Distribution and seasonal variability of trace elements in atmospheric particulate in the Venice Lagoon

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ABSTRACT

Size distribution and selected element concentrations of atmospheric particulate matter (PM) were investigated in the Venice Lagoon, at three sites characterised by different anthropogenic influence. The PM_{10} samples were collected in six size fractions (10–7.2, 7.2–3.0, 3.0–1.5, 1.5–0.95; 0.95–0.49 and <0.49 μm) with high volume cascade impactors, and the concentration of 17 elements (Al, As, Ca, Cd, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V, Zn) was determined by inductively coupled plasma quadrupole mass spectroscopy. More than 1 year of sampling activities allowed the examination of seasonal variability in size distribution of atmospheric particulates and element contents for each site.

At all the stations, particles with an aerodynamic diameter <3 μm were predominant, thus accounting for more than 78% of the total aerosol mass concentration. The highest PM_{10} concentrations for almost all elements were found at the site which is more influenced by industrial and urban emissions. Similarity in size distribution of elements at all sites allowed the identification of three main behavioural types: (a) elements found mainly within coarse particles (Ca, Mg, Na, Sr); (b) elements found mainly within fine particles (As, Cd, Ni, Pb, V) and (c) elements with several modes spread throughout the entire size range (Co, Cu, Fe, K, Zn, Mn).

Factor Analysis was performed on aerosol data separately identified as fine and coarse types in order to examine the relationships between the inorganic elements and to identify their origin. Multivariate statistical analysis and assessment of similarity in the size distribution led to similar conclusions on the sources.

1. Introduction

Epidemiological studies worldwide have indicated a strict relationship between airborne particulate matter (PM) and detrimental effects on human health (Pope, 1996; Schwartz et al., 1996). The percentage of matter inhaled through the respiratory tract as well as the degree of toxicity depend on the particle size; indeed, the chemical composition, which varies significantly in connection with particle size, regulates the toxicity of any specific element. Several studies have indicated the water-soluble metal content as a possible harmful component of airborne PM, and transition metals such as Cu, Fe, and Zn, associated with aerosol, have been hypothesised to cause cellular inflammation, as they mediate the release of free radicals in lung fluids (Donaldson et al., 1997). Moreover, different sources emit PM with different size distribution, which are deposited at different rates. Particles with diameters in the range of 0.1–1.0 μm (accumulation mode) deposit slowly and can be transported far from emission sources with effects on remote areas (Allen et al., 2001).

A bimodal distribution of atmospheric particulates has been reported for many urban sites (Chan et al., 2000; Karanasiou et al., 2007). The coarse particles (aerodynamic diameter >3 μm) are usually formed by mechanical action at high temperatures, crustal erosion, road dust resuspension and sea salts, being the fine fraction a mixture of primary and secondary aerosol, principally emitted from anthropogenic sources (combustion, high-temperature industrial activities, automotive traffic, etc.). Therefore, detailed information on the aerosol mass distribution and on its chemical composition is essential to identify their sources as well as to assess the environmental and health risks. Improvements in analytical techniques, together with the increase in awareness of ultraclean procedures have drawn on reliable information about trace element concentrations in the different size ranges of airborne particles. As trace element contents in aerosol can frequently be associated with specific anthropogenic sources, the trace metals may be used as tracers in order to identify the source of atmospheric PM (Weckwerth, 2001; Birmili et al., 2006).

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The Lagoon of Venice is a complex system situated in the northeast of Italy between the Adriatic Sea and a heavily industrialised and densely populated mainland (the urban area's inhabitants are more than 300000). Numerous local anthropogenic sources contribute to contaminate Lagoon atmosphere, particularly thermoelectric, petrochemical and incineration plants in the large industrial zone of Porto Marghera, glass factories, vehicular traffic, intense commercial and tourist harbours as well as airport traffic are involved in the process.

In the framework of a study, that was carried out to define the quality of the atmosphere of the Venice Lagoon, the size distributions of particulate matter and the element concentrations in atmospheric aerosol were investigated at three sites characterised by aerosol of different origin. Of these three sites, one was mainly affected by aerosol of marine origin and associated with long range transport, another one by aerosol of industrial and urban sources and the last one was affected by urban and vehicular traffic. Here, we report the results obtained for each site by the analysis of samples, which have been collected for more than 1 year with the aim of examining seasonal variability of particulate matter and its element size distribution. In order to study the differences observed in the relevant size distributions to the selected elements, factor analysis was performed separately on fine and coarse aerosol data. The examination of the relationship between the different inorganic elements actually helps in identifying the principal emission sources at the different stations.

