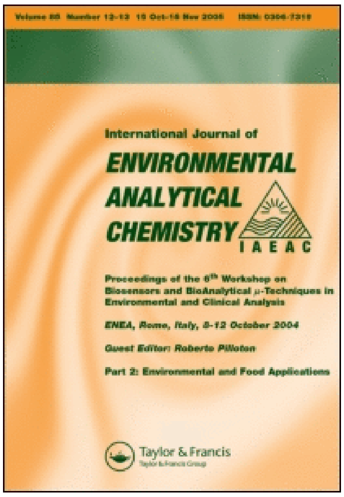

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Assessment of the sources of the inorganic fraction of aerosol in a conurbation

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Two intensive sampling campaigns for coarse ($PM_{2.5–10}$) and fine ($PM_{2.5}$) particulate matter were carried out in August 2003 and March 2004 in the multi-impacted centre of the Athens (Greece) conurbation. Receptor modelling by means of Positive Matrix Factorization was utilised in order to provide an insight to the poorly characterised sources of the chemically analysed inorganic fraction of the sampled aerosol mass. Using elemental concentrations, seven factors have been resolved for both fractions for August 2003. Combining elemental and ionic concentrations, nine factors were resolved in the coarse particulate matter and eight in the fine particulate matter for March 2004. The greatest contributors of primary origin are (re)suspended dust/soil and sea salt. Secondary aerosol contributions were resolved in the form of secondary sulphate, secondary nitrate as well as an aged sea salt factor which was characterised by the replacement of chloride with sulphate and, secondarily, nitrate. Furthermore, throughout sites and fractions, primary anthropogenic emissions were identified in a series of factors, including a Pb-rich profile, representing non-catalytic exhaust emissions, a Cu-Mo-Sb-rich profile representing brake emissions, a Zn-Ba-rich profile representing tyre-wear and heavy vehicle brakes, and, lastly, a V-Ni-rich factor representing industrial heavy oil-combustion. Local anthropogenic emissions predominated, outweighing long-range transport as it was suggested by the lack of direct relationship between changes in the wind speed and direction and species mass burdens, as well as factor contributions.

Keywords: aerosol; particulate matter; source apportionment; Athens; Greece; Positive Matrix Factorization

1. Introduction

Airborne particulate matter, in its micrometric diameter size, the 'inhalable' PM_{10} and the 'respirable' $PM_{2.5}$ fractions, can cause adverse health effects to humans [1–3]. While it is not ascertained which characteristic parameter (e.g. chemical composition, number concentration, size distribution, surface area or mass concentration), is primarily responsible for these effects [4], it is certain that there is a need for cost-effective strategies on the control of aerosol sources. Characterisation of the aerosol's bulk chemical composition can assist in the determination of its origins. Thence, and since current

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air quality standards are mostly expressed in terms of aerosol mass concentrations, the aforementioned strategies necessitate the identification of source categories contributing to the aerosol mass concentrations.

Qualitative and quantitative information on the sources contributing to atmospheric aerosol can be obtained by retrospective methods such as receptor modelling. One methodology used to date is Chemical Mass Balance (CMB). However, CMB input requires *a priori* knowledge on the physicochemical characteristics of the sources contributing to the sampled aerosol. In locations where emission inventories have not been systematically researched, knowledge of this kind is difficult to ascertain. Another methodological approach is the implementation of Factor Analysis (FA) techniques which do not require such input, and their use for source apportionment is based on the following assumptions; firstly, that highly correlated species might: (i) have originated from the same sources, (ii) have originated from different sources but have been chemically combined in the atmosphere, (iii) have originated from different sources but share common transport processes, and secondly, that the sources' emission profiles remain constant throughout the period under study. *Positive Matrix Factorization* (PMF) [5,6] constitutes a newer alternative to the traditionally used FA technique, Principal Component Analysis (PCA). Its advantages over the latter have been thoroughly discussed elsewhere [6–8]. A new mathematical approach to the solution of the multi-linear problem, the *Multilinear Engine* (ME), was introduced by Paatero in 1999 [9]. ME-2 is the second implementation of the multilinear engine which has been recently used in a number of source apportionment studies [10–13], as well as the current study.

To date relatively few aerosol source apportionment studies have been presented for Mediterranean conurbations [14–17], and even fewer and non-systematic for eastern Mediterranean ones. The missing scientific understanding for the aerosol pollution of these conurbations, originates from the non-widely studied unique combination of atmospheric and geochemical conditions that prevail in the region. These prevailing atmospheric conditions are characterised by high insolation, high aerosol crustal or dust content, high sea-salt aerosol content, lower aerosol ammonium or gaseous ammonia and generally lower aerosol black carbon. In the current study, we have applied the aforementioned powerful PMF method on our aerosol pollution data from the centre of Athens [18], in order to assess a qualitative and quantitative instance on the sources contributing to the inorganic fraction of the aerosol mass.

2. Experimental

The data analysed in this study were obtained during two intensive sampling campaigns, consisting of 12 hour long sampling sessions, in the centre of Athens (Figure 1). The first campaign was carried out during August 2003 at a roadside site, in Athinas St., at a height of 1.5 m above ground. This was the first time that aerosol sampling within the 'breathing zone' [19] was carried out in the centre of Athens. August was selected as the warm period month with minimum human activity in the city, due to the summer vacations. The second campaign took place during March 2004 at the same point in Athinas St. and at an urban background site, on the roof of a governmental building (AEDA), at approximately 25 m above ground. The AEDA site lies roughly 700 m from the Athinas St. site. March was selected to represent typical cold period conditions with maximum human activity and without high precipitation levels, as February of the same year, which was initially

Figure 1. Map of the region under study.

selected, was untypically cold with extensive snow storms in Athens that reduced traffic and human activity in the city.

A detailed description of the sampling campaigns, including description of sites, sampling apparatus and filter types employed, QA/QC procedures, analytical and quantification methods and their detection limits, as well as extensive discussion on the chemical characterisation results can be found elsewhere [18].

A summary of the procedures and results is presented in Table 1 and a more detailed description is given in the supporting information of the present study (see the note at the end of this paper). A brief description of the methods used follows. In March 2004, two identical Dichotomous Stack filter Units (hereafter, DSFUs) were employed in every site and both elemental and ionic concentrations were obtained on virtually equally loaded filters for two fractions, a coarse ($PM_{2.5-10}$) and a fine one ($PM_{2.5}$). In August 2003, only elemental concentrations were obtained. Ionic concentrations were assessed by means of Ion Chromatography (IC) while elemental concentrations were quantified by Proton-Induced X-Ray Emission (PIXE). Compound-specific and sample-specific error estimates were analytically obtained for all elements, while compound-specific and batch-specific (in batches of ten samples) error estimates were analytically obtained for all ions. Source apportionment analysis was carried out separately for every fraction and every site. During both campaigns, some fine fraction filters broke due to overloading. PMF is very useful in such cases of incomplete parallel samplings (March 2004 campaign) when one of the simultaneously sampled-through filters has been lost, as it allows them to be included in the analysis, while providing ways to effectively prevent them from imposing distortions on the analysis results. Otherwise, entire such sessions would have to be subtracted from source apportionment analysis, resulting in loss of information existent in the data set. Values corresponding to the incomplete sampling sessions were considered missing and, together with the quantified uncertainties, were treated according to Polissar et al. [20]. For the March 2004 campaign, 41 coarse and 36 fine fraction samples were included in the source apportionment analysis for Athinas St., while 35 coarse and 30 fine fraction samples were included for AEDA. For the August 2003 campaign, 39 and 34 sampling sessions were maintained for Athinas St. coarse and fine fraction, respectively.

