Comparison of traditional moss bags and synthetic fabric bags in magnetic monitoring of urban air pollution

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Abstract

In this study, the properties and collection efficiencies of two different sample materials are compared for seasonal and spatial variation of traffic-induced particle matter in Turku city centre, southwest Finland. The sampling was done by exposing *Sphagnum papillosum* moss bags and Filtrete™ fabric bags simultaneously in spring during the road dust period and in autumn during the leafless period for about 47 days in 2015. Most polluted areas are located near heavily trafficked areas and intersections. PM accumulation in the city centre at the air quality monitoring station is the lowest among the sample sites, which indicates that the station underestimates air pollution levels and its relocation should be considered. Magnetic and elemental comparisons show that both bag materials function well in air pollution monitoring. However, the magnetic enhancement in the fabric bags is four times higher in spring than in autumn, while such observation is not detected in the moss bags. This indicates that the collection efficiency of moss bags is similar when the mitigating effect of vegetation is in minimal. Furthermore, we suggest it is more suitable to use the fabric bags in dry and dusty conditions and the moss bags in wet conditions. Based on the results, we consider that overall the moss bags are a better choice for air monitoring studies in the Nordic conditions than the fabric bags.

Keywords: environmental magnetism, magnetic biomonitoring, material comparison, traffic, particle matter, road dust

1 Introduction

In the absence of heavy industry, traffic is the major source of air pollution in urban areas. Typical traffic emissions include exhaust gases, such as carbon monoxide (CO) or dioxide (CO_2), liquids (leakages), and particle matter (PM) from the abrasion of various car parts and road surfaces (Kupiainen, 2007; HEI, 2010). In the world's sub-arctic regions, such as the Nordic countries, North America and Japan, the road dust period in spring is a significant source of PM (Kupiainen, 2007). Road dust originates from road sanding and salting and the surface abrasion caused by studded tires. After the snow melts, the road dust is re-suspended in the air through wind, traffic-induced turbulence and street spring cleaning activities. The road dust period typically lasts for four to eight weeks.

Air quality in urban areas is regularly monitored using fixed monitoring stations. Their temporal accuracy is high but spatial coverage and representativeness is typically poor because of their high costs and limited number (Hansard et al., 2011). The spatial resolution of air quality studies needs to be enhanced so that urban air quality can be managed more effectively. Magnetic techniques combined with biomonitoring provide a practical, efficient, and economical approach to air quality investigations. Magnetic methods function as a proxy for iron-bearing minerals and particle matter (PM) as well as associated heavy metals; thus they can be used, for example, in the identification of pollution sources and determining the properties and distribution of PM (e.g. Petrovský et al., 2000; Chaparro et al., 2015; Marié et al., 2018; Wuyts et al., 2018). Biomonitors can be applied, these include leaves, needles, lichens, plants, and active moss bags (e.g. Salo et al., 2012; Sant'Ovaia et al., 2012; Castañeda-Miranda et al., 2014; Cao et al., 2015; Vuković et al., 2015; Paoli et al., 2017). Moss bags collect various pollutants simultaneously and since they are easy to place, they enhance the spatial and temporal resolution of the data. Moss bags are very useful in urban areas lacking native biomonitor species due to high pollution levels or seasonal conditions (Salo & Mäkinen, 2014; Salo et al., 2016a).

Since the moss bag technique has no international standard, the results from different studies or countries may be difficult to compare. Protocols are currently recommended (see Ares et al., 2012, 2014; Giordano et al., 2013; Capozzi et al., 2017). The moss bag technique was standardised in Finland in the 1990s (SFS 5794; Finnish Standards Association, 1994). The principal difference between the Finnish standard and recommended protocols is in the devitalisation process of the moss material: acid washing is used in the Finnish standard while treatment with cellular extractants (EDTA and dimercapol) and oven drying is outlined in the protocols. Acid washing increases the bioconcentration capacity of moss and balances the element levels (Finnish Standards Association, 1994; Ares et al., 2012). In oven drying, the capacity increase requires the use of chelating agents. Comparison between acid washed and oven dried moss bags showed similar accumulation efficiency but oven drying was suggested due to its eco-friendliness (Adamo et al., 2007).

Furthermore, the preparation of moss bags is rather laborious and suitable species may not be available. It would thus be beneficial and solve the issue of comparability if a ready-made material was substituted for the moss material. Attempts to find a replacement material and a new approach to moss bags, or biomonitors in general, have emerged. Comparisons between moss bags, lichen bags and synthetic filters resulted in filters showing a poor performance and a recommendation to use moss material in air monitoring studies (Adamo et al., 2007; Giordano et al., 2013). A passive sampler design using natural wool as a sorbent showed similar results to needles and thus could be an alternative for biomonitoring (Cao et al., 2015). In addition, preliminary magnetic test indicated that the synthetic fabric bags made of Filtrete™ could be a potential substitute for moss and lichen bags (Salo, 2014).

In this study, we compare traditional moss bags (*Sphagnum papillosum*) and new synthetic fabric bags (Filtrete™) by investigating the seasonal and spatial variation and distribution of magnetic PM in Turku city centre, Finland. The bags were exposed to air pollutants for two seasons in 2015: the first season was in the spring during a road dust period and the second season in the autumn in a leafless period. Our main aim was to compare the collection efficiencies and properties of moss bags and fabric bags in order to evaluate their applicability in air monitoring studies.

2 Material and methods

2.1 Study area and collection periods

The city of Turku is located in the southwest of Finland; its total area is 306.4 km^2 and it has a population of 183,000. Traffic-derived nitrogen oxides (NOx) and PM significantly impact the air quality in the Turku region, while emissions from industry or energy production mainly have a low effect (Air Quality Expert Services, 2010). Traffic intensity ranges from below 2,000 to 30,000 vehicles per day in the centre (City of Turku, 2013). Two air quality monitoring stations operate in Turku: CO, NO_2 and PM_{10} are measured in the city centre at Kauppatori, and ozone (O_3) in Ruissalo 10 km to the west of the city. In the neighbouring cities, the stations measure NO_2, SO_2, and PM_{10} in Naantali, and NO_2 and PM_{10} in Raisio.