2. Materials and methods

Aerosol sampling was conducted from March 2002 to July 2003 at three sites in the Venice Lagoon (Fig. 1): site 1 (lat. 45°25′38.5″N, long. 12°12′47.6″E), located downwind from the Porto Marghera industrial area and influenced by industrial and urban aerosol sources; site 2 (lat. 45°25′21.8″N, long. 12°26′12.2″E), affected by marine aerosol and long range sources; and site 3 (lat. 45°29′37.9″N, long 12°19′27.2″E) located downwind from a mainland urban area, close to Venice Airport and highway A27. Sixteen samples were collected at site 2, eleven at site 1 and 5 at site 3; they were then split into two groups based on season characteristics: October–March (cold season) and April–September (warm season).

Atmospheric PM sampling was performed by high volume six-stage cascade impactors (Tisch Inc.) with cut-offs for the aerodynamic particle sizes in μm: 10–7.2, 7.2–3.0, 3.0–1.5, 1.5–0.95, 0.95–0.49 and <0.49 (flux of 1.13 m^3 min^{-1}). Samples were collected when the wind blew from selected quadrants: southeast

at site 2, northeast at sites 1 and 3. A more comprehensive description of the sampling sites and the strategy was previously reported (Gambaro et al., 2004; Manodori et al., 2006).

The preparation of the material, which was previously described, was carried out under a laminar flow clean area (class 100). In short, filters were conditioned for 24 h at a temperature of 20° ± 5 °C and a relative humidity of 30 ± 5% and weighted with 0.01 mg precision.

The analytical procedure was previously described in detail, and is presented here only in short, some more details are reported on the supplementary file for analytical methodology (Toscano et al., 2009).

The samples were digested by a microwave oven (Milestone, Ethos 1600) in 100 ml tetrafluoromethoxyl vessels. The digestion mixture was composed of HNO$_3$, H$_2$O and HF at a ratio of 5:1.5:1; all the reagents were ultra-pure grade (Romil Ltd., Cambridge).

Al, As, Ca, Cd, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V and Zn were determined by inductively coupled quadrupole mass spectroscopy (Agilent model 7500). Quantification was carried out by a matrix-matched calibration curve, with 11 points to cover the entire concentration range of elements in the aerosol samples (Toscano et al., 2009).

Blank concentrations for the slotted membranes and the back filters, including the contribution from filter handling during sampling, were measured and used to correct the concentrations measured in the dissolved filters. The blank metal contents as μg/filter for the slotted membrane and the back filter are reported in the Supplementary Table A. The blank contribution to the total concentration was regularly under 20% for all the elements, only for arsenic and litium in samples collected in the site 2 and 3 blank frequently represented more than 50% of the total content, therefore element concentrations were under the detection limit so that such elements were excluded from the multivariate statistical analysis. In order to assess the significance of data, which have been separately identified as fine and coarse particles data, the LODs in term of ng m^{-3} were calculated as three times the SD for the blank concentration for the two classes (Supplementary Table A).

Accuracy and precision (repeatability) were measured using Standard Urban Dust Reference Material (NIST, SRM-1648) following the procedure reported in supplementary analytical methodology. The minimum recovery value was 80% for K and the maximum was 120% for Zn (Supplementary Table B).

3. Results and discussion

3.1. Particle mass concentration and size distribution

The PM$_{10}$ mass concentration measurements taken from March 2002 to June 2003 and separately identified as cold and warm season data at the three stations ranged from some units to some tens of μg m^{-3} (see Supplementary data in Table C), The values are consistent with the concentrations detected in many European cities (Heal et al., 2005; Hueglin et al., 2005; Viana et al., 2007; Pey et al., 2009; Makkonen et al., 2010; Vercauteren et al., 2011). The statistical tests did not show differences (at the 0.05 level) between the two season groups for sites 1 and 2. Site 3 showed a similar behaviour, however no statistical evaluation was possible because of the reduced number of samples collected during the warm season.

