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Comparison of PM_{10} concentrations and metal content in three different sites of the Venice Lagoon: An analysis of possible aerosol sources

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Abstract

The Venice Lagoon is exposed to atmospheric pollutants from industrial activities, thermoelectric power plants, petrochemical plants, incinerator, domestic heating, ship traffic, glass factories and vehicular emissions on the mainland. In 2005, construction began on the mobile dams (MOSE), one dam for each channel connecting the lagoon to the Adriatic Sea as a barrier against high tide. These construction works could represent an additional source of pollutants. PM_{10} samples were taken on random days between 2007 and 2010 at three different sites: Punta Sabbioni, Chioggia and Malamocco, located near the respective dam construction worksites. Chemical analyses of V, Cr, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Tl and Pb in PM_{10} samples were performed by Inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) and results were used to identify the main aerosol sources. The correlation of measured data with meteorology, and source apportionment, failed to highlight a contribution specifically associated to the emissions of the MOSE construction works. The comparison of the measurements at the three sites showed a substantial homogeneity of metal concentrations in the area. Source apportionment with principal component analysis (PCA) and positive matrix factorization (PMF) showed that a four principal factors model could describe the sources of metals in PM_{10}. Three of them were assigned to specific sources in the area and one was characterised as a source of mixed origin (anthropogenic and crustal). A specific anthropogenic source of PM_{10} rich in Ni and Cr, active at the Chioggia site, was also identified.

Key words: MOdulo Sperimentale Elettromeccanico; metals; Venice Lagoon; PM_{10}; principal component analysis; positive matrix factorization

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Introduction

Atmospheric particulate matter (PM) is a worldwide issue, involving factors like atmospheric emissions, anthropogenic activities, air quality, human health and climate change. Estimates of global emissions show how natural and anthropogenic sources can contribute to atmospheric aerosol in the form of particles of different size (Liousse et al., 1996; Chung and Seinfeld, 2002; Zender et al., 2004; Liao and Seinfield, 2005), which may have different adverse effects on human health (Brunekreef and Holgate, 2002; Ibald-Mulli et al., 2002; Schwarz et al., 2002). The PM chemical characterization can give information about the aerosol sources. Commonly, PM studies have performed using various "bulk" techniques to evaluate the contribution of the different sources with statistical receptor models (Thurston and Spengler, 1985; Viana et al., 2008a; Amato et al., 2009). Moreover, in recent years several studies have been performed with chemical characterization of single particles with qualitative and quantitative techniques such as Aerosol Mass Spectrometer (AMS), Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) (De Carlo et al., 2006; Drewnick et al., 2008; Johnson et al., 2008; Takegawa et al., 2009), as well as Scanning Electron Microscopy (SEM) (Shao et al., 2007) or Transmission Electron Microscopy (TEM) (Li and Shao, 2009).

Based on their origin, major and trace inorganic elements composing particulate matter can often be distinguished in natural (e.g., Na, Mg, K, Ca, Si, Al) and anthropogenic (e.g., V, Cr, Mn, Ni, Cu, Zn, Cd, Pb) emissions. In the case of anthropogenic emissions, fossil fuel combustion is believed to be one of the main sources of PM (Sahu et al., 2011). Elements such as As, Se, Cd, Pb, Sb, Se, Cr, Co, Cu, Ga, and Mo well represent this source because they are emitted by coal combustion (Godoy et al., 2005; Grgić et al., 2009; Thurston et al., 2011); while

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V, Ni, Pb are emitted mostly by oil combustion sources (Viana et al., 2008b; Horemans et al., 2011). V and Ni may also be tracers of ship traffic emissions (Yuan et al., 2006; Minguillòn et al., 2008; Amato et al., 2009; Viana et al., 2009), which could be an important source for the Venice area. Industrial processing of materials and non-ferrous minerals can represent an important source of Cd, Zn, Cu, Hg (Sànchez de la Campa et al., 2011), while industrial production of iron, cast iron and steel, represent a good source of elements like Ni, Zn, Pb, Cu (Gladtke et al., 2009). Further, Cu, Zn, Pb and Sb are often associated to traffic emissions and road dust (Weckwerth, 2001; Manoli et al., 2002; Birmili et al., 2006).

The Venetian area, studied here, is located at the edge of the Po Valley and is subjected to long-range transport of particulate from the valley (Prodi et al., 2009). Furthermore, it is an area with significant local anthropogenic emissions due to the presence of two medium size urban areas, to the presence of one of the largest Italian industrial zone (about 12 km^2), to the presence of artisan glass factories (Murano island) and to the emissions of ship traffic within the lagoon. Since the beginning of 2005, the Venice Lagoon has also been affected by emissions linked to the construction of the MOSE mobile dams, one dam for each channel that connects the lagoon to the Adriatic Sea (Chioggia, Malamocco and Punta Sabbioni).

The present work illustrates and discusses the results of measurements of PM_{10} concentration and its metal content, obtained at three different sites. Measurements were taken between 2007 and 2010 and were statistically analysed, using both correlation with local meteorology, analysis of enrichment factors (Watson et al., 2002; Lu et al., 2007) and well established source apportionment methods: principal component analysis (PCA) and positive matrix factorization (PMF). These methods are widely used approaches for studying aerosol sources in specific areas (Krecl et al., 2008; Viana et al., 2008a; Xie et al., 2008). The objectives of the analysis were to characterise the sources of aerosols in the Venice area, estimate the spatial variability in concentrations and sources, and identify any eventual contribution due to the MOSE construction work. A cluster analysis (CA) of the data-set was also performed for comparison purposes, which could furnish valuable information on the stability of the source identification in cases where the chemical composition is characterised by a limited number of species (Prendes et al., 1999; Ho et al., 2006). In addition, the sources found were compared with other source apportionment studies of PM_{10} and $PM_{2.5}$ performed at other sites in the Venice area (Rampazzo et al., 2008a; Stortini et al., 2009).