The majority of the sample sites (40) were focused on the grid plan area of Turku (Fig. 1A). The sampling area was delineated by using the most traffic intensive roads and was extended to both the southern and northern sides of the Aurajoki River. Three sample sites were situated at the air quality monitoring stations: site 38 in the centre of Turku, site 37 in Naantali (about 14 km west of Turku) and site 36 in Raisio (about 7 km northwest of Turku). The background sites were located on Ruissalo island (BKGD 1, air quality monitoring station close to the city centre) and Parainen island (BKGD 2, in the countryside about 35 km to the south of Turku centre).

The sampling was done by simultaneously exposing the moss bags and synthetic fabric bags for two seasons in 2015. The first bag sets were placed from March to April (road dust period in spring) and the second set from November to December (leafless period in autumn). The collection periods were 47–48 days and 45–47 days, respectively. In the text, the following abbreviations are used for seasonal bag sets: MbS (moss bags spring), MsA (moss bags autumn), FbS (fabric bags spring), and FbA (fabric bags autumn).

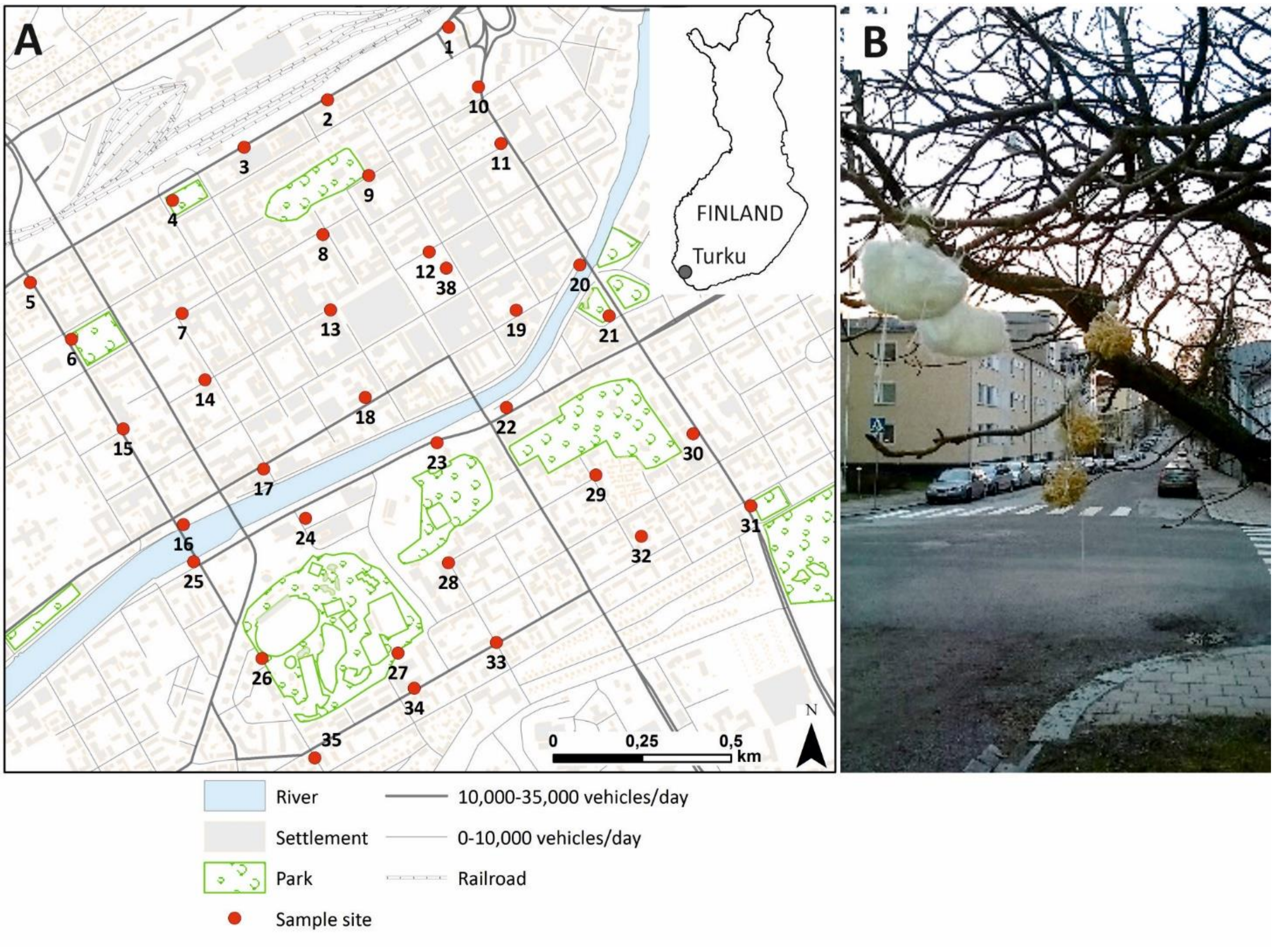

Figure 1. Sampling was targeted to the city centre of Turku, SW Finland (A). Site 38 was located at the air quality monitoring station. Outside of the map view sites 36 and 37 were located in the neighbouring cities of Naantali and Raisio, respectively, as well as the background sites 1 and 2. Moss bags and fabric bags were exposed together at all sites (B). © National Land Survey of Finland, 2013.

The prevailing wind directions and the strongest winds (>4 m s^{-1}) in the study area were from the northeast and southeast in spring, and the northeast and east in autumn. The conditions were drier and dustier in spring than in autumn (Fig. 2); the total precipitation was 21.55 and 112.5 mm while the total PM load was 24,426.6 and 8,543.2 µm m^{-3} respectively during the study seasons (City of Turku, 2015).