The general particulate distribution in the three sites in the warm and in the cold seasons was bimodal, registering the highest abundance in the 0.49–1.5 μm fraction and a relative maximum for the particulates with an aerodynamic diameter >3 μm (see Supplementary Fig. A). Only at site 3 a unimodal distribution with a maximum of the fine particulates was observed during the cold

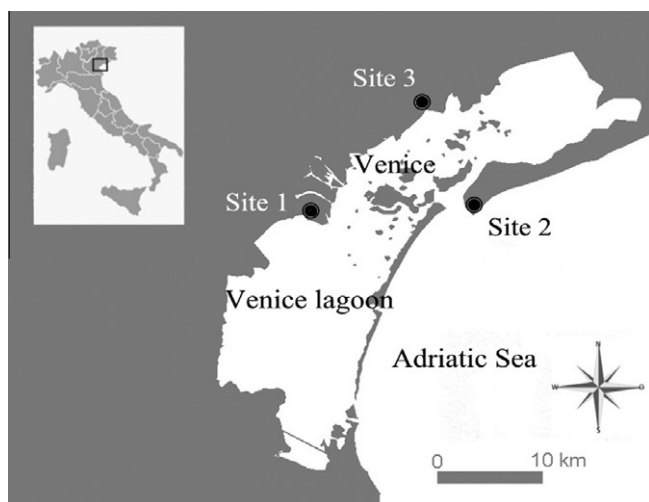Fig. 1. Sampling sites at the Venice Lagoon.

Table 1
Mean concentration (standard deviation) in ng m^{-3} measured from March 2002 to June 2003 in the three sites and mean concentration observed in some European urban areas.

	Al[a]	As	Ca[a]	Cd	Co	Cu	Fe[a]	K[a]	Li	Mg[a]	Mn	Na[a]	Ni	Pb	Sr	V	Zn[a]
Site 1	0.4 (0.2)	3 (2)	0.7 (0.4)	2 (2)	0.3 (0.1)	10 (6)	0.4 (0.2)	0.2 (0.1)	0.5 (0.1)	0.2 (0.1)	16 (8)	0.37 (0.05)	14 (5)	19 (10)	2 (1)	12 (3)	0.06 (0.06)
Site 2	0.13 (0.05)	Udl	0.16 (0.09)	0.6 (0.8)	0.06 (0.04)	4 (1)	0.14 (0.05)	0.13 (0.06)	0.11 (0.05)	0.10 (0.03)	5 (2)	0.5 (0.2)	3 (1)	10 (3)	1.1 (0.5)	5 (2)	0.03 (0.02)
Site 3	0.11 (0.05)	6 (5)	0.3 (0.1)	3 (3)	0.09 (0.04)	9 (5)	0.2 (0.1)	0.2 (0.1)	0.10 (0.01)	0.10 (0.04)	7 (3)	0.20 (0.07)	2 (1)	18 (9)	1.0 (0.4)	2 (1)	0.05 (0.04)
Flanders[b]	0.16	3.8	0.43			14	0.73	0.24		0.10	8.9	0.88	3.6	21		7.6	0.067
S-E Finland[c]	0.25	0.85		0.31	0.13	2.6	0.27				7.3		1.3	13		2.7	0.020
Stockholm[d]			0.88	0.11	0.15	7.7					5.5		2.3	3.4		1.6	0.017
Barcelona[e]		0.38		0.18	0.45	37	0.3	0.28		0.4	4.3	1.7	3.2	6.6	3.2	6.2	0.046
Birmingham[f,*]	0.53			0.21	0.08	10	0.09				4.0		0.93	9.6			0.033
Edinburgh[g]		0.37		0.34		4.9	0.18				2.9		3.4	14		1.1	0.013
Swiss urban areas[h]	0.103	0.54	0.41	0.27		31	0.77	0.23		0.06	10	0.38	2.2	26		1.3	

Udl = under detection limit.
[a] μg m^{-3}.
[b] Vercauteren et al., 2011.
[c] Makkonen et al., 2010.
[d] Johansson et al., 2009.
[e] Pey et al., 2009.
[f] Birmili et al., 2006.
[*] PM$_{7.5}$ metal concentration.
[g] Heal et al., 2005.
[h] Hueglin et al., 2005.

season. The particles with an aerodynamic diameter <1.5 μm were more than 70% of the PM$_{10}$, with the coarse fraction (>3 μm) ranging between 18% (site 3) and 22% of the PM$_{10}$ (sites 1 and 2). These results are generally in tune with literature data for urban and industrial areas (Chan et al.,1997, 2000; Manoli et al., 2002; Heal et al., 2005; Karanasiou et al., 2007).

