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Spatial variation of PM elemental composition between and within 20 European study areas — Results of the ESCAPE project

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Abbreviations: AUV, Vorarlberg, Austria; BNL, Belgium & the Netherlands; DCO, Copenhagen, Denmark; FIH, Helsinki/Turku, Finland; FPA, Paris, France; GMU, Munich/Augsburg, Germany; GRA, Athens, Greece; GRH, Heraklion, Greece; GRU, Ruhr Area, Germany; HUG, Gyor, Hungary; IRO, Rome, Italy; ITU, Turin, Italy; LIK, Kaunas, Lithuania; NOS, Oslo, Norway; SPB, Barcelona, Spain; SPC, Catalunya, Spain; SST, Stockholm, Sweden; SWL, Lugano, Switzerland; UKM, Manchester, United Kingdom; UKO, London/Oxford, United Kingdom; ESCAPE, European Study of Cohorts for Air Pollution Effects; $PM_{2.5}$, mass concentration of particles less than 2.5 μm in size; $PM_{2.5}$, absorbance measurement of the blackness of $PM_{2.5}$ filters, this is a proxy for elemental carbon, which is the dominant light absorbing substance; PM_{10}, mass concentration of particles less than 10 μm in size; PM_{coarse}, mass concentration of the coarse fraction of particles between 2.5 μm and 10 μm in size; ST, street site; UB, urban background site; RB, regional background site; Cu, copper; Fe, iron; K, potassium; Ni, nickel; S, sulfur; Si, silicon; V, vanadium; Zn, zinc.

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ABSTRACT

An increasing number of epidemiological studies suggest that adverse health effects of air pollution may be related to particulate matter (PM) composition, particularly trace metals. However, we lack comprehensive data on the spatial distribution of these elements.

We measured $PM_{2.5}$ and PM_{10} in twenty study areas across Europe in three seasonal two-week periods over a year using Harvard impactors and standardized protocols. In each area, we selected street (ST), urban (UB) and regional background (RB) sites (totaling 20) to characterize local spatial variability. Elemental composition was determined by energy-dispersive X-ray fluorescence analysis of all $PM_{2.5}$ and PM_{10} filters. We selected a priori eight (Cu, Fe, K, Ni, S, Si, V, Zn) well-detected elements of health interest, which also roughly represented different sources including traffic, industry, ports, and wood burning.

PM elemental composition varied greatly across Europe, indicating different regional influences. Average street to urban background ratios ranged from 0.90 (V) to 1.60 (Cu) for $PM_{2.5}$ and from 0.93 (V) to 2.28 (Cu) for PM_{10}. Our selected PM elements were variably correlated with the main pollutants ($PM_{2.5}$, PM_{10}, $PM_{2.5}$ absorbance, NO_2 and NO_x) across Europe: in general, Cu and Fe in all size fractions were highly correlated (Pearson correlations above 0.75); Si and Zn in the coarse fractions were modestly correlated (between 0.5 and 0.75); and the remaining elements in the various size fractions had lower correlations (around 0.5 or below). This variability in correlation demonstrated the distinctly different spatial distributions of most of the elements. Variability of PM_{10}_Cu and Fe was mostly due to within-study area differences (67% and 64% of overall variance, respectively) versus between-study area and exceeded that of most other traffic-related pollutants, including NO_2 and soot, signaling the importance of non-tailpipe (e.g., brake wear) emissions in PM.

1. Introduction

Particulate matter (PM) is a heterogeneous mixture of natural and anthropogenic components including sulfates, nitrates, ammonium, elemental and organic carbon, mineral dust, trace elements, sea salt, pollens, spores, which has been linked to long-term adverse health effects (Brunekreef & Holgate, 2002; Pope & Dockery, 2006; WHO, 2006). However, the focus has been primarily on different size fractions of PM mass and soot content and much less on PM composition (HEI, 2010). In recent years, there has been increasing interest also in chemical components of PM as possibly more specific markers for health effects in air pollution research (Grahame & Schlesinger, 2007; Heal et al., 2012; Kelly & Fussell, 2012; Stanek et al., 2011). Several studies have examined the association between short-term exposure to trace elements monitored at sparsely distributed sites of the U.S. Chemical speciation network and acute health outcomes (Bell et al., 2009; Mostofsky et al., 2012), but far fewer have looked at long term health effects (Ostro et al., 2010). Schwarze et al. (2006) reviewed the consistency of both epidemiological and toxicological studies with regard to various PM properties, and saw the most convincing effect between metals (particularly copper, vanadium, iron and nickel) and the development of pulmonary and cardiovascular disease. Chen & Lippmann (2009) specifically reviewed metals in ambient air and focus on nickel and vanadium from residual oil fly ash as the most toxic source-related markers of exposure. Both reviews comment on the paucity of speciated PM data and the need for better exposure assessment considering the spatial variability of concentrations and personal exposure.

Within the framework of the European study of cohorts for air pollution effects (ESCAPE, www.escapeproject.eu), we measured NO_2, NO_x, $PM_{2.5}$ (particles smaller than 2.5 μm), PM_{10} (particles smaller than 10 μm), PM_{coarse} (difference between $PM_{2.5}$ and PM_{10}), $PM_{2.5}$ absorbance ($PM_{2.5abs}$: a proxy for elemental carbon) in twenty European areas (see Fig. 1). Within each area, distinct sites were chosen to capture local PM ($n = 20$) and $NO_{2/x}$ ($n = 40$) contrasts. All data were collected with identical instrumentation and analyzed centrally facilitating comparison of exposure contrasts between and within areas for NO_2, NO_x, $PM_{2.5}$, PM_{10}, PM_{coarse}, $PM_{2.5abs}$ (Cyrys et al., 2012; Eeftens et al., 2012). These latter pollutants, heretofore referred to as the 'main' pollutants, have been described in previous manuscripts (Cyrys et al., 2012; Eeftens et al., 2012). We have already shown that some of these main pollutants have a North–South gradient across Europe and that there is significant variability in spatial distribution within urban areas. Other studies have also reported North–South gradients for a number of pollutants; however, most have depended on one or just several monitoring sites per city (Beelen et al., 2009; Dingenen et al., 2004; Götschi et al., 2005; Lianou et al., 2011; Tørseth et al., 2012; von Arx et al., 2004) precluding characterization of local variability. Furthermore, although the European Monitoring and Evaluation Programme (EMEP), with nearly four decades worth of harmonized monitoring, has been important to document spatial patterns and long-term trends, their focus has been on ozone, SO_2, NO_2, sulfate and nitrate with much less data on PM and its constituents (Tørseth et al., 2012).

Here we present concentrations for eight elements (Cu, Fe, K, Ni, S, Si, V, Zn) in both the $PM_{2.5}$ and PM_{10} size fractions and explore their spatial distributions in twenty European areas. A separate paper has described the development of land use regression models based on these measurements (de Hoogh et al., 2013). Although trace elements by energy dispersive X-ray fluorescence (ED-XRF) analysis make up only 10–20% of PM mass (depending on size fraction and time of year), they can often be linked to certain types of sources. We will further assess their spatial differences between and within areas, as well as examine their correlation with the main pollutants and between themselves to see how much new information these constituents add.

2. Materials and methods

2.1. PM sampling

PM sampling design and methods have been previously described in Eeftens et al. (2012). Briefly, PM was measured in 20 of the 36 study areas of ESCAPE (for map of PM study areas, see Fig. 1) and NO_2/NO_x was measured in all areas. In each study area, 20 sites were measured for PM (except in the Netherlands/Belgium (40 sites) and Spain Catalunya (40 sites)).

Sampling campaigns in each area were conducted over an entire year. All measurements took place between October 2008 and April 2011. Participating centers used identical sampling protocols, common criteria for the selection of sampling sites, the same equipment, and all samples were gravimetrically analyzed and reflected (for black smoke) centrally at one laboratory (IRAS, Utrecht University). Trace element analysis is described below. All PM samples were collected using Harvard impactors (Air Diagnostics, Harrison, ME, USA), which were designed to collect $PM_{2.5}$ and PM_{10} at a flow rate of 10 l/min (Brunekreef et al., 2005; Hoek et al., 2002). Sites were selected to capture a large diversity in potential air pollution sources and contrasting concentration levels while also considering the spatial distribution of cohorts of

Fig. 1. The ESCAPE study areas where PM measurements were taken.

interest. These sites were categorized as regional background (RB), urban background (UB), and street (ST) sites. Regional background sites were located outside of major urban areas, and were not influenced directly by traffic sources. Urban background sites were located inside an urban area, but at least 50 m away from major roads. Street sites were selected at building facades representative of homes, in streets with traffic intensities of around 10,000 vehicles per day or more. All sites were selected so that the influence of other local sources of particulate matter and combustion gases (e.g., construction works, district heating plants, parking lots) within 100 m was minimized. The focus was on ST and UB sites with only several RB sites. Site selection proposals were evaluated centrally, to ensure that all centers applied the same selection criteria (Eeftens et al., 2012).

