PM10 concentrations, trace elements and sources' identification in three representative receptors of Western Macedonia, Greece.

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Abstract Many epidemiological studies have revealed consistent associations between ambient concentrations of inhalable (PM10) particles and their elemental composition with adverse respiratory health effects. On the other hand, suspended particulate matter emissions from several types of sources can be identified by the investigation of their particle element composition.

The objectives of this work were to present the results of PM10 concentrations and trace elements obtained from 1-year sampling/analysis campaign.

Three different sampling sites of the region of Western Macedonia in Greece were selected to investigate the PM10-associated elements fingerprints in samples of airborne particles: S1 in the center of Kozani, where urban activities and traffic density occur, S2 in the city of Ptolemaida located close to the industrial area, and S3 in the village of Eratyra in a rural residential district.

The PM10 samples were analyzed by ISP-MS instrument. Twenty five elements were detected at quantifiable concentrations in the examined PM samples.

Finally, an attempt was made to identify the main PM10 sources that affect the sampling sites. For this purpose was applied the multivariate Positive Matrix Factorization (PMF) receptor model.

Keywords: PM10, elemental composition, PMF

1. Introduction

Atmospheric particles produced by both natural (soil dust erosion, sea salt, volcanism, natural forest, etc.) and anthropogenic sources (industries, transports, biomass burning, combustion of fossil fuels …).

In general, suspended particulate matter emissions from several types of sources can be identified by the investigation of their particle element composition. On the other hand, trace element concentrations in airborne particulate matter are of great concern to people living in urban areas. Many epidemiological studies have revealed consistent associations between ambient concentrations of inhalable (PM10) particles and their elemental composition with adverse respiratory health effects (Dockery and Pope, 1994; Schwartz *et al.*, 1996). Moreover the implementation of the EU directive on air quality demands the monitoring of PM10 and atmospheric lead concentrations, while proposes new more stringent standards. In addition, the monitoring of atmospheric concentrations of Cd, As, Hg and Ni was also proposed due to their detrimental effect on human health (EC, 1998; WHO, 2000).

It is of great importance to develop a series of evaluation procedures for efficient air quality control strategies.

As an attempt to evolve an effective air quality management technique it is useful to be able to observe the contribution of each primary source to the chemical composition of ambient particulate matter.

Receptor modelling is an assessment method for sources of PM10 based on chemical species data collected at the receptor. Among a number of multivariate statistics, positive matrix factorization (PMF) has superior applicability for an area with diverse source profiles (Paatero and Tapper 1994).

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The PM10 samples were analyzed by ISP-MS instrument (Method IO-3.5, EPA). Twenty five elements were detected at quantifiable concentrations in the examined PM samples.

Finally, an attempt was made to identify the main PM10 sources that affect the sampling sites. For this purpose was applied the multivariate Positive Matrix Factorization (PMF) receptor model.

It should be noticed that Tolis *et al*. (2011) carried out source apportionment of PM10 using PMF technique but for very limited number of PM samples and only for the city of Kozani.

2. Methods

2.1. Sampling site

The Eordea basin in the axis of the Greek cities of Kozani and Ptolemais is a heavily industrialized area and can be characterized as a broad, relatively flat bottomed basin surrounded by mountains. It is approximately 50 km in length and the width ranges from 10 to 25 km. The basin axis has a northwest to southeast direction. Four lignite power stations in the basin are operated by the Greek Public Power Corporation, while recently a new power station has been constructed and started operating. The climate in the area is continental with strong temperature inversions during the whole year (Triantafyllou, A.G. 2001).

Three representative sampling sites of the region were selected to investigate the PM10-associated elements in samples of airborne particles: S1 in the center of Kozani (40.299^o N, 21.799^o E), where urban activities and traffic density occur. Kozani is the major city in West Macedonia, Greece (50,000 inhabitants) located on the south sector of the Eordea basin at about 711 m above sea level. S2 in the city of Ptolemaida (32,000 inhabitants) located (40.513^o N, 21.677^o E and 610 m) close to the industrial area with opencast coal mining and lignite combustion activities. S3 in the village of Eratyra (1,400 inhabitants) located (40.341^o N, 21.511^o E and 740 m) 30 km away from the industrialized area (on the south-west sector) in a rural residential district. It can be considered as a background station, not directly influenced by traffic or industrial emissions.

