Bulk deposition close to a Municipal Solid Waste incinerator: One source among many

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HIGHLIGHTS

- Metals and soluble ions were determined in bulk deposition collected nearby a MSWI.
- PMF was applied to assess the contribution of the MSWI among the affecting sources.
- Three of the six PMF identified sources are associated with natural matrices.
- The highest contribution of toxic metals is due to resuspended soil dust.
- MSWI's relative contribution to the total inorganic pollutant load is negligible.

ARTICLE INFO

ABSTRACT

In order to assess the contribution of a Municipal Solid Waste incinerator to the area's total contamination, metals and soluble ions have been determined in bulk deposition collected at sites affected by different levels of plant emissions, according to the results of the Calpuff air dispersion model. Results show that in general fluxes monitored at the different sites during the same period are quite similar for each analyte. Deposition fluxes of nitrite and ammonium are significantly lower at the more distant site, while copper is significantly higher at this site, possibly because of copper fungicide used on the nearby agriculture land. The presence of sea spray and resuspended soil dust can be inferred from Pearson correlation coefficients, while enrichment factors indicate that Cu, Pb and Zn have a probable anthropogenic origin. A more complete evaluation of the sources affecting the area was obtained with PMF analysis. The sources associated with each factor were identified from the source profile and temporal trends. Six factors were identified, three sources associate with natural matrices, while three factors represent anthropogenic sources. The greatest contribution of heavy metals, the most toxic and persistent components determined, is associated with resuspended soil dust, especially when weighted according to their toxicity. The anthropogenic source contribution is similar at all sites, and therefore the incinerator's relative contribution to the total pollutant load appears to be negligible compared to other sources affecting the area.

1. Introduction

Waste incineration is a disposal method increasingly used in Municipal Solid Waste (MSW) management. In the Europe–27 countries, about 256 million tons of MSW were produced in 2009 and about 20% of them were incinerated (Blumenthal, 2011). New generation plants, built after European Directive 2000/76/EC and the implementation of Best Available Techniques (according to IPPC Directive 96/61/EC), have appreciably reduced environmental emissions, especially of the most dangerous pollutants, such as organic compounds and heavy metals. Thanks to new incineration processes and flue gas treatments, less than 1% of Cu, Pb, Zn, Cd and Hg contained in the waste are emitted to the atmosphere in the flue-gas discharge (European Commission, 2006).

From a global perspective, fossil fuel combustion and industrial activities are the main sources of heavy metals; in Italy, MSW incinerators release less than 2% of the total amounts of heavy metals (such as As, Cd, Cu, Cr, Hg, Ni, Pb, Zn) (ISPRA, 2012). However, even though the incinerator contribution to the national total emissions is very

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low, it may be more relevant locally. In addition to this, since there are no degradation processes for metals, soils, vegetation and waters undergo an overall enrichment of metals, and this results in their introduction and accumulation in the food chain.

Atmospheric deposition is a major pathway for air pollutants into the surface environment (Mijić et al., 2010): for example, 90% of the total plant uptake of Pb and As and 50% of the total plant uptake of Cd are due to atmospheric deposition (Bradl, 2005). From a biogeochemical perspective, the characterization of total atmospheric deposition is relevant in order to identify the variability and sources of atmospheric pollutants (Azimi et al., 2005). During the past few decades the field of analysis and monitoring of atmospheric deposition has grown dramatically, since deposition monitoring serves the following purposes: determination of atmospheric loadings to determine impacts upon receptors; analysis of temporal and spatial trends, e.g. to evaluate the consequences of emission changes; need for a fundamental understanding of mechanisms transferring chemical constituents from the atmosphere to surfaces (Draaijers et al., 1996; Krupa, 2002).

Many studies on bulk (wet and dry) deposition of metals have been used to estimate the influence of atmospheric inputs of metals on the surface environment (Huston et al., 2009; Huston et al., 2012; Mijić et al., 2010; Rossini et al., 2010; Sharma et al., 2008; Tasić et al., 2009). These studies provide information on the contaminant fluxes, allow comparison of contamination in different areas and can also yield information about the sources affecting the area. To this end, several chemometric tools can be applied. Principal Component Analysis has been used widely to establish the chemical composition profiles of sources affecting a receptor (Rossini et al., 2010; Sharma et al., 2008). The related Positive Matrix Factorization (PMF) program is more powerful and provides quantitative information on source contributions. There are only few studies (Huston et al., 2012; Tasić et al., 2009) which have applied this source apportionment method to bulk (wet + dry) deposition. Thus, very little is known on the potential for application of the method to this kind of matrix and more studies are required to assess it. Moreover PMF analysis was previously never used to assess the contribution of a specific point source among many affecting an area. This kind of application is worthy of assessment.

In order to determine the contribution of a medium-sized (according to Italian standards) municipal solid waste incinerator (MSWI) located near the city of Rimini (Northern Italy) to local pollution, a monitoring system of bulk atmospheric deposition was activated in 2006. In this study, heavy metals, and the main soluble ions were investigated in bulk deposition. Our previous studies (Vassura et al., 2011) assessed the temporal trend of atmospheric deposition of PCDD/Fs in different environmental media. It demonstrated that the locality was affected by homogeneous contamination and suggested that more sources of these contaminants are present in the whole area. Nevertheless the low number of samples did not allow the application of chemometric techniques, to enter into a more comprehensive data analysis.

In this work, the study of contaminants affecting the monitored area was extended. Furthermore PMF analysis was applied in order to elucidate the different sources affecting the area and to evaluate their relative contribution to the total pollutant load.

2. Material and methods

2.1. Sampling network

The MSWI studied in this research, which is authorized to burn 140,000 tons per year of urban, hospital, and cemetery solid waste (127,600 until 2008), has been described elsewhere (Vassura et al., 2011). The sampling campaign took place from 2006 to 2010. During this period the plant worked at full capacity in 2006–2007 (3 incineration lines) and at reduced capacity in 2008–2009, due to a reconstruction

process. The plant shut down its activities for six months, while for the other part of the period only one line worked, while the others were dismantled. In 2010, a new line commenced the activity.

The study area, together with an orographic map and an indication of sampling sites appears in Fig. 1. The sampling network was designed on the basis of the dispersion map calculated by the atmospheric dispersion model Calpuff, applied to incinerator emissions, and reported in a previous paper (Vassura et al., 2011). The incinerator is located in a valley; the model identifies the main fallout zone on the surrounding ridge (Fig. 1b). Indeed, the hill ridge height varies from 60 to 70 m ASL, which is almost the same height as the emission stack of the incinerator. According to the model, the hill ridge attenuates the dispersion of plant emissions beyond the surrounding hills. Three sites (1, 2 and 3) were located on the hill ridge. Site 1 was located 1.8 km from the plant, in an area strongly affected by incinerator emission fallout and by the nearby A14 highway (800 m). Site 2 was placed in a rural area 1.2 km from the plant, in the main incinerator emission fallout zone. Site 3 was located following the main wind axis between the incineration plant and the site itself. It is located in a suburban area approximately 2 km from the incinerator, 1.5 km from the Adriatic Sea and 600 m from the highway, so it is also affected by pollutants coming from the coast and from road traffic. Finally, site 4 was located 4 km from the plant, in a zone of minimum fallout and used as a control site. Since it is located beyond the hill ridge it is not affected by plant emissions but it is sufficiently close to other sites to have the same background contamination.

