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ORIGINAL PAPER

Moss bag (*Sphagnum papillosum*) magnetic and elemental properties for characterising seasonal and spatial variation in urban pollution

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Abstract This study investigates the seasonal and spatial variation of traffic-induced particle matter in order to evaluate the pollutant distribution and the representativeness of the single air quality monitoring station in the city centre of Turku, southwest Finland. Study focused on parks, kindergarten and school yards as well as heavily trafficked sites. Sampling was done using active magnetic biomonitoring, which is highly applicable in polluted areas lacking native species. *Sphagnum papillosum* moss bags were exposed separately in road dust period, which is experienced after snow melt and the resuspension of sanding material in spring, and summer season for about 60 days in 2013. Moss bags are magnetically and elementally (e.g. Al, Cr, Fe, Na, Ni, Pb) more enriched in road dust period and near heavily trafficked sites than in summer season and in the courtyard or park sites. Magnetic properties indicate that particle matter is composed of fine-grained pseudo-single-domain magnetite towards superparamagnetic–single-domain grain sizes. Intensive road dust period overrides the variation of prevailing conditions as indicated by three paired samples showing finer grain sizes and higher element levels in courtyard/park sites than in traffic sites in summer. The results emphasise the effectiveness of active magnetic biomonitoring for the assessment of spatially representative air quality monitoring stations and related modelling approaches.

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Introduction

Urban air quality is typically surveyed with fixed monitoring stations, which have high temporal accuracy but poor spatial coverage and representativeness due to their limited number. There is an apparent need for enhancing the spatial resolution of air quality studies. By combining magnetic techniques with biomonitoring, the data of atmospheric deposition are obtained easily and efficiently, e.g. for the identification of pollution sources and determining the properties and distribution of particle matter (PM). Practical surrogate indicators of airborne PM (containing iron oxides and heavy metals) include active moss bags (e.g. Salo and Mäkinen 2014; Vuković et al. 2015), epiphytic lichens (e.g. Bajpai 2013; Chaparro et al. 2013), plants (e.g. Castañeda Miranda et al. 2016), tree leaves and needles (e.g. Jordanova et al. 2010; Hansard et al. 2012). Moss bags are easy to place, incorporate various pollutants simultaneously and provide spatially as well as temporally accurate data. Therefore, they are very useful in urban areas lacking native biomonitor species due to high pollution levels or seasonal conditions (Salo et al. 2012, 2016).

Traffic is the major air pollution source in urban areas especially when heavy industry is not present. Traffic emissions include exhaust gases such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and hydrocarbons (HC), liquids (leakages), and PM from the abrasion of car parts, such as brakes and tires, and road pavement (Kupiainen 2007; HEI 2010). The amount of road dust is impacted by traffic intensity, vehicle velocity, road type, neighbouring environment and meteorological conditions (Duong and Lee 2011). After snow melt in spring, many countries in the northern hemisphere experience a short but intensive road dust period, which typically lasts for 4–8 weeks. This road dust period is due to road sanding and salting (mainly sodium chloride) as well as the use of studded tires in winter conditions. Dust particles are resuspended through wind, traffic-induced turbulence and spring clean of the streets.

Anthropogenic PM is typically composed of iron oxides and heavy metals such as Cd, Fe, Ni, Pb and Zn. Some metals such as Cd are toxic even at very low concentrations (Järup 2006), but heavy metal levels are rarely investigated with monitoring stations. Road dust is a substantial source of PM_{10} ($\leq$10 μm) and especially $PM_{2.5}$ ($\leq$2.5 μm) in the air (Vallius 2005; Shah and Balkhair 2011). $PM_{2.5}$ is more harmful than coarser particles because they contain more heavy metals (Li et al. 2013), and they can be inhaled deeply in the lungs (e.g. Pope and Dockery 2006; Kampa and Castanas 2008). Exposure to air pollution causes asthma and respiratory or cardiovascular symptoms (Schwartz 2004; Schwarze et al. 2006; Kampa and Castanas 2008). The relative impact of air pollution is greater for children than adults because children's lungs and immune system are not developed to full functionality and children usually spend more time outdoors exposed to air pollutants (Schwartz 2004; Gasana et al. 2012).

The aim of this paper was to investigate the seasonal and spatial variation of traffic-induced PM in order to evaluate the pollutant distribution and accordingly estimate the representativeness of the single air quality monitoring station in the city centre of Turku, southwest (SW) Finland. Study emphasised heavily trafficked sites and places where children typically spend their day, i.e. kindergarten, school and park areas. Magnetic and elemental data were collected by exposing *Sphagnum papillosum* moss bags separately for road dust period, which is experienced in spring season, and summer season in 2013.