For each site, PM measurements were done for 14 days, in three different seasons. A single reference monitoring site with 14-day average measurements was maintained in each area for the entire year. Due to the limited number of samplers, all sites could not be simultaneously monitored within a study area; instead, five sites and the reference site were measured simultaneously (in each of the four rounds per season) representing all different site types (RB, UB, and ST).

To adjust for the temporal variability of concentrations, we used the data from the above mentioned centrally located reference site in each study area where measurements were taken over an entire year (see previous studies (Hoek et al., 2002), and other land use regression (LUR) studies (Hoek et al., 2008)). The reference site was chosen at a regional or urban background location that was not directly impacted by local sources.

2.2. XRF analyses

All PM_{10} and $PM_{2.5}$ samples were analyzed for elemental composition using energy-dispersive X-ray fluorescence. Analyses were performed by Cooper Environmental Services (Portland, OR, USA). Filters were analyzed between December 2010 and July 2011. Forty-eight elements were measured (see supplement 1 for details). Quality assurance and control included analysis of NIST reference material (SRM 1228 and SRM 987), repeated analysis of a multi-elemental quality control standard (Multi 30585) and replicate analysis of about 10% of the samples (see supporting information S1, Table S1 for coefficient of variation of duplicates). In addition, about 20 field blanks and field duplicates were taken in each study area.

Concentrations were calculated by multiplying the reported concentration of an element ($\mu g\ cm^{-2}$) with the exposed filter area (7.8 cm^2), subtracting the study area-specific mean field blank and dividing by the sample volume. Limits of detection per study area were calculated as three times the standard deviation of field blanks divided by the

nominal sample volume of 25.2 m^3. If an element had more than 25% of its samples below the detection limit, that element was not evaluated. Concentration values of individual samples below the DL were retained and not replaced with a standard value. In these calculations we removed 6 of the about 400 blanks, because of extreme values. Field duplicates were used to calculate the precision of measurements. We additionally removed 12 samples (1% of the total) with erroneous PM_{10}–$PM_{2.5}$ differences. This was evaluated by first checking whether the $PM_{2.5}$ concentration was larger than 1.4 times the PM_{10} concentration and then if an element-specific absolute difference between $PM_{2.5}$ and PM_{10} was exceeded. The latter condition was added as, for low concentrations (close to 0), a ratio may easily be above 1.4. The ratio of 1.4 was selected based upon an assumed precision of 10% of both measurements, resulting in a precision of the difference of 14% ($\sqrt{2} \times 10$), with the principle to only exclude observations that were clearly impossible (3 times the precision of the difference, $3 \times 14\%$, or approximately 40%).

We have a priori chosen to focus on eight of the 48 elements reported by ED-XRF analyses (copper (Cu), iron (Fe), potassium (K), Nickel (Ni), sulfur (S), silicon (Si), vanadium (V), and zinc (Zn)). These elements were chosen for both their varied documented toxicity to human health as well as their representation of a variety of sources: brake and tire wear (Cu, Fe), tire wear (Zn), secondary inorganic aerosols (S), soil material (Si), oil combustion (V, Ni), biomass burning (K).

2.3. Calculation of annual averages

Annual averages were calculated after adjusting for temporal variation measured at the ESCAPE reference site. We used the difference method for temporal correction (Eeftens et al., 2012; Hoek et al., 2002). In this method, the overall annual mean concentration at the reference site ($C_{ref,avg}$) was determined and then the 2-week measurement at time t at the reference site ($C_{ref,t}$) was subtracted to calculate the difference ($C_{diff\ ref,t} = C_{ref,avg} - C_{ref,t}$). Next, this difference was added to the 2-week mean concentration at short-term monitoring site x to obtain the corrected concentration at time t ($C_{corr\ x,t} = C_{x,t} + C_{diff\ ref,t}$).

Negative concentrations occurred only when extreme concentrations occurred at the reference site, suggesting that the adjustment procedure did not work in these extreme cases. Log-transformation of the concentrations did not resolve this problem. We decided to exclude these extreme sampling periods from the analysis by element. Outliers were defined as an elemental concentration at the reference site higher than four times the interquartile range above the 75th percentile of the reference site measurements. Ultimately, 31 outliers were detected out of 8320 (20 areas × 26 periods × 16 elements) sampling periods and removed. In 11 study areas, PM sampling occasionally failed at the reference site; in such cases, elemental concentrations were estimated using routine monitoring sites, provided that the squared correlation between the measured element and the routinely measured component was higher than 0.50. With the exception of the London study area, no elemental composition was available from routine networks and we therefore used PM_{10}, $PM_{2.5}$, NO_2 and NO_x. In particular, the non-traffic elements (Ni, K, S, V) were at times not well predicted and left missing. Site-specific annual averages were only calculated if two or three valid adjusted samples were obtained. These procedures resulted in 92 missing average values for all elements, sites, and areas out of a possible 7040.

2.4. Data analysis

Cleaning, preparation of elemental data, and calculation of annual elemental averages were done in SAS 9.2; All subsequent analyses were done in R (R Development Core Team, 2011) To quantify the amount of spatial variation, the total range (maximum–minimum) was calculated as a percentage of the mean. For each study area, we used ANOVA to test for significant differences between urban background and street sites and (where applicable) between urban and regional background sites. Percentages of between and within area variance of annual means were determined using analysis of variance with LME (linear mixed-effects; method = REML) (Pinheiro et al., 2012). We also analyzed overall patterns in three groups of study areas: Northern (Oslo, Stockholm County, Helsinki/Turku, Copenhagen), Southern (Turin, Rome, Barcelona, Catalunya, Athens and Heraklion) and Western/Central Europe (all other areas).

3. Results & discussion

Quality control results and the relevance of temporal adjustments in the derivation of annual means are described in the online supporting information S1 and S2, respectively.

3.1. Spatial variability between and within study areas

Different aspects of spatial variability are characterized in Table 1 (annual mean and overall spatial contrasts), Fig. 2 (trends across Europe), and Table 2 (within area variability by site type). Table 1 shows spatial contrasts defined as a percentage of the range divided by the mean for the eight elements by area and region. For a quick overview of patterns of concentrations and variability across Europe, Fig. 2 is more readily accessible. For S, in both $PM_{2.5}$ and PM_{10}, the spatial contrasts are relatively small and stable within and between areas with all contrasts below 100%. For K, most contrasts were below 100% for both PM size fractions. V and Zn are the next two elements that still have somewhat stable but greater spatial variability in both size fractions across and within areas with contrasts between 100 and 200%. Si is similar to V and Zn, but with slightly larger contrast. The last three elements (Ni, Fe, Cu) in both size fractions are quite variable with large spatial contrasts within and between areas. A pair of unusually high contrasts were observed in Vorarlberg for Ni, which resulted from the division of range by very low average concentrations. Regional differences in spatial contrasts are noticeable for $PM_{2.5}$_Cu, Fe, Zn, K, and both size fractions of V and Si.

Fig. 2 shows boxplots of the spatial distribution of eight elements in the $PM_{2.5}$ and PM_{10} size fractions across Europe. Table 2 describes the spatial variability within study areas by creating ratios using the average concentrations by site type; i.e., street versus urban background (ST/UB); regional background versus urban background (RB/UB). Across Europe, The highest ST/UB ratios in both $PM_{2.5}$ and PM_{10} were for Cu and Fe. In both size fractions, across Europe and in nearly all regions, Cu, Fe, Zn, Si had significantly different ratios across all site types demonstrating their local (traffic-related) sources. In contrast, S, Ni, and V ST/UB ratios were approximately 1.0 and non-significant (non-traffic source). For K, in all areas and most regions, the $PM_{2.5}$ ST/UB and RB/UB ratios were not significant; whereas, for PM_{10}, they were mostly significant indicating the different non-traffic versus traffic-related sources of the fine versus coarse fractions. It is important to note that the site type categorization may vary by area and that there are fewer RB sites, making those ratios less reliable.