2.2. Meteoclimatic conditions

Pollutant dispersion and deposition are affected by meteoclimatic conditions. Wind data were provided by Arpa SIM (Servizio IdroMeteorologico) Emilia Romagna (http://www.arpa.emr.it/sim/? osservazioni_e_dati/dexter). They were obtained by real time measurements at a monitoring station 8 km from the incinerator. The average over the 5-year period (2006–2010) is reported in Fig. 2. Results confirm, as previously reported in Morselli et al. (2011), that wind direction (south-west–north-east) and speed are mainly dominated by the land and sea breezes. Since rainfall contributes to atmospheric pollutant removal, it influences atmospheric deposition collection by bulk samplers. The rainfall trend (mm of rain for month) from 2006 to 2010 is very variable (Supporting information (SI), Fig. S1). In 2006 rainfall was heavy in summer and light in winter, while in other years rainfall followed the typical seasonal trend; it was almost absent in the warmest months and heavier in cold months. In 2010, May and June also were particularly rainy. More details on meteoclimatic conditions are reported in Table S1.

2.3. Sampling

Atmospheric deposition was collected monthly by Depobulk® samplers. They consist of an HDPE funnel directly connected to a collection bottle and placed in a PVC structure hanging from a pole 2 m from the ground. Bulk sampler characteristics are those recommended by the Italian National Institute of Health (ISS) (Menichini et al., 2006) and CEN EN — Method 15841 (2009). Before environmental exposure, the collecting bottles (20 L) were carefully washed using a 0.2% solution of HNO₃, then by distilled water and lastly bi-distilled water.

2.4. Sample preparation and analysis

After collection, samples were immediately sent to the laboratory, where they were weighed for the determination of total precipitation; then atmospheric deposition samples were filtered through cellulose nitrate filters (Millipore, 0.45 μm), in order to separate the soluble and insoluble fractions. All filters were stored at 4 °C until mineralization, whereas two 250 mL representative aliquots of
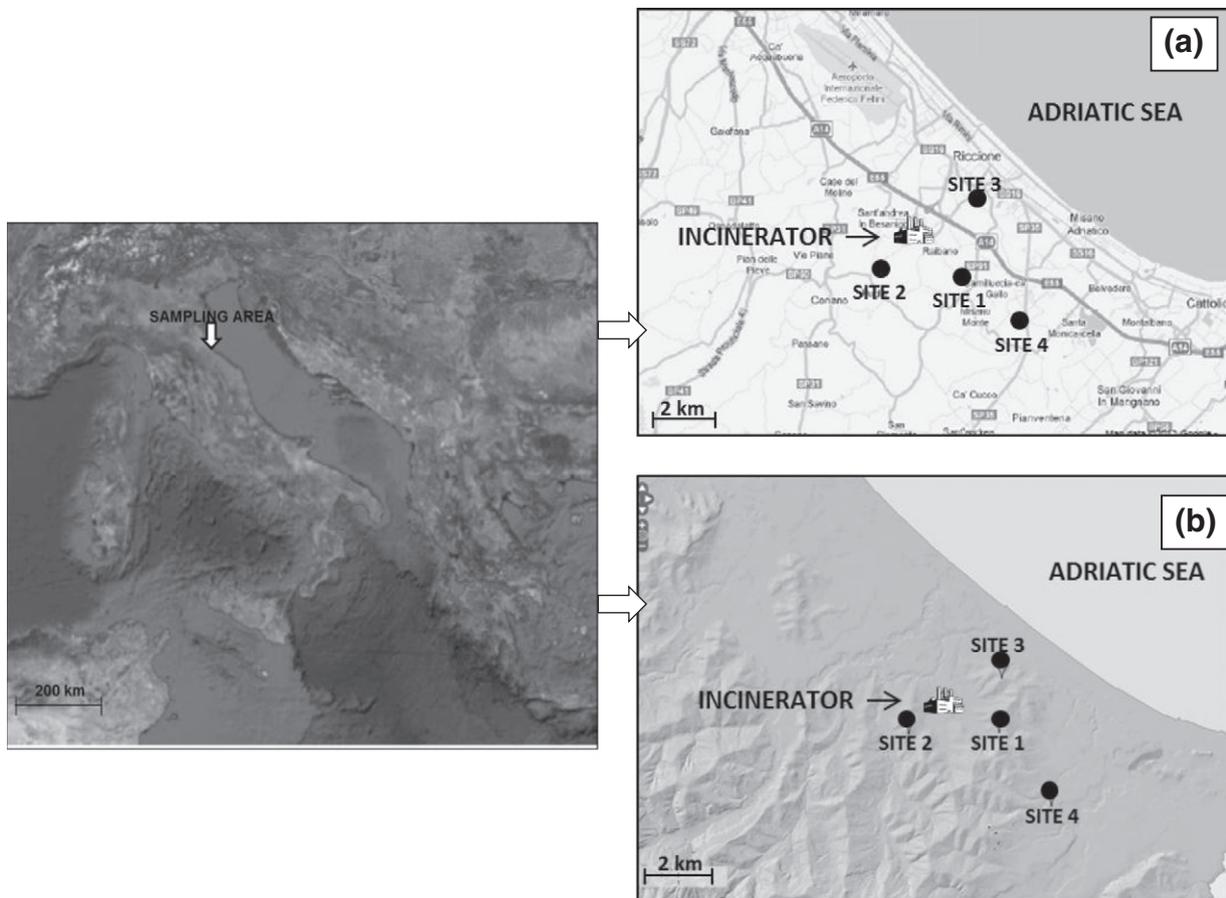
Fig. 1. Studied area and monitoring sites on a large-scale map and (a) a local map (from Map data © 2012 Google — modified) and (b) on an orographic map (from Emilia-Romagna website: http://geo.regione.emilia-romagna.it/geocatalogo/).

water solution were collected and stored in HDPE bottles at 4 °C until metal and ion analysis. HNO_3 (65%, Suprapur, Merck) was added to the aliquot for metal determination, until pH < 2.

Fig. 2. Wind rose from study area (average of years 2006–2010).

The filters were mineralized in a Multiwave 3000 (Anton Paar) microwave oven. Each was placed in a Teflon bomb with 5 mL of HNO_3 and 0.5 mL HCl (30%, Suprapur, Merck). The procedure did not allow a complete digestion of silicate. However for the application of this study, i.e. having information of contaminant flux in the environment, the results are fit for purpose. Digested solution was made up to 50 mL with bi-distilled water. Metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were analyzed with the Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer equipped with an air–acetylene flame atomizer for the determination of Fe and Zn in the insoluble fraction and electro-thermal (graphite tube) atomizer for other metals. Standard solutions were prepared daily in 0.2% HNO_3, by serial dilutions of stock standard solutions (Carlo Erba Reagenti and Merck kGaA).

Soluble ions (NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, K^+, Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}) were determined by Ion Exchange Chromatography (Metrohm 761 Compact IC). Cations were separated on a Metrosep C2/150 column (150 × 4 mm), with isocratic elution (dipicolinic acid (Sigma Aldrich) 4 mM, tartaric acid (Sigma Aldrich) 1 mM) and a flow rate of 1.5 mL/min. Anions were separated on a Metrosep A supp 4 column (250 × 4 mm), followed by a suppressor, with isocratic elution ($NaHCO_3$ (>99.8% Carlo Erba Reagenti) 1.7 mM, Na_2CO_3 (anhydrous, >99.5%, Carlo Erba Reagenti) 1.8 mM and acetone (Sigma Aldrich, HPLC grade, >99.8%) 2%) and a flow rate of 1.5 mL/min. Stock standard solutions (Ultra Scientific) were used for the determination of concentrations by an external standard method.