3.2. Element concentrations and seasonal variability

The element PM$_{10}$ mean concentrations are reported in Table 1. The values detected at site 1 and site 3 were similar and in line with those reported for urban-industrial areas in Northern and Central Europe, mean concentrations detected in some European urban areas are reported in Table 1 (Heal et al., 2005; Hueglin et al., 2005; Birmili et al., 2006; Viana et al., 2007; Johansson et al., 2009; Pey et al., 2009; Makkonen et al., 2010; Vercauteren et al., 2011). The highest metal concentrations for almost all elements (either typical crustal or anthropogenic) was found at site 1, which is located downwind from the industrial zone of Porto Marghera and affected by urban emissions. Petrochemical production and refining, waste incinerators, or thermal-electric plants (fed by fossil fuels) are the main industrial activities. Moreover, a non-ferrous metal industry as well as glass factories are active in this area ("Rapporto ambientale d'area di Porto Marghera, Bilancio Ambientale", 1998–2007).

Gypsum landfill activities and relevant building works to renovate plants could account for the high PM$_{10}$ concentrations of typical crustal elements (Al, Fe, and Ca particularly).

The high concentrations and the size distribution of V, Ni, As and Cd can be related to electric power plants in the industrial zone. It is known that the combustion of coal is an important source of As and oil combustion is a significant source of V and Ni, being the non-ferrous metal industry accountable for emissions of As, Cd, Cu, Pb and Zn (Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001).

The average concentrations of Cd and As at sites 1 and 3 were higher – sometimes up to threefold – than those reported by many literature data, (Heal et al., 2005; Moreno et al., 2006; Salma et al., 2002). However, the data reported are in line with those obtained by different studies conducted in the Venice Lagoon (Mantovan et al., 2004; Gambaro et al., 2007; Rampazzo et al., 2008).

Arsenic is present in the environment of the Veneto region, its concentration in soils being currently above the regulatory threshold (20 mg kg^{-1}). The high concentration of As in soils is due to rock composition as well as to human activities; volcanic and mine areas contribute to naturally high As concentrations, while the fossil fuels, the agrochemical applications, the smelting and glass factories are the main anthropogenic As sources (Bini, 2008).

Table 2 reports the mean PM$_{10}$ and element concentrations separately defined as fine and coarse fractions as they have been measured in the warm and in the cold seasons. Significant season differences were observed in the fine fraction at site 2 for Ni, Cu, Zn and Pb (at the 0.05 level). Site 3 showed similar behaviour; the concentrations of Ni, Cu, Zn, Cd, Pb and As determined in the cold season were almost double than those determined in the warm season. However, because of the small amount of data, no statistical evaluation was possible at this station. A higher concentration of anthropogenic elements in the cold season has been regularly observed in urban regions (Lee et al., 1994; Voutsa et al., 2002), this can be ascribed to higher emissions from the combustion of fossil fuels and to the frequent and persistent thermal inversions at ground level of the Po Valley during the cold season (Marcazzan et al., 2001).

3.3. Seasonal element size distributions

On the basis of the size distributions (Fig. 2 and Supplementary Fig. B), elements could be roughly divided into three main groups: (a) elements, showing a large mode in the coarse fraction (3–10 μm), (b) elements showing a large mode in the very fine fraction (0.49 − 1.5 μm) and (c) elements presenting several modes spread throughout the size distribution. This behaviour is generally in line with the findings reported by other authors (Wang et al., 2006; Karanasiou et al., 2007); however, the size distribution of some elements was different as regards the three sites and the two seasonal groups.

3.3.1. Elements (Na, Mg, Sr, Ca)

The distribution of Na, Mg, Sr and Ca showed a large mode in the coarse fraction (3–10 μm) in all stations, indicating that they are mainly originated from natural sources. Their percentages in the coarse fraction ranged from 71% (Na) to 57% (Sr) at site 2,

Table 2
Mean concentration of PM (µg m^{-3}) and elements (ng m^{-3}) in the fine (PM$_3$) and corse fractions (PM$_{3-10}$) during warm and cold seasons.