2.2. Ambient sampling

Ambient air sampling of PM10 was conducted throughout 1 yr at three receptor sites S1 (August 2015 to July 2016), S2 and S3 (November 2013 to October 2014).

Particles were collected by filtration on PTFE membrane filters (teflo, Pall) using low volume air samplers equipped with size-selective inlet (PM162M Environnement S.A. and Derenda LVS).

The duration of each sampling was 24h starting at midnight. In total 64, 163 and 62 samples were available for each site S1, S2 and S3 respectively.

Before and after sampling the filters were exposed for 24–48 h on open but dust-protected sieve-trays in an air-conditioned weighing room (T=22±2^{o}C and R.H.=43±5%). The gravimetric determination of the mass was carried out using an analytical microbalance, located in a weighing room. Static electricity from the filters was eliminated with a special static eliminator.

2.3. Elemental analysis

Representative number of filters, after collection and weighing, underwent a chemical analysis in order to determine the metals and metalloids in the atmosphere.

Specifically, were chosen samples one per ten, eight and fifteen days for S1 (n=33), S2 (n=44) and S3 (n=21) receptor site respectively. The selection of sampling filters was at least representative and encountered a variety of meteorological conditions in order to avoid possible distorting effects.

The PM10-bound concentrations of elements (Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th and U) were determined by ICP-MS (Agilent 7500 ICP-MS).

Sampled filters were extracted by hot acid procedure (Method IO-3.1, EPA) with 8 mL mixed acid (1:3 ratio of high purity HNO^3 and HCl). All the extracts were then transferred to clean polypropylene tubes and diluted to 25 mL with high purity de-ionised water.

An internal standard mix (Li, Sc, Ge, Rh, In, Tb, Lu and Bi isotope) has been added in all standards, blanks and samples at a concentration of 0.4 μgmL^{-1} in order to monitor the drift in the ICP-MS signal due to plasma instability and sample cone clogging.

The instrumental conditions were basically similar to those reported by the instrument manufacturer. The standard calibration curves for ICP-MS analysis were in general in line with those obtained by the standard addition method (r value above 0.999). The final concentrations were corrected with the recovery rates and filter blanks.

2.4. Positive matrix factorization

Positive matrix factorization (PMF) is a powerful multivariate technique developed by Paatero and Tapper (1993). Suppose X is an n by m data matrix consisting of the measurements of n chemical species in m samples. The objective of multivariate receptor modeling is to determine the number of aerosol sources p, the chemical composition profile of each source and the contribution of the p sources contributes to each sample. The factor analysis model can be described with the general equation (Eq. 1):

$$X = GF + E \quad (1)$$

$$Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} (e_{ij} / s_{ij})^2 \quad (2)$$

where G is an n by p matrix of source chemical compositions (source profiles) and F is a p by m matrix of

source contributions (factor scores) to the samples. Each sample is an observation along the time axis, so G describes the temporal variation of the sources. E represents the part of the data variance unmodeled by the p-factor model (residual matrix). The main process of this model is minimizing the Q-value which is defined (Eq. 2) as the sum of square of the residuals (eij) weighted inversely with error estimates (sij) of the data point.

The features of PMF are: (1) it uses weighted least-squares fits for data that are normally distributed and maximum-like hood estimates for data that are log-normal, (2) it weighs data points by their analytical uncertainties, (3) it constraints factor loadings and factor scores to non-negative values and thereby minimises the ambiguity caused by rotating the factors, (4) it expresses factor loadings in mass units, which allows factors to be used directly as source signatures and (5) it provides uncertainties for factor loadings and factor scores, which make them easier to use in quantitative procedures such as chemical mass balance.

3. Results and discussion

3.1. PM10 concentrations

The measurement campaign was conducted throughout a year at three receptor sites S1 (August 2015 to July 2016), S2 and S3 (November 2013 to October 2014) and the PM10 concentrations determined gravimetrically.

The mean annual concentrations of PM10 measured at the three sampling sites are presented in Table 1. As seen, the mean PM10 values at Kozani and Eratyra were below the EU proposed annual limit value of 40 μgm^{-3} (83/399/ECC) while the mean annual concentration at Ptolemaida was equal to the current standard.