2.5. Quality assurance

Quality assurance information is reported in Table S2. Recovery results are based on analysis of the NIST standard reference material
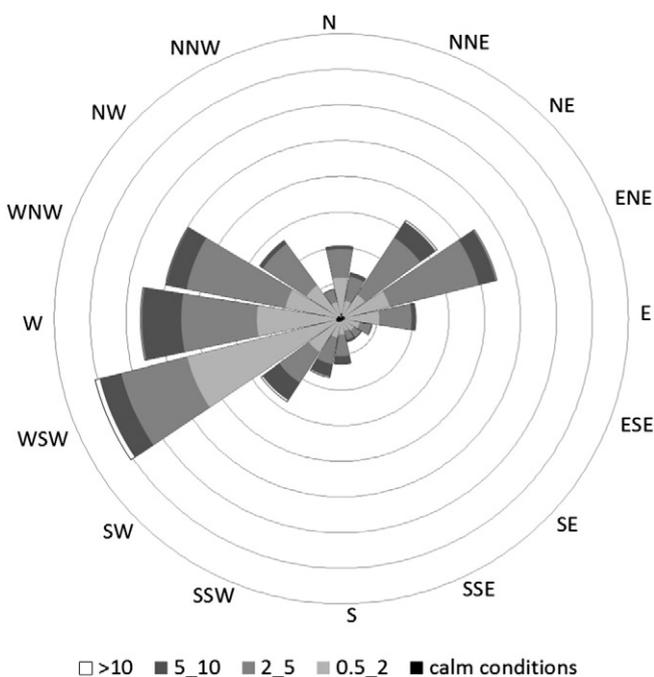
(SRM), 1648 urban dust (mean values for four tests). Al, Cd, Cu, Mn, Ni, Fe and Pb recoveries generally ranged from 80% to 120%, with a standard deviation always lower than 7% (for cadmium it is little higher, 10%). Zinc recovery is quite high, 144%, but RSD is good (6%). On the contrary As and Cr recoveries are low, 55% for the first and 44% for the latter. Nevertheless As and Cr fluxes are low and the study area can be considered weakly contaminated by these metals. RSD (9% for both) demonstrates that the reproducibility is good. Since the main aim of the study is the comparison among sampling sites, we decided not to discard Zn, As and Cr results.

Blank filters were digested with the same procedure as that for samples, to assess filter contamination. As and Cd blank values were below the graphite furnace AAS LoQ. For other metals, blank filter and sample concentrations were compared. Only a few samples registered a concentration lower than 10 times filter blank concentrations and therefore blank contamination did not significantly affect the sample results. Nickel and zinc showed higher contamination; 18% of samples for the former and 12% for the latter showed a concentration lower than 10 times the blank values. Since PMF analysis allows the association of an error with each value, it was decided not to discard these data as the weighting process in PMF would allow for the greater uncertainties.

Tests were performed to assess the effect of the acid matrix on the AAS signal. Standard solutions in the same matrix as samples and in 0.2% HNO_3 solution were prepared. The test demonstrated that no matrix effect was present and the AAS signal did not depend on the acidity of the solutions. Therefore it was decided to prepare the standards in 0.2% HNO_3 solution.

2.6. Enrichment factors (EF)

Atmospheric deposition is affected by the contribution of resuspended crustal material. EF determination allows a distinction between anthropogenic and natural origins of a certain element (Mijić et al., 2010). The enrichment factor calculation is based on standardization of the measured element against a reference element, assumed to be completely of crustal origin. In this work, Al was used.

$$EF(M)_{atm.dep} = \frac{(F.d.D_M / F.d.D_{Al})}{([M]_{soil} / [Al]_{soil})}$$

where

F.d.D_M   Daily deposition flux of metal (M) (mg/m² day)
F.d.D_Al   Daily deposition flux of Al (mg/m² day)

$[M]_{soil}$ Metal concentration in soil (mg/kg ss)
$[Al]_{soil}$ Al concentration in soil (mg/kg ss).

Soil composition was determined by chemical analysis of soils sampled in the study area in January 2011.

2.7. Positive Matrix Factorization (PMF)

Details of this method appear in the SI. In PMF, the choice of the number of factors is a compromise. Using too few factors will combine sources of a different nature together. Using too many factors will make a real factor further dissociate into two or more non-existent sources (Lee et al., 1999).

The appropriate number of factors extracted and the value of C3 were then determined based on satisfying most of the following criteria (the first four criteria were based on Lee et al. (1999) and Chan et al. (2008)):

- Value of Q close to n × m−p × m−p × n (i.e. the degree of freedom of the analysis).
- R90 (the 90 percentile of the scaled residuals, r_{ij}) is within ± 2. That is, most of the residuals are within 2.
- A sharp drop in IM (the maximum of the mean values of r_{ij} of each species) and/or IS (the maximum of the S.D. of r_{ij} of each species).
- A significant increase in the largest rotmat element.
- Comparison of the mass profile of the marine aerosol factor with sea water composition (Goldberg, 1963).
- Comparison of the resuspended soil dust factor mass profile with the composition of the soil in the study area, by comparison of the Ca/Al ratio and the Fe/Al ratio in soil and in the PMF profile.

Three to 11 factor solutions were tested, but only six factors and C3 = 0.12 were found to obey all the required constraints and resulted in a physically meaningful solution. The optimal Q-value obtained with this model was 3192, which compares reasonably well with the theoretical value of 2638 for the six factor model. The observed difference between theoretical and calculated Q-value (factor of 1.2) is reasonable given the empirical nature of the equations used for estimating the input error values and the presence of missing data (Ogulei et al., 2006a). Six factors explained >75% of the variations in most species; however >30% of the variations in As, Fe and Pb were not explained by these factors. These species have large number of samples which have concentrations below the detection limit; this could be the reason for such a high variation explained by residuals (Chan et al., 2008).
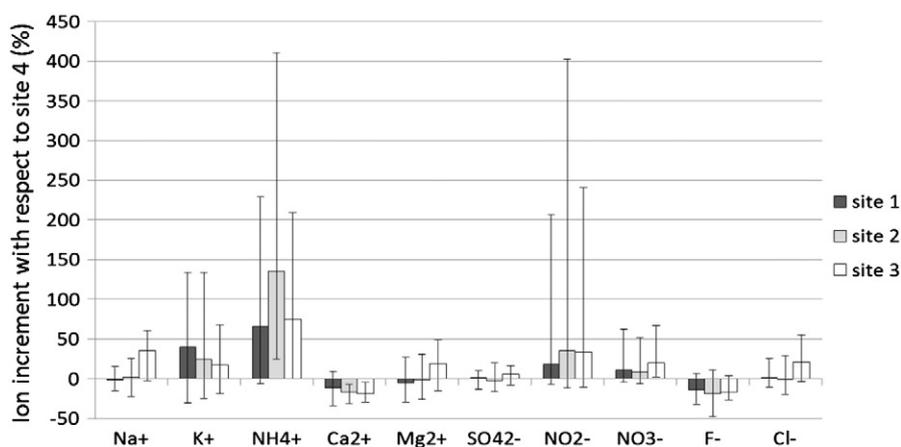
Fig. 3. Median ionic deposition difference for each month at sites 1, 2 and 3 with respect to site 4 for ionic component. The bars represent the upper and lower quartile.