| | Site 1 | | | | Site 2 | | | | Site 3 | | | |
| | Fine | | Coarse | | Fine | | Coarse | | Fine | | Coarse | |
	Warm[a]	Cold[b]	Warm[a]	Cold[b]	Warm[a]	Cold[b]	Warm[a]	Cold[b]	Warm[a]	Cold[b]	Warm[a]	Cold[b]
PM	26.4	24.5	7.81	6.77	22.4	20.2	6.81	4.73	21.7	29.7	5.53	5.70
Al	272	228	154	140	84	75	54	54	75	48	55	41
As	2.0	3.9	0.040	0.24					3.5	6.9	0.048	0.25
Ca	373	317	377	330	46	42	122	105	140	113	178	160
Cd	1.1	2.2	0.044	0.18	0.22	0.95	0.009	0.027	1.1	3.3	0.026	0.23
Co	0.19	0.23	0.065	0.084	0.040	0.039	0.016	0.018	0.046	0.069	0.028	0.026
Cu	6.3	6.4	2.9	3.9	2.2[c]	3.0[c]	1.1	1.1	4.7	7.0	2.7	2.9
Fe	227	196	135	157	88	94	47	55	126	147	73	77
K	144	219	50	59	81	117	34	24	91	273	31	31
Li	0.343	0.344	0.143	0.137	0.071	0.056	0.045	0.040	0.069	0.067	0.042	0.029
Mg	117	99	112	93	34	33	74	64	57	38	70	45
Mn	9.1	10.7	4.8	7.9	3.3	4.3	1.5	1.5	3.7	6.0	1.8	2.0
Na	195	217	169	165	140	173	422	339	91	99	144	71
Ni	11.8	12.9	2.1	2.6	2.1[c]	3.0[c]	0.17	0.48	1.1	2.2	0.22	0.41
Pb	16	18	2.2	3.3	8.2[c]	11.1[c]	0.62	0.88	8.8	21	0.81	1.9
Sr	1.22	0.97	0.96	0.84	0.45	0.53	0.64	0.64	0.64	0.44	0.57	0.41
V	9.8	10.7	1.5	1.9	4.6	5.3	0.39	0.61	1.7	2.1	0.18	0.27
Zn	43	55	9.1	23.6	20[c]	39[c]	3.8	6.0	20	58	1.9	9.9

[a] April–September.
[b] October–March.
[c] Seasonal difference significant at 0.05 level.

from 50% (Ca) to 45% (Na, Sr) at site 1 and from 57% (Ca) to 48% (Sr) at site 3. Yet at site 1, which is affected by industrial and urban sources, about 50% of these elements was present in the fine fraction. Therefore, we can hypothesise a significant contribution of the anthropogenic emissions in addition to the natural sources.

3.3.2. Elements (Cd, Pb, Ni, V, As)

These elements showed a large mode between 0.49 and 1.5 µm at all sites; Cd, Ni, V and As also showed an additional mode for $d_p < 0.49$ µm at site 1 which could be associated with the accumulation of particles probably related to emissions from local sources (Fig. 2 and Fig. B). As regards these elements both the enrichment factors and the dimensional distribution indicated a significant anthropogenic contribution indeed. The enrichment factor calculated by Al ranged between 72 for V and 3190 for Cd and, at site 1, the fraction with an aerodynamic diameter <0.49 µm was the highest.

The percentages of these combustion-derived elements were very low in the coarse fraction, ranging from 4% (As) to 16% (Ni) at site 1, from 3% (Cd) to 11% (Ni) at site 2 and from 3% (As) to 16% (Ni) at site 3. High concentrations were found in the fine fraction (<1.5 µm) with contribution rates ranging from 95% (As) to 77% (Ni) at site 1, from 94% (As) to 74% (Ni) at site 3 and from 93% (Cd) to 82% (Ni) at site 2. At all sites lead showed a homogeneous size distribution as far as concentrations are concerned. In spite of the fact that gasoline with lead additives was phased out in the Northern European countries during the period of this study, in many countries in Eastern and Southern Europe, it was still used in vehicles lacking catalytic converters (Allen et al., 2001; Karanasiou et al., 2007) and lead is present as an impurity of the gasoline. Measurements of isotopic composition of lead (Howearth et al., 2005) have shown a significant change in the radiogenic lead composition in comparison with the composition observed one decade before; the afore said observations emphasised that the fine particles transported by long-range mechanisms and coming from Eastern Europe can contribute to the total amount of lead particulates in the Venice Lagoon.

3.3.3. Elements (Al, Fe, Mn, Cu, Zn, Co, K)

Al, Fe, Mn, Cu, Zn, Co and K presented a bimodal distribution; the first at 0.95–1.5 µm and the second at 3–10 µm, in accord with

multiple sources. However, during the cold season, the second mode was much reduced or absent for Mn, Cu and Zn at site 2. This indicates that this site is slightly affected by local crustal erosion especially in winter season, being anthropogenic sources predominant. Furthermore, during the cold season, the "long range" transport contribution to the content of Mn, Cu and Zn in the atmosphere of the Venice Lagoon is remarkable. These size distributions are in tune with literature data from different geographical regions (Chan et al., 1997; Rizzio et al., 1999; Manoli et al., 2002; Wang et al., 2006).

