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An evaluation of the $PM_{2.5}$ trace elemental composition in the Venice Lagoon area and an analysis of the possible sources

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ABSTRACT

Global emissions reported by many authors have shown as natural and anthropic sources can contribute to the principal aerosol classes, but values change according the local scenario. The Venice Lagoon is exposed to different anthropic source emissions like vehicular traffic, industrial thermoelectric power plant, petrochemical plant, incinerator plant, domestic heating, ship traffic, glass factories and airport. Samplings of $PM_{2.5}$ were daily performed between March and November 2007 in Sacca San Biagio island (Venice), and values of $PM_{2.5}$ concentration and element concentration were obtained. Monthly average concentrations ($\mu g\ m^{-3}$) during this period show higher values during the spring and the autumn. A good relationship between data obtained and concentration values from environmental local agencies is evidenced, both for $PM_{2.5}$ from urban area (Venezia Mestre), and for PM_{10} sampled in the same area, as well as the influence of some meteorological parameters on $PM_{2.5}$ concentration sampled. Trace elements samples were measured by an Inductively Coupled Plasma-Quadrupole Mass Spectrometry (ICP-QMS), and values ($ng\ m^{-3}$ and $\mu g\ g^{-1}$) for elements regulated by European directives (As, Cd, Ni, Pb), as well as, other elements (Na, Al, K, Ti, V, Mn, Fe, Co, Zn, Se, Ag) are also reported. Data analysis by mean of Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) pointed out four principal groups of elements like Mn–Fe–K, As–Se–Cd, V–Co, and Pb that could be assigned to specific sources of the Venetian wetland basin.

1. Introduction

Estimations of global emissions, as reported by many authors, have shown that natural and anthropogenic sources can contribute to the principal dimensional classes (coarse, fine and ultrafine) (Chung and Seinfeld, 2002; Liao et al., 2004) of atmospheric particulate matter (PM). About 10%–20% of the aerosols can be characterized as anthropogenic on a global scale (Seinfeld and Pandis, 1998), but these values may drastically change due to local scenarios, human activities, and the prevailing particle cut-off. Coarse particles originate from industrial powder resuspension, soil/crustal resuspension (agriculture, rural activities, mining activities, biological sources, constructions, demolitions, etc.) and natural intrusions (Saharan dust, sea spray, etc.); while the fine fractions could be due to diesel engines, firewood, road traffic, power plants, domestic and residential emissions, industrial activities (Seinfeld and Pandis, 1998). This type of aerosol, introduced directly into the air by natural or anthropogenic sources, is defined as primary aerosol. Instead, the secondary aerosol is the result of processes, such as gas-to-particulate formation, nucleation, coagulation and condensation, that induce new particle formation.

Recently, particulate matter in urban areas has been increasing due to increased anthropogenic emissions, as a consequence levels of PM have become high with respect to the Air Quality Standards (AQS) specified by EC directives and by local regulations. Fine and ultrafine PM represent a health hazard due to their potential roles in some respiratory (Kampa and Elias Castanas, 2008) and cardio-vascular diseases (Riediker et al., 2004).

In urban areas at the European Mediterranean latitudes, the annual aerosol concentration has varies with season, showing higher values in winter and lower values in summer (Van Dingenen et al., 2004; Putaud et al., 2004). Winter increases are principally

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due to the use of domestic heating, as well as unfavourable meteorological conditions for the dispersion of pollutants (common ground and low altitude thermal inversions). In summer, the atmospheric boundary layer is higher resulting in an improvement in pollutant dispersion.

Major and trace elements in particulate matter can be classified as natural (Na, Mg, K, Ca, Si, Al, Mn, etc.) or anthropogenic (V, Cr, Mn, Ni, Cu, Zn, Cd, Pb, etc.). According to Pacyna (1994), the principal anthropogenic emission sources are attributed to fossil fuels; Cr, Mn, Sb are good markers for this source as they are present in coal, while V, Ni, Pb are emitted by fuel oil combustion. Industrial processes and non-ferrous mineral extraction are important sources for Cd, Zn, Cu, Hg; while elements like Ni, Zn, Pb, Cu are emitted during industrial processing of iron, cast iron and steel.

In this study results following a $PM_{2.5}$ monitoring campaign in 2007, of the Venice Lagoon are reported. The study area was the central portion of the Venice Lagoon which is exposed to different emissions sources (biogenic as well as anthropogenic). Results of major and trace element levels, as well as a comparison with past data obtained from the Venice Lagoon are also reported along with comparison data from some European cities. We applied Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) with the aims of characterizing the elemental composition with relation to their sources, and to have a comparison between the results using two independent methods of multivariate analysis.

2. Materials and methods

2.1. The study area

Venice is located at the northern end of the Adriatic sea at the north-eastern most part of the Po river plain. The whole study area corresponds to almost 550 km^2, and is composed of 8% dry land, 11% water, the other 80% being composed of intertidal mud plains, and salt and artificial marshes. The lagoon area includes the mainland areas of Venezia Mestre and Marghera, and the historical centre of Venice. Mainland sources of $PM_{2.5}$ are vehicular traffic (road and aircraft), a thermoelectric power plant, a petrochemical plant, an incineration plant, and domestic heating; while ship traffic (public transport, touristic and merchant shipping), glass factories, aircraft over flights and domestic heating, represent the main anthropogenic sources of the historical centre.

Monthly average temperature values registered (from station EZI-n. 23 – industrial area) (Ente della Zona Industriale di Marghera (EZI), 2007) in Venice from 1975 to 2006 (ARPAV, 2006) showed a seasonally pattern with high temperatures in summer (July–August 20–25 °C) and low temperatures in winter (December–January 0–5 °C). Precipitation events were variable over a solar year, with peaks in spring and autumn. Prevailing winds were from NNE or from SE for sea breezes in the summer, with wind speeds between 2 and 4 $m\ s^{-1}$ for 57% of the time during the summer, and for 43% of the time during the winter.