1 Experimental

1.1 Description of measurement sites and sampling strategy

The Venice Lagoon area (almost 550 km^2) consists of 8% emerged land, 11% water and around 80% of mud plains, salt marshes and artificial marshes. The city of Venice (about 270,000 inhabitants) is located in the lagoon, in the northern part of the Adriatic Sea, and at the northeast boundary of an extensive plain (Po Valley). The area (Fig. 1) is subjected to significant emissions also from the urban area of Mestre and from road traffic (highways and main roads) and from the airport located in the mainland. Other significant sources are the industrial area, having a size of about 12 km^2 and located near the city of Porto Marghera, that include oil refinery, thermo-electrical power plant and a waste incinerator. Ship traffic (public transport, tourist and merchandise activities) and glass factories (accounting for about 10% of primary PM_{10} according to the Venice administration, Comune di Venezia, 2005) are also influencing the pollution in the area. At the beginning of 2005, construction began on three large mobile dams (MOSE) for the protection of Venice City from high tides.

The presented work focused on the analysis of PM_{10} concentrations and their possible sources at the three sites shown in Fig. 1. The three sites, located in proximity to the construction works of the large MOSE mobile dams, were almost aligned in a row in the NNE-SSW direction at about 12 km one from the other. Specifically, the sites were: Punta Sabbioni located at 45°26′12.49″N, 12°25′29.05″E), Malamocco (located at 45°19’56.43″N, 12°19’15.48″E) and Chioggia (located at 45°13′48.55″N, 12°17′51.88″E). At the three sampling sites, daily samples of PM_{10} were collected from 2007 to March 2010 in several campaigns (generally 2 weeks), distributed to cover the different seasons. The total number of samples were 83 at Punta Sabbioni, 90 at Chioggia and 88 at Malamocco, making a total of 261 samples. Two meteorological stations were used for this work. The first was the station of Ceppe, located at 45°20′5.82″N, 12°18′59.40″E, about 1.2 km SSE of the Malamocco measurement site, and managed by the Venice Water Authority, providing reference data for

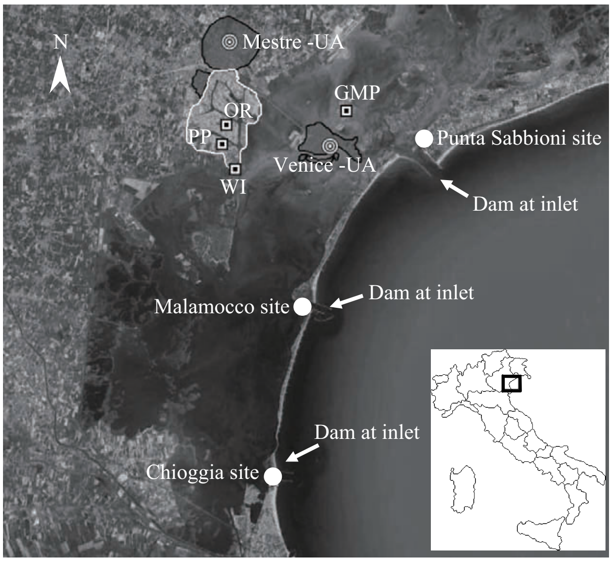

Fig. 1 Map showing the location of the three measurement sites (stars), the position of the urban areas of Venice and Mestre (UA), the position of the industrial area of Porto Marghera (bordered in white) with the indication of the position of the main sources: PP (power plant), OR (oil refinery) and WI (waste incinerator). The position of the GMP (glass-making production) is indicated together with the positions of the mobile dams construction at the three lagoon inlets.

the sites of Chioggia and Malamocco. The second station is located at the Punta Sabbioni sampling site.

The Venice area was characterised by prevailing winds from NNE-NE (frequency about 25%) and from SSE-SE (frequency about 11%). The wind velocity (using the year 2009 at Ceppe as reference) had a median value of 2.8 m/sec, with an interval (covering 5%–95% of the data) between 0.7 and 7.9 m/sec. Wind direction, especially in spring and summer, was characterised by a local daily circulation, with wind blowing from NNE-NE during the night and the early hours of the morning, and from SSE-SE during the diurnal hours of the day (Contini et al., 2007; Gambaro et al., 2007). This was due to the presence of a circulation with wind coming from the Alps during the night, and from the Adriatic sea during the day (Camuffo, 1981).

1.2 Equipment used and analytical protocol

The PM_{10} samples were collected using low volume sequential aerosol samplers (Skypost PM-TCR Tecora) operating at 2.3 m^3/ hr with 16 filters capacity (two filters were used as field blanks for each sampler load). The filters in quartz, Sartorius (diameter 47 mm), were used after careful decontamination, in a controlled atmosphere, using a procedure described elsewhere (Capodaglio et al., 1994). Filters for samplings and for blanks were weighted before and after sampling (a three-time-weight average with time interval of 24 hr), by means of a Sartorius Competence CP64-0CE balance (± 10 µg). The balance and the filters were kept within a nitrogen box, where temperature (20 ± 3°C) and humidity (50% ± 5%) were controlled before and during weighting, and field blanks were used to control systematic and random uncertainties. Each filter was digested by a temperature controlled microwave (Ethos1-Milestone®) with Teflon vessels (100 mL) in a carousel device (Milestone® HPR-1000/10S High Pressure) using a mixture of acids and reagents, as described in Buccolieri et al. (2005): HNO_3, H_2O_2 and HF (ultra pure quality).

The steps of the microwave digestion procedure consisted of a first slope (20 min) from room temperature to 100°C, followed by a time sequence (5 min/step), allowing the maintenance and increase (Δt 20°C) of temperature up to 180°C, after which this value was maintained for 10 min. The content of all vessels was diluted to ca. 30 mL with ultrapure water (weighted volume), and in all digestion sessions one or two vessels were used as control for acids and reagents. Between two sample treatments, the vessels were cleaned using a mixer of 10 mL of HNO_3 (Romil® Suprapur) and 1 mL HF (Romil® UPA), following a temperature controlled program (20 min/slope from room temperature till 160°C and 10 min. at 160°C).

Inorganic elements (V, Cr, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Tl and Pb) in PM_{10} samples were measured by an Inductively coupled plasma-quadrupole mass spectrometer (ICP-QMS, Agilent 7500I, USA). Results of analytical determinations were obtained through the removal, for each chemical species, of the average level present in the blank samples. For each PM_{10} sample, the concentration calculated for a specific species was quantified if it was larger than the standard deviation (σ_B) of the blank filters, otherwise a threshold value equals to σ_B was considered. In cases of concentrations below the limit of detection (LOD), or not detectable above the average variability of the field blanks, a threshold concentration equals to the maximum between the LOD and σ_B was assumed. Some difficulty was experienced in the quantification of specific trace elements, mainly Mo, Co and Tl. Therefore, a threshold was adopted for the data analysis, with only elements with more than 60% of quantified data being maintained in the post-processing. Specifically, Mo was removed at all sites, while at Chioggia and Malamocco, Co and Tl were removed. Recoveries were evaluated using standard reference material (NIST® 1684). The relative errors were calculated for different elements and were in the range between 1% and 11%. Specifically the absolute values of recoveries were: V (2%), Cr (3.5%), Fe (10%), Co (6%), Ni (1%), Cu (3%), Zn (9%), As (2.5%), Cd (2%), Sb (0.4%) and Pb (8%).