It has been previously shown that the choice of chemical species to be included in receptor modelling is critical and that 'bad variables' with low signal-to-noise ratios may hinder successful modelling as well as the physical interpretability of results [21,22]. Of the 34 chemical species analysed [18], some were in both elemental and ionic forms. Inclusion of such 'duplicate' species should be avoided in receptor modelling. Hence, one of the forms should be chosen, preferably the one which is a 'better variable' [21]. In light of this, 24 species were finally included in the PMF analysis for the March and 18 for the August campaign, with the rest being excluded either as 'duplicates' or as 'bad variables' (Ga, Rb, Zr, Sr, Se and Sn), on the basis of their low signal-to-noise ratio and a large number of their values being below detection limit [21,23]. In the case of the duplicate species, K was preferred over K^+ and Ca over Ca^{2+}, due to the lower signal-to-noise ratio of the ionic forms and the higher contribution of the 'total elemental concentrations' (as given by PIXE) to the total mass concentrations. On the other hand, Cl^- was included instead of Cl, due to the Cl–loss in the PIXE analysis as clarified elsewhere [18]. In the absence of ionic concentrations for the August campaign, elemental Cl has been inevitably used, yet taken into consideration qualitatively only. Sulphate was preferred over 'total elemental sulphur' and was included in the analysis with the exception of the August campaign when, in the absence of sulphate, 'total elemental sulphur' was used. Species As and elemental

Table 1. Summary of the sampling and analytical procedures and results.

March 2004	Site 1: Athinas St.		Site 2: AEDA		August 2003	Site 1: Athinas St.	
	$PM_{2.5–10}$	$PM_{2.5}$	$PM_{2.5–10}$	$PM_{2.5}$		$PM_{2.5–10}$	$PM_{2.5}$
Sampler	DSFU	DSFU	DSFU	DSFU		DSFU	DSFU
Volume (m^3)	4.32					4.32	
Filters	Polycarbonate Membrane					Polycarbonate Membrane	
Pore size (μm)	12	0.4	12	0.4		12	0.4
Species	mean ± stdev	mean ± stdev	mean ± stdev	mean ± stdev	Species	mean ± stdev	mean ± stdev
Quantification	PIXE					PIXE	
Al	663 ± 439	338.5 ± 353.5	419.5 ± 247.5	296.5 ± 174	Al	558.5 ± 222	308.5 ± 124
Si	1829 ± 1204	644.5 ± 754.5	1075 ± 619.5	439 ± 315.5	Si	1287 ± 582	450 ± 201
S[a]	732.5 ± 375.5	2716 ± 1245	505.5 ± 304	2914 ± 1764	S	322.5 ± 188	4472 ± 2126
Cl[a]	1131 ± 1093.5	183.5 ± 301	721.5 ± 688	123.5 ± 78.505	Cl	121.5 ± 91.8	37.35 ± 17.95
K	417.5 ± 234	270.5 ± 197	239.5 ± 131.5	299 ± 145.5	K	304.5 ± 139.8	345 ± 96.85
Ca	15542.5 ± 9409	3563 ± 1847.5	7528.5 ± 4746.5	1684.5 ± 826	Ca	5263.5 ± 3374.5	1390 ± 2773
Ti	125.5 ± 85.4	58.35 ± 54.65	57.2 ± 36.05	27 ± 16.45	Ti	48.2 ± 24.75	18.45 ± 8.09
V	5.965 ± 3.87	9.9 ± 8.9	4.41 ± 2.795	12.87 ± 7.365	V	5.205 ± 3.855	13.75 ± 11.25
Cr	8.405 ± 4.815	2.675 ± 2.105	8.165 ± 6.135	3.56 ± 1.405	Cr	4.69 ± 2.785	2.415 ± 1.24
Mn	17.85 ± 11.35	12.65 ± 11.55	12.85 ± 8.26	11.67 ± 4.13	Mn	12 ± 6.43	9.105 ± 4.105
Fe	1019 ± 607.5	410.5 ± 348	743.5 ± 451	372.5 ± 126.5	Fe	698.5 ± 320	367.5 ± 137.5
Ni	5.135 ± 3.825	4.4 ± 3.71	3.69 ± 2.77	5.35 ± 2.72	Ni	3.94 ± 2.38	5.52 ± 4.055
Cu	31.75 ± 17.06	19.9 ± 16.25	60.95 ± 47.25	58.6 ± 27.6	Cu	106.55 ± 51.15	113.4 ± 50.8
Zn	64.2 ± 38.7	97.2 ± 90.95	33.965 ± 22	63.45 ± 51.7	Zn	30.4 ± 16.65	55.1 ± 39.15

(*Continued*)

Table 1. Continued.

Ga^a	0.29 ± 0.29	0.19 ± 0.17	0.165 ± 0.145	0.185 ± 0.08	Ga	0.23 ± 0.15	0.28 ± 0.26
As	0.825 ± 0.41	1.65 ± 0.39	0.485 ± 0.315	0.65 ± 0.185	As	0.475 ± 0.325	0.995 ± 0.6
Se^a	0.155 ± 0.145	0.54 ± 0.36	0.09 ± 0.06	0.72 ± 0.365	Se	0.04 ± 0.1	1.05 ± 0.605
Br	3.755 ± 2.245	7.06 ± 2.03	2.395 ± 1.485	7.305 ± 1.995	Br	1.115 ± 0.485	5.28 ± 1.76
Rb^a	1.84 ± 1.165	0.915 ± 0.705	1.05 ± 0.535	0.925 ± 0.565	Rb^a	1.41 ± 0.56	1.085 ± 0.335
Sr^a	18.7 ± 14.55	5.155 ± 6.15	6.73 ± 3.71	2.61 ± 1.28	Sr^b	5.485 ± 2.72	1.985 ± 0.82
Zr^a	5.035 ± 3.595	1.87 ± 1.48	3.54 ± 2.21	1.57 ± 0.665	Zr^a	3.1 ± 1.57	1.575 ± 0.61
Mo	1.815 ± 1.035	1.59 ± 0.965	3.2 ± 1.855	4.865 ± 2.34			
Sn^a	2.515 ± 1.905	4.02 ± 4.52	2.235 ± 1.74	4.875 ± 4.48	Sn^a	1.33 ± 0.855	2.32 ± 1.67
Sb	3.85 ± 2.695	2.565 ± 2.285	4.295 ± 2.66	3.075 ± 1.39			
Ba	33.3 ± 26.8	14.25 ± 11.94	26.35 ± 28.05	9.05 ± 6.16	Ba	17.85 ± 10.955	10.525 ± 6.115
Pb	18.13 ± 16.53	42.45 ± 41	21.05 ± 20.445	32.2 ± 58.1	Pb	11.47 ± 6.45	31.4 ± 21.2
Quantification		IC				IC	
Na$^+$	785 ± 522	264.5 ± 164.75	631 ± 401.5	246 ± 255		–	–
NH$_4^+$	212.5 ± 112.5	1518.5 ± 1130	162 ± 145	1636.5 ± 1718.5		–	–
K$^{+\ a}$	187 ± 109	145 ± 61.5	158 ± 170.5	83.55 ± 56.1		–	–
Mg^{2+}	302 ± 153	109.75 ± 44.4	213.5 ± 110.5	83.3 ± 59.2		–	–
Ca$^{2+\ a}$	11669.5 ± 3575	3293 ± 1411.5	5622 ± 2557	1322.5 ± 785.5		–	–
Cl$^-$	2695.5 ± 1016	324 ± 253	1238.5 ± 898	195.5 ± 189		–	–
NO$_3^-$	2481 ± 1527.5	343 ± 200	1891 ± 1387	259 ± 268.5		–	–
SO$_4^{2-}$	1862 ± 832	6680.5 ± 3249	1153.5 ± 509.5	7613 ± 6423		–	–
Quantification		Gravimetry				Gravimetry	
PM*	*80.05 ± 37*	*40.45 ± 27.45*	54.8 ± 26.25	31.55 ± 10		–	–