Venice area is characterized by atmospheric stability and thermal inversion inducing cold masses at the ground level during the winter time. Humidity is high causing foggy events in winter and intermediate seasons, with low pollutants dispersion. Temperature increase is coupled with an increase of the Planetary Boundary Layer, consequently both pollutants mixing and dispersion increase in summer time. In Venice this phenomenon is further increased by breezes and windy events (ARPAV, 2006) from SE during the day, while winds from the mainland (NNE) prevail during the night.

An overview of PM_{10} data from the regional environmental agency (ARPAV), such as annual average concentration values from Sacca Fisola (near Sacca San Biagio), in the time interval 2004–2008 shows values respectively of 41 $\mu g\ m^{-3}$, 40 $\mu g\ m^{-3}$, 37 $\mu g\ m^{-3}$, 43 $\mu g\ m^{-3}$, and 36 $\mu g\ m^{-3}$, as well as, exceedances (>50 $\mu g\ m^{-3}$ in 24 h) during the same period of 83, 96, 73, 101, and 58 time $year^{-1}$ respectively. Instead, data collected from 2001 to 2006 in the industrial area of Venice (station EZI-n. 3) (Ente della Zona Industriale di Marghera (EZI), 2007) shows that monthly average concentration values oscillate between 20 $\mu g\ m^{-3}$ and 100 $\mu g\ m^{-3}$ (ARPAV, 2006). At the same station, concentrations of trace elements like arsenic (As) are at their highest during the cold periods (2–6 $ng\ m^{-3}$) with peaks of around 10–15 $ng\ m^{-3}$. Cadmium (Cd) values were lower in the second half of the year and ranged between 2 and 10 $ng\ m^{-3}$. For nickel (Ni) no particular trend was observed, with values ranging between 2 and 10 $ng\ m^{-3}$. Lead (Pb) concentration values were lower in the summer (0–20 $ng\ m^{-3}$) and higher in the winter (20–60 $ng\ m^{-3}$).

Sources of PM emissions in Venice have been identified by different studies carried out by national and regional environmental agencies, with data available from 2000 onwards. For heavy metals in PM_{10} the thermoelectric power plant and the glass factories are considered the most important emission sources, even though there are some discrepancies for glass factories emissions due to differences between assessment criteria adopted by the Municipality of Venice, the Province of Venice, the Murano glass factories trade-union. The results from the municipality of Venice seem to be the most conservative, but in any case under or overestimations can occur due to the fact that they have been made in different moments and with some differences in protocol assessment. Data from the national environmental agency (APAT) for ships in the two principal berthing areas of Venice has shown that 69% of the emissions come from the Marghera area (petrochemical industry deliveries), and 31% from the Venice area (tourism and local activities).

2.2. Sampling and samples processing

Sampling of $PM_{2.5}$ was carried out daily from 28th of March 2007 to 5th of November 2007 (195 samples) on the Sacca San Biagio island (Lat. 45°25′40.14″N–Long. 12°18′36.73″E) near the "Canale della Giudecca", which is located southeast of the harbour area (Fig. 1). Samples were collected using a low volume aerosol sampler (Skypost PM-TCR Tecora) equipped with a sequential sampler (Charlie) with an electronically adjustable flow (flow value 38.33 $l\ min^{-1}$) and

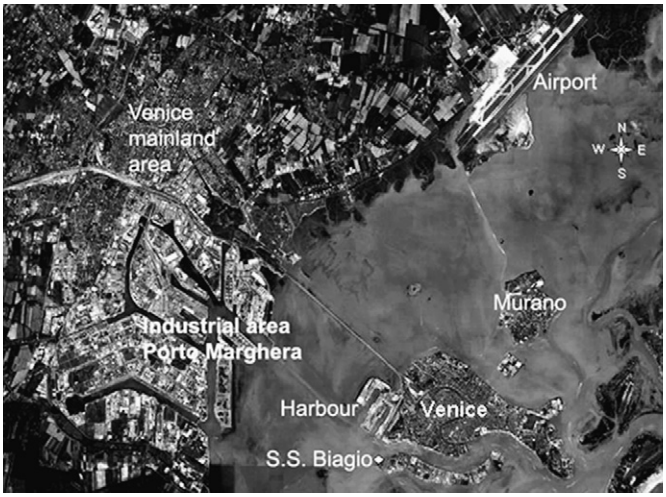


Fig. 1. Sampling area (from Google maps 2009 – modified).

a sequential sampling module (Sentinel PM) for automatic filter changing after 24 h (16 filter capacity). $PM_{2.5}$ was collected on quartz fibre filters (Sartorius diameter 47 mm – porosity Ø 0.45 μm), and two of the 16 filters were used as field blanks. Meteorological data was downloaded from meteorological station n. 252 of the Venice Lagoon area (Meteorological Observatory Cavanis).

The materials were decontaminated using procedures described elsewhere (Capodaglio et al., 1994) in an atmosphere-controlled laboratory along with sample pre-treatment. Blank and sample filters were weighed three times (%RSD 5–10%) over 24 h before and after the sampling using a Sartorius Competence CP64-0CE Balance (precision of 0.01 mg). The balance and the filters were kept in a temperature (20 ± 3 °C) and humidity (50% ± 5%) controlled Nitrogen glove box before and during the weighing procedure.

Each filter was microwave digested (Ethos1-Milestone®) inside a Teflon vessel (100 ml) held in a 10 place high pressure carousel (Milestone® HPR-1000/10S High Pressure), using the mixture of acids and reagents as described by Buccolieri et al. (2005) (HNO_3, H_2O_2 and HF Romil®UPA). The digestion temperature program consisted of a ramp from room temperature to 100 °C in 20 min, followed by a step gradient (5 min per step, ΔT 20 °C) up to 180 °C, this value is then maintained for 10 min before cooling. The sample digests and blanks (one or two per carousel) were diluted to ~30 ml with ultrapure water (by weigh). Between digestion batches, the vessels were cleaned with a mix of 10 ml of HNO_3 (Romil®Suprapur) and 1 ml of HF (Romil®UPA) using a temperature controlled program (20 min ramp from room temperature to 160 °C then 10 min at 160 °C).