Table 1
Intra-site Pearson correlation coefficients among the soluble ions at sites 1 (a), 2 (b), 3 (c) and 4 (d). Significant correlations (p = 0.001) are reported in bold.

Site 1	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	F^-	NO_2^-
Na^+	1.00									(a)
NH_4^+	−0.05	1.00								
K^+	0.12	0.41	1.00							
Ca^{2+}	0.43	0.08	0.28	1.00						
Mg^{2+}	**0.65**	−0.04	0.10	0.32	1.00					
SO_4^{2-}	**0.74**	0.16	0.03	0.38	**0.67**	1.00				
NO_3^-	0.19	0.05	0.15	0.18	0.17	0.11	1.00			
Cl^-	**0.75**	−0.01	0.27	0.37	**0.92**	**0.80**	0.24	1.00		
F^-	0.21	0.23	**0.47**	0.45	**0.59**	**0.55**	0.32	**0.70**	1.00	
NO_2^-	−0.05	−0.02	−0.01	−0.07	−0.10	−0.09	−0.07	−0.06	−0.09	1.00

Site 1	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	F^-	NO_2^-
Na^+	1.00									(b)
NH_4^+	0.01	1.00								
K^+	0.27	0.16	1.00							
Ca^{2+}	0.30	−0.07	0.17	1.00						
Mg^{2+}	**0.69**	0.00	0.18	0.44	1.00					
SO_4^{2-}	**0.76**	0.21	0.28	0.41	**0.64**	1.00				
NO_3^-	0.24	0.07	0.16	0.40	0.44	0.41	1.00			
Cl^-	**0.78**	0.03	0.20	0.39	**0.91**	**0.84**	0.36	1.00		
F^-	−0.02	0.13	0.13	0.09	0.10	0.22	0.27	0.25	1.00	
NO_2^-	−0.12	0.12	0.01	−0.12	−0.12	−0.08	−0.29	−0.09	−0.06	1.00

Site 1	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	F^-	NO_2^-
Na^+	1.00									(c)
NH_4^+	0.07	1.00								
K^+	0.29	−0.06	1.00							
Ca^{2+}	0.20	−0.19	0.44	1.00						
Mg^{2+}	**0.83**	0.06	0.33	0.41	1.00					
SO_4^{2-}	**0.75**	−0.02	**0.49**	**0.66**	**0.78**	1.00				
NO_3^-	0.27	0.39	0.17	**0.48**	0.42	**0.53**	1.00			
Cl^-	**0.72**	0.27	0.21	0.30	**0.92**	**0.85**	**0.62**	1.00		
F^-	−0.07	0.27	0.08	0.07	−0.03	0.13	0.32	0.17	1.00	
NO_2^-	0.04	-0.06	−0.02	0.05	0.03	0.05	−0.04	−0.03	−0.09	1.00

Site 1	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	F^-	NO_2^-
Na^+	1.00									(d)
NH_4^+	0.12	1.00								
K^+	0.21	0.22	1.00							
Ca^{2+}	0.23	−0.31	−0.01	1.00						
Mg^{2+}	**0.72**	0.03	0.33	0.41	1.00					
SO_4^{2-}	**0.73**	0.32	0.41	0.22	**0.68**	1.00				
NO_3^-	0.36	0.31	0.34	0.18	**0.56**	**0.50**	1.00			
Cl^-	**0.76**	0.16	0.42	0.27	**0.94**	**0.82**	0.44	1.00		
F^-	−0.05	-0.06	−0.02	0.34	−0.06	0.09	0.06	0.02	1.00	
NO_2^-	0.13	-0.06	−0.05	0.08	0.05	0.03	0.06	0.06	−0.04	1.00

3. Results and discussion

3.1. Inorganic ions

Fluxes of ions were calculated using the concentration, volume collected, area of funnel and number of days deployed to give a value in mg m^{-2} day^{-1}. The mean daily deposition fluxes of inorganic ions registered at the different sites are reported in SI, Table S3. Fluxes of most analytes monitored during the same period, are quite similar from one site to another. Generally, no large differences can be seen among the values found at the most affected sites (according to the dispersion model, i.e. sites 1, 2 and 3), and the reference site (site 4). On the contrary, temporal variability is quite high. Nitrate fluxes decreased from 2006 to 2010, especially at sites 1, 2 and 3, and in the last years deposition fluxes were similar to site 4. In comparison with another study undertaken in the same region (Pieri et al., 2010), deposition fluxes show a high load of chloride and sodium due to the influence of the coastal area, while nitrates, sulfates and ammonium fluxes are lower.

In order to assess the differences between the most affected sites (according to the dispersion model, i.e. sites 1, 2 and 3) and the reference one (site 4), the percent difference of ionic load with respect to the control site for each of the sites 1 to 3 has been evaluated for each month. In Fig. 3 median, lower and upper quartile are reported for each component. Potassium, ammonium, nitrate and nitrite usually show a lower flux at site 4. Specifically, more than 60% of data show a higher flux at the most affected sites. For ammonium at site 2 and nitrate at site 3, more samples show a lower flux at site 4, 82% for the former and 75% for the latter.

In order to better evaluate inter-site differences for each chemical species, a significance test was also used. First of all the frequency distribution of the concentrations was examined, represented by the mean daily deposition fluxes for each month. All the chemical species proved to be log-normally distributed (goodness of fit was tested with the Kolmogorov–Smirnov method) except for nitrite, nitrate and ammonium. For these species, the non-parametric Mann–Whitney test was used, while for the others a t-test, using the logarithm of deposition fluxes, was used. Deposition fluxes of nitrite and ammonium at site 4 were confirmed to be significantly lower (p-level 0.05) than at other sites.

A preliminary study on the origin of the ions in the area used Pearson correlation coefficients between deposition fluxes of ions for each site (Table 1a–d). A significant correlation may be reflective of a common source of contaminants. At all sites, ions due to the marine spray contribution (Cl$^-$, Na$^+$, Mg^{2+} and SO$_4^{2-}$) correlated significantly (p = 0.001), indicating a strong contribution of sea spray. This is the only source that can be identified with this technique. There are other significant correlations, but they did not occur at all 4 sites and were not typical of any known emission source.

3.2. Heavy metals

Even if metal solubility can provide insights into the origin of the metal itself (Guieu et al., 1997), it is influenced by several other factors, such as pH, anion-cation balance, redox potential, temperature, complexing agents and so on. For this reason, even though metals were determined separately in the soluble and the insoluble fractions, results will be discussed by considering the sum of the two fractions.

Mean daily deposition fluxes of heavy metals registered each month are reported in SI Table S4.

The percent differences of metal load with respect to the control site for each of the sites 1 to 3 for each month were calculated. Median and lower and upper quartiles for each component are reported in Fig. 4. Considering the total sampling period (2006–2010), a high variability can be observed and it was concluded that there are no important spatial differences in the area. The study area is characterized by a low metallic load, similar to other suburban areas (Guieu et al., 1997; Sandroni and Migon, 2002).

A significance test (t-test, since all the species are log-normal distributed) demonstrated that the deposition flux of copper at site 4 is significantly higher than that at sites 1 and 2 (p-level 0.05), while the p-value for site 3 is 0.06. Copper can be a marker of several processes, such as vehicular traffic (brake wear emissions) (Napier et al., 2008; Thorpe and Harrison, 2008) and also Municipal Solid Waste incineration (Pacyna and Pacyna, 2001). Since copper is the only vehicular traffic marker higher at site 4 and the location of the site itself, the greatest contribution to copper may be due to copper fungicide used on the nearby agriculture land (Komárek et al., 2010; Ötvös et al., 2003).