Materials and methods

Study area and sampling

The city of Turku is located on the coast of SW Finland (Fig. 1). It has an area of 306.4 km^2 and a population around 180,000. The air quality of Turku region is significantly impacted by traffic-derived NO_x and PM, whereas the industrial or energy production emissions have mainly low effect (Ilmanlaadun asiantuntijapalvelut 2010). The single air quality monitoring station measures only PM_{10} values and operates in the city centre. In 2013, PM_{10} values were 19.0 μg m^{-3} for road dust period and 11.6 μg m^{-3} for summer season (Ilmanlaatuportaali 2015). The majority of 19 sites were located in the city centre (Fig. 1). One of the sites (site 6) was situated at the air quality monitoring station, and the rest of the sites were located near major roads, and kindergarten, school and park areas. Traffic sites were located within 1–5 m from the road sides. Six city sites (2–3, 4–5, 10–11) formed paired samples with one of the sites in a kindergarten/school courtyard and the other in an adjacent traffic area. The rural background (BKGD) sites were located in Piikkiö (BKGD 1), about 15 km in the southeast, and in Parainen (BKGD 2), about 35 km in the south from Turku. Site 1 was lost in road dust period, and site 5 was lost in summer season.

The sampling was done with standardised moss bag method (SFS 5794, Finnish Standards Association 1994). The green parts of moss *Sphagnum papillosum* were collected from a natural area and cleaned from litter and other vegetation parts in the laboratory. Moss was acid-washed in 0.5 M HCl and rinsed three times (à 20 min) with deionised H_2O for evening out the element levels and neutralising the material. One part of the acid-washed moss was stored in the laboratory as control moss, which was not exposed to air pollution. The initial magnetic and elemental concentrations were determined from the control moss, and the averages were subtracted from the exposed moss bags. Therefore, the final moss bag data reflect the accumulation of air pollutants during the study periods.

About 30 g (wet wg.) of moss was placed in a nylon net with 0.64 cm^2 mesh and closed with a cotton thread. At each site, three spherical moss bags were tied in the outer branches of the trees at a height of 2.5–3 m. Sampling was done as two sets in 2013: the first set was placed from April to June (road dust period in spring), and the second set from June to August (summer season). The collection times were 61–62 and 60 days, respectively. For each site, a composite sample was formed in the laboratory. The samples were dried to constant weight in $T < 40$ °C and ground to fine powder with Retsch PM100 planetary ball mill (500 rpm, 30 s) equipped with a zirconium oxide (ZrO_2) grinding jar and balls.

Magnetic methods

Mass-specific susceptibility ($\chi \times 10^{-8}$ m^3 kg^{-1}) is a concentration-dependent parameter, which represents the concentration of magnetic minerals in a sample. Mass-specific susceptibility was measured using Bartington MS2B dual-frequency (0.47 and 4.7 kHz) sensor in the Department of Geography and Geology, University of Turku. Six separate subsamples of two control moss and two separate subsamples of each site were prepared in standard 10 cm^3 plastic containers and were measured five times in the low frequency. Thus, the final mass-specific susceptibility of each moss bag site is the average value of two subsamples (10 measurements in total) corrected with