Notes: All values in ng m^{-3}; (*) Denotes values in μg m^{-3} obtained gravimetrically; ^{a}Species excluded from PMF analysis.

Cl during the August campaign, were down-weighted by a factor of 3, as ‘weak variables’ [21]. Concentrations for Mo and Sb were not available for the August campaign.

3. Results and discussion

3.1 *Determination of the number of factors*

3.1.1 *Understanding of the influences in the region under study; preliminary considerations for the number of factors*

There exists no globally applicable rule-of-thumb for the determination of the number of factors in source-to-receptor modelling. Various solutions with different numbers of factors have to be calculated and the final, among the ones that satisfy certain statistical criteria, is identified as the ‘correct’ solution on the basis of the physical interpretability of the extracted profiles. Solutions with too few factors to explain the observed variation in the concentrations result in mixing of species with widely different origins into non-interpretable profiles. On the contrary, too many factors impose a breakdown of physically meaningful profiles into two or more non-realistic ones. Hence, it is largely up to the analyst’s understanding of the influences in the region under study to identify *a priori* and anticipate the presence of certain source categories.

3.1.2 *Determination of the correct solution*

Utilising 50 random starting points (executed runs), several solutions with different numbers of factors were examined. For error estimates realistically representative of the actual error distribution in the experimental dataset, the sum of errors (Q-robust) function of the ‘correct solution’ should be close, e.g. within 50% [24], to theoretical Q value [25]. A good fit of the model to the observed data is indicated by the compound-specific and sample-specific residuals of a solution (e_{ij}) being approximately equal to the respective error estimates (s_{ij}). The obtained standardised residual distributions (e_{ij}/s_{ij}) were reviewed and the statistically good solutions were identified by (a) the lack of patterns/anomalies (e.g. positive or negative unimodality) and (b) verifying that $\geq 97\%$ of the e_{ij}/s_{ij} distribution lied within ±3. In order to check how representative of the variation in individual species concentrations an obtained solution has been, we have additionally reproduced the ME-2 runs in the ME-2 based, EPA PMF (version 1.1) [57] (see supporting information), utilising its built-in routines for the calculation of *compound-specific* regression diagnostics between modelled and experimental concentrations. A slope ≥ 0.7 and a determination coefficient (r^2) e0.8 were set as quality thresholds. Thence, in addition to the standardised residuals, the regression diagnostics were used to verify good species-specific fit quality.

Some rotational ambiguity may be inherent in all factor analysis solutions since a global minimum value for Q may be achievable by more than one combination of source composition (G) and source contribution (F) matrices. Hence, research is required upon the identification of potential statistically equivalent solutions (hereafter ‘rotations’) and the determination of the most physically meaningful among them. The FPEAK parameter was thus utilised in the ME-2 script [7,26,27]. A non-zero value of FPEAK tries to impose rotations on the emerging solutions throughout the iteration sequence [28]. In our case, the $[-1, +1]$ domain of FPEAK was examined at a step of 0.05. Theoretically, a rotation may be considered valid when the increase it causes in Q-robust is smaller than the number of (near) zero values the rotation introduces in the factor matrices [7]. Statistically valid rotational ambiguity was detected in some of the solutions, with Q-robust being pushed within ~10% higher than the original value for FPEAK[−0.1, +0.1]. Beyond this FPEAK domain, a significantly worse fit was obtained, with a steep proportional increase by more than 20% in Q-robust so that the rest of the rotated solutions were excluded from further consideration.

Based on the above, a number of statistically good solutions with their rotations were carefully examined, and the final solutions were chosen on the basis of their physical interpretability. Multiple regressions of individual factor contributions on the chemically characterised particulate mass concentration was used as a post-analysis tool for the fit quality and verification upon the correct choice of the number of factors, as is further discussed below.

3.2 *Identification and description of the extracted factors*

For the March 2004 campaign the solution contains nine resolved factors for the coarse and eight for the fine fraction in both sites. Certain differences are evident in both the profiles and their contributions between the two sites. For the August 2003 campaign, when only elemental concentrations were available, seven factors have been resolved in the coarse and fine fraction.

As derived from near-surface meteorological data (Patission Station, near the sampling sites, Ministry of Environment/PERPA) and back trajectories (Hysplit, NOAA), during the August campaign, the location under study is under the influence of wind blowing from NW/N/NE. During most of the March campaign, in the city centre stronger winds come from N/NE, while on some of the days weaker winds come from S/SW/W. However, there has been established no clear relationship between this change in the wind origins and the variation in the bulk concentrations of the marker species for the resolved factors. Similarly, there has been identified no clear relationship between the aforementioned change in the wind origins and the factor contribution time-series. Additionally, excluding the species that represent primary marine emissions (Na^+, Cl^-, Mg^{2+}), no significant correlations are observed in the concentrations of the marker species for the resolved factors between the two sites. The above might suggest that, owing to the sparse precipitation events, as well as the densely-built and multi-impacted urban environment, the chemical composition of particles in the location is strongly dependent on an intense mixing of mostly local contributions from different sources and on atmospheric interactions throughout several days. Hence, the criteria employed for the source identification included the presence of certain markers in the factor profiles in relation to the possible origin and use of the species [29,30], the seasonal and spatial variation of their marker species concentrations and their similarity with previously reported factors for urban environments. A qualitative list of the resolved factors and their markers is shown in Table 2. The factor composition profiles are shown in Figures 2, 3 and 4. As the current study does not account for the total mass closure, it should be noted that factor total mass contributions refer to the chemically characterised mass.