Table 2a–d reports Pearson correlation coefficients among deposition fluxes of metals for each site.

At all sites, major constituents of soil (Fe, Al and Mn) correlate significantly (p = 0.001), indicating a contribution of resuspended soil dust. At some sites, Cr also correlates with these metals, indicating that the presence of Cr in atmospheric deposition is mainly due to the contribution of the soil. Other significant correlations are Cu–Ni and Cu–Pb at site 2, Zn–Ni at site 3 and Cu–Ni and Cu–Zn at site 4. Cu, Zn and Pb could be markers of the incinerator (Pacyna and Pacyna, 2001), but the Cu–Zn correlation is significant also at site 4 and these elements correlate significantly also with Ni, which is a marker of oil combustion, and may be related to vehicular traffic emissions (Horemans et al., 2011; Karar and Gupta, 2007). These
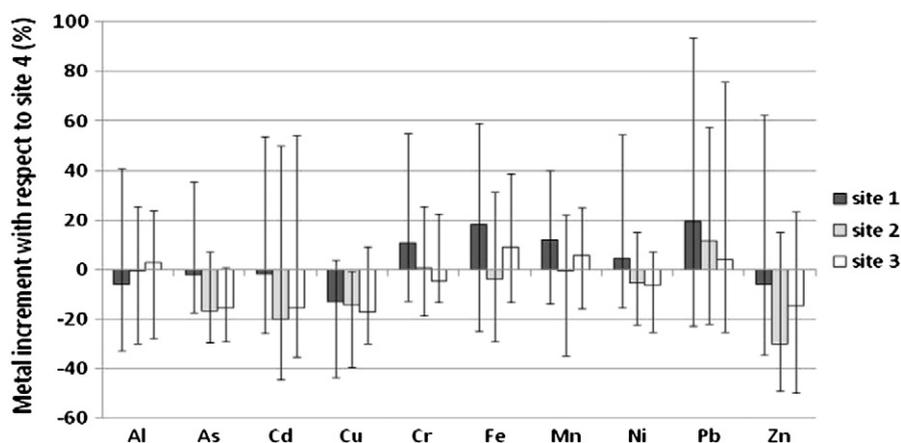

Fig. 4. Median deposition difference for each month at sites 1, 2 and 3 with respect to site 4 for trace metals. The bars represent the upper and lower quartile.

Table 2
Intra-site Pearson correlation coefficients among metals at sites 1 (a), 2 (b), 3 (c) and 4 (d). Significant correlations (p = 0.001) are reported in bold.

Site 1	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	0.17	1.00								
Cd	−0.15	−0.15	1.00							
Cu	−0.14	0.05	0.10	1.00						
Cr	**0.52**	0.44	0.12	−0.08	1.00					
Fe	**0.74**	0.17	0.00	−0.05	0.44	1.00				
Mn	**0.75**	0.23	−0.22	−0.01	**0.66**	**0.74**	1.00			
Ni	0.40	0.27	0.29	0.31	**0.64**	**0.50**	**0.52**	1.00		
Pb	−0.07	−0.05	0.04	0.29	−0.13	−0.05	−0.08	0.03	1.00	
Zn	0.03	0.14	0.30	0.26	0.21	0.20	−0.08	0.33	0.39	1.00

(a)

Site 2	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	−0.08	1.00								
Cd	−0.10	−0.14	1.00							
Cu	−0.13	−0.09	−0.15	1.00						
Cr	0.27	0.45	−0.23	−0.08	1.00					
Fe	**0.74**	−0.12	−0.03	−0.04	0.25	1.00				
Mn	**0.46**	−0.10	−0.19	0.17	0.38	**0.49**	1.00			
Ni	0.34	0.09	−0.13	**0.48**	0.34	0.20	0.27	1.00		
Pb	−0.09	0.04	0.05	**0.51**	−0.06	−0.23	−0.01	0.42	1.00	
Zn	−0.06	**0.55**	0.17	−0.03	**0.51**	−0.04	−0.03	0.12	−0.09	1.00

(b)

Site 3	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	0.06	1.00								
Cd	−0.07	−0.05	1.00							
Cu	0.06	0.06	0.19	1.00						
Cr	0.40	−0.02	0.28	0.17	1.00					
Fe	**0.76**	0.08	−0.03	0.37	0.38	1.00				
Mn	**0.72**	0.29	−0.16	0.14	0.36	**0.57**	1.00			
Ni	−0.02	−0.02	0.04	0.17	0.22	−0.01	−0.04	1.00		
Pb	−0.05	0.00	−0.07	0.15	0.14	−0.01	−0.09	0.15	1.00	
Zn	0.04	0.08	0.13	0.44	0.37	0.06	0.01	**0.65**	0.14	1.00

(c)

Site 4	Al	As	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	0.09	1.00								
Cd	0.01	0.01	1.00							
Cu	0.16	0.19	0.49	1.00						
Cr	0.44	0.04	0.09	0.13	1.00					
Fe	**0.59**	0.37	0.36	0.34	0.36	1.00				
Mn	**0.57**	0.30	−0.09	0.05	**0.65**	**0.63**	1.00			
Ni	0.47	0.12	0.41	**0.62**	**0.52**	0.44	0.37	1.00		
Pb	0.00	−0.05	0.07	0.42	0.04	−0.03	−0.12	0.20	1.00	
Zn	0.19	0.23	0.40	**0.64**	0.04	0.46	0.13	0.42	0.26	1.00

(d)

correlations appear to indicate the contribution of vehicular traffic, since Cu, Pb and Zn are markers also of this source (Horemans et al., 2011; Karar and Gupta, 2007; Napier et al., 2008).

The enrichment factors (EF) may help to identify a resuspended soil dust contribution and thus an external contribution which is generally, but not always anthropogenic (Table 3). Usually anthropogenic contamination is considered significant if EF > 100, modest if 10 < EF < 100 while the origin is mainly natural if EF < 10 (Mijić et al., 2010). EF data (Table 3) confirm that Cr and Mn are mainly due to resuspended soil dust, as indicated by the Pearson correlation coefficients. According to the EF, Ni also is mainly due to the soil contribution. Deposition fluxes of Cd are usually below the method detection limits, as for As, so it is difficult to interpret information from its EF. However, in 2010, the deposition flux of Cd was above the method detection limit and the EF indicates that it is mainly due to resuspended soil dust. Cu, Pb and Zn are instead due to anthropogenic sources. For Cu and Pb the EF decreased from 2006 to 2010 and they are lower than 10 in the last year, indicating a mainly natural origin. These metals could be considered as markers both of vehicular traffic and incineration plants, but since similar values of EF were registered at site 4 and at other sites, they seem most probably due to vehicle emissions.

3.3. Positive Matrix Factorization

The overall mass concentration profiles of the six factors affecting the four sites are shown in Fig. 5. The first factor consists of mainly potassium, calcium and iron, but also sodium, magnesium and sulfates give an appreciable contribution. This factor is characterized by elements typical of Saharan dust, in particular of the western part of the region, which is richer in calcium rather than aluminum (Dall'Osto et al., 2010; Moreno et al., 2006). Temporal trends of the factors (Fig. 6) show that in March–April 2007 the contribution of this factor at the sites was about 10 times higher than the mean value. The study area is often characterized by Saharan dust events and probably they were particularly strong in this month. In order to confirm this event, back trajectories were studied. Site 3 was considered as the arrival point, but other sites will be affected by the same back trajectories. A transport time of 48 h was considered suitable to assess long-range contributions. In Fig. 7 an example which considers the period 23–26 March 2007 is reported. Meteorological parameters of the database GDAS1 and an arrival level height of 2 m AGL were chosen as input data. Back trajectories were computed by the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model for calculating air parcel trajectories for complex dispersion and deposition simulations. Back trajectories confirmed a Saharan dust event.