The percentage of metals was lower in the coarse fraction than in the fine fraction. It ranges from 40% (Fe) to 23% (Zn) at site 1, 40% (Al) to 14% (Zn) at site 2 and 44% (Al) to 14% (Zn) at site 3. The metal content prevailed in the very fine fraction (<1.5 µm) with contributions to PM$_{10}$ ranging from 68% (K, Zn) to 46% (Fe) at site 1, from 73% (Zn) to 40% (Al) at site 2 and from 77% (K) to 37% (Al) at site 3.

3.4. Multivariate data analysis

The data processing was performed using Statgraphics Centurion XVI. Only the chemical species with concentrations above the detection limit in more than 40% of the samples were included in the datasets; therefore, As, Ca and Li were excluded from the multivariate analysis. The data set from site 3 was excluded from the analysis because only five campaigns were carried out.

The principal component analysis (PCA) was performed in order to emphasise differences between site 1 and 2 on the basis of PM$_3$ and/or PM$_{3-10}$ composition. Fig. 3 shows the 27 object scores for the PM$_3$ fraction and the variable loadings in the space of the first two principal components (the biplot for the PM$_{3-10}$ is presented in Fig. C). For both PM$_3$ and PM$_{3-10}$, the first two principal components explained for more than 80% of the total variance and the first principal component differentiated the two sites. As almost all variables had similar weights on the first PC, we hypothesised this component being related to the elemental concentration; indeed, the two sites differed in almost all metal concentrations. The biplot of the coarse fraction showed the relevance of Na in the coarse fraction of the site 2 samples derived from marine aerosol.

Factor analysis was used to explore the relationship between variables using a Varimax rotation procedure to maximise the explained variance. Table 3 presents the factor loading obtained
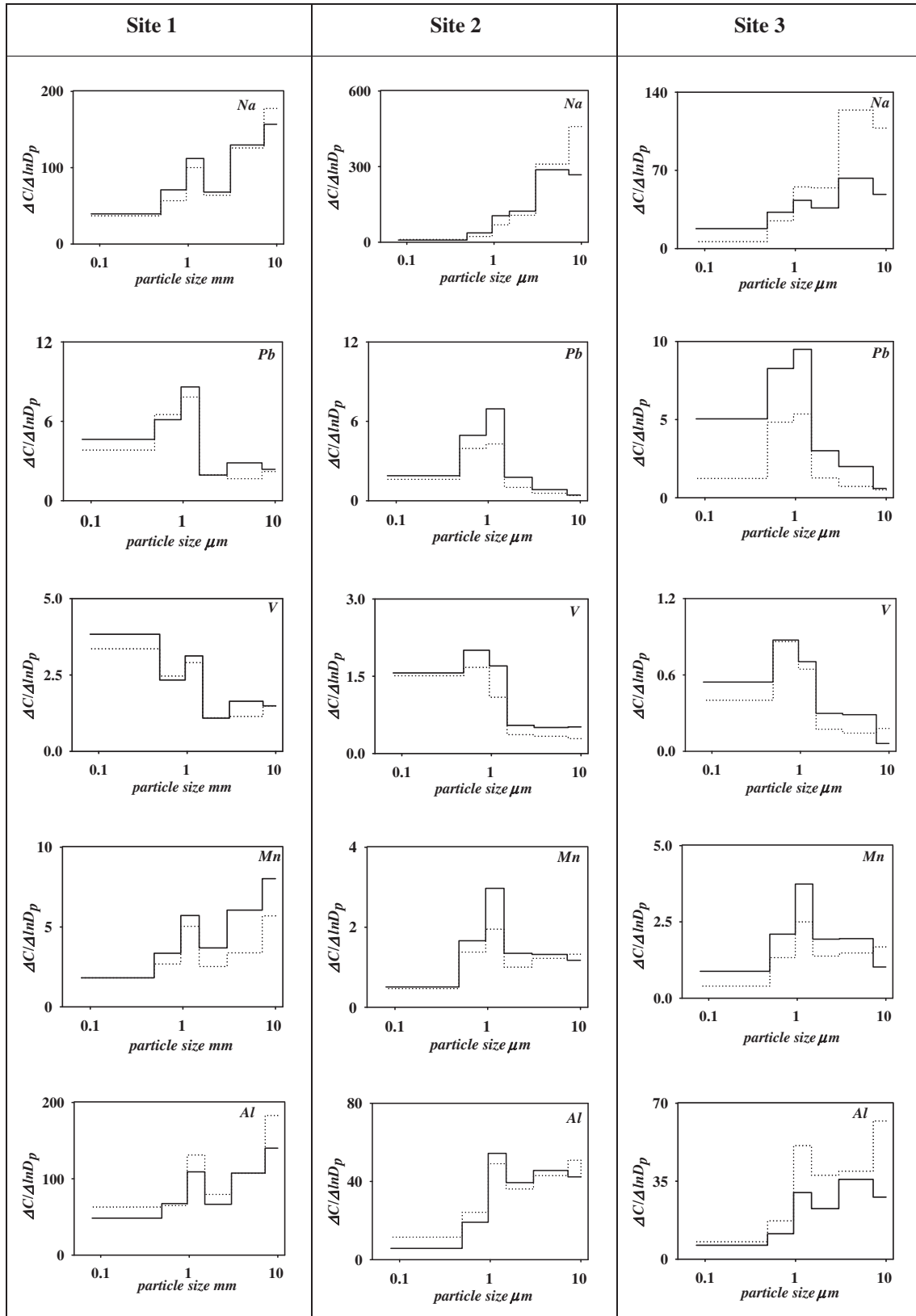
Fig. 2. Element size distribution at the three sampling sites expressed as differential mass concentration ($\Delta C/\Delta \ln D_p$ = incremental mass concentration/increment in ln particle diameter) in winter (——) and summer (…………); concentration in ng m^{-3}.