1.3 Source apportionment methods applied and their implementation

To identify and characterise the possible sources of PM_{10} at the three different sites, the PMF approach was used. This is a source apportionment method described in detail in Paatero and Tapper (1994) and in Paatero (1997). The software adopted was the freeware version EPA PMF 3.0, which works under the Multilinear Engine (ME-2) developed by Paatero (1999). PMF is a multivariate factor analysis that decomposes a matrix X ($n\times m$) of data, n being the number of samples and m the number of species, into two matrices, namely Z ($n\times p$) and C ($p\times m$), p being the number of factors identified. Thus the matrix X can be written as

$$X = ZC + E \tag{1}$$

where, E representing a matrix of the unexplained part of X. The objective of PMF analysis is based on a point-by-point weighted least squares minimization approach, and aims to minimize Q, defined as:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \frac{e_{ij}^2}{s_{ij}^2} \tag{2}$$

and:

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} z_{ik}\, c_{kj} \tag{3}$$

where, s_{ij} corresponds to the uncertainty of the concentration x_{ij}. Moreover, the PMF approach has the constraints: $z_{ik} \geqslant 0$ and $c_{kj} \geqslant 0$, where z_{ik} and c_{kj} are single elements of the matrix Z and C, respectively. For the present study it was decided to use, as uncertainty data, the same values used as a threshold for non-quantified data, adding an "extra modelling uncertainty" of 10% to all species. This value encompassed various errors not considered as measurement or laboratory errors, including source profile variations, and chemical transformations in the atmosphere.

The PMF data handling required a discrimination of "bad", "weak" and "strong" variables, according to signal-to-noise ratio criterion (Paatero and Hopke, 2003). Here, the species Sb was defined as "weak" for all datasets (Chioggia, Malamocco, Punta Sabbioni and Cumulative dataset), species As was defined "weak" only for the Chioggia dataset, while the other elements were defined as "strong". For all datasets, the choice of solution was carried out by analyzing the results obtained by the model with 3, 4, 5 and 6 factors. The resulting parameters, obtained from the scaled residual matrix, IM (the maximum individual column mean), and IS (the maximum individual column standard deviation), together with Q values, were examined to find out the most reasonable solution (Lee et al., 1999; Hopke, 2000; Viana et al., 2008a). In particular, for Q values, the solution to the system was the point where the slope of the curve showed a marked change. Conversely, in the case of IM and IS parameters, when the number of factors increased to a critical value, these parameters experienced a very marked drop. In the present work, the Q, IM and IS values showed a reasonable solution in correspondence to 4 factors for all of the analysed datasets.

The correlations between the identified factors were very small, indicating the absence of ambiguity in the solutions due to possible rotations in the same solution space. As further confirmation, the PMF solutions were explored for multiple values of the peak coefficient (F_{peak}, between −1.0 and +1.0, with steps of 0.2). The resulting solutions were similar and the analysis gave no further information for the identification of factors. Therefore, it was decided to adopt the standard solution with the coefficient $F_{\text{peak}} = 0$. To evaluate the quality of the model results, the examination of the frequency distribution of the residuals, scaled by the standard deviation, showed that all the distributions of the residuals were close to normal distributions, and it was therefore possible to assume that all the species were reasonably modelled by the PMF.

To improve the understanding of the profiles found with the PMF, a CA was performed on the cumulative data-set. Cluster analysis could be an effective statistical method for the qualitative study of atmospheric aerosol composition, even if its application to atmospheric problems is rather limited (Ho et al., 2006). One difficulty concerns the interpretation of the dendrograms, because environmental variables can force unclear groups in the dendrograms. Nonetheless, the method is quite useful at least for confirming and interpreting groups of variables obtained with other multivariate statistical methods (Prendes et al., 1999; Ho et al., 2006; Contini et al., 2010). The CA was carried out using Euclidean distance and the method of Ward.

The PMF results were compared with those obtained by the PCA, performed on the cumulative data-set, using the Statistica 6.0 software (Statsoft, Inc.). The PCA was applied to normalised concentrations:

$$\varepsilon_{ij} = \frac{x_{ij} - < x_j >}{\sigma_j} \tag{4}$$

where, σ_j was the standard deviation of the measured concentration series of species j and $<x_j>$ was the average concentration of species j. Varimax rotation was applied to the matrix of loads. This rotation is widely used in the analysis of atmospheric aerosol (Thurston and Spengler, 1985; Swietlicki et al., 1996; Senaratne and Shooter, 2004; Karar and Gupta, 2007), and maximizes the number of factors loading near zero and near one, maintaining unchanged the explained variance and the communalities of the species. For example, in Miranda et al. (1996), it was shown that Varimax rotation helped to separate a second soil constituent of the aerosol sampled in the area of Mexico City.

To further investigate the similarities among the sites, the coefficients of divergence, COD_{sp} between the sites s and p, evaluated on the average concentrations, were calculated as:

$$\text{COD}_{\text{sp}} = \sqrt{\frac{1}{m}\sum_{j=1}^{m}\left(\frac{\left(< x >_{j\text{s}} - < x >_{j\text{p}}\right)}{\left(< x >_{j\text{s}} + < x >_{j\text{p}}\right)}\right)^2} \tag{5}$$

where, $< x >_{js}$ and $< x >_{jp}$ were the average concentrations of the chemical component j at sites S and P, respectively, and m was the number of chemical components. In a previous analysis (Wilson et al., 2005), the values of the coefficient of divergence were used to infer the spatial homogeneity of aerosol composition at different sites. Values of CODs coefficients lower than 0.2 indicates a relatively homogeneous spatial distribution.