2.3. Samples measurements

Trace elements in the $PM_{2.5}$ samples were measured by Inductively Coupled Plasma-Quadrupole Mass Spectrometry (ICP-QMS-Agilent 7500I), the accuracy and precision of the method was controlled using the standard reference material (Urban Particulate Matter NIST®1684). Elements concentrations in samples have been obtained after subtraction of their field blank values.

The limit of detection (LOD) was calculated for each element using the formula $LOD = \overline{B} + 3\sigma$, where $\overline{B}$ corresponds to the average value for the element measured in the blank and 3σ corresponds to three times the standard deviation of the blank value; values lower than the LOD were reported as none detected. Accuracy was evaluated against the standard reference material and the relative error was calculated using the formula $\mathrm{RE\%} = V_{\mathrm{det}} - V_{\mathrm{cert}}/V_{\mathrm{cert}} \times 100$ in which V_{det} is the determined value and V_{cert} is the certified value. For elements assessed, the determined (% or mg kg^{-1}), certified (% or mg kg^{-1}) and RE% values are: Fe (3.97/3.91/1.53), Al (3.21/3.42/−6.14), K (0.89/1.05/−15.23), Pb (0.663/0.655/1.22), Zn (0.471/0.476/−1.05), Na (0.356/0.425/−16.23), Mn (712/786/−9.41), Cr (417/403/3.47), V (117/127/−7.87), As (102/115/−11.30), Ni (70/82/−12.20), Cd (72/75/−4.00), Se (24/27/−11.11).

2.4. Data analysis

Principal Component Analysis (PCA) was performed using software for multivariate statistical analysis (Statistica 6.0 – Statsoft, Inc.). This allows similarities and differences to be highlighted in multi-dimensional data, by reduction of the number of dimensions (Jolliffe, 2002), without a significant loss of information. Data rotation has been performed using the Varimax rotational algorithm. Positive Matrix Factorization analysis has been also performed on data using software (PMF 3.0) developed by the US Environmental Protection Agency (EPA). The method is described in detail by Paatero and Tapper (1994) and in Paatero (1997). It should be noted that the principal difference between PCA and PMF is the non-negativity of factors (both loadings and scores) that is built into the PMF model. Moreover, PMF does not rely on information from the correlation matrix but utilizes a point-by-point least-squares minimization scheme. Therefore, the profiles produced can be directly compared to the input matrix without transformation.

3. Results and discussions

3.1. Concentration measurements

In Table 1 the monthly average $PM_{2.5}$ concentrations, as well as data from past research programs of the Consortium for Coordination of Research Activities Concerning the Venice Lagoon System (CORILA) are reported (Contini et al., 2007; Gambaro et al., 2007; Prodi et al., 2009). Values are higher in spring and in autumn compared to summer. Higher values than those reported by us have been obtained from local studies in the 2003 and 2004 summer seasons with sampling stations near to the glass factories (Murano) and the navigable channels of Burano island. All the data obtained from sampling campaigns in Venice for $PM_{2.5}$, have confirmed the seasonal behaviour of $PM_{2.5}$. According to Guerzoni et al. (2004), sources of pollution in the Venice Lagoon are emissions from the industrial area of Porto Marghera (central part of the lagoon), untreated domestic sewage from the historical city of Venice; traffic from motorboats and the nearby city of Mestre (Fattore et al., 1997; Wenning et al., 2000). Also, according to Rampazzo et al. (2008), the impact on Venice air quality of glass manufacturing factories has recently decreased, but will not cease in the near future.

In Fig. 2 a comparison between daily concentrations of $PM_{2.5}$ at Sacca San Biagio and in Venezia Mestre at the ring road (ARPAV – Via Circonvallazione) between April–October 2007 is reported. There is a good agreement between the results, and in both cases the gravimetric procedures used are comparable. Moreover, some meteorological effects are common to all campaigns, which could be linked to polluted or clean atmospheric conditions (Prodi et al., 2007). In fact, there are circulation patterns above the Venice Lagoon induced by local breezes and long range transport from the "Pianura Padana" (the Po river flood plain) (Prodi et al., 2009). A comparison with the PM_{10} data collected by ARPAV at Sacca Fisola (near our site) is reported in Fig. 3. A good correlation for the

Table 1
Monthly average concentration values (μg m^{-3}) of $PM_{2.5}$ in Sacca San Biagio during the monitoring period in 2007. Average concentration values (μg m^{-3}) from past monitoring campaigns are also reported (Murano and Mazzorbo – CORILA 2000–2004 project).

Month		Average concentration		N. days
March		24.9		3
April		27.3		21
May		18.6		27
June		12.1		27
July		12.7		29
August		13.7		31
September		10.9		23
October		22.3		30
November		23.0		4
Total		16.9		195
CORILA's campaigns				
Local study		Average concentration		
Murano		27.2		June 2003
Mazzorbo		23.7		July 2004
Seasonal study	All day	Diurnal (8 am–8 pm)	Nocturnal (8 pm–8 am)	
	16.7	14.2	19.2	Summer 2004
	41.8	36.3	48.0	Winter 2005
	16.9	15.7	18.4	Spring 2006

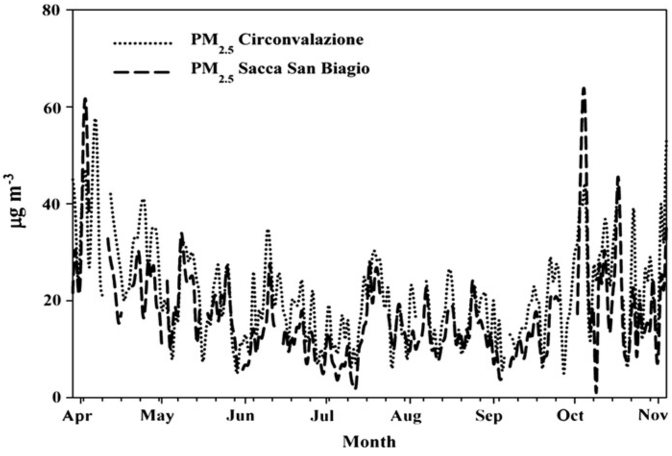


Fig. 2. Comparison between PM$_{2.5}$ values of Sacca S Biagio and the Venezia Mestre principal way “Circonvalazione” (ARPAV) from April to October 2007.