3.1.1. Similar trends and the non-tailpipe story of Cu, Fe, Zn

In the $PM_{2.5}$ fraction, both Cu and Fe show very similar patterns with consistently low levels that are slightly increasing from northern to Western/Central Europe (with a notable Fe high in the Ruhr area) before a big jump in levels in the southern Mediterranean areas. Similarly for the PM_{10} fraction, Cu and Fe levels are also low across northern and central Europe (with a few more Fe highs in Oslo, Stockholm, Paris and the Ruhr area) before high levels in the south. Cu and Fe mass is mostly in the PM_{10} fraction. Table 2 shows that Cu and Fe have the highest ratios–well over 1 for ST/UB and well below 1 for RB/UB. In fact, of the selected elements, Cu and Fe clearly have the greatest number of significantly different ratios (at $p < 0.05$) with more than half of the areas having significantly different ST/UB ratios. Regionally, all but one ratio is significant with particularly high ST/UB ratios in Northern Europe (2.52

Table 1
Adjusted annual mean concentrations [ng/m^3] and overall spatial contrasts (% range/mean) of eight elements from $PM_{2.5}$ and PM_{10} size fractions by study area. Additionally, means were calculated for all areas, Northern Europe, Western/Central Europe, and Southern Europe. The specific ordering of ESCAPE study areas can be grouped into: northern Europe at the top (Oslo, Norway to Copenhagen, Denmark); central/western European areas in the middle (Kaunas, Lithuania to Lugano, Switzerland); and southern European areas at the bottom (Turin, Italy to Heraklion, Greece).

Study area	pm25-CU	pm25-FE	pm25-ZN	pm25-SI	pm25-K	pm25-S	pm25-NI	pm25-V
Oslo	3.3 (345%)	79.8 (259%)	13.5 (142%)	91.8 (284%)	86.4 (149%)	369.3 (86%)	0.6 (262%)	1.4 (250%)
Stockholm County	4.0 (265%)	142.3 (207%)	11.7 (79%)	212.9 (221%)	112.7 (96%)	524.9 (22%)	1.3 (286%)	1.4 (146%)
Helsinki/Turku	1.8 (199%)	75.2 (204%)	15.7 (46%)	112.1 (172%)	113.3 (65%)	648.9 (37%)	1.4 (208%)	2.5 (157%)
Copenhagen	3.8 (298%)	70.9 (184%)	12.8 (64%)	49.4 (142%)	115.3 (39%)	710.6 (14%)	1.0 (146%)	2.4 (69%)
Kaunas	4.3 (116%)	75.1 (220%)	49.4 (189%)	116.7 (131%)	269.4 (88%)	887.6 (18%)	0.3 (431%)	1.0 (122%)
Manchester	3.0 (162%)	67.0 (137%)	11.8 (90%)	51.4 (90%)	71.1 (91%)	687.4 (25%)	0.7 (121%)	1.1 (94%)
London/Oxford	5.0 (290%)	111.1 (296%)	15.1 (90%)	60.1 (106%)	76.9 (62%)	696.2 (36%)	0.8 (129%)	1.9 (108%)
Netherlands/Belgium	5.0 (210%)	120.2 (204%)	28.1 (262%)	101.5 (243%)	119.2 (77%)	915.1 (72%)	2.3 (174%)	3.7 (209%)
Ruhr_Area	6.7 (132%)	241.9 (236%)	41.2 (164%)	155.9 (105%)	209.0 (75%)	1202.6 (31%)	1.9 (211%)	1.8 (39%)
Munich/Augsburg	7.9 (120%)	138.2 (182%)	20.4 (84%)	115.7 (166%)	269.1 (33%)	831.8 (26%)	0.5 (177%)	0.3 (158%)
Vorarlberg	3.9 (141%)	69.8 (94%)	22.0 (86%)	63.0 (60%)	338.3 (97%)	616.1 (25%)	0.1 (711%)	0.3 (90%)
Paris	7.6 (360%)	128.6 (298%)	22.8 (128%)	65.9 (154%)	104.0 (45%)	813.9 (49%)	0.8 (156%)	1.3 (86%)
Gyor	4.4 (137%)	89.5 (223%)	31.8 (154%)	114.3 (327%)	337.0 (48%)	1227.8 (16%)	0.2 (326%)	0.7 (62%)
Lugano	5.6 (251%)	144.5 (221%)	22.5 (90%)	113.2 (64%)	151.0 (52%)	917.1 (41%)	0.9 (133%)	0.7 (105%)
Turin	13.0 (179%)	253.4 (171%)	34.8 (90%)	184.1 (104%)	384.3 (47%)	1066.1 (35%)	2.6 (137%)	2.0 (68%)
Rome	14.2 (149%)	283.2 (136%)	22.9 (82%)	231.0 (128%)	297.1 (63%)	972.0 (22%)	1.5 (86%)	2.9 (82%)
Barcelona	11.1 (194%)	236.3 (173%)	57.8 (126%)	181.2 (96%)	175.2 (81%)	1041.7 (41%)	4.4 (121%)	9.5 (156%)
Catalunya	8.5 (282%)	196.1 (226%)	39.3 (243%)	185.0 (94%)	184.5 (208%)	952.8 (71%)	3.3 (213%)	6.4 (258%)
Athens	11.5 (227%)	257.6 (152%)	42.1 (128%)	291.9 (63%)	214.1 (46%)	1656.7 (18%)	2.5 (142%)	6.2 (130%)
Heraklion	2.4 (272%)	115.1 (75%)	12.7 (63%)	256.2 (81%)	275.5 (118%)	1514.2 (51%)	4.3 (173%)	9.7 (173%)
Mean all-areas	6.4 (216%)	144.8 (195%)	26.4 (120%)	137.7 (142%)	195.2 (79%)	912.7 (37%)	1.6 (217%)	2.9 (128%)
Mean north	3.2 (277%)	92.0 (214%)	13.4 (83%)	116.6 (205%)	106.9 (87%)	563.5 (40%)	1.1 (225%)	1.9 (156%)
Mean west/central	5.3 (192%)	118.6 (211%)	26.5 (134%)	95.8 (145%)	194.5 (67%)	879.6 (34%)	0.9 (257%)	1.3 (107%)
Mean south	10.1 (217%)	223.6 (156%)	34.9 (122%)	221.6 (95%)	255.1 (94%)	1200.6 (40%)	3.1 (145%)	6.1 (145%)
Study area	pm10-CU	pm10-FE	pm10-ZN	pm10-SI	pm10-K	pm10-S	pm10-NI	pm10-V
Oslo	15.8 (280%)	552.0 (219%)	22.4 (157%)	728.1 (286%)	222.9 (154%)	413.5 (58%)	1.2 (146%)	2.4 (164%)
Stockholm County	20.1 (268%)	816.9 (237%)	24.5 (174%)	1432.8 (236%)	377.3 (178%)	579.5 (33%)	1.7 (105%)	2.4 (122%)
Helsinki/Turku	7.3 (344%)	363.1 (301%)	22.9 (166%)	681.3 (236%)	262.6 (151%)	692.3 (42%)	1.6 (203%)	3.9 (250%)
Copenhagen	15.1 (256%)	361.8 (204%)	19.9 (103%)	280.6 (146%)	187.6 (39%)	786.6 (28%)	1.0 (119%)	2.7 (78%)
Kaunas	8.1 (165%)	357.2 (118%)	58.0 (158%)	654.6 (90%)	399.2 (58%)	964.6 (23%)	0.3 (668%)	1.6 (126%)
Manchester	10.4 (166%)	306.1 (146%)	18.0 (95%)	263.6 (136%)	149.8 (61%)	790.9 (33%)	0.9 (288%)	1.6 (65%)
London/Oxford	18.7 (397%)	520.6 (358%)	23.5 (140%)	304.5 (103%)	138.8 (57%)	789.7 (44%)	1.0 (115%)	2.5 (87%)
Netherlands/Belgium	19.2 (289%)	547.0 (278%)	43.5 (278%)	474.9 (290%)	223.2 (85%)	1070.3 (49%)	2.8 (167%)	4.5 (201%)
Ruhr_Area	22.3 (211%)	874.3 (204%)	64.6 (168%)	658.1 (96%)	336.2 (64%)	1309.9 (35%)	4.0 (244%)	2.1 (99%)
Munich/Augsburg	29.1 (229%)	687.9 (273%)	34.0 (173%)	557.6 (262%)	393.5 (33%)	898.5 (26%)	1.2 (405%)	0.4 (154%)
Vorarlberg	11.2 (156%)	359.5 (99%)	31.9 (76%)	402.3 (78%)	405.8 (90%)	664.5 (33%)	0.1 (1820%)	0.6 (206%)
Paris	33.8 (431%)	747.2 (343%)	40.2 (208%)	466.6 (204%)	182.5 (70%)	905.4 (62%)	1.3 (254%)	1.8 (91%)
Gyor	10.1 (217%)	394.0 (194%)	39.8 (132%)	519.3 (115%)	442.3 (53%)	1264.1 (19%)	0.3 (448%)	1.4 (62%)
Lugano	28.0 (338%)	741.1 (276%)	35.4 (128%)	505.0 (54%)	235.9 (47%)	905.8 (15%)	1.4 (70%)	0.9 (74%)
Turin	53.5 (197%)	1343.4 (165%)	61.8 (124%)	1233.3 (111%)	565.6 (51%)	1134.4 (36%)	5.7 (133%)	3.7 (88%)
Rome	57.6 (207%)	1296.8 (168%)	45.0 (131%)	1086.1 (153%)	513.3 (97%)	1085.6 (28%)	2.5 (168%)	4.2 (100%)
Barcelona	51.6 (261%)	1365.0 (201%)	104.8 (122%)	1243.6 (80%)	482.4 (75%)	1228.7 (42%)	6.1 (117%)	12.5 (119%)
Catalunya	41.0 (335%)	1164.5 (238%)	72.6 (219%)	1282.6 (108%)	485.6 (143%)	1104.1 (69%)	4.6 (191%)	8.0 (281%)
Athens	42.3 (332%)	1214.0 (202%)	68.3 (103%)	1266.8 (84%)	380.0 (53%)	1793.1 (19%)	4.7 (120%)	7.6 (116%)
Heraklion	9.6 (220%)	539.0 (113%)	21.3 (87%)	1107.5 (85%)	555.1 (87%)	1704.6 (36%)	5.9 (146%)	11.9 (165%)
Mean all-areas	25.3 (265%)	727.6 (217%)	42.6 (147%)	757.5 (148%)	347.0 (82%)	1004.3 (37%)	2.4 (296%)	3.8 (132%)
Mean north	14.6 (287%)	523.4 (240%)	22.4 (150%)	780.7 (226%)	262.6 (130%)	618.0 (40%)	1.4 (143%)	2.9 (153%)
Mean west/central	19.1 (260%)	553.5 (229%)	38.9 (156%)	480.6 (143%)	290.7 (62%)	956.4 (34%)	1.3 (448%)	1.7 (117%)
Mean south	42.6 (259%)	1153.8 (181%)	62.3 (131%)	1203.3 (103%)	497.0 (84%)	1341.8 (38%)	4.9 (146%)	8.0 (145%)