The second factor is more difficult to interpret, since it is characterized by Zn, Cu, Pb, Fe and Cd, which can be markers both of vehicular traffic and incinerators (Chan et al., 2008; Gratz and Keeler, 2011; Lee et al., 1999; Mijić et al., 2010; Nicolás et al., 2008; Ogulei et al., 2006b). For this reason it was called "Metals". Cl^- is not represented by this factor and since it is also a marker of incineration (Keeler et al., 2006), this suggests that vehicular traffic is better represented by this factor. However Cl^- has been reported also in a vehicular emissions factor (Lee et al., 1999; Nicolás et al., 2008). Further insights can be gained by considering the factor contribution at each site (Fig. 6). In 2009–2010, the temporal contribution of this factor at each site decreased. In 2008 the incinerator was reconstructed, possibly giving an explanation for this behavior. However, in 2008 the plant was closed entirely for six months, but the contribution of the factor is higher than in 2009–2010. Additionally, the contribution at site 4 is not lower than that at the other sites. For these reasons, this factor is very unlikely to be associated with the incinerator and is more probably due to vehicular traffic.

Table 3
Enrichment factors of metals in bulk deposition.

a	Site 1					Site 2					Site 3					Site 4				
	2006	2007	2008	2009	2010	2006	2007	2008	2009	2010	2006	2007	2008	2009	2010	2006	2007	2008	2009	2010
Cr	**1.3**		**0.9**	**1.9**	**1.1**	**1.8**		**1.2**	**1.9**	**1.1**	**1.9**		**1.2**	**2.1**	**1.3**	**1.2**		**1.0**	**2.4**	**0.6**
Cu	<41	19	9	6	6	<42	14	15	6	6	<40	27	12	13	6	<36	19	17	16	5
Mn	1.3	0.8	1.0	1.3	0.7	1.5	0.6	1.4	1.3	0.8	1.5	1.2	1.4	1.4	0.8	1.1	**0.5**	1.2	1.4	0.6
Ni	<5.0	<2.6	**1.1**	<2.0	**0.8**	<4.2	**1.2**	**1.3**	<2.0	**0.8**	<5.3	**1.8**	**1.3**	**1.5**	**0.9**	<3.2	**1.5**	**1.5**	<2.8	<0.9
Pb	47	27	**7.1**	**6.9**	**7.3**	<78	**11**	**10.4**	**6.9**	**7.3**	57	15	**14.2**	**10.5**	**6.8**	69	23	**11.1**	<13	**3.7**
Zn	52	67	17	16	18	31	32	20	16	18	40	70	22	21	19	50	38	38	26	14
As	<68	<15	<55	<65	<37	<82	<10	<77	<64	<41	<113	<14	<76	<61	<30	<62	<10	<93	<75	<20
Cd	<62	<93	<16	<4	4	<102	<81	<19	<4	4	<15	<85	<19	<5	11	<12	<42	<25	<8	4