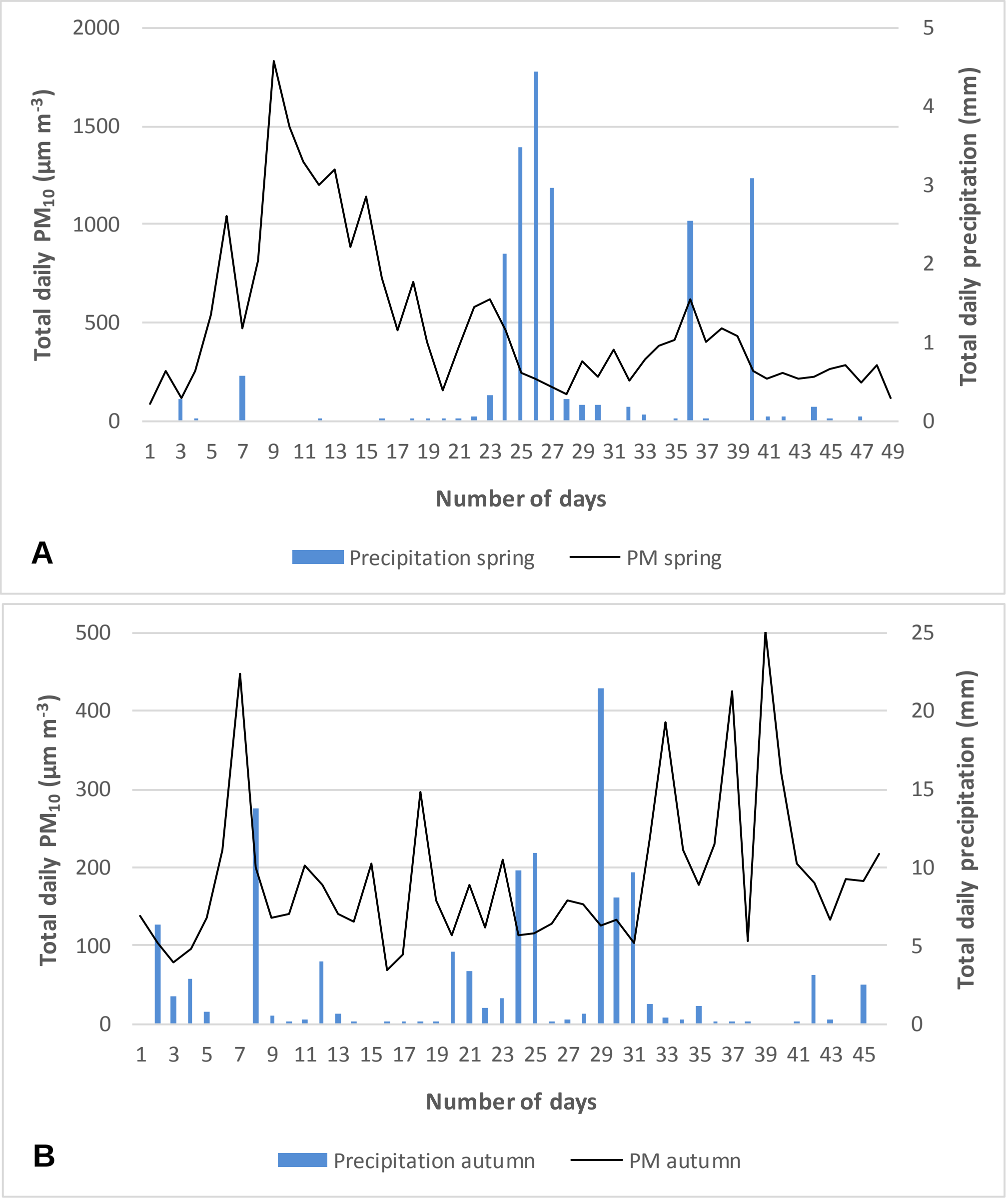

Figure 2. Total daily precipitation and PM$_{10}$ loads measured in Turku centre site 38 in spring (A, 4.3.–21.4.2015) and autumn (B, 6.11.–21.12.2015).

2.2 Sampling design

2.2.1 Moss bags

The moss bags were prepared according to the Finnish standard SFS 5794 (Finnish Standards Association, 1994). The green parts of moss *Sphagnum papillosum* were collected from a natural area and manually cleaned from litter and other vegetation in the laboratory. The moss was acid-washed in 0.5 M HCl and rinsed three times with deionized H_2O to balance the element levels and neutralise the material. Fifteen grammes (wet wg.) of moss was placed in a nylon net with an 0.64 cm^2 mesh and closed with a cotton thread. At each site, three spherical moss bags were tied to the outer branch of a tree at a height of 2.5–3 m. Three moss bags were used to ensure that there would be enough moss material to measure after the exposure periods since moss bags may experience some loss during, for example, windy conditions. A composite sample for each site was formed in the laboratory.

The samples were dried to a constant weight in T <40 °C and ground to a fine powder with a Retsch PM100 planetary ball mill (500 rpm, 20 s) equipped with a zirconium oxide (ZrO_2) grinding jar and balls. One part of the acid-washed moss (an amount corresponding to 30 bags) was stored in the freezer as a control moss, and this was not exposed to air pollution. The ground moss material was used for magnetic and chemical analyses.

2.2.2 Fabric bags

The fabric bags were made of a synthetic Filtrete™ (GSU-100 in spring, GSU-60 in autumn). However, GSU-100 was then replaced in the markets by GSU-60, which is the thinnest Filtrete™ material. The fabric has an electrical charge, which makes it effective for trapping small particles, such as pollen and air pollutants. It is used as a filter fabric in ventilation windows to clean the incoming air. First, the fabric was ripped into 5 cm by 10 cm pieces. Four pieces (dry wg. 2.5 g in spring, 2.0 g in autumn) were loosely packed in a nylon net with an 0.64 cm^2 mesh and closed with a cotton thread. At each sampling site, two spherical fabric bags were tied on the outer branch of a tree at a height of 2.5–3 m. Fabric bags do not experience a similar material loss as moss bags do during exposure, and thus two fabric bags were considered adequate. In the laboratory, a composite sample for each site was made and dried to a constant weight in T <40 °C. Grinding was not possible due to the properties of the material. Half of the fabric strips (uniform composition) were measured as a magnetic susceptibility control before the exposure, and part of the material was stored for control measurements of elements and other magnetic properties.