and 2.10 for PM_{10}_Cu and PM_{10}_Fe, respectively) despite low absolute levels. Zn mass, on the other hand, is more evenly split between $PM_{2.5}$ and PM_{10} with also slightly increasing levels across Europe interspersed with more frequent highs but relatively more modest southern levels.

Likely the most interesting story here is that of Cu/Fe/Zn (indicators of non-tailpipe emissions–brake and tire wear). From the ANOVA analysis of all areas combined, within area variability of Cu and Fe in the PM_{10} and PM_{coarse} fraction (Cu: 67%, 70%) and (Fe: 64%, 66%) was higher than either NO_2 (60%) or $PM_{2.5abs}$ (52%) and much higher than $PM_{2.5}$ (19%), PM_{10} (27%), and PM_{coarse} (29%) (Eeftens et al., 2012); furthermore, contrasts for Cu and Fe were greater than for Si, indicating that, in addition to their presence in direct non-tailpipe emissions, resuspension from traffic on major roads adds more than just crustal material to the coarser fraction (Schauer et al., 2006). Lower spatial contrasts of Fe in Southern Europe, but with higher concentrations in both $PM_{2.5}$ and PM_{10} fractions, are indicative of Fe of crustal origin from both resuspension in the drier climate combined with unpaved areas and possibly also some long-range Saharan dust events (Viana et al., 2008). Emitted primarily in the coarse size fraction, Cu and Fe's dispersion are more limited than NO_2 or soot while their availability for local resuspension persists. High within area spatial contrasts, in terms of local ST/UB ratios (ratios around 2), also confirms the relatively greater variability of these two traffic-related elements compared to the main PM pollutants (e.g., for ST/UB: 1.14 for $PM_{2.5}$; 1.38 for $PM_{2.5abs}$; 1.23 for PM_{10}; and 1.42 for PM_{coarse}) (Eeftens et al., 2012). Despite lower sample numbers, local UB/RB also have a twofold concentration difference. Similar observations of greater elemental PM variability have been made regionally in the Netherlands (higher contrasts of Cu, Fe and chromium than BC, NO_x, NO_2) (Boogaard et al., 2011; Strak et al., 2011) and London (Gietl et al., 2010). Interestingly, unlike other southern areas, Heraklion,