3.2.1 *(Re)suspended soil/dust*

A (re)suspended soil/dust profile is easily identified as it contains the bulk of the calcium concentrations while being rich in typical crustal species Al, Si, Fe and Ti. Mineral dust is a major component of the Athenian atmosphere due to the geochemistry of the region in

Table 2. Qualitative presentation of the PMF-obtained factors with their characteristic tracer-species; *in the absence of ionic form, the 'total elemental' concentration of the species was used for the August 2003 campaign. Theoretical and robust Q values of the final solutions.

Factor characterisation		March 2004				August 2003	
	Tracer-Species	Athinas coarse	Athinas fine	AEDA coarse	AEDA fine	Athinas coarse	Athinas fine
(Re)suspended soil/dust	Al, Si, Ca, Ti, Fe,	+	+	+	+	+	+
Secondary sulphate	SO_4^{2-}, Ca, S*	+	+	+	+	+	+
Secondary nitrate	NO_3^- Ca, Mg^{2+}	+	–	+	–	–	–
Primary sea-salt	Na^+, Cl^-, Mg^{2+}, Cl*	+	+	+	+	+	+
Aged sea-salt	SO_4^{2-}, NO_3^- Na^+, Mg^{2+}	+	+	+	+	–	–
Oil-combustion	V, Ni	+	+	+	+	+	+
Brakes	Cu, Mo, Sb (Ba)	+	+	+	+	+	+
Tyre wear & heavy vehicle brakes	Zn, Ba	+	+	+	+	+	+
Combustion/ Non-catalytic exhaust	Pb	+	+	+	+	+	+
Solution Diagnostics	Q_{robust}	681	422	630	311	447	343
	$Q_{theoretical}$	533	504	455	420	377	328

combination with the low precipitation levels and wind speeds that favour an increased aerosol atmospheric residence time. The great abundance of calcium in the Athenian atmosphere, where it predominates particularly in the coarse particle fraction, has been thoroughly discussed elsewhere [18,31]. Mass-wise, the contribution of the soil/dust factor is significantly higher in Athinas near the ground than in AEDA. In addition to the constant overall activity (e.g. pedestrians walking) and the constant geochemical influence, during the sampling period the extensive construction activity for the 2004 Olympic Games that was taking place at the centre of the city, 24 hours a day, 7 days a week, further contributed to the aerosol enrichment with mineral dust. It is noteworthy that the influence of (re)suspended dust/soil is evident in the form of calcium and crustal species 'contamination', in some of the other profiles as well.

3.2.2 *Primary marine aerosol*

Resolved in all sites and fractions for March 2004 is a factor explaining the larger part of the Na^+, Cl^- and Mg^{2+} concentrations. This profile can be easily attributed to primary marine aerosol emissions in the form of salts such as NaCl and $MgCl_2$. The greatest contribution is seen in the coarse fraction, in agreement with the typical partitioning of its characteristic species. The proximity of the city to the sea from all directions, and most closely to the Saronicos Gulf in the S-SW, indicates the origin of this burden. A comparison of the factors' composition with sea salt average chemical composition [32] is shown in Figure 5. As can be seen, the coarse fraction sea salt profiles are very similar to

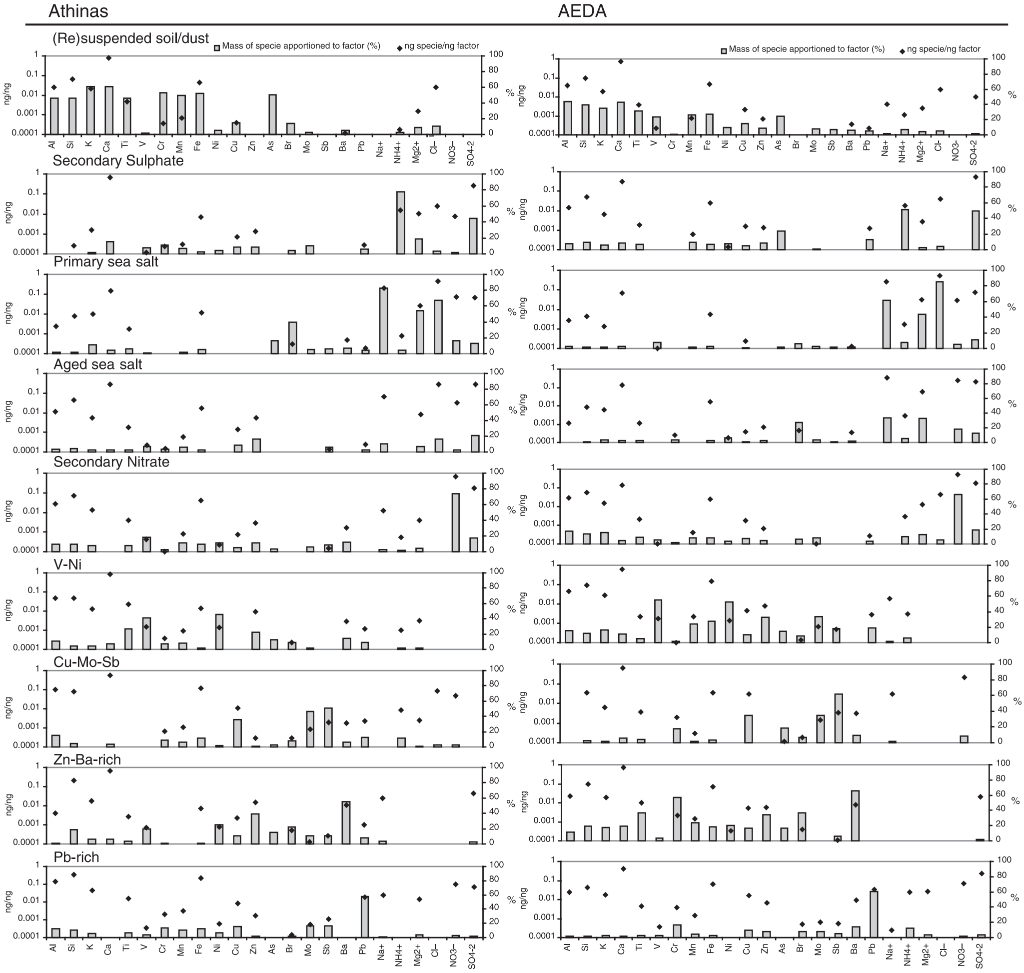

Figure 2. Source composition profiles for the $PM_{2.5–10}$ fraction during the March 2004 campaign.

the seawater profile, while the fine fraction profiles deviate most probably due to the partial chloride depletion and its replacement by the enriched fine-fraction sulphate.