a Often metal concentration in atmospheric deposition resulted below the detection limit (BDL). When in both the datasets (soluble and insoluble fractions) 50% of the monthly values at least were BDL, the annual flux was calculated by using the detection limit for a BDL value and the enrichment factor was reported as "lower than". When only in one dataset (soluble or insoluble) 50% of the monthly values at least were BDL, the fraction which makes the highest contribution to the total flux was considered. If it were the fraction with 50% of the monthly values at least were BDL, the annual flux was calculated by using the detection limit, for a BDL value, and the enrichment factor was reported as "lower than". If it were the other, annual flux was calculated by using 1/2 DL for BDL value, as suggested by the Italian National Institute of Health (ISS) (Menichini et al., 2004). The enrichment factor is reported in bold and it is just an estimate of the real value.
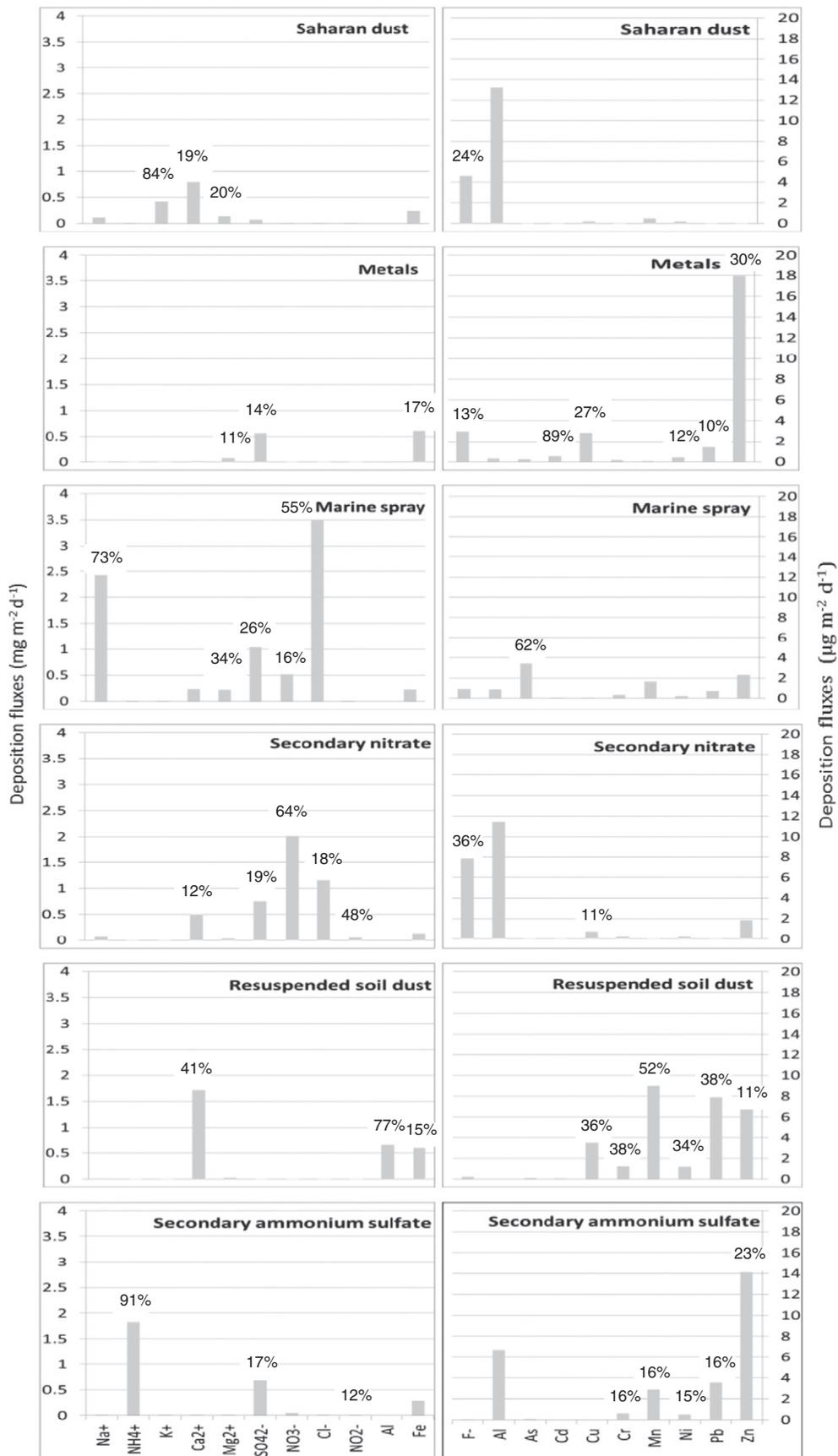
Fig. 5. Sources profiles in mass concentration. For each factor, the left box reports soluble ions, and Fe and Al (the latter only for resuspended soil dust) profiles (mg m^{-2} day^{-1}). In the right box, Zn, Pb, Ni, Mn, Cr, Cu, Cd, As and Al (for the other five factors) profiles are reported (μg m^{-2} day^{-1}). The percentage contribution of the factor to each chemical component is also reported.
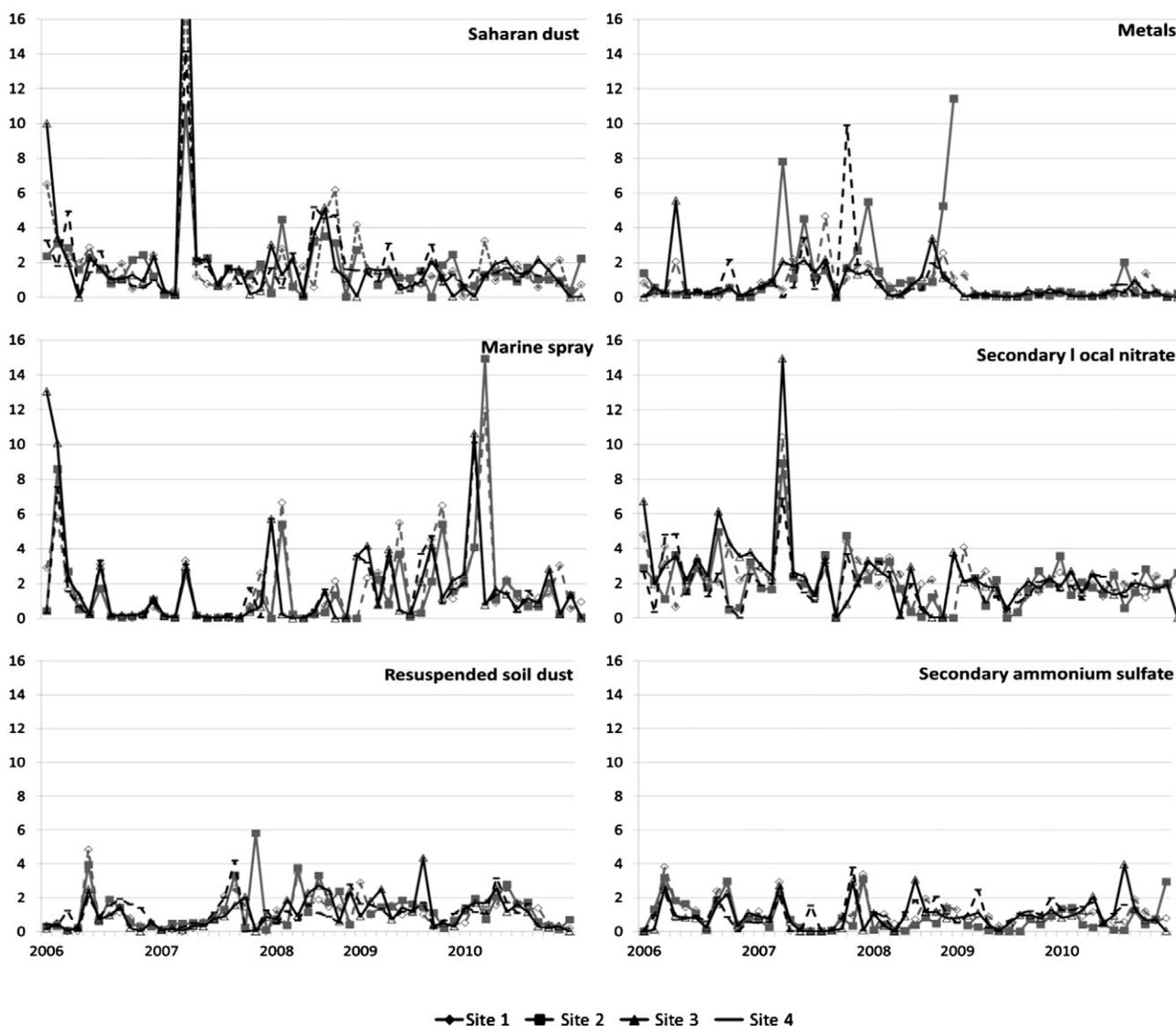
Fig. 6. Temporal variation of source contributions at the four sites.

The third factor is characterized by the chemical species present in sea water, i.e. Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^-, so this factor represents the marine aerosol contribution. One of the criteria chosen to evaluate the solution obtained with PMF analysis is comparison of this factor with sea water composition (Goldberg, 1963). The results are reported in SI Table S5. They are quite similar. The major difference between the two profiles is due to the lower % of chloride in the PMF profile, which is balanced out with a higher contribution of nitrate and sulfate. The deficit of chlorine, referred to as "chlorine depletion", is caused by reactions of acids (i.e. H_2SO_4 and HNO_3) not completely neutralized by ammonia, with sodium chloride to expel HCl. As a result, $NaNO_3$ or $Ca(NO_3)_2$ are produced in the particle (Dongarrà et al., 2010; Lee et al., 1999; Pathak and Chan, 2005). The sum of these three anions is very similar in sea water and in the PMF profile.

Temporal trends of the factors indicate that the marine spray contribution is particularly high during some months (Fig. 6). In order to better understand these events, the mean hourly wind direction and speed were assessed. It was possible to conclude that in general marine spray events occur when, at least for few hours (e.g. 5 h can be sufficient) wind direction is from over the sea with a wind speed equal or higher than 8 m/s.

The fourth factor is mainly characterized by nitrates, but also by chlorides and sulfates. It could represent secondary nitrates due to the conversion of NO_x, emitted both by vehicular traffic and by other combustion processes. The absence of potassium, a marker of biomass combustion processes is suggestive of a contribution from other sources of combustion.

The fifth factor is clearly resuspended soil dust, since it is characterized by Ca, Al and Fe but also by other metals that can be found in soil. Another criterion chosen to evaluate the solution obtained with PMF analysis is the comparison of this factor with soil composition. The mass profile was compared with the composition of the soil in the study area, which was analyzed in January 2011. The results are quite similar. The ratio Ca/Fe in the factor is 2.84, which is similar to what is found in soil (2.99), while the Ca/Al ratio is 2.60, while in soil it is 2.03. Finally the ratio between all other analyzed metals and Ca is 0.018 in the PMF factor and 0.013 in soil.