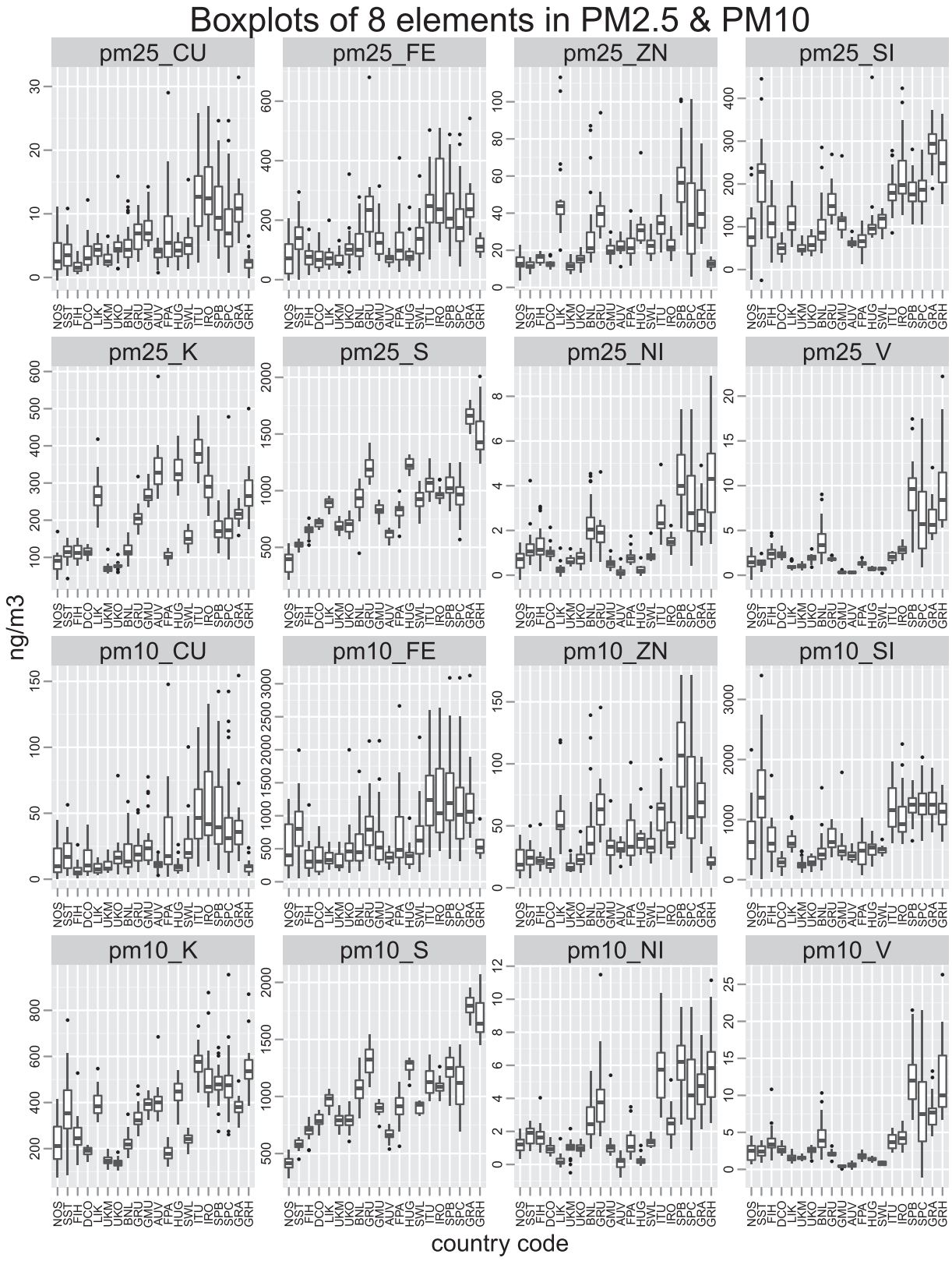

Fig. 2. Distribution of eight elements in both $PM_{2.5}$ and PM_{10} size fractions across Europe. The city codes are indicated in the abbreviations list at the beginning; the specific ordering of ESCAPE study areas can be grouped into: Northern Europe on the left (Oslo, Norway to Copenhagen, Denmark); Central/Western European areas in the middle (Kaunas, Lithuania to Lugano, Switzerland); and Southern European areas on the right (Turin, Italy to Heraklion, Greece).

Greece has low levels of Cu and Fe, which is most likely due to the relatively lower traffic density as levels of NO_2 and NO_x are also low in this smaller city (Cyrys et al., 2012).

Zn's story is more complex as it is more equally present in both size fractions (see Fig. 3) and its percentage of total variance is quite evenly split into between and within area variability indicating its presence in

Table 2
Ratios between mean regional background (RB) and mean urban background (UB) concentrations, and between mean street (ST) and mean urban background (UB) concentrations for all study areas (RB/UB; ST/UB). Additionally, these ratios were also calculated for all areas and the regions of Northern Europe, Western/Central Europe, and Southern Europe.

Study area	pm25-CU	pm25-FE	pm25-ZN	pm25-SI	pm25-K	pm25-S	pm25-NI	pm25-V
Oslo	0.13; 3.01**	0.68; 3.95**	0.61; 1.26*	0.71; 2.74**	0.83; 1.21	0.84; 0.97	0.06*; 0.95	0.22; 1.00
Stockholm County	0.45; 1.25	0.30**; 1.54**	0.78; 1.12	0.24**; 1.49**	0.68**; 1.19**	0.98; 1.02	0.71; 0.78	0.69; 1.19
Helsinki/Turku	0.72; 1.89**	0.34; 1.43	1.05; 1.23**	0.54; 1.12	1.02; 1.12	0.90; 1.00	0.46; 1.18	0.51; 1.05
Copenhagen	0.64*; 2.55**	0.74; 2.30**	0.92; 1.08	0.60; 0.96	1.03; 1.01	0.96; 1.04	0.87; 1.16	0.80; 1.03
Kaunas	0.77; 1.06	0.64; 0.84	0.71; 0.83	0.86; 1.10	0.86; 0.83**	1.02; 1.00	0.58; 0.45	0.94; 1.19
Manchester	NA; 1.73**	NA; 1.53**	NA; 1.16	NA; 1.32**	NA; 1.10	NA; 1.00	NA; 1.15	NA; 1.07
London/Oxford	0.33*; 1.63*	0.29*; 1.79**	0.79; 1.13	0.54; 1.18	0.97; 0.99	1.08; 0.93	0.25**; 0.78*	0.45**; 0.94
Netherlands/Belgium	0.70**; 1.77**	0.74**; 1.81**	0.95; 1.05	1.07; 1.70**	1.01; 1.06	0.91; 1.02	0.75; 0.94	0.75; 0.92
Ruhr_Area	0.60**; 1.25	0.56; 0.93	0.62; 0.89	0.77; 0.98	0.84; 0.90	0.90**; 1.02	0.54**; 1.16	0.91; 1.01
Munich/Augsburg	0.66**; 1.26	0.54**; 1.33	1.09; 1.15	0.84*; 1.08	1.08*; 1.07	1.07; 1.07*	0.84; 1.25	1.21; 0.85
Vorarlberg	0.59; 1.03	0.77; 1.25*	0.71**; 0.98	1.21*; 1.04	0.87; 1.02	0.97; 0.99	-0.33*; 0.44	1.08; 1.10
Paris	0.36; 2.00*	0.41**; 2.22**	0.65**; 1.23	0.79; 1.30*	0.92; 1.08	0.93; 1.06	1.40; 1.50**	1.00; 1.26**
Gyor	0.34; 1.06	0.78; 1.70**	0.68; 0.88	0.96; 1.69	0.85; 0.94	0.98; 1.01	0.56; 0.56	1.03; 1.04
Lugano	0.42**; 1.42	0.45**; 1.32	0.72**; 1.12	0.65**; 0.81*	0.70**; 0.94	0.78**; 0.88*	0.88; 0.69	0.74; 1.11
Turin	0.27**; 1.87**	0.38*; 1.81**	0.62**; 1.28**	0.55**; 1.36**	0.78; 1.03	0.87; 1.06	0.62*; 1.35**	0.68; 1.14
Rome	0.61*; 1.54**	0.59; 1.61**	1.00; 1.28**	0.84; 1.33*	1.18; 1.08	0.98; 1.03	0.88; 1.10	0.73; 1.00
Barcelona	0.41**; 1.96**	0.48**; 1.83**	0.63; 1.56**	0.62; 1.14	0.67; 1.04	0.82*; 1.09**	0.51; 0.99	0.57; 0.97
Catalunya	0.30**; 1.85**	0.48**; 1.77**	0.38**; 1.30	0.79*; 1.17**	0.75; 1.08	0.77**; 1.04	0.38**; 0.85	0.40; 0.86
Athens	0.70; 1.64**	0.93; 1.44**	0.54; 0.97	1.02; 1.07	0.75**; 1.07*	0.91; 1.02	0.66; 1.01	0.62; 0.95
Heraklion	NA; 1.13	NA; 1.05	NA; 1.04	NA; 1.03	NA; 1.05	NA; 1.00	NA; 0.80	NA; 0.77
Mean all-areas	0.54**; 1.60**	0.55**; 1.52**	0.78**; 1.15**	0.66**; 1.17**	0.87; 1.03	0.84**; 0.97	0.53**; 0.97	0.48**; 0.90
Mean north	0.52; 2.03**	0.47**; 2.00**	0.84*; 1.17**	0.42**; 1.42*	0.92; 1.16**	0.98; 1.07	0.66; 1.08	0.60**; 1.10
Mean west/central	0.65**; 1.39**	0.66**; 1.37**	0.89; 1.02	1.00; 1.27**	0.97; 1.04	0.96; 1.01	0.93; 0.99	0.97; 1.01
Mean south	0.51**; 1.78**	0.58**; 1.62**	0.59**; 1.34**	0.71**; 1.08	0.81; 1.04	0.73**; 0.94	0.46**; 0.95	0.44**; 0.86
Study area	pm10-CU	pm10-FE	pm10-ZN	pm10-SI	pm10-K	pm10-S	pm10-NI	pm10-V
Oslo	0.29; 3.49**	0.49; 3.07**	0.67; 1.88**	0.65; 2.78**	0.77; 1.75**	0.86; 1.06	0.74; 1.31	0.42; 1.52**
Stockholm County	0.25**; 1.73	0.30**; 1.77**	0.56**; 1.51**	0.30**; 1.68**	0.49**; 1.49**	1.04; 1.06	0.45**; 0.98	0.61**; 1.45**
Helsinki/Turku	0.64; 2.07*	0.48; 1.67	0.83; 1.29	0.60; 1.33	0.85; 1.21	0.85*; 0.99	0.51; 1.23	0.49; 1.24
Copenhagen	0.50**; 3.37**	0.56; 2.58**	0.81; 1.31**	0.55; 1.12	0.96; 1.00	0.95; 1.03	0.72; 1.01	0.77; 1.02
Kaunas	0.71; 1.44*	0.63*; 1.12	0.74; 0.90	0.97; 1.32**	0.92; 0.92	1.03; 1.02	0.20; 0.44	0.76; 1.22
Manchester	NA; 1.82**	NA; 1.77**	NA; 1.30**	NA; 1.56**	NA; 1.02	NA; 1.04	NA; 1.91**	NA; 1.08
London/Oxford	0.43; 2.11**	0.35; 2.06**	0.91; 1.36**	0.54; 1.15	0.80; 1.09	1.17; 0.92	0.78; 1.03	0.58; 1.01
Netherlands/Belgium	0.61**; 2.55**	0.66**; 2.08**	0.79; 1.13	0.86; 1.53**	0.94; 1.13**	0.92*; 1.05	0.76; 1.07	0.73; 0.92
Ruhr_Area	0.59**; 1.73**	0.50; 1.10	0.60*; 0.91	0.75; 1.04	0.83; 0.92	0.92; 1.01	0.56*; 1.23	0.80*; 0.84*
Munich/Augsburg	0.54**; 1.80*	0.53**; 1.72	0.99; 1.37	0.86; 1.43	1.08; 1.12**	1.05; 1.06*	0.84; 1.66	0.99; 1.13
Vorarlberg	0.69; 1.63**	0.78; 1.42**	0.75**; 1.12	1.05; 1.24**	0.92; 1.04	0.96; 1.00	46.67; 47.60	0.99; 0.77
Paris	0.19**; 3.54**	0.42**; 2.90**	0.60**; 1.77**	0.83; 1.67**	0.97; 1.19**	0.85*; 1.13*	0.95; 2.24**	0.85; 1.26**
Gyor	0.63; 1.63**	1.02; 1.71**	0.77; 0.97	1.22; 1.37**	0.95; 0.97	1.04; 1.00	0.30; 0.92	0.96; 1.09
Lugano	0.40**; 1.86	0.46**; 1.62	0.68**; 1.31*	0.77; 0.90	0.77**; 1.03	0.90**; 0.91**	1.13; 0.89	0.80; 0.98
Turin	0.32; 2.40**	0.44; 2.06**	0.56*; 1.55**	0.64; 1.53**	0.82; 1.08	0.97; 1.08	0.64; 1.54**	0.71; 1.33**
Rome	0.44**; 2.29**	0.58*; 2.17**	0.80; 1.72**	0.92; 1.72**	1.08; 1.31**	0.93; 1.03	0.56**; 1.48**	0.68*; 1.14
Barcelona	0.29**; 2.81**	0.40**; 2.06**	0.59; 1.72**	0.53*; 1.09	0.58; 1.07	0.76; 1.05	0.52; 1.14	0.58; 0.94
Catalunya	0.27**; 2.65**	0.61**; 2.00**	0.40**; 1.52**	0.93; 1.24**	0.80; 1.12	0.73**; 1.00	0.44*; 0.97	0.52; 0.79
Athens	0.68; 2.10**	0.73; 1.65**	0.53; 1.12	0.83; 1.17*	0.78**; 1.07	0.91; 1.00	0.47*; 1.16	0.59; 0.92
Heraklion	NA; 1.50*	NA; 1.15	NA; 1.17	NA; 1.09	NA; 1.06	NA; 1.02	NA; 0.89	NA; 0.79
Mean all-areas	0.44**; 2.28**	0.52**; 1.83**	0.71**; 1.35**	0.67**; 1.36**	0.81**; 1.12**	0.84**; 0.98	0.51**; 1.12	0.49**; 0.93
Mean north	0.39**; 2.52**	0.43**; 2.10**	0.72**; 1.48**	0.47**; 1.69**	0.75*; 1.37**	0.98; 1.09	0.59**; 1.14	0.60**; 1.31**
Mean west/central	0.56**; 2.03**	0.62**; 1.67**	0.85; 1.16*	0.96; 1.35**	1.00; 1.08	0.98; 1.03	0.95; 1.24	0.88; 1.01
Mean south	0.43**; 2.52**	0.60**; 1.95**	0.56**; 1.59**	0.82**; 1.27**	0.82**; 1.13**	0.73**; 0.94	0.44**; 1.10	0.51**; 0.87