3.2.3 *Sulphate and nitrate; secondary aerosol I & II*

The next factor in both fractions, during the March 2004 campaign, is identified by its enrichment in SO_4^{2-}, the bulk of which results from the transformation of primarily emitted SO_2 by activities such as fuel combustion. Automotive diesel in Greece is the richest in sulphur-content in the EU [19,33], while its adulteration with domestic heating and sailing diesel results in a further increase of the sulphur content [34,35]. In the coarse fraction the secondary sulphate factor is rich in Ca, which shows the neutralisation of sulphate into salts such as $CaSO_4$. In the absence of ionic concentrations for the August 2003 campaign, the secondary sulphate factor has been identified by the high sulphur loadings. Additionally, a distinct secondary nitrate profile has been identified in the coarse

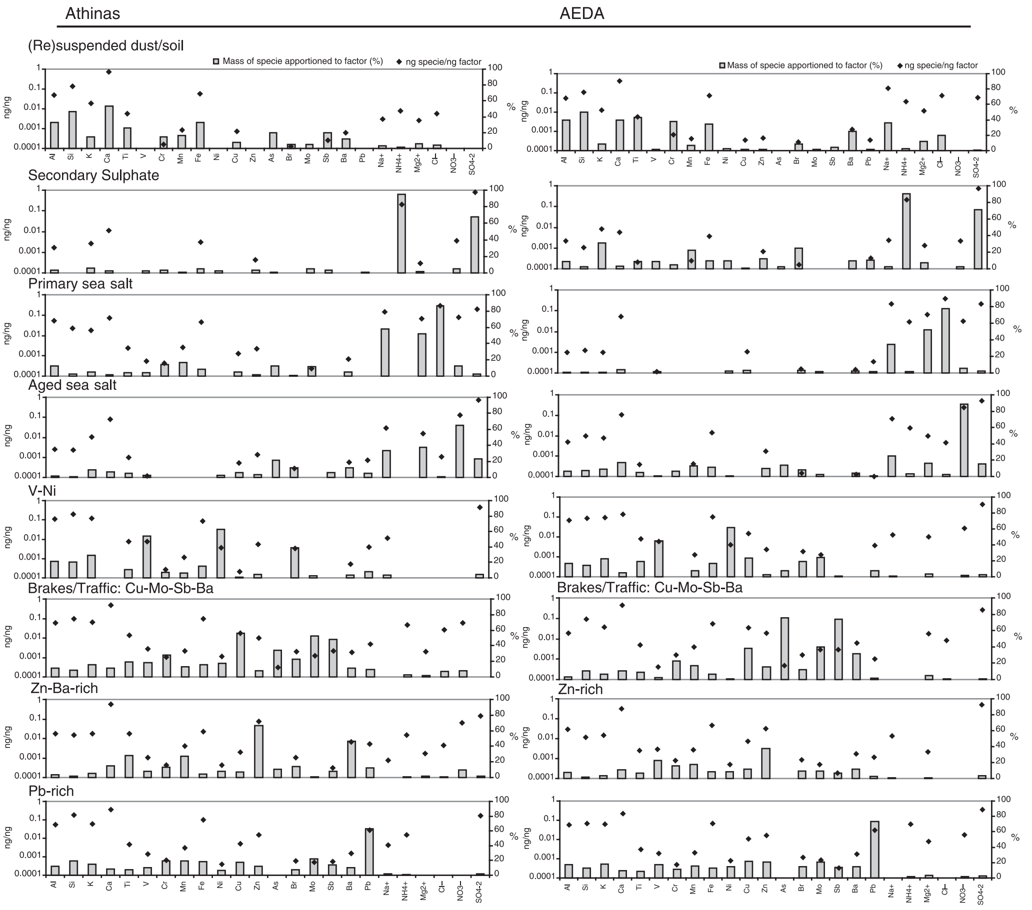

Figure 3. Source composition profiles for the $PM_{2.5}$ fraction during the March 2004 campaign.

fractions of the two sites. Nitrate originates from the atmospheric transformation of NO_x, which is directly emitted from high-temperature combustion such as internal combustion engines in cars or domestic heating. Nitrate is deposited mostly into the coarse fraction in the location under study [18] and it is a minor contributor to the fine fraction, where no such profile has been directly resolved. The fine fraction profile ‘binds’ the bulk of NH_4^+, demonstrating the neutralisation of sulphate into ammonium-sulphate salts. In relation to the above, it is worth mentioning the very low presence of NH_4^+ in the secondary nitrate factor. The above suggest that the formation of NH_4NO_3 in the location under study is not favoured, since ammonia is consumed in neutralising sulphate [18].

3.2.4 *Aged sea salt*

Based on its contributions of SO_4^{2-}, Na^+ and Mg^{2+} as well NO_3^- and Ca^{2+}, the next factor is identified as representing aged sea salt particles in which Cl^- is replaced by SO_4^{2-} and, to a lesser extent, NO_3^-, in the formation of secondary salts such as Na_2SO_4, $MgSO_4$, $NaNO_3$ and $Mg(NO_3)_2$. This factor appears in both fractions, while, based on bulk concentrations,

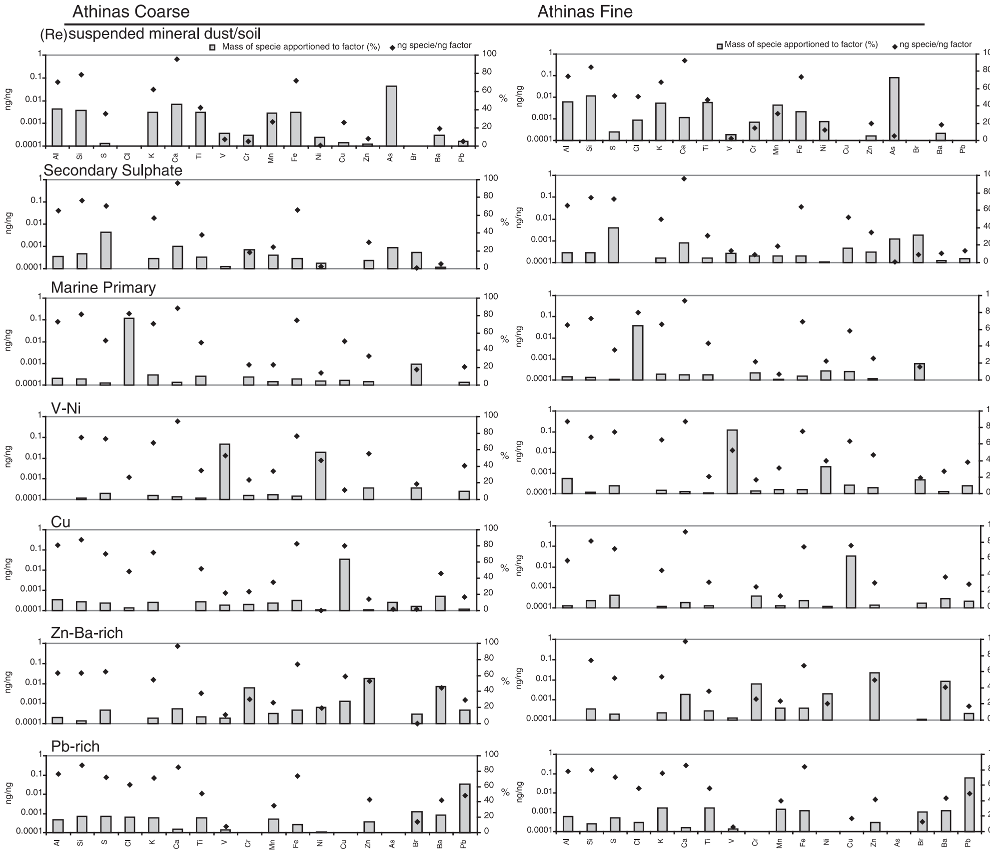

Figure 4. Source composition profiles for both particulate matter fractions in Athinas St., during the August 2003 campaign.