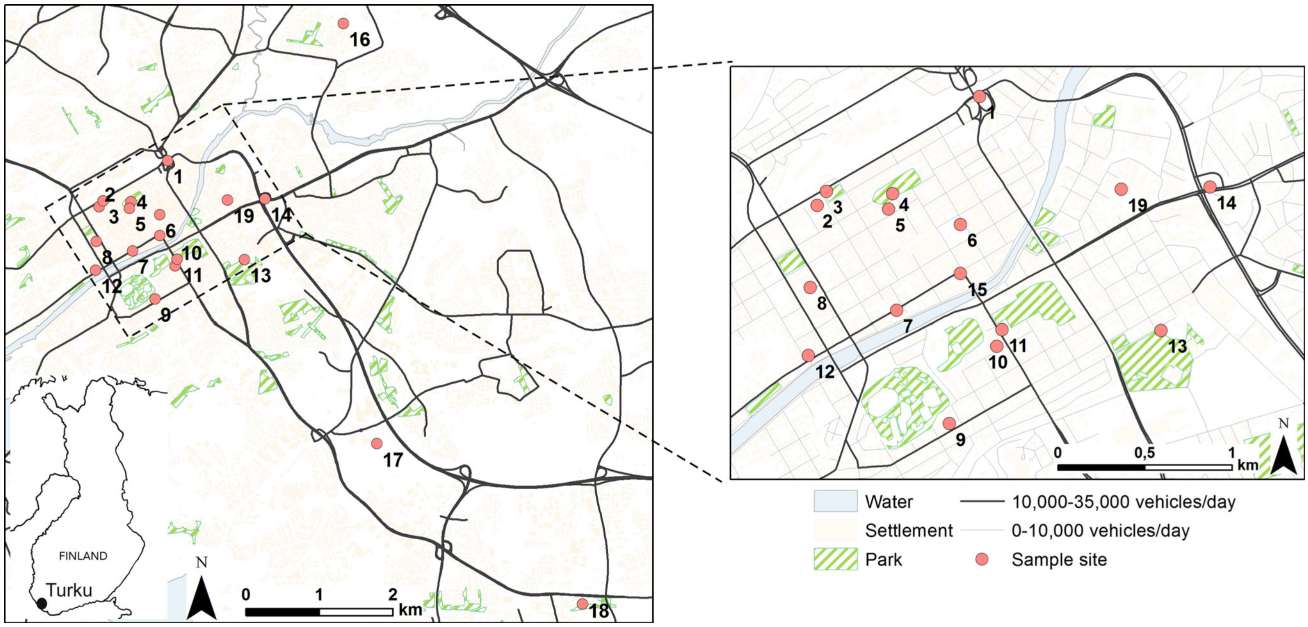

Fig. 1 Map showing the location of sample sites in Turku, SW Finland (rural background sites are located outside the map view). The sites were located mainly in the city centre (© National Land Survey of Finland 2013)

the average value of corresponding control moss (30 measurements in total) (Table 1).

Hysteresis loops and temperature dependencies were investigated in order to identify magnetic minerals and their grain sizes in the samples. Determinations were done using Quantum Design SQUID magnetometer in the Department of Physics and Astronomy, University of Turku. Hysteresis loops were determined at temperatures of 10 and 300 K in a magnetic field up to 1 T (T), whereas temperature dependencies were measured from 300 to 10 K in 10 millitesla (mT). Saturation magnetisation (M_S), saturation remanence (M_{RS}), 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 control moss κ by fitting function

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

to upward 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. M_S was determined as the magnetisation value at zero field M(0). H_{CR} was determined by solving numerically the field where the difference of the upward and downward branches was equal to 0.5.

Chemical analysis

Elements Al, As, Ca, Cd, Cr, Cu, Fe, Hg, Na, Ni, Pb, Ti, V and Zn were analysed in the accredited laboratory, Acme Labs, Canada. The analysis method was VG101. Ground moss samples (1 g) were dissolved in aqua regia and were analysed by inductively coupled plasma mass spectrometry (ICP-MS). Three separate subsamples for two control moss were analysed and the average element concentrations (Table 1) were subtracted from the final moss bag data. Two procedural blanks, two reference materials (STD CDV-1 and STD V16) and two separate sample duplicates were analysed at the same time with acceptable results. The detection limits are given in Table 1.

Statistical methods

Statistical analyses were done with IBM SPSS Statistics version 20. Most of the variables did not follow the normal distribution (Shapiro–Wilk significance (sig.) ≤ 0.05). Hence, statistical differences were tested by nonparametric Wilcoxon signed-ranks test with the null hypothesis (H_0) that the median difference between paired observations is zero. 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. Nonparametric Kruskal–Wallis test was used to test whether the mean ranks of two groups are the same.

Results and discussion

Magnetic characteristics of moss bags

Mass-specific susceptibilities ($\chi \times 10^{-8}$ m^3 kg^{-1}) are the highest at sites next to most trafficked areas (i.e. 10,000–35,000 vehicles per day) and the lowest at

Table 1 Detection limits (DL) for analysed elements and initial average mass-specific susceptibilities ($\chi \times 10^{-8}$ m^3 kg^{-1}, $N = 6$) and element concentrations (mg kg^{-1}, $N = 3$) of two control moss (C1 and C2)

	χ	Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Na	Ni	Pb	Ti	V	Zn
DL		100	0.1	100	0.01	0.1	0.01	10	0.001	10	0.1	0.01	1	2	0.1
C1	−0.7 ± 0.3	<100	0.33 ± 0.05	<100	<0.01	2.0 ± 0.1	1.4 ± 0.1	387 ± 9	0.023 ± 0.001	17 ± 5	0.3 ± 0.1	0.69 ± 0.07	4 ± 0	<2	2.3 ± 0.1
C2	−1.0 ± 0.2	<100	0.30 ± 0.08	167 ± 47	<0.01	2.0 ± 0.1	1.4 ± 0.1	303 ± 5	0.020 ± 0.000	27 ± 5	0.2 ± 0.0	0.54 ± 0.01	4 ± 0	<2	2.0 ± 0.2

Controls are indicated with standard deviation of three subsamples, except when below the DL. The average concentrations of control moss are subtracted from the final moss bag data (Table 2)

courtyards or parks. These findings are similar to observations in other studies (e.g. Maher et al. 2008; Vuković et al. 2015). In road dust period, the magnetic enhancement of moss bags is the greatest at sites 3 and 9, which have significant estimated nearby traffic volumes of 40,000 and 34,100 vehicles per day, respectively (Turun kaupunki 2013). The same sites and site 1, with 13,000 vehicles per day, stand out in summer season. As for paired samples (see Sect. "Study area and sampling"), susceptibilities are slightly higher in traffic than in courtyard sites, except for pair 10–11 (3.2×10^{-8} and 2.4×10^{-8} m^3 kg^{-1}) which show a stronger value in the courtyard site in summer season. Maximum values (Table 2), which seem to be similar for both sampling times, are not fully representative due to the loss of site 1 in road dust period near one of the busiest intersections in Turku. For comparison, the moss bags from this site gave 25.6×10^{-8} m^3 kg^{-1} in road dust period in 2010 (Salo et al. 2012). Rural background values in road dust period and summer season are 0.8×10^{-8} and 0.5×10^{-8} m^3 kg^{-1} in BKGD 1, and 0.3×10^{-8} m^3 kg^{-1} in BKGD 2, respectively. Urban and industrial references show values similar to park and courtyard sites in the centre.