2.2.3 Filters

PM_{10} air filter samples were collected at three locations in the Turku region: in Turku centre (site 38) and in the neighbouring cities of Naantali (site 37) and Raisio (site 36). The samples were collected using a Thermo Scientific TEOM Series 1400A ambient particulate monitor (flow 0.82 m^3 h^{-1}, volume 19.68 m^3 24 h^{-1}) with Munktell quartz microfiber filters (diameter 47 mm, thickness 0.42 mm). The filters are made of high-purity borosilicate glass microfibers. The sampling times were the same as for the adjacent moss bags and fabric bags, i.e. 47–48 days in spring and 45 days in autumn. The filter samples were dried to a constant weight in T <40 °C. Their magnetic and elemental values were used as background information (Table 1).

Table 1. Mass-specific susceptibilities (χ x 10^{-8} m^3 kg^{-1}, spring/autumn) and element values (mg kg^{-1}, spring/autumn) of filter samples exposed at air quality monitoring stations in Turku (site 38), Naantali (site 37), and Raisio (site 36) (n/a = not available).

	χ	Al	Ba	Cr	Cu	Fe	Ni	Pb	Ti	V	Zn
Turku	1.9/5.2	260/240	9.1/11.0	2.8/4.5	6.5/16.0	510/720	110/15	7.9/10.0	19/23	3.1/5.5	38/69
Naantali	4.4/3.0	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Raisio	1.4/2.1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

2.3 Sample analysis

2.3.1 Magnetic methods

Mass-specific susceptibility (χ x 10^{-8} m^3 kg^{-1}), which is a concentration-dependent magnetic parameter, was measured using a Bartington MS2B dual-frequency (0.47 and 4.7 kHz) susceptibility meter in the Department of Geography and Geology, University of Turku. Two subsamples were prepared for each moss bag sample whereas filter samples and fabric bag samples were measured in full (total of one and four subsamples, respectively). To fill the standard 1 cm^3 plastic susceptibility containers, small and light filter samples were measured with 1.0 g of clean cotton wool; the mass-specific susceptibilities of the clean cotton wool having been premeasured. The filters were cut in half using plastic scissors and the halves were placed on the sides of the susceptibility container. All moss, fabric and filter subsamples were measured five times and the average value was used. Furthermore, control values for moss and fabric materials were subtracted from the data (Table 2). For control values, six subsamples were measured for the moss material while half of the fabric strips were measured before the bag preparation. One clean filter sample was used for the control measurements (0.0 x 10^{-8} m^3 kg^{-1}). The final data reflect the accumulation of air pollutants in each sample material during the collection periods.

Hysteresis loops and temperature dependencies were measured using a Quantum Design SQUID-magnetometer in the Department of Physics and Astronomy, University of Turku. Hysteresis loops of selected samples were measured at a temperature of 300 K in a magnetic field up to 1 T. Saturation magnetisation (M_{RS}), saturation remanence (M_S), coercive force (H_C), and coercivity of remanence (H_{CR}) were obtained after the subtraction of the linear paramagnetic signal from the sample holder and clean moss κ using the fitting function

$$M(B) = M_{RS} \times ArcTan((B \pm H_c)/B_s)$$

to upwards the hysteresis loop (with – sign). Here M(B) is the magnetisation as a function of the magnetic field B and B_S is a scaling constant. The saturation remanence was determined as the magnetisation value at the zero field M(0). H_{CR} was determined by solving numerically the field where the difference between the upward and downward branches was equal to 0.5.

2.3.2 Chemical analysis

Moss and fabric bag samples from the sites 1, 2, 9, 10, 16, 38, and BKGD 1 for both seasons were selected for chemical analysis based on 1) availability of both bag types from both seasons, and 2) representativeness of heavily and low trafficked areas. Filter samples from site 38 were also analysed (Table 1). The concentrations of ten elements (Al, Ba, Cr, Cu, Fe, Ni, Pb, Ti, V, and Zn) were analysed in the accredited laboratory of Nablabs, Jyväskylä (Finland). The moss bag samples were dissolved in a Teflon vessel in a microwave oven (Mars X, CEM) with 5 ml concentrated HNO_3 (suprapur). The fabric bags and filter samples were autoclave dissolved with 5 ml concentrated HNO_3 (suprapur). The element concentrations were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Jobin-Yvon Ultima 2) and mass spectrometry (ICP-MS, Agilent 7500CE). Three separate subsamples for each control moss and fabric batches were analysed, and the average element concentrations (Table 2) were subtracted from the final data. Analysis methodologies were SFS-EN ISO 11885 and 17294. Procedural blanks and two certified plant reference samples (BCR CRM 842 Lichen and NIST 1575a Pine Needles) were analysed simultaneously with acceptable results.

Table 2. Quantification limits (QL) for analysed elements, and initial average mass-specific susceptibilities (χ x 10^{-8} m^3 kg^{-1}, N=6 for moss) as well as average element concentrations (N=3, mg kg^{-1}) of control moss (CM1 and CM2) and control fabric (CF1 and CF2). Controls are indicated with standard deviation of subsamples, except when below the QL.