The last factor consists mainly of ammonium and sulfate. Secondary ammonium sulfate aerosol is formed from oxidation of sulfur dioxide in the atmosphere. The ammonium found in this source accounts for more than 85% of the total ammonium concentration. The molar ratio NH_4^+/SO_4^{2-} shows that ammonium is in strong excess which is because ammonium is also associated with other species (e.g. nitrate).
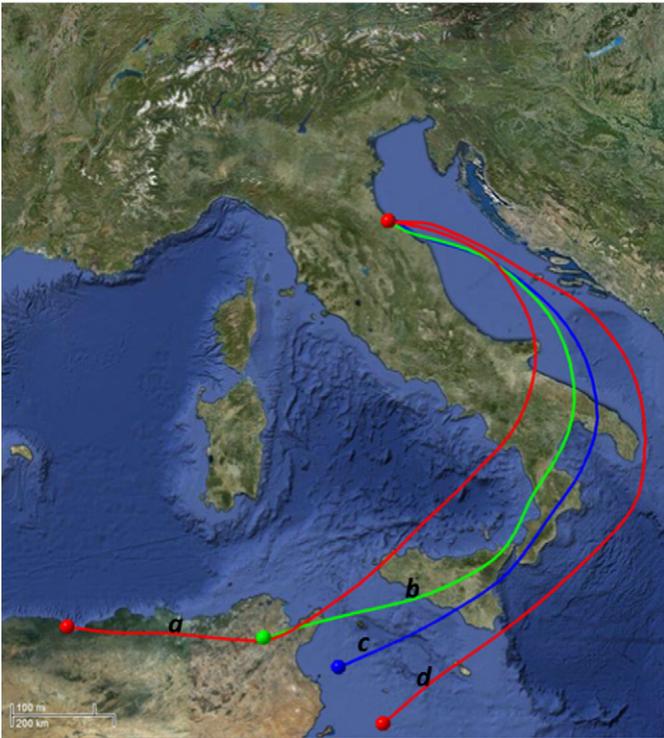
Fig. 7. Back trajectories at site 3 for the period 23–26 March 2007. Back trajectory time: 48 h. a: 6.00 PM 25/03–6.00 PM 23/03/2007. b: 0.00 AM 26/03–0.00 AM 24/03/2007. c: 6.00 AM 26/03–6.00 AM 24/03/2007. d: 12.00 AM 26/03–12.00 AM 24/03/2007.

Among the components analyzed, heavy metals are those which create the greatest concern, due to their toxicity and their persistence in the environment. For this reason the median contribution of each metal (Fe, As, Cd, Ni, Cr, Mn, Cu, Pb and Zn) to toxicity for each source at each site has been evaluated. The concentration of metals in each source (F matrix) has been divided by the acceptable daily intake indicated by WHO (WHO, 1996; 1993; 1989). In this way, evaluation of the total load of metals giving a higher weight to the most toxic metals has been generated. The results appear in Fig. 8. The highest contribution of metals is due to resuspended soil dust. This is especially due to lead, which together with cadmium, is the most toxic metal. The resuspended soil dust factor makes the highest contribution even when considering the sum of metals not weighted by their toxicity. Thus, not only do three of the six identified sources represent natural matrices, but also one of them is the main source of metals in atmospheric deposition. After resuspended soil dust, the secondary ammonium sulfate factor is the most important source of metals, and this is also due to the high concentration of lead associated with this factor.

4. Conclusion

The deposition fluxes recorded in the study area show a low concentration of heavy metals and soluble ions in atmospheric deposition when compared to other studies. Only ammonium and nitrite fluxes are significantly lower at the reference site, while all other components do not show significant differences between the sites.

The whole area seems to be overall affected by a rather homogeneous contamination, suggesting that multiple sources, rather than a single hot spot emission source like the incinerator, are influencing
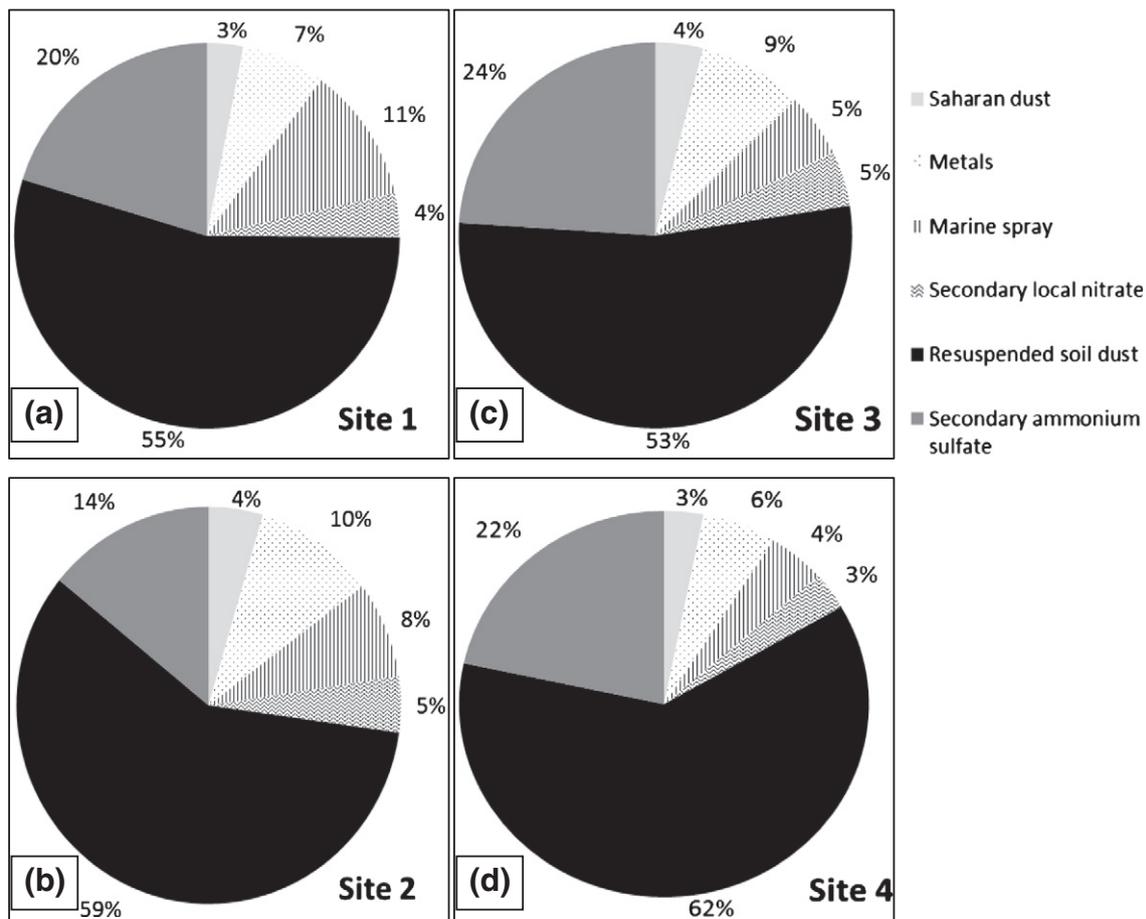

Fig. 8. Percentage contribution of each factor to toxicity based upon the metal content weighted by relative toxicity. (a) site 1; (b) site 2; (c) site 3 and (d) site 4.

the whole area. PMF analysis indicates that six main sources affect the area, three ascribed to natural matrices (sea spray, resuspended soil dust and Saharan dust) and three ascribed to anthropogenic sources (secondary nitrates, secondary sulfates and another one more ambiguous, that probably represents the influence of vehicular traffic emissions). The greatest contribution of heavy metals, which are the most toxic and persistent of the analyzed components, to atmospheric deposition is due to resuspended soil dust, especially when weighted according to their toxicity.

In conclusion, the incinerator's relative contribution to the total inorganic pollutant load seems to be negligible compared to other sources affecting the area.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.03.097.

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