In this study, susceptibilities of about $>8 \times 10^{-8}$ in road dust period and $>3 \times 10^{-8}$ m^3 kg^{-1} in summer season are regarded as typical values indicating traffic impact. Based on average susceptibility values, the magnetic enhancement is approximately three times higher in road dust period than in summer season. A similar ratio was found in road dust period in 2010 between the average susceptibilities of traffic and park sites in Turku (10.1 ($\pm$ 6.9) $\times 10^{-8}$ and 3.1 ($\pm$1.2) $\times 10^{-8}$ m^3 kg^{-1}, respectively) (Salo et al. 2012). Moreover, Wilcoxon signed-ranks test shows statistically significantly higher median susceptibilities in road dust period than in summer season (sig. = 0.000). Road dust period greatly enhances magnetic susceptibilities in spring while normal traffic conditions are the main contributing factor in summer. Seasonal differences in the dust levels have been found in other studies as well (e.g. Kuhns et al. 2003; Gertler et al. 2006).

Rapid saturation of narrow hysteresis loops at 0.2–0.3 T (Fig. 2a, b) is indicative for low-coercivity ferrimagnetic minerals, such as magnetite. Before the subtraction of the linear paramagnetic signal, hysteresis loops indicate iron to be present also either in paramagnetic or superparamagnetic (SP) form. Moreover, M_S and H_C are stronger in low-temperature than room-temperature hysteresis loops. At 10 K, average H_C is 11.0 ($\pm$3.1)mT and H_{CR} 124.6 ($\pm$10.8)mT for road dust period and 10.7 ($\pm$4.5)mT and 111.4 ($\pm$9.6)mT, respectively, for summer season. At 300 K, average values for H_C are 5.8 ($\pm$1.1)mT and 5.3 ($\pm$0.8)mT and for H_{CR} 64.8 ($\pm$8.9)mT and 72.4 ($\pm$9.3)mT, respectively. Low to intermediate H_C values found in this study are typical for magnetite as well as greigite (Sagnotti 2007).

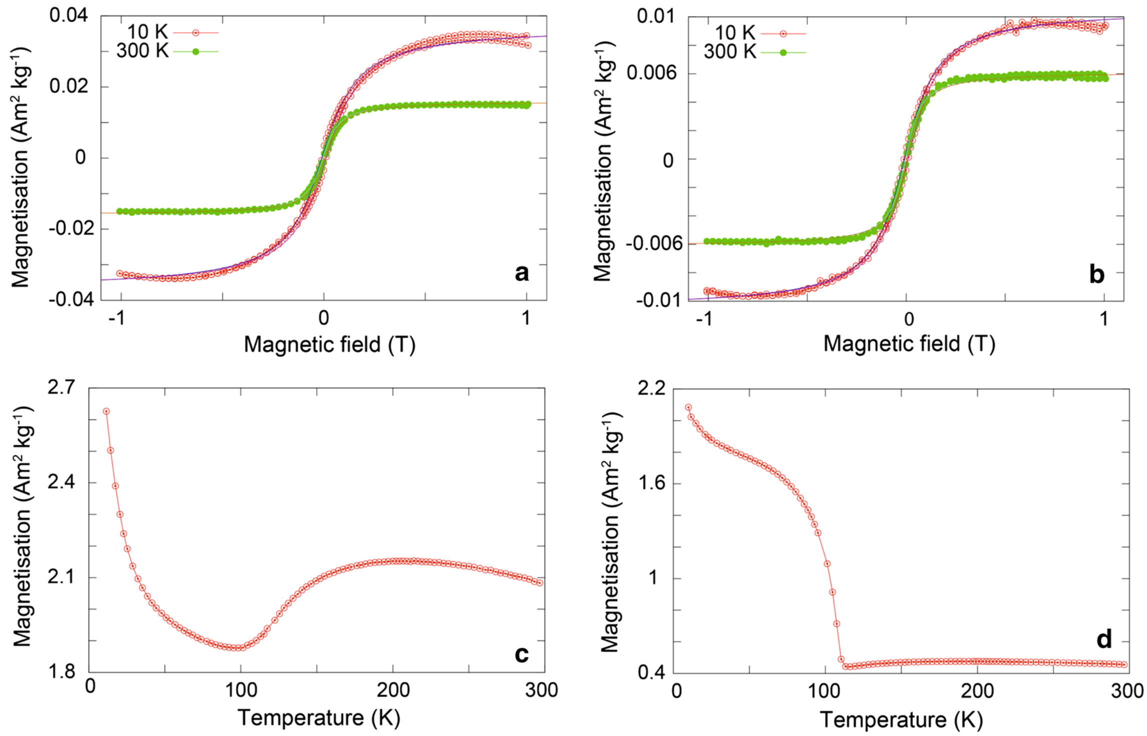

Fig. 2 Hysteresis loops measured at 10 and 300 K for site 9 in road dust period (**a**) and summer season (**b**), and temperature-dependent magnetisation measured at magnetic field of 10 mT for site 3 in road dust period (**c**) and for site 11 in summer season (**d**)