	χ	Al	Ba	Cr	Cu	Fe	Ni	Pb	Ti	V	Zn
QL		5	0.5	0.05	1.0	5	0.05	0.05	0.5	0.05	1.0
CM1	−0.3	47±2	1.1±0.0	0.4±0.4	1.3±0.0	283±9	0.2±0.0	0.5±0.1	4.0±0.2	0.3±0.0	3.0±0.5
CM2	−0.5	36±1	1.0±0.0	0.4±0.0	1.2±0.2	127±5	0.2±0.0	0.3±0.0	4.2±0.1	0.2±0.0	3.0±1.0
CF1	−1.3±0.3	40±1	<0.5	0.4±0.1	<1	8±5	1.1±0.3	0.8±0.9	1.4±0.5	<0.05	2±0.5
CF2	−1.4±0.4	24±8	<0.5	0.18±0.06	<1	<5	0.28±0.21	0.2±0.1	0.8±0.2	<0.05	<1

2.3.3 Statistical

Statistical analyses were performed with IBM SPSS Statistics version 21. All four bag sets showed non-normally distributed magnetic susceptibilities (Shapiro-Wilk test, $p \leq 0.05$). Element concentrations in the moss bags were normally distributed (Shapiro-Wilk test, $p > 0.05$), whereas in the fabric bags Al and Ba in spring and Cr in autumn deviated from the normal distribution (Shapiro-Wilk test, $p \leq 0.05$). Thus, we tested both the mean (with parametric paired samples t-test) and median (with non-parametric Wilcoxon signed ranks test) differences between the pairs of observations of the magnetic susceptibilities and elements. The correlations between the variables were calculated with the Spearman's rank order correlation coefficient (ρ) and the associated level of significance, which is robust to outliers and more appropriate for non-normally distributed data.

3 Results

3.1 Magnetic properties of moss bags and fabric bags

Based on mass-specific susceptibilities (χ x 10^{-8} m^3 kg^{-1}; Table 3), magnetic enhancement was observed throughout the study area in all four bag sets (MbS, MbA, FbS, FbA). Spatially, the enhancement was greatest at sites located next to the most traffic intensive roads (Fig. 3). This was especially the case at sites 1 (maximum χ in MbS, MbA, and FbS), 2, 3 (maximum χ in FbA), 10, and 31, which were all located next to roads with over 20,000 vehicles per day or at busy intersections with traffic lights. The sites in park areas and close to roads with less than or about 10,000 vehicles per day have lower magnetic PM loads. In all the sample sets, site 38, at the air quality monitoring station in the centre, showed lower susceptibilities than the average values of other sites (e.g. the MbS is 2.9 x 10^{-8} at site 38 and the average at the other sites is 13.1 x 10^{-8} m^3 kg^{-1}). The background sites have susceptibility values between 0.0 x 10^{-8} and 1.0 x 10^{-8} m^3 kg^{-1} (Table 3).

Seasonally, in both bag materials, the spring sets have statistically significantly higher median magnetic susceptibilities than the autumn sets (Wilcoxon signed ranks test, $p \leq 0.05$). The mean susceptibility values of the four bag sets showed the following seasonal order: FbS (27.3±16.9 x 10^{-8} m^3 kg^{-1}) > MbS (12.8±13.2 x 10^{-8} m^3 kg^{-1}) > MbA (11.5±12.8 x 10^{-8} m^3 kg^{-1}) > FbA (6.5±7.1 x 10^{-8} m^3

kg^{-1}). The differences in the median values are statistically significant (Wilcoxon signed ranks test, $p \leq 0.05$).

Table 3. Summary statistics (minimum, maximum, mean, median, and standard deviation without background samples, and background values) of mass-specific susceptibilities (χ x 10^{-8} m^3 kg^{-1}) and elements (Al, Ba, Cr, Cu, Fe, Ni, Pb, Ti, V, Zn in mg kg^{-1}) for moss bags (MbS = moss bags spring, MbA = moss bags autumn; N=36/35 for χ, N=6/6 for elements) and for fabric bags (FbS = fabric bags spring, FbA = fabric bags autumn; N=31/34 for χ, and N=6/6 for elements) (n/a = not available). Spearman's correlation coefficients (ρ) between magnetic susceptibilities and elements are calculated without the background samples.

	χ	**Al**	**Ba**	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Ti**	**V**	**Zn**
Moss bags (MbS/MbA)											
Min	2.1/0.8	133/144	2.9/4.1	1.2/0.9	1.9/3.9	187/223	0.3/0.5	0.4/0.7	14.0/9.8	1.0/1.0	25.7/41.0
Max	79.9/62.2	1953/1664	30.9/37.0	14.6/13.6	35.7/50.8	3217/3273	7.6/4.1	2.5/3.0	226.0/185.8	13.7/12.8	116.7/117.0
Mean	12.8/11.5	765/745	12.9/15.8	5.7/4.9	14.4/20.5	1253/1367	2.9/2.3	1.7/2.0	90.5/81.7	5.9/5.3	61.7/67.3
Median	9.5/6.7	683/529	11.9/12.0	4.8/3.3	14.2/15.8	1117/933	2.0/2.3	1.8/2.4	85.5/56.8	6.0/4.2	62.2/59.0
SD	13.2/12.8	670/669	10.1/12.9	4.8/4.8	12.0/17.7	1124/1273	2.6/1.4	0.8/1.0	79.1/77.2	4.5/4.6	31.5/28.5
BKGD 1	1.0/1.0	73/84	1.7/32.0	0.2/0.2	0.9/1.2	77/243	0.3/0.2	0.2/0.2	5.5/7.8	0.3/0.4	22.7/68
BKGD 2	0.0/0.5	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
ρ	*1.000*	*0.943*/0.986**	*0.943*/0.943**	*0.943*/0.943**	*0.928*/0.886**	*0.943*/1.000**	*0.143/0.429*	*0.290/−0.029*	*0.943*/1.000**	*0.886*/0.943**	*0.943*/0.886**
Fabric bags (FbS/FbA)											
Min	5.3/1.0	360/63	3.6/0.6	2.3/0.5	1.6/0.7	623/64	0.0/0.1	0.0/0.0	52.6/5.1	2.1/0.3	7.3/2.5
Max	71.9/32.5	2660/786	24.8/9.7	32.6/8.8	16.5/10.5	4793/1598	4.2/2.9	4.2/1.7	308.6/88.2	16.0/4.7	49.3/23.5
Mean	27.3/6.5	1783/290	16.6/3.5	17.1/2.7	11.0/3.8	3146/549	2.6/1.0	1.7/0.8	207.1/31.9	10.6/1.6	33.7/9.0
Median	21.6/4.2	2310/236	21.3/3.0	21.1/1.9	14.0/3.0	3993/448	3.5/0.5	1.6/0.7	258.6/25.2	13.0/1.1	39.3/7.0
SD	16.9/7.1	1070/267	9.7/3.3	12.1/3.1	6.3/3.6	1900/557	1.9/1.1	1.4/0.6	118.0/30.4	6.2/1.6	17.5/7.5
BKGD 1	0.6/0.0	70/0	0.8/0.0	0.3/0.0	0.8/0.0	113/9	2.3/0.0	1.2/0.0	8.6/0.4	0.3/0.0	2.3/0.5
BKGD 2	-/0.3	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
ρ	*1.000*	*0.551/0.943**	*0.600/1.000**	*0.946*/0.771*	*0.829*/1.000**	*0.600/1.000**	*0.657/-0.029*	*0.600/0.771*	*0.486/0.943**	*0.736/0.943**	*0.829**/1.000**