The crustal enrichment factors (EFs) were also evaluated to help in the identification of anthropogenic elements. The EFs were evaluated for the different elements, taking Fe as reference and using, for comparison, the average upper-crust concentrations reported in Wedepohl (1995). Si, Al, Fe and Ti are generally used as reference elements, being abundant in soils, even if other choices have been made in research works: for example, Sr or Ti (Dongarrà et al., 2007; Teixeira et al., 2009). In the cases analysed Fe appears to be a suitable choice for the reference element because its origin in the Venice area has been indicated as mainly crustal in other research works in PM_{10} (Rampazzo et al., 2008a, 2008b; Masiol et al., 2010), in $PM_{2.5}$ (Stortini et al., 2009), in PM_3 and in PM_{10-3} (Toscano et al., 2011). The EF is the comparison of the ratios of atmospheric concentrations of elements to a reference element with the same ratios in geological material (Watson et al., 2002), and it could furnish information on elements likely to originate from anthropogenic sources (Lu et al., 2007). Values of EF lower than 10 indicate that the crustal origin prevails, while EF values greater than 20 indicate that the element probably has an anthropogenic origin. Between the two thresholds ($10 < \text{EF} < 20$), it is not possible to discriminate between crustal or anthropogenic nature of the element and it is also possible to have more sources, with different nature, contributing to the element (Cesari et al., 2012). Such thresholds are appropriate when generic reference tables for upper crustal composition are used in this work for the evaluation of EFs.

2 Results and discussion

2.1 Analysis of measured PM_{10} composition

Table 1 reports the average concentrations of the different elements, together with their maximum and minimum, measured at the different sites. For all elements, measured values were in agreement with those observed in previous research performed at other sites of the Venice Lagoon (Rampazzo et al., 2008a; Masiol et al., 2010; Toscano et al., 2011). The analysis was performed considering all data, and also separating weekdays (Monday to Saturday) from holidays (Sunday and public holidays) to help to identify the contribution of sources having a weekly cycle. At the Punta Sabbioni site all the elements analysed presented larger average concentrations on weekdays. At Malamocco only, Fe, Sb and Pb were higher on weekdays, while at Chioggia the elements presenting a higher average concentration on weekdays were Cu, Zn, Sb, Pb and PM_{10}. The significance of the observed differences between weekdays and holidays was estimated using a statistical test, at 5% probability level, based on the *t*-Student distribution. Results of the test on absolute concentrations indicated that at Punta Sabbioni and Malamocco the differences were not statistically significant, while at Chioggia Cr was statistically lower on weekdays. In relative terms (i.e. considering the ratio between element concentrations and PM_{10} concentrations), at Chioggia and Malamocco, Ni and Cr presented statistically significant lower concentrations on weekdays. Therefore, in general terms, there was not a clear weekly pattern showing higher concentrations on working days at the three sites.

The differences observed between one site and another showed that Cu, Zn, As, Cd and Sb had lower concentrations in Chioggia, compared to the other two sites, which instead had concentrations that were not statistically distinguishable. The trend observed at Chioggia could be related to a greater distance from glass manufacturing (which could be considered a source of Cu, Zn, As, Cd and Sb) in the area as shown by Rampazzo et al. (2008b). In fact, the distances of Punta Sabbioni and Malamocco from glass factories are about 6 and 14 km, respectively, while Chioggia is located at a distance of about 26 km. The average concentration of V was significantly larger at Malamocco with respect to the other two sites. Since V can be associated to oil combustion, the higher concentration of V could be due to ship traffic emissions, Malamocco lies along the path of commercial shipping to and from Porto Marghera. The conclusion is that the differences between the three sites are quite limited, especially between Malamocco and Punta Sabbioni. Furthermore, PM_{10} concentrations at the three sites were not statistically different.

The values of the CODs calculated at the three sites analysed are between 0.10 and 0.17, suggesting that the area investigated is characterised by a relatively homogeneous

Table 1 Average, minimum and maximum concentrations (ng/m^3) of the different elements and PM_{10}, measured at the three sites

	Punta Sabbioni			Chioggia			Malamocco		
	All periods (83 samples)	Weekdays (71 samples)	Holidays (12 samples)	All periods (90 samples)	Weekdays (74 samples)	Holidays (16 samples)	All periods (88 samples)	Weekdays (76 samples)	Holidays (12 samples)
PM_{10}	41116.6 (8700.0–238438.4)	43005.3 (8700.0–238438.4)	29941.4 (8800.0–93000.0)	44172.6 (6200.0–127938.6)	45284.6 (10020.0–127938.6)	39029.8 (6200.0–109650.8)	37129.4 (2000.0–102121.8)	36965.2 (2300.0–102121.8)	38169.5 (2000.0–82700.0)
V	4.4 (0.3–15.3)	4.6 (0.4–15.3)	3.1 (0.3–7.0)	4.4 (0.3–15.7)	4.3 (0.3–15.7)	4.8 (0.9–12.6)	5.6 (0.1–18.1)	5.5 (0.3–18.1)	6.1 (0.1–17.0)
Cr	5.2 (0.4–21.9)	5.5 (0.4–21.9)	3.3 (1.0–7.2)	4.0 (0.4–72.1)	3.5 (0.4–53.0)	6.6 (0.4–72.1)	3.8 (0.4–12.4)	3.8 (0.4–12.4)	3.9 (0.4–11.6)
Fe	357.0 (24.3–1347.3)	377.8 (24.3–1347.3)	234.1 (66.7–491.8)	394.4 (30.2–3317.4)	390.0 (34.5–3317.4)	414.8 (30.2–1651.7)	319.6 (13.0–941.3)	327.5 (13.0–941.3)	269.6 (43.6–644.7)
Co	0.2 (0.01–2.2)	0.2 (0.01–2.2)	0.1 (0.03–0.6)		0.3		0.2 (0.03–1.0)	0.2 (0.03–1.0)	0.2 (0.03–0.9)
Ni	3.9 (0.2–18.3)	4.2 (0.2–18.3)	2.2 (0.4–4.3)	3.5 (0.3–28.7)	3.2 (0.5–23.4)	4.8 (0.3–28.7)	4.6 (0.5–17.0)	4.5 (0.5–17.0)	5.0 (0.7–16.4)
Cu	9.8 (0.5–43.2)	10.2 (0.5–43.2)	7.4 (1.2–17.8)	6.4 (0.5–30.8)	6.7 (0.5–30.8)	5.0 (1.0–17.5)	8.9 (0.2–28.8)	8.7 (0.2–28.7)	9.8 (0.3–28.8)
Zn	57.4 (1.1–177.3)	59.3 (1.1–177.3)	45.8 (2.1–109.3)	33.0 (0.3–102.8)	33.1 (0.7–102.8)	32.4 (0.3–86.7)	43.0 (1.3–129.6)	42.7 (2.0–129.6)	44.9 (1.3–103.1)
As	2.0 (0.1–13.3)	2.2 (0.1–13.3)	0.9 (0.1–5.6)	1.1 (0.1–6.1)	1.1 (0.1–6.1)	1.1 (0.1–4.4)	2.1 (0.1–13.9)	2.0 (0.1–11.8)	2.4 (0.1–13.9)
Mo		5.2			5.5			5.8	
Cd	2.2 (0.01–20.7)	2.4 (0.01–20.7)	1.0 (0.01–8.0)	1.5 (0.01–13.2)	1.4 (0.01–10.9)	2.2 (0.01–13.2)	2.7 (0.01–35.6)	2.4 (0.01–35.6)	4.7 (0.01–22.0)
Sb	8.6 (0.6–35.9)	9.1 (0.6–35.9)	6.2 (1.1–14.6)	4.7 (0.1–53.7)	5.0 (0.1–53.7)	3.1 (0.1–13.6)	7.3 (0.2–34.5)	7.4 (0.2–34.5)	6.9 (0.6–25.5)
Tl	0.06 (0.001–0.5)	0.06 (0.001–0.5)	0.04 (0.001–0.08)		0.05			0.04	
Pb	21.3 (1.6–161.8)	22.1 (1.6–161.8)	16.0 (1.9–36.0)	16.1 (0.5–93.1)	16.6 (1.1–93.1)	13.7 (0.5–37.8)	21.2 (0.8–325.1)	21.5 (1.8–325.1)	18.9 (0.8–39.8)