for the fine aerosol fractions from site 2. Four factors were obtained with eigenvalues >1, summing 80% of the total variance in the fine particle data set.

The first factor, accounting for 25% of the total variance, presented highest loading for Pb, K, Mn, Cu and Zn. These elements have been reported as being predominant in road dust, deriving
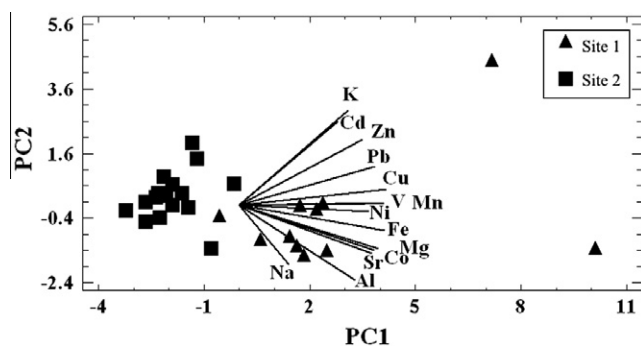
Table 4
Variable loadings in the factors obtained by Varimax rotation for the PM$_3$ at site 1.

Element	Factor 1	Factor 2	Factor 3
Al	−0.202	**0.850**	−0.097
Cd	**0.759**	0.052	0.310
Co	0.232	**0.906**	−0.178
Cu	**0.705**	0.649	0.226
Fe	0.418	0.887	0.141
K	**0.924**	0.033	0.207
Mg	0.220	**0.917**	0.155
Mn	0.713	0.578	−0.032
Na	−0.028	−0.012	**−0.920**
Ni	**0.863**	0.014	−0.293
Pb	**0.821**	0.469	0.030
Sr	0.242	**0.913**	0.039
V	**0.886**	0.216	−0.209
Zn	**0.763**	0.582	0.246

In bold loadings higher than |0.6|.

Fig. 3. PCA biplot relative to the PM$_3$ elemental composition of the sites 1 and 2, in the plane defined by the first two components.

Table 3
Variable loadings in the factors obtained by Varimax rotation for the PM$_3$ at site 2.

