long-term exposure to air pollution. Elemental deposition in moss bags has been shown to be highly correlated both spatially and temporally with PM_{10} measurements, with Pearson correlations for, e.g., Cu reaching 0.94 in mosses versus PM_{10} (Cao et al., 2009). Recent studies have used moss bags to measure urban pollution from several sources (Fernandez et al., 2004; Makholm and Mladenoff, 2005; Tretiach et al., 2007), and a few have focused on traffic-related pollution (Anicic et al., 2009a; Cao et al., 2009; Naszradi et al., 2007; Viskari et al., 1997). Our study is the first to use the technique to characterize home outdoor exposure at people’s residences which is of particular relevance in epidemiological research. In fact, our study is part of the exposure assessment strategy of the REGICOR-Air project (www.regicor.org), an ongoing cohort study conducted in Girona, Spain, which aims to determine the long-term effects of local traffic-related air pollution on cardiovascular health, including atherosclerosis. (Kunzli et al., 2005).

2. Materials and methods

We monitored ambient air concentrations of heavy metals by placing moss bags on balconies of REGICOR participants’ homes for 2 months. The moss bags were distributed over 23 sites across Girona and Salt (Spain). The heavy metal concentrations in mosses were then measured in order to define their distribution. Traffic-related variables were collected to establish their relationship to the metal concentrations. Palmes NO_2 passive samplers were deployed in parallel with the moss bags.

2.1. Study area

The geographic area of study is located in Girona and Salt, neighboring cities of the Girona province, in northeastern Spain, with 96.188 and 29.985 inhabitants (INE, 2009) and an area of 39.1 and 6.59 km^2 respectively. These cities were chosen because of their broad contrasts in NO_2 levels. NO_2 is considered a marker of traffic-related emissions, and thus, substantial contrast of other traffic-emitted pollutants such as heavy metals was expected.

The monitoring was performed at 23 sites: 20 homes of the REGICOR study participants and research partners, two street locations and one park (see map in Fig. 1), selected to cover all residential sectors of the study area and to be homogeneously spread across space and the previously characterized NO_2 distribution. Only non-smoking households with an accessible balcony were selected for the deployment of the mosses and NO_2 samplers. In line with our objective of small-scale pollutant characterization monitoring density was rather high (one moss bag per 0.5 km^2).

2.2. Collection, pre-treatment and exposure of mosses

Hylocomium splendens was chosen as the biomonitor because it has been widely used and its uptake capacity has been investigated thoroughly (Zechmeister et al., 2003). Collection and pre-treatment were made following internationally approved techniques (Harmens et al., 2010; Rühling and Steinnes, 1998). On March 2008, naturally grown mosses were collected in a 50-m^2 parcel in the Großarl Valley, a rural area close to Salzburg (Austria). The moss was cleaned from any litter and adhering macroscopic particles, brown leaves were cut off and discarded and only the green parts of the mosses representing the growth of the last two years were kept. The remaining moss material was rinsed three times with double distilled water, dried at 40 °C for 72 hours and homogenized by mixing all materials to prevent differences in the moss bags composition. Four subsamples were taken for pre-exposure analysis to determine pollutants background levels. Mosses (5 g) were packed in polypropylene bags, airtight sealed and sent to the study center (Barcelona) where the preparation of the moss bag for exposure took place.

The bags were prepared by putting moss loosely on a wooden frame of 10 cm × 10 cm, equipped with a fine polypropylene net of 1 cm × 1 cm mesh size that maintained the leaves within the frame using the system (see Fig. 1) developed by Zechmeister et al. (2006). The monitors were exposed for 8 weeks in May and June 2008. The moss bag was set on the balcony at a sheltered location to avoid any wet deposition as well as a potential washout of already deposited particles. When such a location did not exist, an acrylic roof was fixed on top of the moss frame. The balconies were at heights between 3 and 21 m above the street level.

Most studies using moss bags expose them for 1–4 months. We selected an exposure time of eight weeks knowing that accumulation of air pollution tracers increases linearly with time over a 4-month period (Anicic et al., 2009b).

While exposed, the mosses were not irrigated as few differences between wet and dry moss bags have been found (Anicic et al., 2009b) and the simpler logistics of the dry moss technique makes it more suitable for monitoring at participants’ homes.

To measure NO_2, a diffusion tube was installed next to the moss, exposed for one month and then replaced by a new tube deployed during the second visit. During this visit (June 2–6) we also verified that the measurement instruments were working properly. At the third and final visit (June 30–July 4) the samplers were collected and packed in tightly sealed PVC bags. Questionnaires were administered during the visits to identify unusual situations related to the measurement instruments and environmental conditions.

2.3. Chemical analysis

After monitoring, the chemical analysis was performed in the University of Natural Resources and Applied Life Sciences, and the Umweltbundesamt GmbH laboratories (Vienna). A detailed description of the analytical method is given in the Supplementary data. Briefly, the moss was dried at 30 °C and grinded prior to microwave digestion in nitric acid and hydrogen peroxide. Concentrations of Al, As, Cd, Cr, Cu, Mo, Pb, Sb, Sn and Zn were measured by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) carried out on an Element 2 ICP-SFMS (Thermo Fisher, Bremen, Germany). Quality control was performed by analyzing microwave digestion blanks prepared with ultra-pure water; adding Indium (1 μg/L) to all samples before ICP-SFMS as an internal standard; and using the certified reference material TM 27.2 (low level fortified sample for trace elements) for calibration quality.

The chemical analysis of the NO_2 samplers was performed at the AEA Energy & Environment laboratories (London). NO_2 was analyzed colorimetrically (Bran and Luebbe autoanalyzer) as described by Targa et al. (2008).

2.4. Determinants of spatial distribution of pollutants

To identify local determinants of the distribution of heavy metals in ambient air, geostatistical techniques were used to derive information on potential variables for each location, namely traffic intensity (average daily traffic ADT), percentage of heavy vehicles, number of bus lines and stops in the nearest street, distance from sampler to traffic, height above the street, degree of urbanization and characterization of the site’s surroundings such as crossroads and open areas. The proximity from the site to a river was also considered as three rivers cross Girona. The Onyar River, flowing through downtown, has major streets on both sides. Traffic count data were provided by several sources including the urban mobility plan (PMU-Girona, 2007) and a city noise mapping project (Deltell, 2005). Site characterization data were collected by manual measurements using high-resolution maps from the