Data are also presented separating samples taken on weekdays and holidays.

distribution of aerosol, probably because of the similarity of the sources influencing them. In order to emphasize a potential contribution of the MOSE construction works at each measurement site, a wind direction sector associated to the position of the dams was identified. The sectors are: 170°–360° for Punta Sabbioni, 320°–120° for Malamocco and 350°–70° for Chioggia. Only data taken on weekdays were used for the analysis. A prevalent wind direction was evaluated for each PM_{10} sample, excluding cases of wind calm (when the direction is not well defined) and cases when it was not possible to identify a prevalent wind direction due to an excessive variability during the sampling period. Results are reported in Table 2. In some cases a reliable average is not indicated because of the presence of more than 40% of non quantified data. The application of the *t*-Student test (at 5% probability) to the data in Table 2 showed that at Malamocco the differences in the two sectors of wind directions were not significant for any metals, with the exception of Zn, which presented a lower average concentration when the site was downwind of the construction site. Furthermore, this difference was limited to absolute concentrations of Zn, as it was not present in relative concentrations.

At the Chioggia site, the only element presenting a significant correlation with wind direction was Fe, which had lower average concentrations when the site was downwind of the construction works. In relative terms, Cr, Zn and Sb showed a statistically significant increase in concentrations when the site was downwind of the MOSE dam.

At the Punta Sabbioni site, V, Fe, Co, Ni, Cu, Cd, Sb and Pb had higher absolute average concentrations when the measurement site was downwind of the construction works. However, in relative concentrations this was limited to Co, Cu, Sb and Pb. It should be noted that the wind direction sector includes not only the construction activities but also the city of Venice and the industrial site of Porto Marghera (Fig. 1). Therefore, the increase in metals generally originating from different sources (like Fe, As and Sb) was likely to be due to contributions from several emission activities.

Moreover, at all sites PM_{10} concentrations were not statistically different in the two wind direction sectors. The conclusion was that the analysis of the correlation with wind direction did not highlight a specific contribution of the construction works to atmospheric PM_{10} and its metal content.

Figure 2 shows the EFs evaluated at the three different sites, with the exclusion of elements having more than 40% of non quantified data. The results indicated significant enrichment for Pb, Cd, Sb, As, Zn, Cu and Ni, while elements mainly of crustal origin were Tl, and Co. V and Cr are enriched but the valuees of EFs are lower than the threshold of 20 so that it is not possible to exclude also a contribution of crustal nature. The EF of V is larger at Malamocco and this is compatible with a possible contribution of ship traffic emissions (characterised by V and Ni) at the Malamocco site, which is located near the path of commercial shipping.

Table 2 Average, minimum and maximum concentrations (ng/m^3), separating samples taken on days with prevalent wind direction in the sector associated to the position of the MOSE dams and samples associated to other wind directions

	Punta Sabbioni		Chioggia		Malamocco	
	Work directions (16 samples)	Other directions (25 samples)	Work directions (23 samples)	Other directions (22 samples)	Work directions (40 samples)	Other directions (16 samples)
PM_{10}	41363.3 (8800.0–81633.4)	30024.6 (12400.0–70500.0)	36208.5 (17794.4–98100.0)	46032.7 (10020.0–111900.0)	33584.0 (2300.0–85900.0)	39388.1 (10100.0–80200.0)
V	5.6 (1.5–15.3)	3.1 (0.4–8.4)	4.4 (0.3–15.7)	4.5 (0.7–14.3)	5.2 (0.3–15.5)	5.5 (2.3–15.6)
Cr	6.5 (1.1–17.4)	4.7 (0.4–16.1)	4.3 (0.4–53.0)	3.2 (0.4–11.2)	3.3 (0.4–12.4)	4.6 (1.1–10.4)
Fe	467.3 (77.0–999.8)	254.2 (94.6–826.1)	281.0 (34.5–1017.3)	504.4 (51.0–3317.4)	296.8 (13.0–941.3)	359.6 (165.3–816.7)
Co	0.5 (0.03–2.2)	0.1 (0.03–1.0)	0.4		0.2	
Ni	5.9 (0.4–18.3)	2.5 (0.5–6.2)	3.4 (0.5–23.4)	2.9 (0.5–6.8)	4.0 (0.5–17.0)	5.1 (1.7–11.9)
Cu	11.6 (1.9–28.9)	5.8 (0.7–21.9)	5.0 (0.5–17.3)	6.8 (1.3–30.8)	7.5 (0.2–25.6)	10.9 (3.5–28.7)
Zn	72.3 (14.1–173.4)	45.8 (1.1–170.2)	30.6 (12.0–82.2)	27.6 (0.7–102.8)	34.9 (2.0–109.2)	57.0 (5.8–129.6)
As	2.4		0.9 (0.1–3.5)	0.8 (0.1–2.4)	2.1 (0.1–11.8)	1.7 (0.2–8.8)
Mo	4.9		5.0		5.8	
Cd	2.8 (0.2–13.7)	1.2 (0.01–6.6)	1.2 (0.01–6.6)	1.3 (0.01–10.9)	2.8 (0.01–35.6)	2.8 (0.1–8.6)
Sb	11.5 (1.8–22.9)	3.9 (0.6–14.6)	6.7 (0.3–53.7)	4.5 (0.6–32.7)	6.8 (0.2–18.9)	8.2 (0.6–34.5)
Tl	0.06 (0.01–0.2)	0.03 (0.001–0.1)	0.05		0.04	
Pb	25.0 (5.6–61.9)	12.5 (1.6–45.8)	11.8 (1.6–40.9)	14.8 (1.1–89.8)	15.3 (1.8–50.6)	20.3 (4.4–37.0)