Table 1. Statistical analysis of PM10 concentrations during measurement period

	n	Average [$\mu g/m^3$] (min - max)	Exceedances N^o (%)
Kozani	64	29 (6 - 90)	4 (6.2%)
Ptolemaida	163	40 (6 -116)	46 (28.2%)
Eratyra	62	18 (5 - 47)	0 (0%)

The percentage of daily PM10 concentrations higher than the 24-h limit value of 50 μgm^{-3} (not to be exceeded over 35 times in a year) ranged between 0% and 28.2%, across the three sites. The highest PM10 values were recorded at Ptolemaida. 28.2% of PM10 concentrations exceeded the daily limit value (50μgm^{-3}, EC 1999).

Table 2. Particle mass and elemental concentrations in PM10 (**Not Detected*)

		Kozani (n = 33)		Ptolemaida (n = 44)		Eratyra (n = 21)	
		Average	**SD**	**Average**	**SD**	**Average**	**SD**
PM10	$\mu g/m^3$	29	16	40	24	18	10
Be	ng/m^3	0.02	0.02	0.03	0.06	0.02	0.02
Na	ng/m^3	103	207	179	225	-*	
Mg	ng/m^3	300	252	412	253	131	129
Al	ng/m^3	232	332	239	166	60	63
K	ng/m^3	95	176	127	187	5.6	23
Ca	ng/m^3	2248	1501	3379	2397	673	902
V	ng/m^3	2.5	1.6	2.3	1.6	0.58	0.49
Cr	ng/m^3	5.2	2.9	3.9	2.5	0.54	0.92
Mn	ng/m^3	10.2	10.0	12.3	8.0	3.7	3.6
Fe	ng/m^3	570	569	631	402	159	152
Ni	ng/m^3	4.0	4.7	4.1	2.8	0.53	0.90
Co	ng/m^3	0.27	0.26	0.60	0.85	0.08	0.09
Cu	ng/m^3	3.1	2.8	4.2	14.6	-*	
Zn	ng/m^3	48.9	26.0	35.3	20.2	26.7	16.1
As	ng/m^3	0.62	0.41	0.83	0.64	0.16	0.21
Se	ng/m^3	0.20	0.24	0.10	0.18	0.03	0.08
Mo	ng/m^3	0.26	0.75	0.07	0.08	-*	
Ag	ng/m^3	0.06	0.19	0.02	0.01	0.001	0.004

Cd	ng/m^3	0.09	0.07	0.22	0.25	0.04	0.04
Sb	ng/m^3	0.64	0.32	0.65	1.06	0.08	0.13
Ba	ng/m^3	7.2	5.6	7.0	4.3	1.6	1.64
Tl	ng/m^3	0.02	0.02	0.02	0.02	0.007	0.007
Pb	ng/m^3	0.56	0.95	3.1	7.9	0.06	0.23
Th	ng/m^3	0.07	0.11	0.09	0.08	0.02	0.03
U	ng/m^3	0.01	0.03	0.09	0.08	0.005	0.008