Temperature-dependent magnetisation shows Verwey transition (T_V) near 120 K (Özdemir et al. 2002), which points to magnetite as the main magnetic mineral in both sampling times (Fig. 2c, d). However, most samples have a smeared transition and a gradual rise of magnetisation after T_V (Fig. 2c). This indicates that magnetite is partly SP or partially oxidised, i.e. non-stoichiometric (Smirnov 2006; Mitchell and Maher 2009). The previous study (Salo et al. 2012) suggested that urban dust of Turku contains SP particles. In the Day plot (Fig. 3a, b), samples site in the pseudo-single-domain (PSD) region is close to the theoretical mixing line for superparamagnetic (SP)–single-domain (SD) grains. Samples are more dispersed in summer than in road dust period indicating a wider range of magnetite grain diameters (Fig. 3a). In road dust period, magnetite PM is quite similar regardless of site location, while in summer season indications for magnetite PM to be closer to SP-SD mixing line at courtyard/park sites than at traffic sites are shown (Fig. 3b). According to Dearing (1999), PSD and SD particles tend to form in fossil fuel combustion while SP particles form for example in pedogenic processes.

Element concentrations of moss bags

Based on mean concentrations, the element order is almost the same between sampling times: Ca > Fe > Al > Na > Ti > Zn > Cu > V > Cr > Pb > Ni > As > Cd > Hg in road dust period and Ca > Fe > Al > Na > Zn > Ti > Cu > Cr > Ni = Pb > V > As > Cd > Hg in summer season (Table 2). Sites 3, 9, 15 and sites 1, 2, 10, respectively, are distinct by means of higher element concentrations. Sites 2 and 10 are located at kindergarten courtyards but close to heavily trafficked roads and the others are sited at traffic areas. Sites next to heavy traffic show typically greater element enhancement (e.g. Maher et al. 2008; Salo et al. 2012). Wilcoxon signed-ranks test shows that the difference in median values was statistically significant (sig. < 0.05) between paired variables, excluding As, Hg and Zn. Furthermore, ranking the differences indicates higher element values in road dust period, except for Hg which was higher in summer. The rural background sites are among the lowest element values (Table 2).

For paired samples 2–3, 4–5 and 10–11 (see Sect. "Study area and sampling"), courtyard/park sites show higher concentrations for several elements in both sampling times compared to traffic sites: especially Cd, Hg, Pb and Zn stand out in all pairs while, for example, As, Ni, Ti and V are distinctive in most pairs (Table 3).

Average monthly concentrations (mg kg^{-1} per month) of this and previous study (Salo and Mäkinen 2014) show the most elemental levels to be significantly lower (e.g. Cu about 120 and 130 times lower in road dust period and summer season, respectively) in the city of Turku than in the

Table 2 Summary statistics for mass-specific susceptibility ($\chi \times 10^{-8}$ m^3 kg^{-1}) and elements (Al, As, Ca, Cd, Cu, Cr, Fe, Hg, Na, Ni, Pb, Ti, V, Zn in mg kg^{-1}) for investigated sampling times after the average concentrations of control moss are subtracted (Table 1)