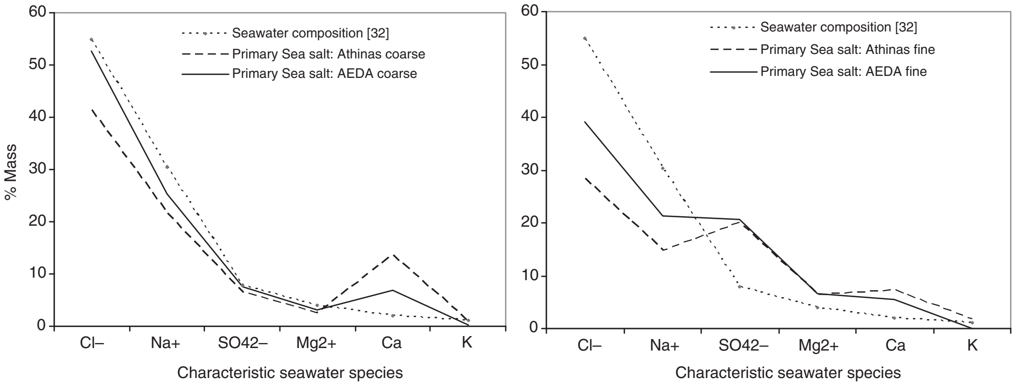

Figure 5. Comparison of the primary sea salt profiles for the coarse and fine fraction, with the average seawater composition [Ref. 32].

chloride depletion has been identified primarily in the fine fraction. In addition to this, based on the high Ca^{2+}/Na^{+} as well as the overall composition, some 'contamination' of the factor profiles with mineral elements and particularly Ca^{2+} is evident. The above might suggest that fine, chloride-depleted, aged sea salt particles, are probably adsorbed on occasionally larger dust/soil particles that may undergo a further size increase due to gravitational and turbulent aggregation phenomena, eventually achieving coarse fraction size after the Cl^{-} replacement. Additionally, it might also indicate a mixture of particles of one fraction into the other in sites with a multitude of contributions and resuspension patterns such as the discussed.

3.2.5 *Vanadium-nickel; oil/petroleum combustion*

The next factor resolved in both sites and fractions is characterised by the distinct loadings of vanadium and nickel, which have been identified as typical marker elements for residual/heavy-oil combustion [29,36,37]. A V/Ni ratio of approximately 1.03 to 1.05 has been previously reported for residual oil burning [24,38]. The pertinent ratios are very close in our coarse fraction factors; 1.07 (Athinas coarse), 1.24 (AEDA coarse), 1.19 (Athinas coarse – August 2003). The fine fraction profiles appear slightly enriched in V compared with the literature and the coarse fraction profiles, with the pertinent ratios being: 1.82, 1.48, 1.59 for Athinas, AEDA and Athinas-August 2003, respectively. By an examination of the human activity in the region, a variety of sources could be responsible for these contributions. A first possible source is domestic heating, as in Greece heavy/residual oils such as Mazut had been extensively used for domestic heating for decades however, they are now limited to only very old buildings. Further possible sources include ship and shipyard emissions from Piraeus, the largest port in Greece, and Perama respectively (both to the S/SW of the sampling locations), power-generation plants like the oil-burning 450 MW unit in Lavrion to the E/SE of Athens, and a series of other industrial practices, such as catalytic reforming in the oil industry, since two major oil industries and some of the largest heavy industries in Greece (steel manufacturing, cement production) are located in Aspropirgos and Thriassion Pedion (~20–30 km from the centre to the W/NW of Athens) (see Figure 1). In the absence of an increase in V and Ni concentration levels during the cold season, it is unlikely that this factor represents domestic heating. The possibility that it might represent ship/shipyard emissions is difficult to ascertain since neither the concentrations of the factor's markers, nor the factor contribution time-series, demonstrate clear influences by the sparse events when air parcels arrive from the direction of the Saronicos Gulf. Additionally, while different wind patterns are observed between the August campaign and certain dates of the March campaign, V-Ni levels remain relatively similar. The above suggest the formation of a background of contributions, which is non-directly influenced by the wind, and is maintained most probably by the aforementioned industrial and shipyard activities, particularly to the SW/W/NW of the city.

3.2.6 *Copper-molybdenum-antimony; automotive brake linings*

Another distinct profile is rich in Cu, Mo and Sb. Molybdenum is commonly used as an alloying agent and Cu-rich profiles have been often attributed to steel production facilities in the literature. However, the above did not suffice for the identification of emissions from industrial practices and especially steel production from Thriassion Pedion (W/NW) in this factor. The reason is that, should the profile represent long-transported industrial burden, despite the distance of several hundred metres and the densely-built urban environment between the sites, one would expect that the marker species concentrations be on similar levels in both sites in the centre of Athens. On the contrary, the concentrations of the factor's marker species are higher in AEDA, which implies additional local burden in this site. Additionally, Mo has been used in automotive applications [39,40] and both Cu and Mo have been used in diesel-engine catalytic applications [41]. Given the fact that an association of Sb and Cu ambient concentrations with traffic density and distance from roads has been reported [42], that all three typical markers Cu, Mo and Sb are released from brake linings [43,44], as well as that in both sites and particularly AEDA, which lies near a busy cross-roads, stop-and-go traffic patterns are common, traffic-related emissions, primarily from brake linings, are most probably represented by this profile. A mean Cu/Sb ratio of 4.9 ± 1.7 has been reported for brake-lining emissions in Cologne, Germany [43]. The pertinent ratios in our factors were close in Athinas, ranging from 5.8 to 6.4, and strongly Cu-enriched in AEDA, ranging from 11.2 to 9.3, close to the 9.1 reported in a recent study for heavily trafficked roads in Taiwan [45]. Emissions from copper-made overhead cables by passing trolley-buses have been previously identified as a source for such Cu emissions [43], which might be the explanation for the additional Cu burden in AEDA, since the site lies beside a trolley-bus route.

3.2.7 *Zinc-barium; large vehicle brake/tyre wear emissions*

The next factor identified is rich in contributions from Ba and Zn. Coarse and fine fraction profiles for this factor differ in that the coarse fraction profiles contain the bulk of Ba concentrations as well as contributions from mineral elements (soil/dust), while the fine fraction profiles are particularly enriched with Zn. Zinc is used in the lubricant additive zinc diethyldithiophosphate and is therefore likely to be incorporated into road dusts through oil leakage, and exhaust particles through oil combustion from two-stroke motorcycle engines. Zinc-rich PMF-resolved factors have been attributed to emissions from lubricant oil, brake linings and tyre wear [46], since zinc is also widely used as a filler in car tyres [43,47]. Additionally, a strong correlation between particulate barium, which is commonly used in brake linings, and large vehicle traffic (i.e. articulated lorries/trucks and city-buses) has been reported [44], suggesting that large vehicles have higher brake-wear emission rates for airborne particles than small vehicles. These emissions would include both mechanically generated coarse particles and the formation of finer particles due to high temperatures at the brake/rotor interface [48]. It is also reported that heavy vehicles are stronger emitters of Ba, but not of Cu, than lighter vehicles, which (a) indicates that the reason why Ba and Cu have been resolved in separate factors in our study is that they most probably represent different traffic patterns, and (b) probably explains some Cu loadings present in the Ba-rich factor [44,49]. A difference between the two sites is observed in the composition of the fine fraction profiles. The Athinas profile is rich in both Zn and Ba, while in AEDA, the bulk of Ba shows up in the 'brake linings' factor, together with Cu, Mo and Sb, which might be indicative of qualitative differences in the traffic patterns at the two receptor sites [50–53]. Hence, this factor has been attributed to large vehicle traffic, representing emissions from brake and tyre wear.