* correlation is significant at the 0.01 level

** correlation is significant at the 0.05 level

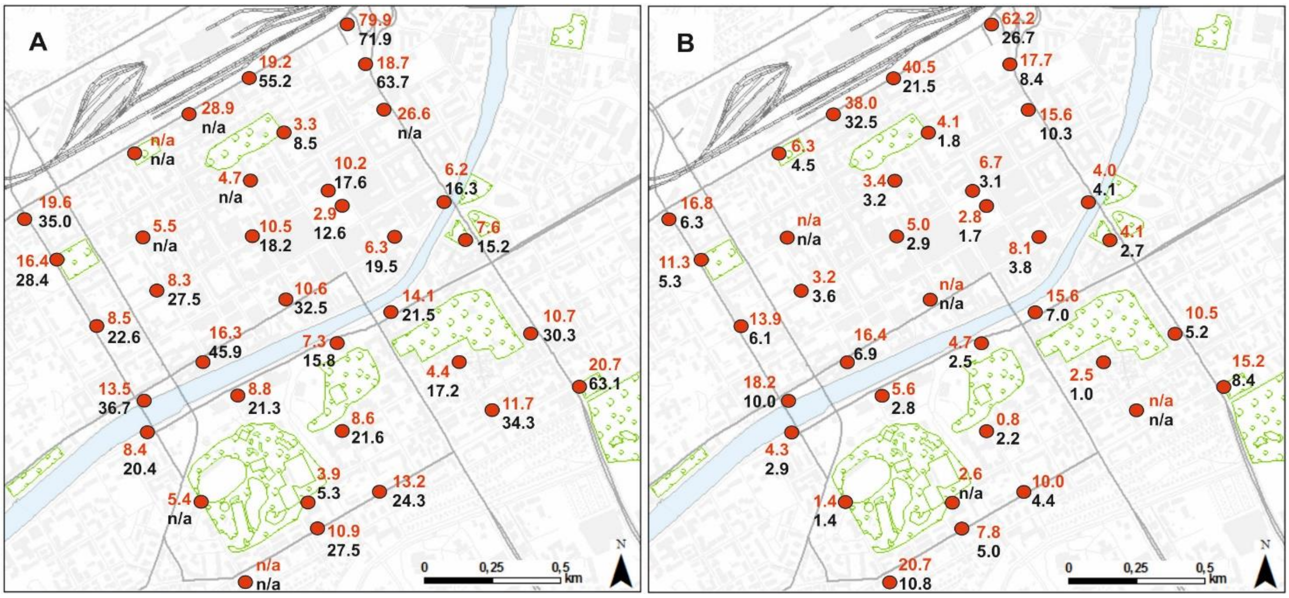

Figure 3. Mass-specific susceptibilities ($\chi \times 10^{-8}$ m^3 kg^{-1}, n/a = not available) of moss bags (upper value in red) and fabric bags (lower value in black) for spring (A) and autumn (B).

The hysteresis loops of the investigated samples are narrow and saturate rapidly at 0.2–0.3 T. The average values of H_C and H_{CR} are low to intermediate (Table 4). All the investigated samples were located in the pseudo-single-domain (PSD) region closer to the theoretical mixing line for superparamagnetic (SP)–single-domain (SD) grains than the mixing line for SD–multi-domain (MD) grains in the Day plot (Fig. 4). The samples, especially from the air quality monitoring station in Turku and the background sites, show this behaviour.

Table 4. Summary statistics (minimum, maximum, mean, standard deviation, and background value) of coercivity (H_C in mT) and coercivity of remanence (H_{CR} in mT) for filters, moss bags and fabric bags (spring/autumn). Background 1 is presented separately (n/a = not available).

	Filters		Moss bags		Fabric bags	
	H_C	H_{CR}	H_C	H_{CR}	H_C	H_{CR}
Min	4.6/4.0	56.2/57.0	4.1/4.1	60.3/58.1	3.5/3.9	639./65.6
Max	6.9/5.3	72.6/62.6	8.5/10.4	81.9/78.3	5.1/7.8	80.0/75.5
Mean	6.0/4.5	62.8/58.9	5.9/6.3	68.3/67.0	4.1/5.4	70.9/70.8
SD	1.0/0.6	7.1/2.6	1.4/1.9	5.9/5.4	0.5/1.3	4.7/3.6
BKGD 1	n/a	n/a	9.5/13.6	69.9/69.8	8.8/3.5	62.4/61.1