* Significant difference between the site types at $p < 0.10$ level.
** Significant difference between the site types at $p < 0.05$ level. NA means that no regional sites were measured in the study area.

local and regional emissions. As a traffic related pollutant, it is present in tires, lubrication oil, and some brake pads, thereby appearing in both size fractions. Regionally, Zn is also emitted in certain industrial processes. This split is observed in the correlograms with decreased correlations between fine and coarse fraction compared to Fe and Cu. This less obvious mix of sources is also seen in its moderate level of spatial contrast and its quite moderate but varied ST/UB ratios between regions. Unlike Cu and Fe, the ST/UB ratios are greatest in Southern Europe. In the PM_{10} fraction, this could mean a combination of more tire wear along with greater resuspension in the south due to the warmer drier climate; and in the $PM_{2.5}$ fraction, this could be due to the greater number of mopeds and motorcycles which are more likely to burn lubrication oil (Hopke et al., 2008).

Undoubtedly, non-tailpipe emissions from traffic are a major contributor to the coarse mass fraction, considered to be of health relevance as well (Brunekreef & Forsberg, 2005); therefore, a focus on tail-pipe emissions control is likely only part of the solution for improved air quality and public health.

3.1.2. Ni & V

Both Ni and V have their mass primarily in the fine fraction. For Ni, the RB/UB ratios for both size fractions are well below 1; whereas for ST/UB for $PM_{2.5}$, it is about 1, but for PM_{10} greater than 1. Again, we see three curious Ni ratios for Vorarlberg (AUV) that are due to the ratioing of very low concentrations of Ni and a negative value from temporal adjustment. Just as for Ni, the RB/UB of V is below 1 for both size fractions. In contrast to Ni, both PM ratios of V are around 1. Interestingly, for Northern Europe, we see a mean ST/UB ratio for PM_{10}_V of 1.31.

Ni & V are emitted from both industrial activities and residual oil combustion. Although emitted in varying ratios depending on type

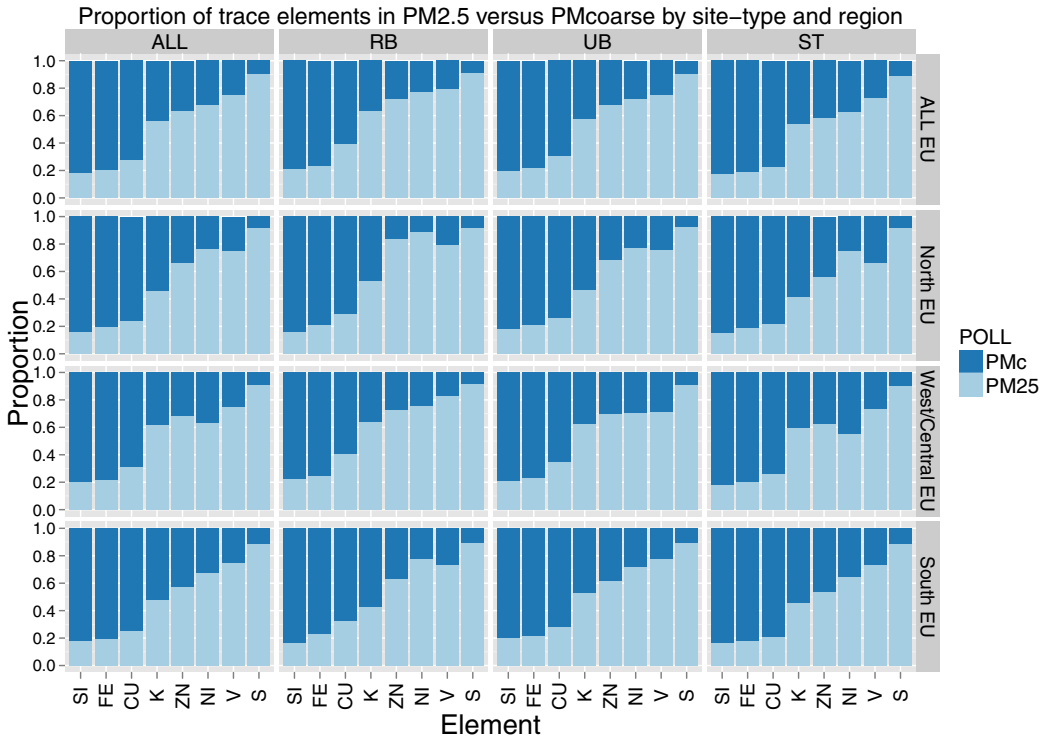

Fig. 3. Proportion of $PM_{2.5}$ and PM_{coarse} by element, site type, and region.