Element	Factor 1	Factor 2	Factor 3	Factor 4
Al	−0.064	0.023	**0.817**	−0.185
Cd	0.532	**0.603**	−0.279	−0.397
Co	0.145	−**0.831**	0.146	−0.021
Cu	**0.785**	0.022	0.089	0.253
Fe	0.452	−0.021	**0.833**	0.128
K	**0.712**	−0.312	0.105	−0.080
Mg	0.090	0.203	**0.904**	0.002
Mn	**0.723**	−0.027	**0.632**	0.148
Na	0.027	**0.770**	0.519	0.065
Ni	0.324	0.277	−0.027	**0.853**
Pb	**0.655**	0.096	0.367	0.187
Sr	0.154	**0.823**	0.432	−0.055
V	−0.102	−0.221	−0.060	**0.836**
Zn	**0.880**	0.278	−0.103	−0.209

In bold loadings higher than |0.6|.

from soil and other sources, such as tyre wear (Zn), brake drum abrasion (Fe), brake linings and diesel engines (Cu) (Weckwerth, 2001; Manoli et al., 2002; Birmili et al., 2006). Moreover, it is well known that vehicle emissions are sources of Pb. Therefore, we have hypothesised that this factor describes vehicular emissions and road dust resuspension. The second factor, accounting for 19.1% of the variance, has been associated with marine aerosol because of the high loading of Na and Sr (0.8). The third factor, accounting for 23.6% of the total variance, is characterised by high loading of Mg, Fe, Al and Mn, therefore it can be associated with crustal contribution. The fourth factor, accounting for 13.0% of the total variance, presented high loading for Ni and V. Vanadium is generally considered a marker of oil combustion (Pacyna and Pacyna, 2001) therefore this component can be associated with static combustion sources and "long range" transport; nevertheless, ship emissions from local maritime traffic cannot be excluded according to different studies carried out in the Venice Lagoon, (Rampazzo et al., 2008; Stortini et al., 2009).

Four factors were obtained for the coarse particles data set, which explained 84% of the total variance and showed a loading pattern similar to the fine particle data set. Remarkable differences were observed in the case of Pb and Mg, which presented high loading on the factors associated with oil combustion and marine aerosol, respectively.

Three factors were obtained with eigenvalues >1, summing 87% of the variance, for the fine data set from site 1 (Table 4). The first factor, accounting for 40% of the total variance, was characterised by high loading for Cu, Mn, Cd, Zn, Pb, Ni, V and K. This can be interpreted as incorporating traffic and road dust sources as well

as industrial emissions. The second factor, accounting for 38% of the total variance and showing the highest loadings for Al, Fe, Co, Mg, Sr and Mn, has been associated with crustal material. The third factor accounting for 9.4% of the total variance, is associated with marine sources as the Na presented the highest loading. Three factors were also obtained for the coarse particles data set, which are the reason for 94% of the total variance and showed a loading pattern similar to the fine particle data set one.

4. Conclusions

Atmospheric particulate samples were collected for more than 1 year at three sites in the Venice Lagoon to examine size distribution and seasonal variability of the particulate mass as well as the concentration of selected elements. The value of PM$_{10}$ content, separately identified in fine and coarse fractions, is in tune with values found in North European towns; such content was uniformly distributed in the Lagoon area, with an evident predominance of the fine fraction (diameter <3 μm). The size distributions at site 1 and site 2 appeared bimodal in both winter and summer seasons, but at site 3, the distribution of PM was unimodal in the cold season and bimodal in the warm one.

The mean element concentrations in PM$_{10}$ were similar at sites 2 and 3 and in line with values reported for urban-industrial sites in Northern and Central Europe. The highest PM$_{10}$ metal concentration for almost all elements was found at site 1, downwind from the industrial area of Porto Marghera and the Venice mainland urban area (Mestre).

Significant seasonal variations were observed at site 1 and site 3 for Ni, Cu, Zn and Pb in the fine fraction, which were ascribable to the higher contribution of fossil fuel combustion for heating and to the increase in traffic in the cold season, as well as to winter frequent thermal inversions at ground level.

The similarity in size distribution at all sites allowed the identification of three different element behaviour types: (a) associated to coarse particles (Na, Mg, Sr, Ca); (b) associated to fine particles (Cd, Pb, Ni, V, As) and (c) with multi-modes distribution spread throughout the entire size range (Fe, Zn, Cu, Co, Mn).

Factor analysis was performed on fine and coarse aerosol data to investigate the relationship between the inorganic elements and to identify their origin. A similar trend was observed for the coarse and fine particle data sets from sites 1 and 2. At site 2 four sources were identified according to the factors: vehicular and road dust, crustal sources, marine sources and fuel oil combustion emissions. At site 1, only three factors were significantly accounting for vehicular-road dust and industrial, crustal and marine emissions as sources. Multivariate data analysis and assessment on similarity in the size distribution drew on analogous conclusions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2011.09.045.

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