3.2.8 *Lead; non-catalytic automotive emissions*

A distinct lead-rich source profile has been resolved for all sites and fractions. The profile also features large amounts of bromide, which are emitted from the combustion of leaded gasoline, as well as re-suspended dust/soil. Owing to the introduction of unleaded gasoline Pb has been greatly reduced in the Athenian atmosphere in the last 15 years [54]. However, leaded gasoline is still used in older, non-catalytic vehicles, which are estimated as constituting up to 20–30% of the total fleet in Athens [55]. The Pb concentrations peak in the fine particulate matter and, similarly, fine fraction contributions of these factors appear slightly higher than the coarse fraction ones. Traffic related to non-catalytic vehicles is primarily represented in this factor, with possible additional burden from other combustion and industrial practices.

3.3 *Fit quality check and estimation of source contributions to the chemically characterised mass*

In the absence of EC/OC quantification the current study does not refer to the full PM mass closure. Furthermore, it has to be noted that the analysed inorganic mass constitutes approximately one third of the total PM mass for the $PM_{2.5–10}$ fraction and half for the $PM_{2.5}$ mass, as described in detail elsewhere [18]. The uncharacterised and, hence, unapportioned, part of the particulate mass is estimated to consist of Particulate Organic Matter, including primary and secondary organic carbon, elemental carbon and carbonate, in forms like $CaCO_3$, which has been identified as a major component of the Athenian air [31]. Furthermore, it may include OH^-, strongly bound water, lighter elements that PIXE cannot successfully analyse and other mineral compounds (including bound oxygen and nitrogen), as well as carbon, organics and polymers.

To *a posteriori* check the number of factors of the final solutions, we have applied multiple regression of the factor contributions on the *chemically characterised* mass concentration, calculated as the sum of input species mass concentrations, assuming no intercept. The lack of negative partial (scaling) coefficients suggests that an appropriate number of factors has been used to explain the variation in the species concentrations. Very strong correlations ($p < 0.0005$) were observed for the whole model, with determination coefficients (r^2) ranging from 0.87 to 0.91 throughout sites and fractions.

Normalised to the *chemically characterised* mass concentration, factor bulk contributions are presented in Figure 6. The largest burden comes from soil/dust (re)suspension, ranging from approximately 25 to 39% of the chemically characterised mass ($\sim$5–10 $\mu g\,m^{-3}$ for the coarse fraction), and 11–15% (1.4–2 $\mu g\,m^{-3}$ for the fine fraction), for AEDA and Athinas, respectively. The great influence of dust/soil (re)suspension, which is caused by the overall human activity and favoured by the micrometeorological and geochemical characteristics of the region, is thus outlined. This influence is particularly observed in the coarse fraction, near the ground (Athinas St.). Primary sea salt contributions range between 17 and 19% ($\sim$3.6–4.7 $\mu g\,m^{-3}$) in the coarse and from 5 to 7% ($\sim$0.7–0.8 $\mu g\,m^{-3}$) in the fine fraction. The coarse-fraction-resolved secondary nitrate profiles contribute roughly 8–12% (2.2–2.4 $\mu g\,m^{-3}$), while the contribution of the secondary sulphate ones are larger in both fractions, ranging between 12 and 14% (2.5–3.9 $\mu g\,m^{-3}$) in the coarse fraction and peaking up to 44–48% (5.7–7 $\mu g\,m^{-3}$) in the fine fraction. The aged sea salt factor contributes 6–8% (1.5–1.7 $\mu g\,m^{-3}$) in the coarse fraction and 14–19% ($\sim$1.7–2.8 $\mu g\,m^{-3}$) in the fine. The relative influence of traffic can be approximated by considering the contributions of the three traffic-related factors; Cu-Mo-Sb (Traffic I), Zn-Ba (Traffic II) and Pb-rich (Traffic III). The Cu-Mo-Sb contributes $\sim$4% (0.8–1 $\mu g\,m^{-3}$) in the coarse fraction and 3–5% (0.4–0.6 $\mu g\,m^{-3}$) in the