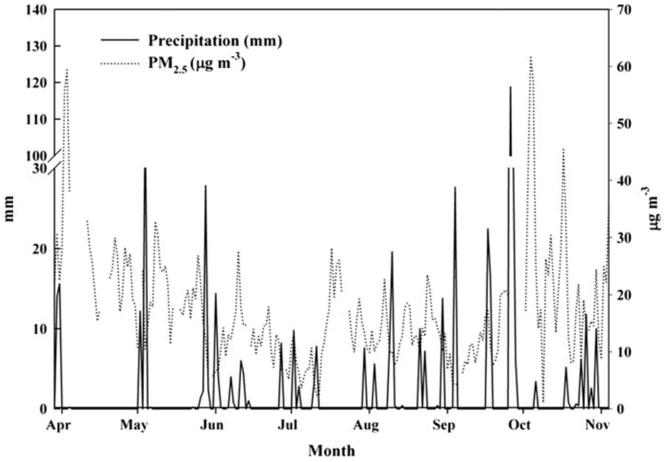


Fig. 4. Daily concentration of PM$_{2.5}$ together with meteorological precipitation.

daily concentration values between both size classes is evidenced ($r^2 = 0.70$), indicating a possible common origin. The mass percentage of PM$_{2.5}$ as a fraction of the PM$_{10}$ was found to be 51.40% which is lower than for other Italian and European cities where values range between 57% and 85%. (Putaud et al., 2004; Van Dingenen et al., 2004).

High values of humidity cause an increase of PM values, while for raining events (>10 mm, see Fig. 4) and high values of wind speed a decrease of PM values is observed. In Fig. 5 the wind rose of the sampling site is reported, while Table 2 shows elements concentrations and their relation to the wind sector and to the wind speed intensity (>2 m s^{-1}). Elements are grouped according the results from PCA and PMF reported hereafter, but the effective number of samples considered has been reduced from 132 to 97 as cases whose direction was too variable during the 24 h of sampling have been eliminated. In fact, in the Venice area the atmospheric circulation often varies, showing a different directions in diurnal and nocturnal hours (Prodi et al., 2009). Therefore, for some of the samples it is not possible to define an effective prevalent wind direction and these cases have been excluded. Results show an increase of some elements (V, Cd and Pb) for wind direction from NNE, in which there are significant anthropogenic emissions (harbour and mainland vehicular traffic). In Table 2 we also reported the number of data available in each sector analysed. Because of the small number of data, it is not possible to have conclusive results for sectors between S and N.

Average values of major and trace elements of sample mass per sampled air volume (ng m^{-3}) and of sample mass per total mass weighed (μg g^{-1}) are reported in Table 3. The elements with the highest daily concentration values are Na (1555.09 ng m^{-3}), Al (634.36 ng m^{-3}), K (229.12 ng m^{-3}) and Ti (186.17 ng m^{-3}). Intermediate values are shown for Fe (97.73 ng m^{-3}), Zn (84.51 ng m^{-3}), Pb (20 ng m^{-3}), V (14.06 ng m^{-3}) and Ni (12.15 ng m^{-3}). Other elements have average concentration values <10 ng m^{-3}. In terms of sample mass per total mass weighed, we can see the same distribution in order of magnitude. A comparison of the average values obtained for As, Cd, Ni and Pb with limit values fixed by European directives and by the World Health Organization (WHO) show that our values are below the limit values indicated for urban areas (see Table 4).

A comparison between the concentrations from this study (PM$_{2.5}$) and PM$_{10}$ from other sites near Venice (ARPAV, 2006), e.g. Parco della Bissuola and Circonvalazione in Venezia Mestre, demonstrates that our values for As and Cd are comparable with respect to previous data took during the same time period

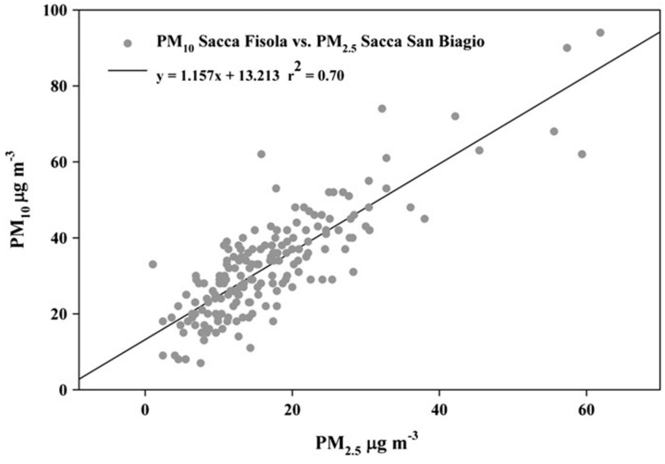


Fig. 3. Correlation between values of PM$_{10}$ from Sacca Fisola and PM$_{2.5}$ from Sacca San Biagio.