	χ	Al	As	Ca	Cd	Cu	Cr	Fe	Hg	Na	Ni	Pb	Ti	V	Zn
Road dust period															
Min	2.6	150	0.00	233	0.003	1.2	0.5	263	0.001	73	0.3	0.4	20	0	5.3
Max	13.9	750	0.57	1950	0.035	7.1	4.2	1213	0.013	523	6.7	4.9	108	10	59.3
Mean	6.3	297	0.13	732	0.013	3.3	1.8	532	0.005	219	1.0	1.3	44	3	24.1
Median	4.0	250	0.09	625	0.013	3.1	1.4	443	0.004	198	0.3	0.8	37	2	23.0
sd	3.8	170	0.14	453	0.010	1.9	1.1	290	0.004	111	1.5	1.2	24	3	12.1
BKGD 1	0.8	0	−0.13	250	0.003	0.1	0.1	33	0.002	163	0.1	0.2	3	0	19.9
BKGD 2	0.3	25	0.02	225	0.003	0.25	0.1	345	0.004	121	0.1	0.6	8	0	62.9
ρ X	1.000	0.918[a]	0.190	0.920[a]	0.148	0.908[a]	0.902[a]	0.951[a]	−0.141	0.495[b]	0.903[a]	0.411	0.943[a]	0.881[a]	0.195
ρ M_S	0.938[a]	0.771[a]	0.035	0.675[b]	−0.105	0.748[a]	0.880[a]	0.862[a]	−0.647[b]	0.158	0.821[a]	0.469	0.825[a]	0.788[a]	−0.210
Summer season															
Min	0.5	0	0.00	250	0.000	1.1	0.2	53	0.000	33	0.1	0.1	5	0	12.8
Max	11.1	450	0.27	1250	0.013	11.4	4.2	653	0.014	103	5.3	2.1	46	3	48.0
Mean	2.9	131	0.08	494	0.007	3.2	0.8	243	0.006	58	0.7	0.7	18	0.6	24.2
Median	1.9	100	0.07	400	0.003	2.5	0.6	208	0.006	43	0.3	0.5	16	0.0	26.3
sd	2.4	126	0.08	264	0.005	2.4	0.9	173	0.003	23	1.2	0.6	11	0.9	9.4
BKGD 1	0.5	0	0.17	250	0.003	0.8	0.0	23	0.010	63	0.1	0.0	2	0	31.5
BKGD 2	0.3	13	0.07	275	0.001	0.6	0.1	71	0.004	41	0.2	0.2	5	0	19.5
ρ X	1.000	0.634[a]	0.172	0.608[a]	−0.083	0.811[a]	0.856[a]	0.793[a]	0.016	0.194	0.729[a]	0.472[b]	0.693[a]	0.715[a]	0.430
ρ M_S	0.906[a]	0.840[a]	0.171	0.645[b]	−0.125	0.727[a]	0.859[a]	0.881[a]	−0.118	0.060	0.752[a]	0.571[b]	0.875[a]	0.784[a]	0.310

Summary statistics are presented separately for sample ($N = 18$) and rural background (BKGD) sites. Spearman rank order correlation coefficients (ρ) between χ, M_S and elements are without rural background sites

[a] Correlation is significant at the 0.01 level

[b] Correlation is significant at the 0.05 level

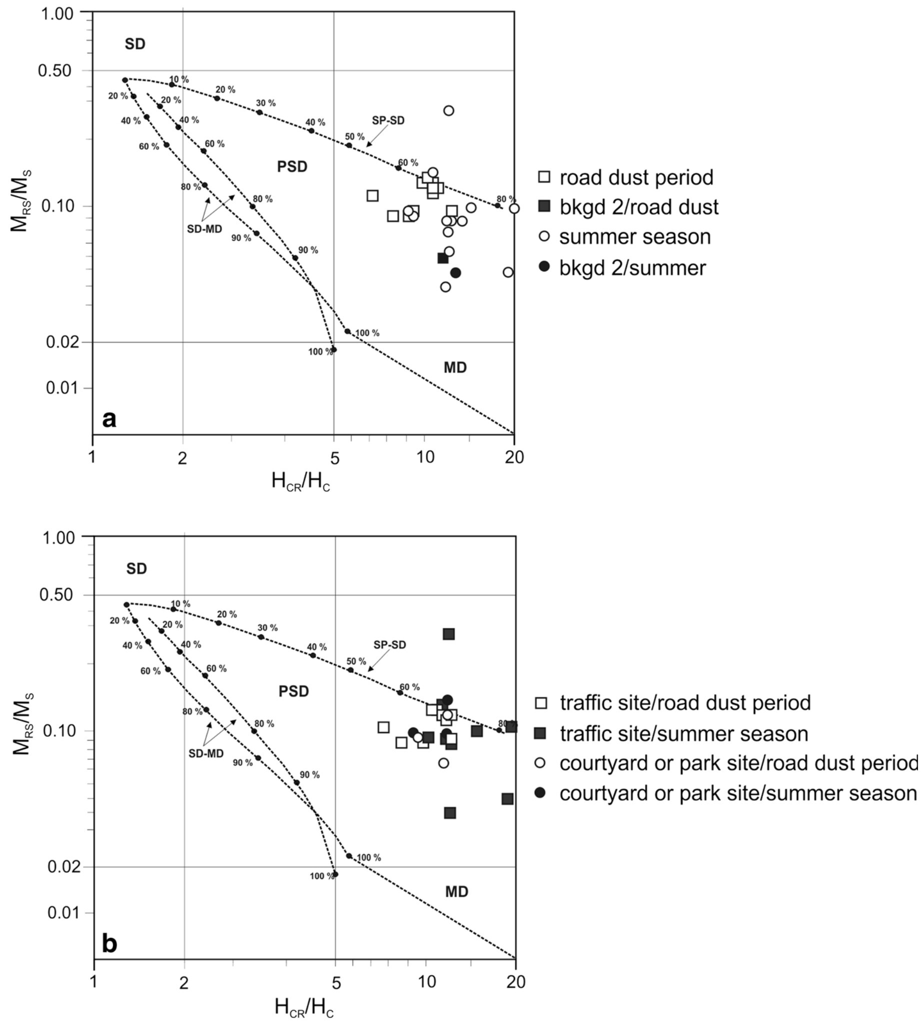

Fig. 3 Day plot of ratios M_{RS}/M_S and H_{CR}/H_C of the moss bag samples in road dust period and summer season (**a**) and different city centre sites in road dust period and summer season (**b**) measured at 300 K. Single-domain (SD), pseudo-single-domain (PSD) and multi-domain (MD) boundaries for grains and mixing lines are shown after Dunlop (2002)