The analysis is limited to samples taken on weekdays.

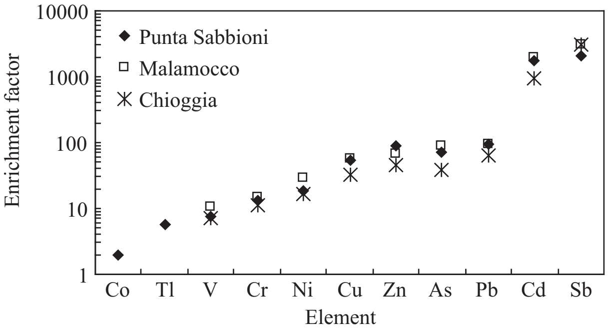

Fig. 2 Average crustal enrichment factors evaluated at the three sites.

2.2 Discussion of a specific source of Ni and Cr identified at the Chioggia site

At the Chioggia site, two days (out of 90) with relatively high correlated concentrations of Ni and Cr, were observed (03/02/2008 and 10/03/2010). These events forced the correlation coefficient between the two elements (Ni and Cr) to 0.87, in an otherwise poorly correlated pair of elements (correlation coefficient 0.49 if the two mentioned days are excluded). Neither of the two days showed important increases in PM_{10} concentrations with respect to the previous and following days. The 03/02/2008 was a weekday and 10/03/2010 was a holiday, with no construction activity in progress. Therefore, this event is not correlated to the emissions of the MOSE construction work. In addition, the concentration peaks were not present at Punta Sabbioni and at Malamocco on 03/02/2008 according to the measurements available simultaneously at the three sites. Both days were characterised, at ground level, by strong winds with a prevalent wind direction from the NE sector.

Figure 3 shows back-trajectories evaluated over 72 hr with the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory Model, HYSPLIT (Draxler and Hess, 1998) for the two mentioned days. Back-trajectories were evaluated as an ensemble at the starting height of 100 m, but similar results were obtained with a 200 m starting height. They indicated that the two days had a different large scale pattern of air mass trajectories. On 10/03/2010 air masses were coming stably from the NE direction, while on 03/02/2008 the trajectories split into two groups, reflecting the meteorological circulation in the lagoon area described in the previous section.

Specifically, a group of trajectories was coming from NE and another from SE. Although the data-set did include other days with similar meteorological conditions at ground level with similar air mass back-trajectories, the concentrations of Ni and Cr showed no significant increase on these days. While the EF of Ni in Chioggia was 16.4 in average terms, on 03/02/2008 it was 147, and on 10/03/2010 it was 100. A similar behaviour was observed for Cr, which had an average EF of 11.2, but reached 196 on 03/02/2008, and 120 on 10/03/2010. The reasonable conclusion of the analysis was that these peaks were related to the emissions of an anthropogenic local source, rich in Ni and Cr, operating non continuously during the measurement period, located in the N-NE sector. It should be noted that the mentioned events were removed from the analysis reported in Section 2.3, since only two cases were identified, and it was not possible to characterise the source statistically.

2.3 Analysis of possible sources using source apportionment models

The PMF was first applied separately to each site. However, because the analysis with the *t*-Student tests mentioned above showed a limited number of significant differences among the three sites, the results were also analysed in a cumulative way, using a data-set of 259 samples obtained from all the measurements taken at the three sites. This data-set was analysed using the PMF, in order to identify the sources affecting the area with a greater statistics than that yielded by the analysis of a single site.

The profiles obtained from the PMF are shown in Fig. 4, together with the variability of the results (error bars).