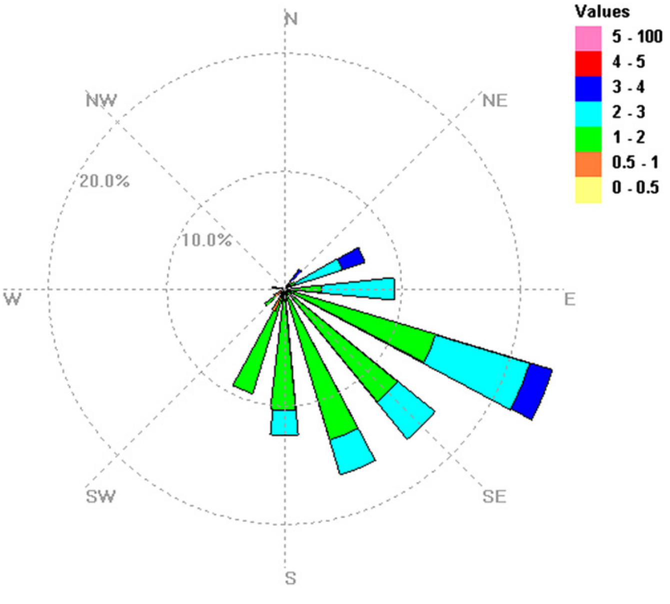


Fig. 5. Wind rose of Sacca San Biagio (April–October 2007).

Table 2
Elements concentrations (ng m^{-3}) with relation to the wind sectors and the wind velocity (>2 m s^{-1}) per sectors. The samples (cases) used are 97 and in bold the maximum values for any element.

	N° data	K	Mn	Fe	V	Co	Se	As	Cd	Pb
N-NNE	**22**	259.02	5.9	105.96	**30.08**	0.37	5.16	5.34	**6.33**	**34.24**
>2 m s^{-1}	**21**	254.02	5.63	103.13	**30.66**	0.38	5.19	5.01	**6.27**	**33.97**
NNE-NE	**23**	180.25	4.52	90.4	**21.47**	0.12	5.29	4.8	**4.33**	**20.31**
>2 m s^{-1}	**23**	180.25	4.52	90.4	**21.47**	0.12	5.29	4.8	**4.33**	**20.31**
NE–SE	**20**	199.2	5.36	102.62	13.81	0.19	4.02	3.95	2.39	15.62
>2 m s^{-1}	**19**	194.64	5.38	104.87	13.92	0.14	4.05	3.43	2.04	15.39
SE-S	**21**	244.54	4.73	109	10.82	0.17	4.13	2.78	1.84	17.36
>2 m s^{-1}	**20**	247.18	4.64	111.83	10.99	0.13	4.23	2.84	1.87	17.55
S–W	**3**	118.13	5.74	88.46	8.87	0.23	2.94	1.49	1.28	9.55
>2 m s^{-1}	**3**	118.13	5.74	88.46	8.87	0.23	2.94	1.49	1.28	9.55
W-N	**8**	332.36	6.17	184.96	7.77	0.48	4.14	2.01	1.81	17.5
>2 m s^{-1}	**8**	332.36	6.17	184.96	7.77	0.48	4.14	2.01	1.81	17.5

(April–October 2007) (Table 4). However, values for Ni are higher than those took previously, both during the corresponding period and for the annual average, but is important to point out that in this study only less than the 50% of the daily values for Ni were above the LOD, raising doubts about the representativeness of the mean value in this study. Values for Pb are generally lower when compared to previous studies carried out on the mainland. The comparable results obtained for the two different size cut-offs could probably be explained by the fact that anthropogenic trace elements are prevalently present in fine particles (Lin et al., 2005; Singh et al., 2002). Past campaigns for PM$_{2.5}$ (Table 5) performed in Venice have shown that elements like K, Mn, Fe, Cd, Pb have values that are comparable with this study, while V, Ni, Zn have consistently higher values. While V and Ni is generally associated to fossil fuel combustion, Zn contribution probably can be strongly associated with industrial activities (Pacyna, 1994; Vallius et al., 2003), and we can consider as its possible sources the industrial area of Marghera and the waste incinerator at Fusina (Guerzoni et al., 2005).

We report also an overview between the data collected in this study and data from some European cities from the Mediterranean basin (Table 6). Values for elements like K and Fe are comparable with those reported here from other European cities. For Ni and V the values obtained are comparable with those from Milan (continental climate + atmospheric stability), which is one of the largest pollution hot spots of Europe (Vecchi et al., 2008). Generally, values obtained in Venice for major and trace elements are higher compared to other European cities, but lower when compared to a city like Thessaloniki (Manoli et al., 2002), which is one of the most polluted coastal cities in Europe (Assael et al., 2008). Comparing our values for As and Cd with the cities considered here it is possible to notice that the values are higher, which may be due to glass factories emissions in Venice that give an important contribution. Tarragona is linked to the harbour and petrochemical and chemical zones, as well as to natural emissions (sea spray, soil resuspension and Saharan dust) (Moreno et al., 2007). In Barcelona vehicular traffic emissions and resuspension contribute to some of the highest average PM$_{10}$ levels in Spain (Moreno et al., 2006). Instead, Huelva is characterized by large industrial estates (metallurgical, petrochemical and fertilizer) surrounded by highly ecologically important areas (Sanchez de la Campa et al., 2007).

3.2. *Multivariate analysis of the data-set*

Principal Component Analysis was applied to the results (ng m^{-3}) of selected elements (variables) in air to identify patterns in the data. Only elements with more than a 60% of their values higher than the LOD were considered (K, Fe, Mn, V, Se, Cd, As, Pb, Co). To reduce the effects of missing data, any days (cases) with more than two elemental values lower than the LOD in the data matrix were eliminated. In this way the percentage of data with values lower than the LOD was diminished by about 15%, and the number of cases was reduced to 132. After this screening, any missing elemental data was substituted with half the LOD value for that element.