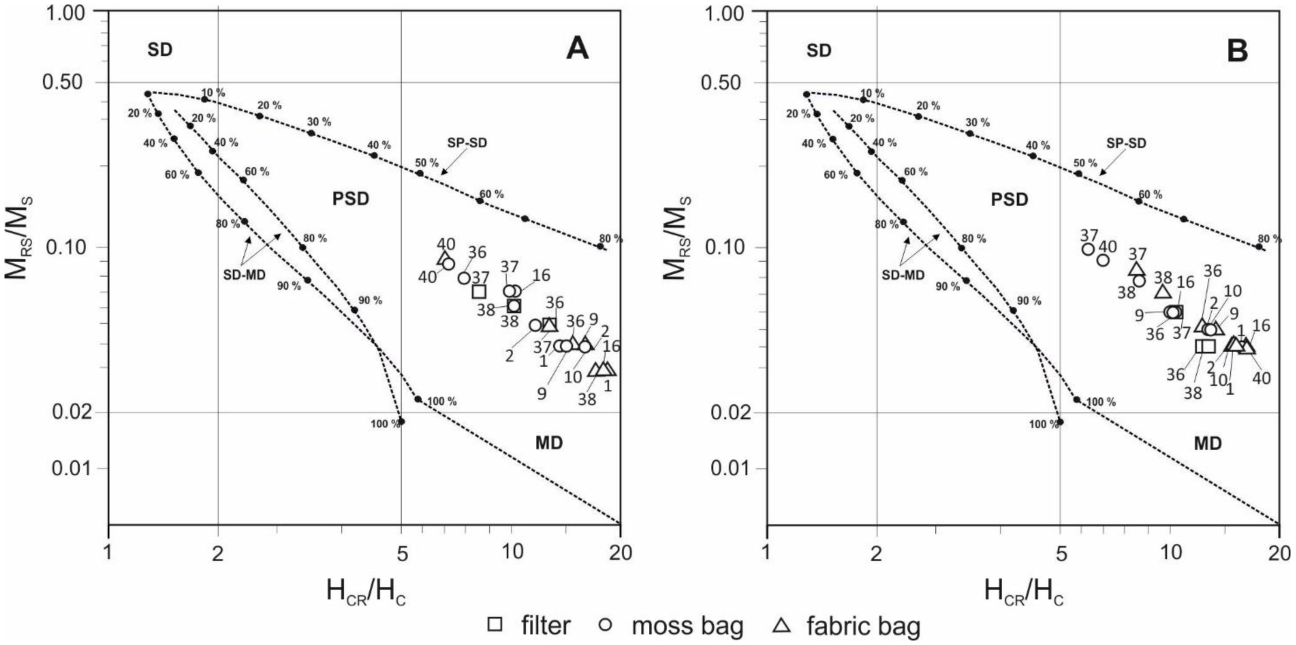

Figure 4. Day plot of ratios M_{RS}/M_S and H_{CR}/H_C of the filters, moss bags, and fabric bags in the road dust period in the spring (A) and the leafless period in the autumn (B). Single-domain (SD), pseudo-single-domain (PSD), and multi-domain (MD) boundaries for grains and mixing lines are shown after Dunlop (2002).

3.2 Element concentrations

Sites next to the most trafficked roads have the highest element concentrations. Site 1 especially, which is near a heavily trafficked intersection stands out as regards the MbS, MbA, and FbA of the sets, whereas site 16 is distinctive in the FbS for having the most elements analysed. For example, site 1 has Fe concentrations that are 12 times (MbS), 14.6 times (MbA), and 25 times (FbA) higher than site 38. The element levels at site 38 are overall lower than the average values of the other sites, except for Ni (MbS, MbA, FbA) and Pb (MbS, MbA).

Based on the mean concentrations, element order in the MbS and MbA is the same: Fe > Al > Ti > Zn > Cu > Ba > V > Cr > Ni > Pb (Table 3). Statistically, the mean values are similar (paired samples t-test, $p > 0.05$). The element order is slightly different in the fabric bags: Fe > Al > Ti > Zn > Ba > Cr > Cu > V > Ni > Pb in the FbS, and Fe > Al > Ti > Zn > Cu > Ba > Cr > V > Ni > Pb in the FbA. Moreover, comparison between FbS and FbA reveals that both the mean and median values of Al, Ba, Cr, Cu, Fe, Ti, V, and Zn are statistically significantly different (paired samples t-test and Wilxocon signed ranks test, $p \leq 0.05$) while values of Ni and Pb are similar (paired samples t-test and Wilcoxon signed ranks test, $p > 0.05$).

Seasonal comparison shows that the median values for six elements (Al, Cr, Fe, Ti, V, Zn) between MbS and FbS, and for all ten elements between MbA and FbA are statistically significantly different (Wilcoxon signed ranks test, $p \leq 0.05$). Furthermore, the rankings of the differences indicate that the element values are higher in FbS than in MbS, and higher in MbA than in FbA.

3.3 Correlations

The Spearman's rank order correlations between magnetic susceptibility and elements for MbS and MbA are in general statistically significant and strong (>0.800), whereas for FbS and FbA they are statistically insignificant and intermediate or strong (0.500–0.800) (Table 3). Al, Fe, and Ni show stronger correlations in MbS than in MbA while Al, Ba, Cu, Fe, Pb, Ti, V, and Zn are stronger in FbS than in FbA. Moreover, the seasonal variable comparison between the two bag materials shows that the correlations are generally intermediate in spring and strong in autumn (Table 3).

4 Discussion

4.1 Properties of magnetic air PM

According to Lecoanet et al. (2003), traffic emissions are dominated by ferromagnetic particles. In Turku, the hysteresis loops of moss and fabric bags (saturation at 0.2–0.3 T) indicated the presence of low-coercivity ferrimagnetic minerals, such as magnetite, in air pollution. In addition, the values of H_C and H_{CR} were typical for magnetite, maghemite, and pyrrhotite (Dekkers, 2007; Table 4). In an earlier study of Turku centre, the Verwey transition (T_V) in the temperature-dependent magnetisation of moss bags pointed to magnetite as the main magnetic mineral (Salo et al., 2016b). Thus, the magnetic enhancement in Turku is induced by the anthropogenic contribution of magnetite.

The size of anthropogenic (magnetic) PM accumulated by each bag set is closer to $PM_{<2.5}$ than PM_{10} because the samples were composed of PSD magnetite of an SP-SD grain sizes (Fig. 4). The upper threshold for PSD grains is about 10 µm while SD grains are between 0.03–0.50 µm and SP grains are below 0.03 µm (Dekkers, 1997). Moreover, the moss bags predominantly capture $PM_{<2.5}$ (79%) over a coarser fraction of $PM_{<2.5\text{-}10}$ (Tretiach et al., 2011). Small particles access respiratory systems and the deeper parts of the lungs, which makes them more harmful to human health than larger particles. Furthermore, PM can contain several pollutants, such as metals, organic compounds, and reactive gases. Health effects can be observed at all exposure levels, which indicates that some individuals are more prone and at risk even at low concentrations (Nel, 2005; WHO 2006). With spatially accurate air quality data, risk areas can be identified and thus effectively targeted protection actions can be initiated.