Table 3 Summary of elements having higher concentrations in paired samples for courtyard/park sites than in traffic sites in road dust period and summer season

Sample pair	Elements, road dust period	Elements, summer season
2 > 3	Ca, **Cd**, Hg, **Pb, Zn**	As, Al, **Cd**, Fe, Na, Ni, **Pb**, Ti, V, **Zn**
4 > 5	Al, Ca, **Cd**, Cu, Cr, Fe, Hg, Na, Ni, **Pb**, Ti, V, **Zn**	–
10 > 11	As, **Cd**, Hg, **Pb, Zn**	Al, Ca, **Cd**, Cu, Cr, Fe, Hg, Na, Ni, **Pb**, Ti, V, **Zn**

The joint elements showing higher concentrations during both sampling times are bolded. Site 5 was lost in summer season

industrial town of Harjavalta. However, the average concentrations of Al and Ti are higher in Turku where traffic is the main pollution source. This might reflect the polluting effect of increased traffic and/or road dust period (e.g. Peltier et al. 2011). Previous moss bag studies from Harjavalta indicate that Ti is the only investigated element that shows notably increasing concentrations (close to the main highways) between 1996/1997 and 2001/2002 despite the reductions in the industrial emissions (Jussila 1997, 2003).

Correlations of magnetic properties and elements

The majority of Spearman's rank order correlations between the elements, χ and M_S are statistically significant (Table 2; Fig. 4). Such associations are typical for enviromagnetic studies and highlight magnetic parameters as good proxy for heavy metal pollution (e.g. Yang et al. 2010; Salo and Mäkinen 2014). In road dust period, elements correlate overall stronger with χ than M_S while situation is vice versa in summer season. Correlations are the weakest with As, Cd, Hg and Zn in both sampling times as well as Na in summer season. First three elements are released to air mainly from industrial sources (Alaviippola et al. 2007), Zn also from traffic activities (Ng et al. 2003) while Na is present in road salt, which is not used in summer (ELY-keskus 2013). Thus, other elements, such as

Al, Fe and Ni, are present in higher volumes in traffic-induced pollution in Turku and are more effectively merged with magnetic PM.

Spatial representativeness of the air quality monitoring station

Data gathered by air quality monitoring stations are extended to apply spatially large areas. Along the same principle, the results of moss bags from site 6 at the only monitoring station in Turku could represent the whole urban centre. Here the susceptibility value is 9.4×10^{-8} in road dust period and 1.9×10^{-8} m^3 kg^{-1} in summer season. The rest of the sites (excluding rural backgrounds) have the average values of 6.1 (range 2.6–13.9) $\times 10^{-8}$ and 2.9 (range 0.5–11.1) $\times 10^{-8}$ m^3 kg^{-1}, respectively. Element values show same order; for example, corresponding values for Al in road dust period are 350 mg kg^{-1} and 294 (range 150–750) mg kg^{-1} while in summer season 50 mg kg^{-1} and 135 (range 0–450) mg kg^{-1}. It seems that in general the accumulation of elements in site 6 is overestimated in road dust period and underestimated in summer season, for example site 10. However, statistically the mean ranks of site 6 and the rest of the sites are not significantly different (sig. > 0.05). Nevertheless, based on the seasonal and spatial differences in the magnetic and elemental data, it is concluded that the current location of air monitoring station in Turku is not ideal and should be further assessed.

The spatial representativeness of monitoring stations is currently under the consideration of EU. Magnetic biomonitoring could be a powerful tool in assessing the impact area of a station. It could also provide spatially and vertically detailed data of pollution levels and distribution required for air quality modelling purposes. More research is needed in order to establish the relationship between monitoring station and biomonitoring data sets.

Results in relation to sampling times and human health

In the spring, traffic sites are highly loaded both magnetically and elementally by road dust. Road dust period is a short but intensive period, which can cause difficulties to even those not suffering from respiratory problems. Thus, summer values represent more of a normal situation where vegetation might have an impact. Vegetation is usually considered to be effective in mitigating air pollution dispersal and trapping PM: for example, Vos et al. (2013) stated that leaves absorb gaseous pollutants through stomata while particles are deposited on the leaves and branches; and Maher et al. (2008) detected higher saturation isothermal remanence (SIRM), Fe and Pb values on roadside than road-proximal tree leaves. On the contrary, vegetation can have locally negative impacts on air quality. For instance, trees and leaves can obstruct wind flow, hold pollutants within the canopy and prevent fresh air ventilation (Roy et al. 2012; Salmond et al. 2013). However, Setälä et al. (2013) reported that trees ability to remove air pollutants is minor in northern climates. In order to investigate the air pollution under normal conditions, i.e. outside road dust period and its masking effect, comparison should be made between summer and autumn seasons.