and quality of hydrocarbon being combusted (Moreno et al., 2010), they nevertheless have a similar trend across Europe. Levels are generally high in Southern Europe and areas with ports such as Belgium/Netherlands (Rotterdam port). These components are of particular interest as they are constituents of residual oil fly ash (ROFA), which toxicological studies have shown to, in addition to providing bioavailable transition metals, produce reactive oxygen species (Dye et al., 1997), release inflammatory cytokines (Veronesi et al., 1999), and affect signal transduction (Samet et al., 1996, 2000). Present primarily in the fine fraction (see Fig. 3), the highest levels are in areas with either shipping, oil heating, or sizable industry, which is mostly in the South (Barcelona, Catalunya, Athens, Heraklion), with some exceptions in Western/Central Europe (Belgium/Netherlands, Ruhr area). Interestingly, despite Rotterdam's significantly busier harbor, levels of V were clearly higher in Heraklion likely indicating different fuel oil use. Ni and V are modestly correlated in all areas, but most highly correlated in Southern Europe (see supplemental Fig. S5) likely due more specifically to port activities. Hedley et al. (2002) has shown that Ni and V, as well as S, levels were greatly reduced in Hong Kong as a result of the mandated switch to low sulfur fuels, which was accompanied by prompt and persistent reductions in daily mortality.

3.1.3. The individuals: Si, K, S

Si, like PM_{10}_K, is elevated in the coastal areas of Northern and Southern Europe. Silicon's RB/UB ratio is less than 1, while its ST/UB is greater than 1. As for Cu and Fe, Si ratios in Northern Europe are higher for ST/UB and lower for RB/UB than in other regions. Of the eight elements, Si is most dominated by the coarse fraction. It is more present in the arid windy coastal areas of the South that are also occasionally affected by Saharan dust events, but is also at high levels in Northern Europe due to its use in winter road treatment; for instance, Stockholm had the highest Si levels despite low PM mass concentrations. In the coarse fraction, it is most correlated with K and Fe both prevalent in resuspended road dust.

K concentrations in $PM_{2.5}$ and PM_{10} follow an entirely different pattern, and differ from one another. $PM_{2.5}$_K has high concentrations in many central European areas but low levels in Spain and Greece and much lower levels in the north. In contrast, PM_{10}_K has a different distribution with high amounts in Northern and Southern Europe. These different profiles by size result from its presence in wood combustion versus sea salt versus low-temperature road salt (in Northern Europe). Although $PM_{2.5}$_K is not a unique indicator of wood combustion, it is often used as a marker as its emission across a variety of wood types is fairly consistent (Fine et al., 2001). As a marker, it can however be confounded by meat cooking and refuse incineration, but, as there was a strong seasonal pattern with high winter levels, it likely reflects wood smoke more than other potential sources.

Within areas, K, after S, exhibits RB/UB and ST/UB ratios next closest to 1.0 for both size fractions with ST/UB slightly above 1, and RB/UB slightly below 1. This demonstrates the evenly distributed nature of this element in the environment. However, for Northern Europe, K ST/UB ratio is noticeably higher. In its fine size fraction, K is not highly correlated with any of the other elements.

S follows a definite rising trend from north to south in both size fractions with lowest levels in Oslo and Stockholm and highest levels in Athens and Heraklion (Fig. 2); however, it is clear that the mass is almost entirely within the $PM_{2.5}$ fraction. Primarily emitted in gas form by industrial (mainly power generation) point sources and transformed into PM (mostly sulfate) by secondary processes, it is homogeneously present regionally and indicative of the intensity of industrial activity. This is consistent with the high $PM_{2.5}$_S levels in both Hungary and the Ruhr industrial regions. The unusually high levels in Greece (higher than in either Barcelona or Rome — also seen in the RUPIOH study (Lianou et al., 2011)), however, may be a result of higher sulfur emissions from extra-European shipping activity and sea-salt aerosols (Tørseth et al., 2012). Its general high between area variance, also seen in area level ST/UB ratios of about 1, enables across area health effects analyses of S. Like $PM_{2.5}$_K, S is also not highly correlated with other elements.

For these elements, the adjustment for temporal variation affected the ranking of average concentrations within study areas, as indicated by the low correlation between unadjusted and adjusted average

concentrations (supplement S2). As temporal variation may not be fully adjusted for with a single site, additional noise may be present in the annual averages. The issue is probably least for S, as previous work showed that a single reference site correlated very highly with other sites for S (Montagne et al., 2014). Comparisons between study areas are not affected. Comparisons between different site types (street, background) are also not affected, as in each sampling period, the different site types were represented.

3.2. Overall trends

3.2.1. Analysis of variance and RB/UB & ST/UB ratios

Table 3 shows the fraction of variance attributed to between and within areas. For the selected elements, we see nearly analogous patterns in the PM_{10} and $PM_{2.5}$ size fractions. The variances of Cu and Fe are mostly explained within area (in PM_{10}: 67 and 64%, respectively). For nearly all the rest of the chosen elements (K, Ni, S, Si, V), the variance is less within area (ranging from 9–41%) compared to between areas. S has particularly high between area variance; whereas, zinc is roughly equally divided into between and within area.

These ANOVA results generally demonstrate at the European level that elements related to traffic emissions (tailpipe or non-tailpipe) had greater within-area variability than PM mass. The ST/UB levels confirmed those results at the area and regional level with significantly different ratios by site type for elements that were more associated with traffic sources (Cu, Fe, Si, and Zn). In general, RB/UB ratios have fewer significantly different ratios than ST/UB — likely due to the lower number of comparable sites. For the most part, RB/UB ratios were similar between the size fractions, but ST/UB ratios were greater for the PM_{10} size fraction (noticeably for Cu, Fe, Ni, Si, Zn); furthermore, more of the PM_{10} ratios are significantly different from 1. This makes good sense as the larger size fraction will disperse less than the finer size fraction for traffic related pollutants. Of note, RB/UB ratios, despite being based on fewer sites, are for the most part consistently below 1.0 and show fairly large contrasts between urban and regional background sites. Elements representing sources of a more regional nature, such as S and K, had ratios closer to 1.0 for both ratios and were only rarely significantly different by site type.

Table 3
Between and within study area variance [fraction] by ANOVA using linear mixed-effect modeling with restricted maximum likelihood (REML) method. These results for the main pollutants (NO_2, NO_x, $PM_{2.5}$, PM_{10}, $PM_{2.5abs}$, and PM_{coarse}) have been reported previously (Cyrys et al., 2012; Eeftens et al., 2012).

	Between_area_var	Within_area_var
NO_2	0.40	0.60
NO_x	0.30	0.70
PM_{25}	0.81	0.19
PM_{25abs}	0.48	0.52
PM_{10}	0.73	0.27
PM_{coarse}	0.71	0.29
pm25_CU	0.46	0.54
pm25_FE	0.45	0.55
pm25_ZN	0.52	0.48
pm25_SI	0.65	0.35
pm25_K	0.85	0.15
pm25_S	0.91	0.09
pm25_NI	0.64	0.36
pm25_V	0.67	0.33
pm10_CU	0.33	0.67
pm10_FE	0.36	0.64
pm10_ZN	0.51	0.49
pm10_SI	0.59	0.41
pm10_K	0.75	0.25
pm10_S	0.90	0.10
pm10_NI	0.67	0.33
pm10_V	0.66	0.34
pmC_CU	0.30	0.70
pmC_FE	0.34	0.66
pmC_ZN	0.46	0.54
pmC_SI	0.57	0.43
pmC_K	0.66	0.34
pmC_S	0.35	0.65
pmC_NI	0.52	0.48
pmC_V	0.37	0.63

3.2.2. Proportion of $PM_{2.5}$ and PM_{coarse}

To help interpret the existing spatial variability, Fig. 3 shows for all ESCAPE areas the median proportion of $PM_{2.5}$ versus PM_{coarse} (PM_{10}–$PM_{2.5}$) for different site types (All, RB, UB, ST) and regions of Europe (All Europe, Northern Europe, Western/Central Europe, Southern Europe). As a reference, we reorder the components in terms of increasing $PM_{2.5}$ proportion for all site types and all of Europe (top left panel). We see Si, Fe, and Cu consistently dominating the coarse fraction. The remaining elements from K, Zn, Ni, V to S are increasingly present in the finer fraction, with S almost entirely in the fine fraction. The coarse proportion of Zn, Ni, and V, although less than the fine fraction in general, increases from regional to urban background to street sites.