4.2 Spatio-temporal characteristics and representativeness of the data

In this study, the spatial intensity of magnetic and elemental enhancement is related to the traffic volume. Similar findings are available from other studies as well (e.g. Maher et al., 2008; Vuković et al., 2015). In Turku, sites with a high traffic volume (>30,000 vehicles per day) have greater magnetic susceptibilities and elemental loads while sites with low traffic volumes (<10,000 vehicles per day) have lower susceptibilities and elemental values (Fig. 3). For example, susceptibility is 24 (MbS), 8 (FbS), and 15 (MbA, FbA) times higher at site 1, a heavily trafficked area, compared to site 9, which is located at a low trafficked park corner.

Mean and median susceptibility values, which are statistically different, indicate that the fabric bags accumulate significantly more magnetic material in spring than in autumn; the magnetic enhancement is approximately four times higher in spring versus autumn. The enhancement in spring is a joint result of the Filtrete™'s properties, dry weather conditions, and suspended high PM loads present in the air and effectively captured by the material. The impacts of road dust to the (magnetic) PM contribution and element levels are reported in several studies (e.g. Kuhns et al., 2003; Gertler et al., 2006; Bućko et al., 2011; Salo et al., 2016b). Our previous study displayed a threefold enhancement in the moss bags' mean susceptibilities in the road dust period versus the summer season (Salo et al., 2016b) but this relationship is not detected between the seasons in this study. We suggest that this reflects the effect of the lack of vegetation mitigating air pollution dispersal and thus the trapping of PM. The results indicate that the moss bags' collection efficiency is good both in the spring and autumn seasons when vegetation, such as leaves, is at a minimal.

Since data from air quality monitoring stations are often extended to apply to spatially large areas, it is possible to review the results of site 38 as representing the whole centre of Turku. In all sample sets, the susceptibility values and almost all element concentrations, except Ni and Pb, at site 38 are lower than the average values of the rest of the sites. This further strengthens our previous conclusion (Salo et al., 2016b) that the air quality monitoring station in Turku underestimates the air pollution levels and its relocation should be considered to better manage the air quality in the area.

4.3 Comparison between the moss bags and fabric bags

The magnetic susceptibilities and element concentrations demonstrated that the moss bags and fabric bags accumulated magnetic air pollutants effectively in both investigated seasons (Fig. 3, Table 3). This indicates that both materials can be used for active monitoring of air PM pollution. However, statistically significant differences reveal that the fabric bags collected PM more effectively in the spring than the moss bags whereas the situation was *vice versa* in autumn. The observed seasonal differences (see 3.2 Element concentrations) between these two bag types are related to the weather conditions prevailing during the exposure periods (Fig. 2) as well as the material properties.

During the exposure periods, the weather in Turku was dryer in the spring and road dust period than in the autumn (Fig. 2; total precipitation 21.55 and 112.5 mm, respectively). According to Omstedt et al. (2005), road surface moisture controls the suspension of road dust particles from the surface into the air. Moreover, studded tyres and road sanding increase the road dust layer in wet conditions while suspension of particles by vehicle-induced turbulence decreases the layer in dry conditions. In Turku, the amount of PM was higher in the spring (24,426.6 $\mu g/m^3$) than in the autumn (8,543.2 $\mu g/m^3$). This indicates that more (magnetic) particles were present and suspended for a longer time in the air in spring than in autumn due to the road dust period and dry weather.

Mosses, especially ectohydric species such as *Sphagnum* spp., efficiently absorb moisture and dissolved substances from wet and dry depositions (Harmens et al., 2011). In addition, the lack of a cuticle enhances the uptake from the atmosphere over their entire surface (Szczepaniak & Biziuk, 2003). Several studies have found higher element concentrations in moss bags exposed to wet conditions than to dry conditions (e.g. Tavares & Vasconcelos, 1996; Adamo et al., 2003; Giordano et al., 2009). The results of our study indicate that the moss thrives and collects PM more efficiently in humid conditions whereas the filter fabric, which is water resistant, effectively captures air suspended PM in dry conditions due to its properties, such as an electrical charge.

Our previous studies show that the moss bags can be used in all seasons, including winter (Salo et al., 2016a), but in the summer season their accumulation capacity can be disturbed by vegetation (Salo et al., 2016b). New results comparing the spring and autumn seasons without vegetation reveal that the moss bags collect pollutants more evenly between the seasons than the fabric bags, where the spring season is distinctive. More research is needed to further develop the sampling design used for the fabric bags, for example, how should the fabric bags be prepared and in what conditions can they best be used for monitoring. Thus, we consider that the moss bags are currently a better choice than fabric bags for air monitoring studies in Nordic conditions.

5 Conclusions

The magnetic enhancement in Turku is induced by the anthropogenic contribution of magnetite. The magnetic and elemental results show PM accumulation especially near heavily trafficked areas and intersections. Interestingly, the accumulation at the air quality monitoring station is the lowest among the collection sites, which implies that the station underestimates the current air pollution levels and its relocation should be considered.

The comparison of moss bags and synthetic fabric bags indicate that both bag materials are suitable for air pollution monitoring. Seasonally, the fabric bags’ magnetic enhancement is about four times higher in the spring versus the autumn. This is not detected in the moss bags, which indicates that their collection efficiency is similar in spring and autumn when vegetation mitigating air pollution is at a minimal. Moreover, comparison between these materials reveals that the fabric bags perform better in the dry and dusty conditions of spring whereas the moss bags accumulate more air pollutants in the wet conditions of autumn. *Sphagnum papillosum* thrives in humid conditions and actively collects pollutants while the filter fabric effectively captures PM due to its electrical charge. Based on the results, we suggest that the moss bags are a better choice for air monitoring studies in Nordic conditions than the fabric bags.

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