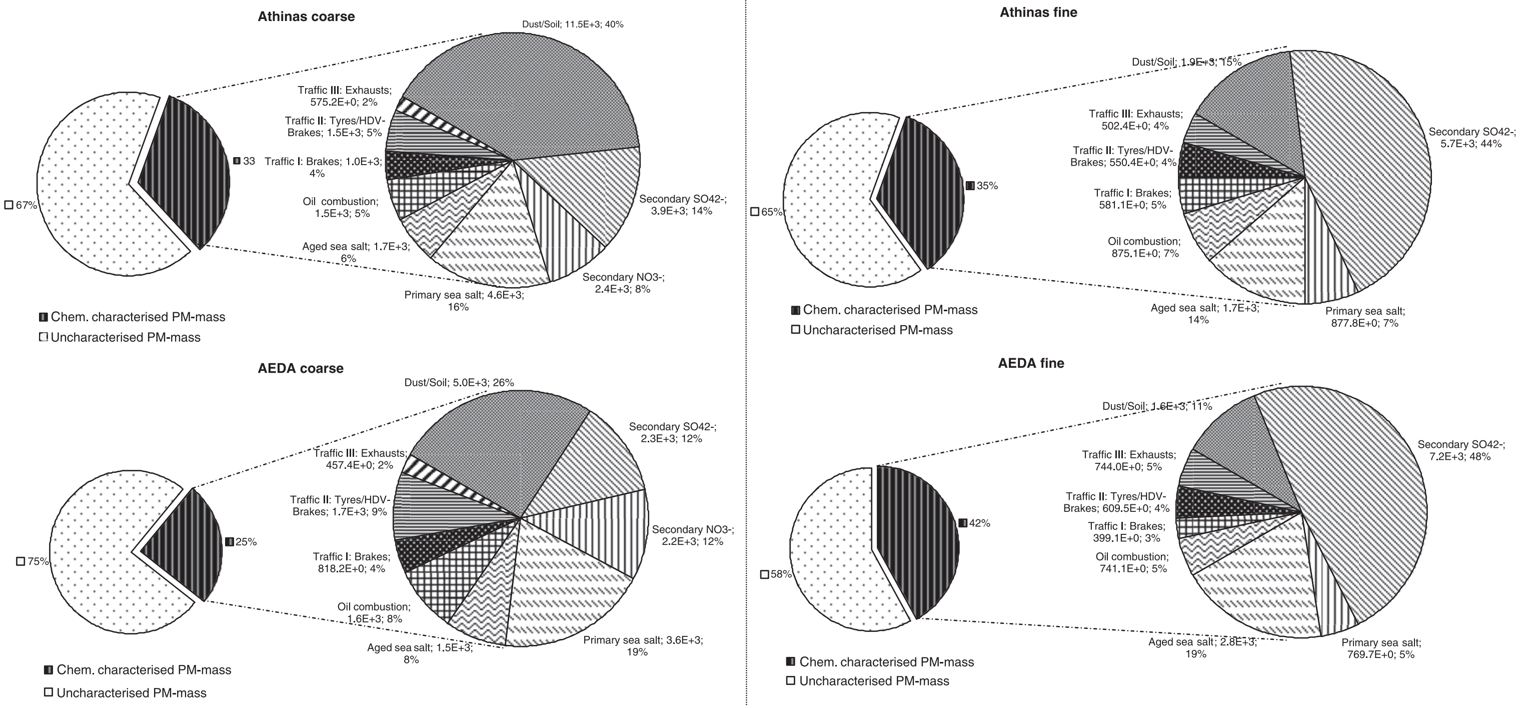

Figure 6. Contributions (mass in ng m^{-3}; percentage) of the PMF-resolved factors to the chemically characterised inorganic fraction of particulate matter mass.

fine fraction, the Zn-Ba profile contributes ~4–9% throughout sites and fractions (~1.5–1.7 $\mu g\,m^{-3}$ in the coarse and ~0.5–0.6 $\mu g\,m^{-3}$ in the fine), and the Pb-rich factor contributes 2–4% (0.5–0.7 $\mu g\,m^{-3}$) throughout sites and fractions. Lastly, the V-Ni factor contributes between 4 and 5% (1.3–1.7 $\mu g\,m^{-3}$) in the coarse fraction and 5 and 7% (0.7–0.8 $\mu g\,m^{-3}$) of the fine fraction.

4. Conclusions

Source apportionment by PMF has been carried out on $PM_{2.5–10}$ and $PM_{2.5}$ data obtained at 1.5 m and at 25 m above ground, during two intensive sampling campaigns in the centre of Athens, Greece. Source apportionment by PMF has been carried out on inorganic species associated with the $PM_{2.5–10}$ and $PM_{2.5}$ collected at 1.5 m and at 25 m above ground, during two intensive sampling campaigns in the centre of Athens, Greece. The results presented in the current study are liable to limitations. The dataset analysed is relatively small and morning and evening samples are examined together, as a result of the short duration of the sampling campaigns. Furthermore, chemical characterisation did not achieve mass closure but instead included major elements and ions, while it took place during two periods of the year, one in late summer and one in early spring. As a result, year-long sampling with full mass closure is still required for a more complete understanding of the seasonal variation of aerosol pollution phenomena and sources. While the current study refers to two sampling sites which are very descriptive of the centre of the city, the results obtained cannot be safely generalised for the urban centre in its entirety due to the vicinity of our measurement sites to major roads and construction works, the multitude of local sources of ambient particulate matter and the urban canyon effect. However, this is the first systematic source apportionment study for the centre of Athens and one of the few that have been presented for Mediterranean urban centres. Furthermore, it is the first study that refers to sources of particles in sampling sites in the very centre of Athens and near the ground, in the 'breathing zone' where aerosol pollution levels often exceed EU imposed limits and constitute a hazard to citizens. Lastly, while some of the profiles identified in this study have been reported elsewhere, other source profiles are region-specific and support findings of recent studies [18,31,56]. Specifically, some of the profiles imply regional geochemical influences, e.g. dust/soil re-suspension owing to human activity and the calcitic nature of crustal rocks in the region under study, and atmospheric phenomena which are characteristic of the region, e.g. consumption of ammonium by sulphates and nitrate neutralisation by other species. Therefore, while for a complete understanding of aerosol pollution mechanisms in the location under study the determination of a larger fraction of aerosol, sampling spanning over all seasons of the year and more sites, is still needed, the current study offers a 'photographic depiction' of the source-to-receptor relationship, in the centre of an urban centre of a region which has not been systematically studied.

The greatest influence of the characterised mass is (re)suspended dust/soil, which originates from the overall human activity, favoured by micrometeorological conditions and the regional geochemistry. Its contribution peaks in the coarse particle fraction, near the ground and during the time of sampling, its influence was further enhanced by construction activities. The region under study is surrounded by sea, the influence of which is shown in a primary sea salt and an aged sea salt factor. Additionally, Secondary sulphate factors are major contributors to the PM, peaking in the fine fraction in accordance to the sulphate partitioning. Nearly all fine fraction NH_4^+ is bound in these secondary sulphate profiles, showing the existence of ammonium-sulphate salts as part of the neutralisation processes. A secondary nitrate profile has been resolved exclusively in the coarse fraction, in accordance to the species fractionation in the region under study. Primary traffic influences are represented by three factors. The first has been identified by its Cu, Mo and Sb markers as depicting brake lining emissions and, possibly, enrichment from overhead trolley-bus cables in one site. The next one is rich in Zn and Ba and represents heavy vehicle tire and brake wear. Another factor is rich in Pb and represents non-catalytic exhaust emissions. Lastly, (residual) oil combustion due to industrial/shipyard activities is depicted in a characteristic V-Ni factor. Based on the species fractionation into $PM_{2.5–10}$ and $PM_{2.5}$ and factor contributions in each particle size range, indications of a mixture of sources contributing to the two particle fractions are present. Indicatively, dust/soil (re)suspension which primarily contributes to the coarse fraction shows an important impact on the fine particles as well as a noteworthy amount of sulphate, the bulk of which is formed secondarily and predominates in the fine fraction, appears to be associated with the coarse fraction, possibly by adhering on larger soil and sea salt particles. Lastly, the anthropogenic, traffic-related profiles demonstrate 'contamination' with dust/soil and, as a general trend, comparable contributions in both size ranges.

During all the first campaign and most of the second, the location is under the influence of winds blowing from N/NE. A few cases of weaker W/SW/S winds have been observed in the second campaign. While the marine influence over the region is evident throughout the sampling periods, no direct relationship has been established between the few changes in the origins of air parcels and the variation of anthropogenic marker species concentrations or the pertinent factor contribution time-series. Particulate pollution in the centre of the city thus seems to be mostly under the direct influence of local sources rather than long-transported burden. Hence, due to the sparse precipitation events, as well as the densely-built and multi-impacted urban environment, the chemical composition of particles in the location seems to be strongly dependent on intense atmospheric interactions and an intense mixture of contributions from different origins throughout several days. The above results emphasise the importance of local anthropogenic emissions, which is to be considered in future epidemiologic studies and policies on human exposure to urban atmospheric pollutants.

Note

Supporting information is accessible at: http://utopia.duth.gr/~vkarageo/LaboratoryandFieldEvaluationofDSFU.pdf.

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