3.2.3. Relation between the pollutants

The correlogram in Fig. 4 presents the median Pearson correlations between ESCAPE main pollutants (NO_2, NO_x, $PM_{2.5}$, PM_{10}, PM_{coarse}, $PM_{2.5abs}$) and trace elements of the three different size fractions of all 20 ESCAPE areas. The addition of PM_{coarse} allows us to see correlations between the non-overlapping fine and coarse size fractions. Generally, PM mass is low to modestly correlated (Pearson R: 0.25 to 0.75) with the selected elements (slightly better for PM_{10}). Element-wise, Cu and Fe were highly correlated ($R > 0.75$) within and between the $PM_{2.5}$, PM_{10} and PM_{coarse} size fractions. Additionally, the coarse fraction of Zn is also well correlated with Cu and Fe in PM_{10} and PM_{coarse} as well as with NO_2, NO_x, $PM_{2.5abs}$, PM_{10} but less well with $PM_{2.5}$ and $PM_{2.5}$_Cu. For the remaining 5 elements (with the exception of Si), the observed high by element correlation of the $PM_{2.5}$ and PM_{10} size fractions disappears when $PM_{2.5}$ and PM_{coarse} are compared showing that the correlation was driven by the overlapping fine fraction.

While we observed that NO_2, NO_x, $PM_{2.5abs}$, using a lower threshold of $R > 0.75$, were consistently correlated with Cu and Fe, this pattern only held true for one (Southern Europe) of the three regional correlograms (see supplemental Figs. S3–S5). Thus, a better way to look at this is to see which elements correlate well (again using $R > 0.75$) with the main pollutants *by region*. From this perspective, we consistently see that K, Ni, S, V cannot be well described by the main pollutants. So, at best three of the main pollutants correlate well with half the eight chosen elements when examining all the data together. But we have also clearly seen that two of the elements (Cu and Fe) are much more variable than any of the main pollutants (except NO_x) and represent a different non-tailpipe emission size fraction. And, even though ANOVA showed that a majority of these elements may have greater between area variability, they still have substantial within area variability and ought to be explored locally. Likely more than half of our eight elements have different spatial distributions thus offering the potential to disentangle different health effects currently ascribed to PM.

4. Conclusion

From our uniquely comparable dataset of PM trace element concentrations across Europe, we focused on eight elements in two size fractions. For these elements and size fractions, we observed great variability across Europe clearly demonstrating different PM composition by area. At the same time, we saw similar patterns between Cu and Fe (coarse fraction) and Ni and V (fine fraction). As expected, elements primarily from combustion sources, such as S, V, Ni, are found in the fine size fraction, while K and Zn are found sizably in both size

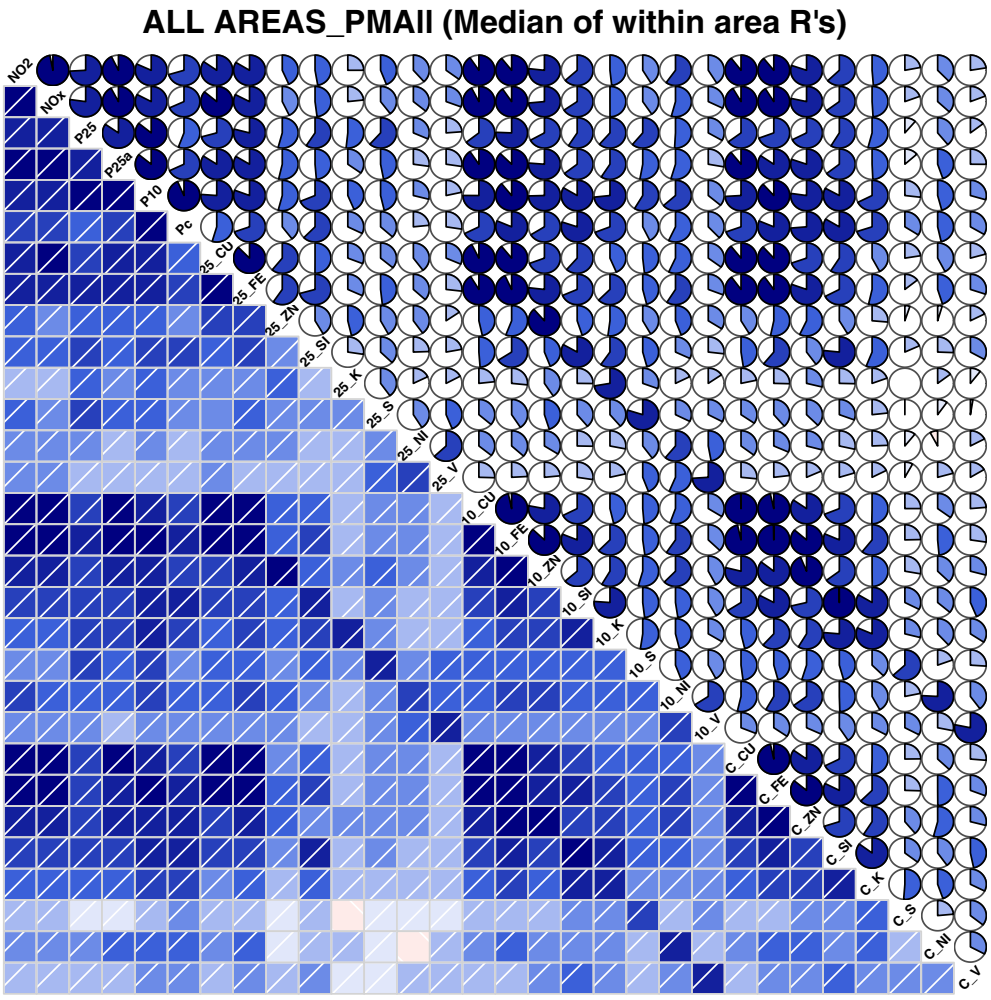

Fig. 4. Correlogram of medians of within area correlations for all areas together. Pearson correlations are shown in two different ways here: on the top right half, we have shaded pies where higher positive correlations are indicated by clockwise filling of the pie with increasingly darker shades of blue (higher negative correlations are shown with counterclockwise filling of pies with brighter shades of red — not observed here); on the lower left half, the waxing positive and negative correlations are simply shown with darker shades of blue or brighter shades of red (white diagonal line indicating a positive or negative relationship), respectively. On the main diagonal, the individual pollutant is labeled (25_*x* referring to element *x* in $PM_{2.5}$, 10_*x* referring to element *x* in PM_{10}, C_*x* referring to element *x* in PM_{coarse}). The correlations can be quantitatively interpreted by the fullness of the pie; e.g., a blue three-quarters full pie indicates an *R* of 0.75 or an R^2 of $(0.75)^2$ or 0.5625.

fractions; and Si, Fe and Cu are predominantly in the coarse fraction. Correlations between main pollutants and elements were mostly low to modest demonstrating distinctly different elemental spatial distributions. Within area variability was different by element and size fraction indicating that source impacts varied locally. Moreover, within-area variability of Cu and Fe in the PM_{10} fraction exceeded that of most other traffic-related pollutants, including NO_2 and soot, signaling the importance of non-tailpipe emissions in PM.

First epidemiological results from the ESCAPE study have already shown significant associations between $PM_{2.5}$ and natural cause mortality (Beelen et al., 2014), and between PM_{10} and lung cancer (Raaschou-Nielsen et al., 2013). As PM is an undoubtedly heterogeneous mixture, the question remains as to how the spatial distribution of its composition may differentially affect health across Europe. Towards that aim, harmonized land use regression models have been created for all selected elements in all 20 areas (de Hoogh et al., 2013). And elemental exposures have been assigned to the respective cohort subjects and a number of health endpoints ranging from respiratory, cardiovascular to mortality have been and continue to be investigated (Wang et al., 2014; Eeftens et al., 2014; Beelen et al., 2015; Wolf et al., 2015).

Conflict of interest

The authors declare that they have no competing financial interests.

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Supplementary data

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