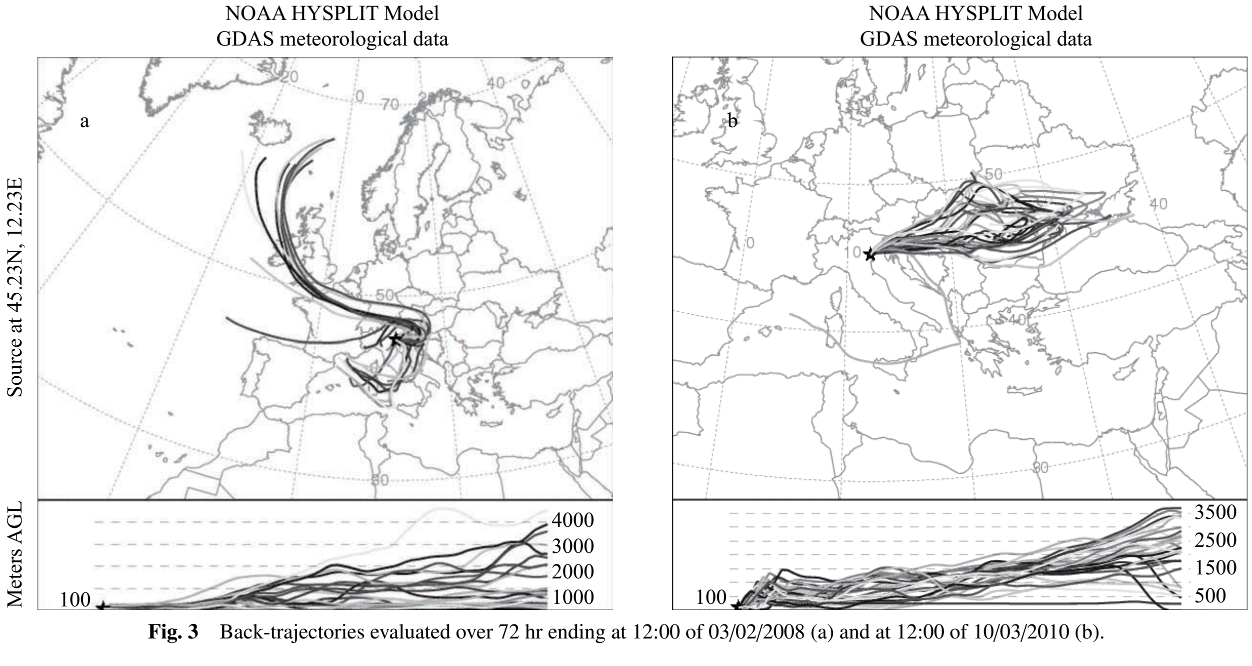

Fig. 3 Back-trajectories evaluated over 72 hr ending at 12:00 of 03/02/2008 (a) and at 12:00 of 10/03/2010 (b).

The variability of the profiles was estimated with the "bootstrapping" method, in which the PMF performed simulations by randomly selecting non-overlapping blocks of data samples, and creating new input data files of the selected samples (Kim et al., 2010). The PMF was then run on the new data files, and the multiple results provided information on the variability of each profile factor. Here, the uncertainty range was assumed to be equal to one-half of the 5%–95% interval of variability of the bootstrapping results.

Four factors (sources) were identified. The first factor was characterised by poorly enriched elements likely of crustal origin (Fe, Co) and highly enriched elements typical of anthropogenic origin (Cu, Zn). This factor represented a complicated mixture of elements and it is likely associable to a mix of sources having different nature and it was present, with minimal changes, at all the sites analysed. Specifically, the couple Cu-Zn could originate from traffic emission from diesel (Cu) and tyre wear (Zn), or from road dust, and it has also been observed in the Venice area in Toscano et al. (2011). It has to be mentioned that factor analysis showing a mix of sources have also been identified in the Venice area in previous studies on PM_{10} (Rampazzo et al., 2008a) and on $PM_{2.5}$ (Stortini et al., 2009). The second factor was characterised by Tl, Pb and Sb. Specifically at the site of Malamocco, this factor also presented a marked percentage of As, which was assumed to be representative of traffic and also industrial emissions, such as ceramic emissions present in the area, which could be partly the source of these elements (Querol et al., 2007a). It is not possible to exclude a contribution from glass factories (Rampazzo et al., 2008b) and from non-ferrous metal industry that is active in this area (Nriagu and Pacyna, 1998; Toscano et al., 2011). The third factor was characterised by Cd and As and could be related to emissions from glass factories. Rampazzo et al. (2008b) reported that particles released by glass factories in the Venice area were characterised by Cd, As and Se. The analysis of $PM_{2.5}$ concentrations in Stortini et al. (2009) also proposed a factor characterised by Se, As and Cd that was potentially associated to glass factory emissions. The fourth factor found was characterised by the key species V and Ni, with a certain percentage of As at the Chioggia site. It was probably associated to fossil fuel combustion (Rodríguez et al., 2004), or refining (Querol et al., 2007b). In the specific area of the Venice Lagoon, it probably originates from shipping traffic emissions, plus a partial contribution of petrochemical emissions from the industrial area of Porto Marghera. A similar factor has also been observed in other source apportionment studies near major harbours in Europe (Isakson et al., 2001; Alastuey et al., 2007; Viana et al., 2009).

The dendrogram of the CA on the cumulative data-set is reported in Fig. 5. The groups found with CA were in good agreement with the factors found with the PMF. In particular, it was possible to identify an isolated V-Ni group analogous to factor 4, representing ship traffic emissions, and a second isolated Cd-As group that was analogous to factor 3, representing glass factory emissions. There was a group in the CA characterised by a link at higher distance between Pb and Sb, analogous to factor 2 found in the PMF. The CA also evidences a group characterised by Zn, Cu, Cr and secondarily linked to Fe, similar to factor 1 of the PMF, identified as a mix of sources of different origin. Interestingly, there was a strong link between Cu and Zn, both of which were highly enriched