In Table 7 are reported the factor-variable correlations (factor loadings) for the first 5 principal components and the total percentage of variances explained by the different components. Only loads with an absolute value larger than 0.3 have been maintained. Eigenvalues from the correlation matrix explain 85.90% of variance, and loading plots have shown five principal components (PC1 31.20%, PC2 23.62%, PC3 13.59%, PC4 8.93%, PC5 8.56%). The elements studied here are distributed as follows:

Table 3
Concentration values (ng m^{-3} and μg g^{-1}) of inorganic elements analysed (minimum, maximum and average).

	Min. (ng m^{-3})	Max. (ng m^{-3})	Average (ng m^{-3})	Min. (μg g^{-1})	Max. (μg g^{-1})	Average (μg g^{-1})
Na	394.08	5408.11	1555.09	1.36E+04	2.53E+05	8.37E+04
Al	414.22	1237.77	634.36	1.74E+04	1.14E+05	5.49E+04
K	100.43	1019.97	229.12	3.84E+03	7.55E+04	1.37E+04
Ti	118.25	252.58	186.17	6.09E+03	4.53E+04	1.63E+04
V	0.85	155.74	14.06	6.19E+01	1.41E+04	1.03E+03
Mn	2.50	21.28	5.22	9.33E+01	3.37E+03	3.83E+02
Fe	36.43	972.29	97.73	1.32E+03	4.56E+04	6.06E+03
Co	0.10	1.12	0.33	2.80E+00	2.39E+02	2.15E+01
Ni	5.71	49.32	12.15	1.28E+02	7.05E+03	9.36E+02
Zn	25.80	161.15	84.51	1.21E+03	1.50E+04	4.55E+03
As	0.46	23.16	3.58	2.22E+01	2.16E+03	2.49E+02
Se	1.63	11.02	4.59	4.96E+01	2.45E+03	3.52E+02
Ag	0.74	1.10	1.02	2.30E+01	1.20E+02	6.08E+01
Cd	0.25	28.47	3.51	1.20E+01	1.45E+03	2.53E+02
Pb	2.42	135.31	18.08	2.12E+02	7.25E+03	1.22E+03

Table 4
Data comparison (averages in ng m^{-3}) between Sacca San Biagio values (this study), World Health Organization (WHO), European community, and some urban zones of the mainland area of Venice (Venezia Mestre).

		As	Cd	Ni	Pb
WHO	Background	1–3	0.1	1	0.6
	Urban	20–30	1–10	9–60	5–500
EC	1999[a]	–	–	–	500
	2004[b]	6	5	20	–
This study	Apr–Oct 2007	3.58	3.51	12.15	18.08
Bissuola	2002	8.4	2.5	5.7	30.5
	2003	5.9	4.1	6	24.8
	2004	3.6	5.5	6.8	25.4
	2005	3.2	3.6	4.7	22.9
	2006	4.5	4.1	5.4	27.5
	Apr–Oct 2006	3.8	3.6	5.28	8.94
	Apr–Oct 2007	3.02	2.88	6.49	12.93
Circonvallazione	2002	5.5	1.6	6.6	32.5
	2003	5.9	4.1	6	24.8
	2004	3.6	5.5	6.8	25.5
	2005	3.2	3.6	4.7	22.9
	2006	4.5	4.1	5.4	25.4
	Apr–Oct 2006	2.67	2.58	7.24	20.11
	Apr–Oct 2007	2.8	2.29	8.38	19.5

[a] 1999/30/EC.
[b] 2004/107/EC.

Table 7
Matrix of loads for the first five principal components obtained with the PCA.

Element	F1	F2	F3	F4	F5
K	**0.87**	–	–	–	–
V	–	–	**0.70**	**−0.66**	–
Mn	**0.86**	−0.32	–	–	–
Fe	**0.82**	−0.42	–		–
Co	–	–	**0.73**	**0.50**	–
As	0.40	**0.74**	–	–	–
Se	–	**0.63**	–	–	**0.54**
Cd	0.32	**0.84**	–	–	–
Pb	**0.53**	–	−0.36	–	**−0.62**
Variance explained (%)	31.20	23.62	13.59	8.93	8.56

K–Mn–Fe in F1; As–Se–Cd in F2; V–Co in F3 and F4; and Se–Pb in F5. While K–Mn–Fe and As–Se–Cd are well defined in F1 and F2 respectively, V and Co are well represented in F3, but also have factor loadings in F4. For Pb no association with other elements is evidenced.

V and Ni are generally attributed to fossil fuel combustion (Rodriguez et al., 2004), or to its refining (Querol et al., 2007), consequently their sources in this study could be attributed to inland urban traffic, airport traffic, ship traffic and the petrochemical plant of Marghera. But in our case is difficult to correlate these two elements because, as previously explained, the number of cases for Ni after LOD screening was significantly reduced. The group of elements As–Se–Cd could be attributed to the Murano glass factories (Rampazzo et al., 2008). According to literature, Se could also have different origin, as it could also be considered as a carbon emission indicator (Manoli et al., 2002). For Pb no specific source association is obtained from our study, but Murano glass factories, fossil fuel and urban traffic could be associated. The group K–Mn–Fe is well associated with the resuspension of crustal material (Rodriguez et al., 2004; Marcanzan et al., 2001), but for the $PM_{2.5}$ cut-off, contributions from industrial processes based on silicates (glass manufacturing) could also be considered (Rampazzo et al., 2008) as a potential source.