According to Dekkers (1997), upper threshold for PSD grains is about 10 µm while SD grains are between 0.03 and 0.50 µm and SP grains below 0.03 µm. Since anthropogenic PM entrapped by moss bags in Turku is composed of PSD magnetite towards SP-SD grain sizes (Fig. 3a, b), it is most likely closer to $PM_{<2.5}$ than PM_{10}. Moreover, Tretiach et al. (2011) stated that moss bags capture $PM_{<2.5}$

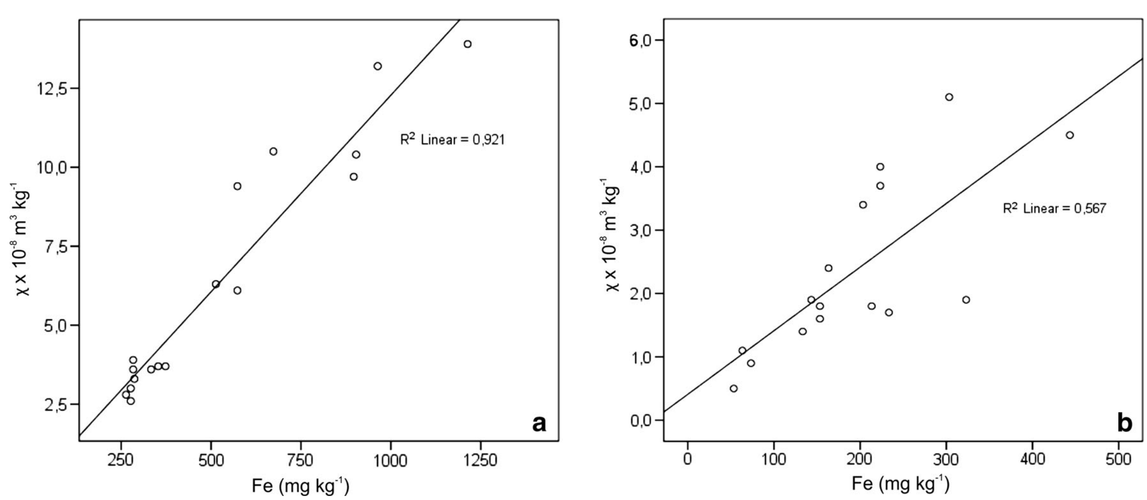

Fig. 4 Representative correlation plot for magnetic susceptibility and Fe in road dust period (**a**) and summer season (**b**) without outliers, i.e. sites 1 and 10

predominantly (79 %) over coarser fraction of $PM_{2.5–10}$. These small particles are harmful to human health because they access respiratory systems and especially deeper parts of the lungs more easily than larger particles. Previous studies have reported urban PM in sizes of about 0.2–5 µm (Chaparro et al. 2013), about 0.1–1 µm (Mitchell and Maher 2009) and about 0.1–5 µm (Sagnotti et al. 2009).

In the city centre, smaller PM as well as higher element levels are found in courtyard/park sites than in traffic sites especially in summer season (Fig. 3b). Courtyard sites are closed and sheltered, so air is not mixed and pollutant levels are not diluted by wind as effectively as in street areas. Children typically spend much time on kindergarten and school courtyards and thus can be exposed to the most harmful PM and elements. Traffic emissions also occur near ground level along streets with pedestrians and cyclists; for example, Maher et al. (2008) reported peak values in traffic-emitted particles at small child height of about 0.3 m and adult head height of 1.5–2 m above the ground level. Since moss bags were located above (~2.5 m) the average height of children, and adults as well, the data might underestimate the conditions for respiratory exposure. The same conditions apply for the air quality monitoring stations with collectors at 3 m. Furthermore, urban air quality data and derived dispersion models are not spatially representative or informative, especially in the case of sheltered areas such as courtyards. By enhancing the representativeness of air pollution data, more accurate information can be provided for environmental management purposes and health studies.

Conclusion

Based on the active magnetic biomonitoring, the single air monitoring station in the city centre of Turku overestimates road dust period and underestimates traffic impact in summer season. The magnetic properties indicate PM in Turku to be composed of fine-grained PSD magnetite towards SP-SD sizes. The presence of iron in SP form is strengthened by original hysteresis loops as well as by temperature-dependent magnetisation. In general, the enhancement is greater in road dust period and near traffic sites than in summer season and in courtyard/park sites. Three paired samples show higher element loads and finer grain sizes in summer at kindergarten courtyard/park sites compared to traffic sites, which is worrying considering children. Therefore, further studies are important for revealing the spatial and vertical distribution of pollutants and their characteristics in urban areas, especially in courtyard sites. Active magnetic biomonitoring can provide elaborate pollution and PM size data necessary for the assessment of the spatial representativeness of air quality monitoring stations, for enhancement of air quality models, as well as for environmental management purposes and health investigations.

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