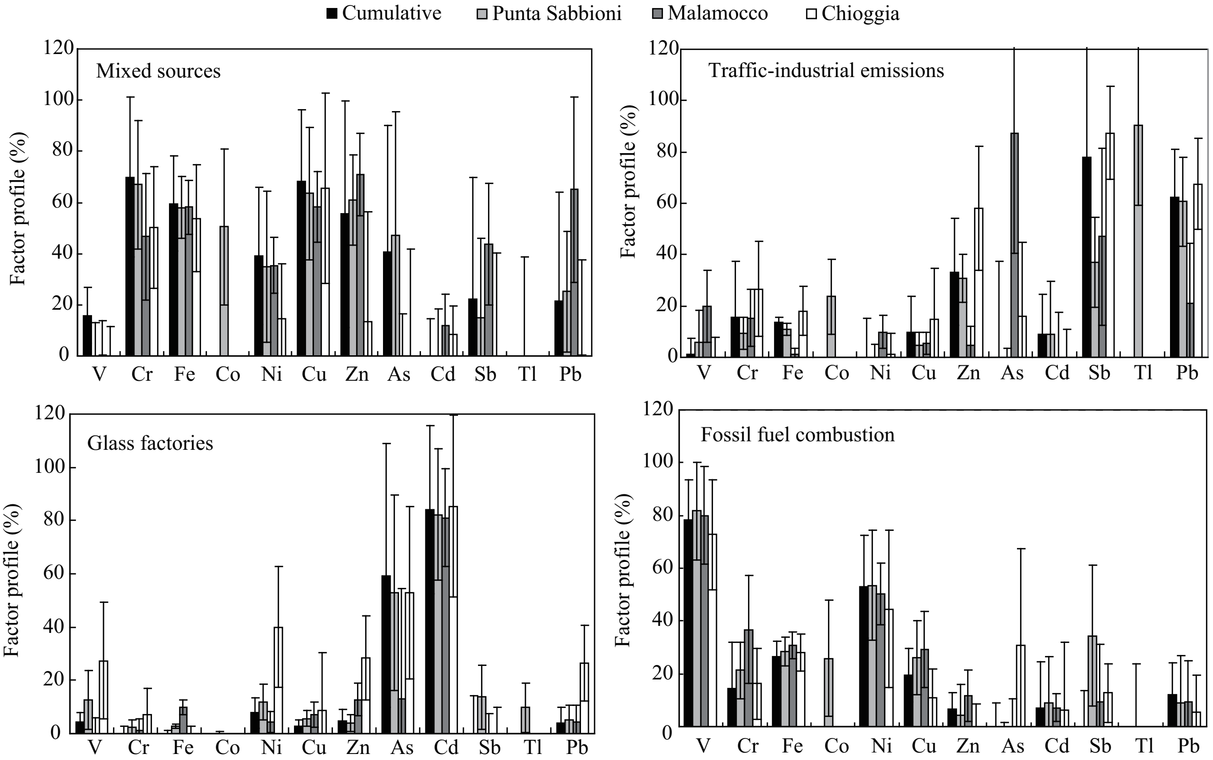

Fig. 4 Profiles of the four factors identified by the PMF, including the uncertainty for each element.

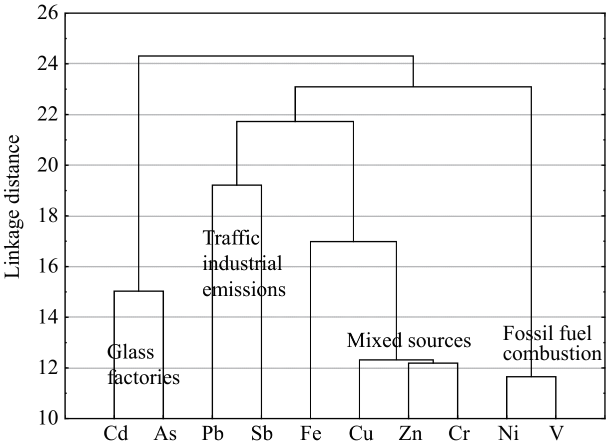

Fig. 5 Cluster Analysis of the cumulative data-set obtained using the Euclidean distance and the method of Ward. The name of the possible sources have been included to facilitate the comparison with PMF and PCA results.

at all sites and likely to be of anthropogenic origin. This pair of elements was linked, to a higher distance, with Fe. This could be explained interpreting this factor as a mix of sources (at least two) of different nature (crustal and anthropogenic).

The results of the PMF were compared with those obtained with the PCA performed on the cumulative data-set, using the software Statistica 6.0 (Statsoft, Inc.). The value of this comparison lies in providing an independent multivariate analysis of the data-set, to assist in the interpretation of the role of the different factors found. The matrix of loads obtained with the PCA is reported in Table 3, together with the indication of the communality of the elements and the variance explained by each principal component (PC). Globally, the four factor model explained 78% of the variance of the data-set. The first PC explained 47.7%, the second 11.2%, the third 10.7% and the fourth 8.2%.

The PCA results were in very good agreement with the factors found with the PMF: the first PC was equivalent to the first factor representing the mixed source, the second was equivalent to the third factor representing the glass factory emissions, the third was equivalent to the fourth factor associated to fossil fuel combustion, and the last was equivalent to the second factor representing traffic and industrial emissions.

It should be emphasised that the identified mix of sources could eventually be separated in specific sources, if more chemical species were characterised in PM_{10}.

3 Conclusions

The present work described an analysis of PM_{10} concentrations and metal content of samples collected at three different sites in the Venice Lagoon basin. The sites were located close to the worksites of the MOSE dams. The statistical comparison of the results showed limited differences in the concentrations measured at the three sites, indicating a relatively homogeneous spatial distribution of metals in PM_{10} in the Venice Lagoon area. This was probably due to the presence of the specific meteorological circulation, which mixes air masses arriving from different directions, favouring the re-circulation and spread of pollutants in the lagoon area. The main differences were smaller concentrations of elements associated to glass manufacturing facilities in Chioggia because of a greater distances from the sources, and a larger concentration of V in Malamocco, likely due to the emissions of commercial shipping traffic.

A specific analysis was performed in order to highlight a possible contribution of the construction works of the MOSE dams, studying the concentration differences between weekdays (when works were in progress) and holidays. However, the differences were not statistically significant (*t*-student test at 5% probability). Furthermore, the correlation of observed concentrations with wind directions did not show statistically significant differences when the sampling sites were downwind of the emissions of the construction works.

The statistical analysis using PMF showed a substantial similarity of the source profiles at the three sites, allowing processing with a single cumulative data-set. The results indicated that a four-source model could describe PM_{10} at the three sites, explaining about 77.8% of the variance of the cumulative data-set. Three of the sources were related to specific emissions in the Venice area (traffic-industrial emissions, glass factories and fossil fuel combustion) and one was a mix of sources including both a typical crustal element, like Fe, and elements with high enrichment factors, like Cu and Zn. The dendrogram of the CA suggested that this factor was composed of at least two sources of different origin (likely of crustal and anthropogenic

Table 3 Load matrix of calculated using PCA on the cumulative data-set

Element	Mixed sources	Glass factories	Fossil fuel combustion	Traffic-Industrial emissions	Communality
V	0.16	0.13	0.93	0.11	0.91
Cr	0.90	0.11	0.15	0.11	0.85
Fe	0.67	–0.01	0.37	0.10	0.60
Ni	0.55	0.23	0.67	0.04	0.80
Cu	0.71	0.26	0.37	0.30	0.79
Zn	0.79	0.29	–0.04	0.35	0.84
As	0.32	0.75	0.22	0.22	0.76
Cd	0.06	0.92	0.08	0.04	0.85
Sb	0.15	0.18	0.40	0.64	0.62
Pb	0.22	0.06	–0.04	0.84	0.76
Variance explained (%)	47.7	11.2	10.7	8.2	77.8

origin).

A local anthropogenic source, rich in Ni and Cr, sporadically active near Chioggia, was identified on the basis of the correlation with local meteorology and enrichment factor evaluation.

The comparison of the different source apportionment methods (PMF, PCA and CA) showed results in good agreement, indicating the robustness of the source identification and of the evaluation of profiles within the experimental uncertainty.

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