Positive Matrix Factorization has been applied to the same dataset used for PCA (132 cases) to obtain a comparative independent analysis of the variables and the principal groups of elements. This was done both to confirm the PCA results and to help us with the interpretation of the results. Initially, PMF data handling needs

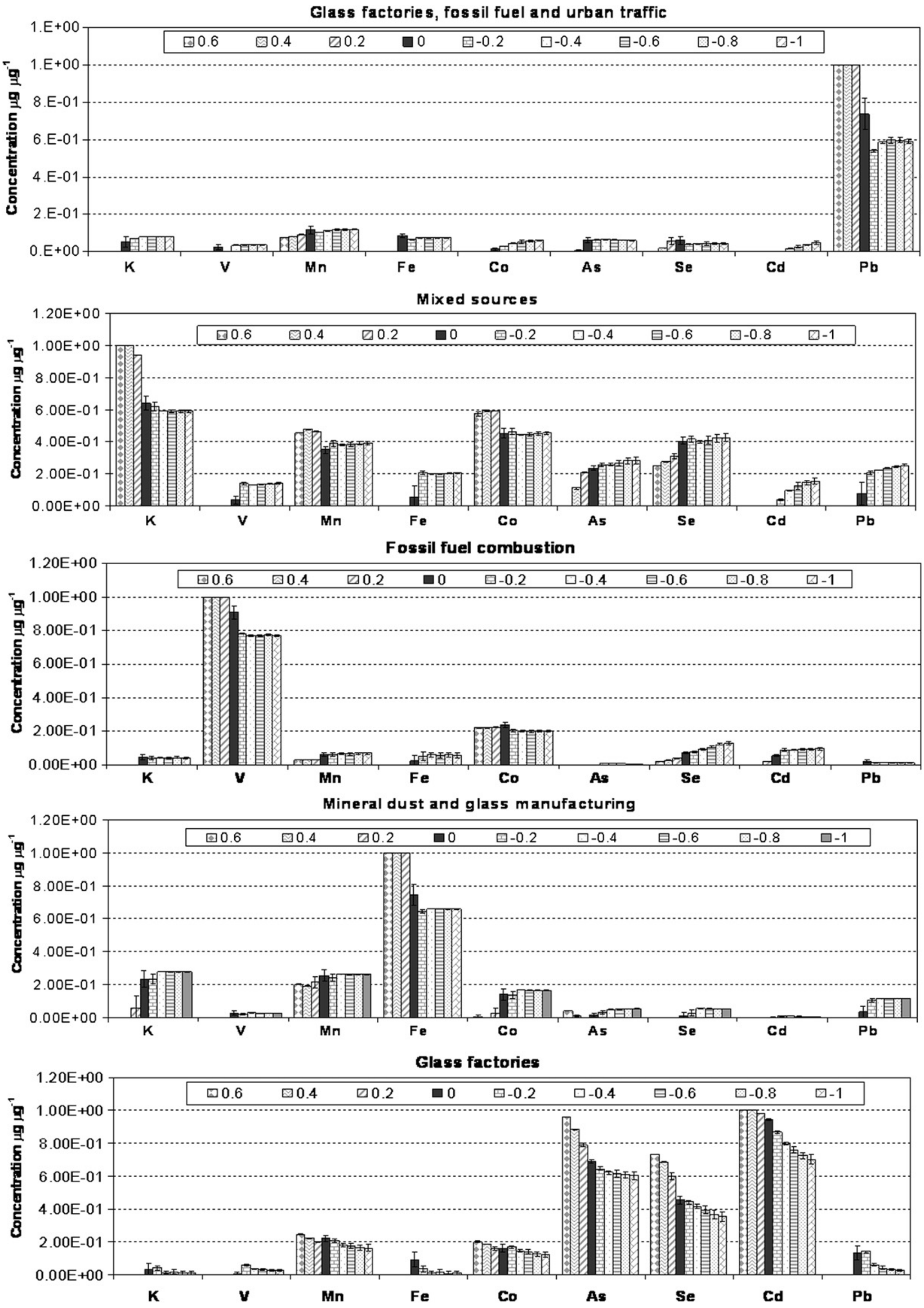
Table 5
Data comparison between this study and data from past campaigns in Venice Lagoon (CORILA 2001–2004 program campaign). Mazzorbo is located near Burano island, Murano correspond to the island with glass factories, P. Sabbioni is located near the sea, and in Marghera is located at the industrial area of Venice.

	Average (this study)	SD (this study)	P. Sabbioni 2001	Marghera 2001	Murano (Jun 2003)	Mazzorbo (Jul 2004)	Mazzorbo (Mar 2005)
K	229.12	143.34	–	–	25	99	309
V	14.06	20.39	–	–	–	5.5	3.3
Mn	5.22	2.95	7.6	11	5.3	2.6	6.5
Fe	97.73	109.58	177	216	213	36	57
Ni	12.15	8.26	–	–	3.7	3.3	2.7
As	3.58	3.53	–	–	–	–	–
Zn	84.51	36.37	32	38	62	31	52
Cd	3.51	4.12	1.4	1.1	38	3.3	6.1
Pb	18.08	16.57	7	14	18	10	20

Table 6
Comparison for some trace elements measured in different European cities.

	This study (Italy)		2001 two samples per week (Spain)[a]			1994 45 days May to June (Greek)[b]	1998 summer 40 samples (Italy)[c]
	Average (ng m^{-3})	SD (ng m^{-3})	Tarragona	Barcellona	Huelva	Thessaloniki	Milan
K	229.12	143.34	–	–	–	–	135 ± 35
V	14.06	20.39	5.30	9.50	3.60	41.00	<12
Mn	5.22	2.95	2.80	9.60	3.20	23.00	11 ± 5
Fe	97.73	109.58	–	–	–	297	170 ± 80
Ni	12.15	8.26	3.50	5.20	3.00	17.00	<6
As	3.58	3.53	0.50	1.10	4.20	1.50	–
Se	4.59	2.21	0.20	0.80	1.10	–	–
Cd	3.51	4.12	0.2	0.60	0.80	0.80	–
Pb	18.08	16.57	17.50	40.30	26.90	127.00	85 ± 70

[a] Moreno et al., 2006.
[b] Manoli et al., 2002.
[c] Marcanzan et al., 2001.


Glass factories, fossil fuel and urban traffic

Mixed sources

Fossil fuel combustion

Mineral dust and glass manufacturing

Glass factories

Fig. 6. PMF. Source profile resolved: results are given for different F_{peak} values but "−0.6" is chosen as the most reasonable solution (visible as dark bars).

to discriminate between "bad", "weak" and "strong" variables, according to signal-to-noise ratio criteria (Paatero and Hopke, 2003). In this way a categorization of "bad" for a variable eliminates it from the model elaboration, while a categorization of "weak" triples the uncertainty of the variables (elements) with a high percentage of data below the detection limit (which could influence the PMF results). While with a categorization of "strong", the variables are elaborated by the PMF as they are. In this work the species: Mn, As, Se, and Cd were defined as "weak" and the species Fe, K, V and Pb as "strong". Analysis of the G-space plot indicates a rotational ambiguity for many factors identified by PMF. For this reason, a PMF solution with multiple values of F_{peak} were systematically explored (F_{peak} between -1.0 and $+1.0$, with steps of 0.2) and the resulting parameters, were obtained from the scaled residual matrix, the IM (the maximum individual column mean), and the IS (the maximum individual column standard deviation). These together with *Q* values, as well as the *Z* and *C* matrices were examined to find the most reasonable solution. Moreover, the F_{peak} analysis allows us to gather additional information on the stability of the resulting solution. An examination of the frequency distribution of the residuals scaled by the standard deviations is one way of evaluating the quality of the model. In this work, all the distributions of the residuals were close to normal distributions so we can assume that all the species are well-modelled. In PMF, the number of sources selected may be determined by looking at a plot of the *Q*, IM and IS values as a function of the number of factors (Lee et al., 1999; Hopke, 2000; Viana et al., 2008). For *Q* values, the solution to the system is the point where the slope of the curve shows a marked change, while for the IM and IS parameters, when the number of factors increases to a critical value, these parameters will experience a drastic drop in value. In this work *Q*, IM and IS values showed a reasonable solution in correspondence with 4 and 5 factors. Our preference was the 5-factors solution as the 4-factors solution combined together sources with a different nature. The PMF analysis partially confirms the results of the PCA, but an additional factor is present, i.e. a group of mixed elements (K, Mn, Co, As, Se). The groups of elements composed of V–Co (fossil fuel combustion); Pb (urban traffic, fossil fuel, glass manufacturing); As–Se–Cd (glass manufacturing) and K–Mn–Fe (crustal sources) were obtained from the data output reflecting the PCA results. Results obtained for the 5-factorial solution are presented in Fig. 6 where the bars represent the computed estimated errors.

In Fig. 6 the chemical profile of each factor is shown for each F_{peak} value considered (the error bars represent the computed error estimated). As mentioned before, all solutions were explored for F_{peak} values within the range between -1.0 and $+1.0$, but for F_{peak} values: $+0.8$ and 1.0 the model solutions were not convergent. Moreover, we can observe that for the other F_{peak} values the different solutions were converged and stable. Finally, the F_{peak} value of -0.6 was chosen as the most reasonable solution (visible in each chemical profile figure as dark bars).

4. Concluding remarks

Data obtained from the study of $PM_{2.5}$ in Sacca San Biagio have shown average concentrations of 16.9 $\mu g\ m^{-3}$ with peaks during April and October 2007, and this is in agreement with the typical trend for the atmospheric particulate matter (PM) in the North of Italy. Values obtained are higher than the limits indicated in the EU directives (Directive 2008/50/EC for $PM_{2.5}$), and the EPA standard for the USA (15 $\mu g\ m^{-3}$). A comparison with Venice mainland $PM_{2.5}$ trend for concentration values evidences a good agreement, and reasons as atmospheric conditions in Venice area, as well as reproducibility in gravimetric procedures could explain this result. A comparison with PM_{10} from a nearby station (Sacca Fisola) shows a good correlation between concentration values that allows us to hypothesizes a possible common origin for PM. Correlations with meteorological parameters show that when precipitation is >10 mm and wind speed is $>2\ m\ s^{-1}$ there is a decrease in fine particles. The correlation of element concentrations with wind sectors and wind velocity $> 2\ m\ s^{-1}$ evidences that some elements like V, Cd and Pb are well associated for wind direction from NNE sector (anthropogenic emissions) and that values for sectors between S and N do not give any meaningful information. Concentration values for elements regulated by EC directives (As, Cd, Ni, Pb) reported in this study show values below the limits indicated for urban areas, and a comparison with PM_{10} values from local environmental agencies confirms that elements typical of anthropogenic emission are prevailing in the $PM_{2.5}$ cut-off. A comparison with other European cities confirms that elements concentrations in Venice area are generally comparable and that anthropogenic emissions represent common contribution for fine particles, even if in Spain natural intrusions are consistent. Factor loadings in PCA have shown five principal components associated to K–Mn–Fe (F1); As–Se–Cd (F2); V–Co (F3 and F4) and Pb (F1 and F5). In the case of V and Co F3 seems to be the most representative, while for Pb a well defined assignation is not achieved probably due to different sources emissions with it in the studied area. K–Mn–Fe could be attributed to the crustal component, while As–Se–Cd could be strongly connected with sources like glass manufacturing, even if generally Se shows different proveniences in source apportionment analysis studies. V and Co could be attributed to emissions from fossil fuels, ship and urban traffic and petrochemical emissions. Elements like Co do not have a well defined trend and probably other sources should be considered in the area. This fact could explain the presence of V and Co in F3 and F4. The analysis of the data-set with PMF, produces a 5-factors output with 4 factors that agree with the PCA output and an additional factor based on mixed elements (crustal and anthropogenic). Rotational freedoms associated with the PMF solution were handled with F_{peak} analysis. In this case, the first group is V–Co, the second group includes Pb, the third group is characterized by the key elements Cd–Se–As and the fourth group consists in K–Mn–Fe. A fifth factor is identified with PMF, and the key elements of this factor are K–Mn–Co–As–Se, that could be representative of a source mixing. It has to be mentioned that in PMF the choice of factor is always a compromise because PMF is a descriptive model and there is no objective criterion to choose the ideal solution.

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