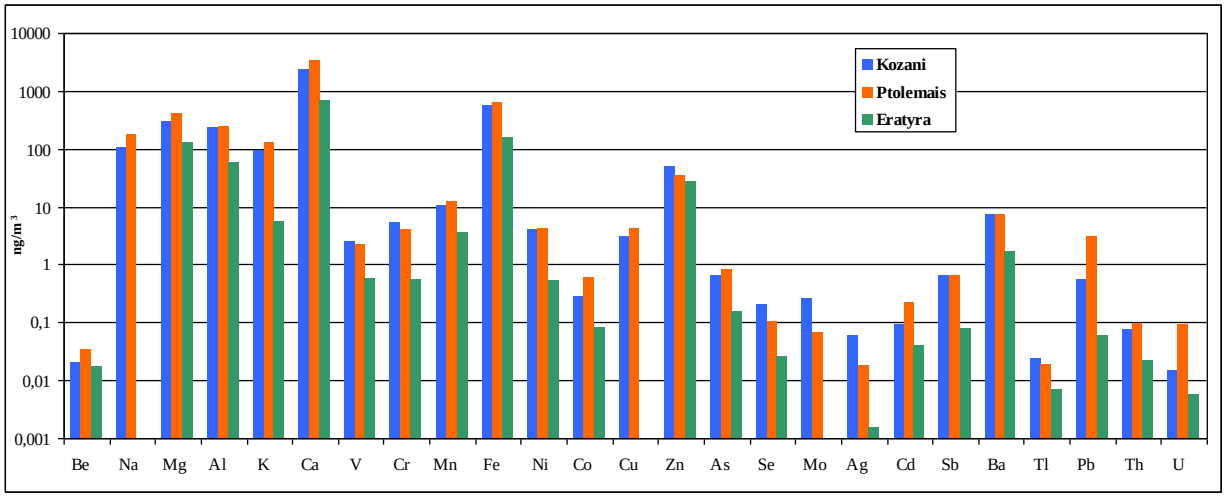

Figure 1. Ambient PM10 profiles at receptor sites Kozani (S1), Ptolemaida (S2) and Eratyra (S3)

These results are fairly lower than those referred in literature for urban-industrial sites (D. Voutsa *et al* 2002).

In the case of Kozani, 4 exceedances (6.2%) in 64 cases were observed. These findings are significant lower than those previous reported regarding the same area for the years 1991 – 1994 (Triantafyllou, A.G. 2001). However, no value recorded on a 24-hour basis exceeded the daily limit in the S3 background station at the village of Eratyra.

3.2. Elemental concentrations

The chemical composition of ambient PM10 at the three receptor sites is summarized in Table 2 and Figure 1.

The summed mass of the 25 elements determined in this study accounted 12.5, 12.6 and 5.9 % of the PM10 mass for S1, S2 and S3 receptor sites respectively.

Crustal matter (as oxides of Al, Ca, Mg, Fe), was the main component of PM10.

The concentrations of Cd, Mn, Ni and Pb were relatively higher at the S2 receptor site in the city of Ptolemaida located close to the industrial area with opencast coal mining and lignite combustion activities. At all three sites mean lead concentrations were well below the ambient air quality standard of 500 ngm^{-3} (as annual mean, EC, 1999). The mean values of As, Cd and Ni were also lower than the proposed assessment thresholds (6, 5 and 20 ngm^{-3}, respectively, EC, 2003). In the case of V, the proposed 24-h concentration is 1μg/m^3 a value never exceeded during the sampling campaign (WHO, 2000). Finally, the mean total concentration of Mn was lower than the annual tolerance concentration included in the WHO Air Quality Guidelines (150 ngm^{-3}, WHO, 2000).

3.3. Source identification

Receptor-oriented source apportionment models allow to identify major air pollution sources and to estimate their relative contribution to ambient air pollutant concentrations.

For this purpose was applied the multivariate Positive Matrix Factorization (PMF) receptor model and an attempt was made to identify the main PM10 sources that affect the sampling sites.

First results obtained from restricted number of samples have shown that:

i. *in case of Kozani (S1)* the identified main sources were coal combustion and road-traffic emissions,

ii. *in case of Ptolemaida (S2)* the main sources were coal combustion, road-traffic emissions and soil dust transferred from open pit mines while

iii. *in case of Eratyra (S3)* the main PM10 sources were the crustal dust and the biomass-wood burning.

It must be noticed that the characterization of specific particle sources is particularly challenging due to a large number of urban and industrial sources presenting similar elemental profiles (Lee *et al* 1999, Kim *et al* 2007, Watson *et al* 2004). For this reason it is imperative further investigation of the PM10 source contribution at the specific receptor sites.

4. Conclusions

- The PM10 measurement campaign was conducted throughout a year's period at three receptor sites.

- The mean PM10 values at Kozani and Eratyra were below the annual limit while the mean annual concentration at Ptolemaida was equal to the current standard value of 40 μgm^{-3}.

- The highest PM10 values were recorded at Ptolemaida. More specifically, 23% of PM10 concentrations exceeded the daily EU limit value.

- Crustal matter (as oxides of Al, Ca, Mg, Fe), was the main component of PM10.

- At all receptor sites, the mean values of Pb, V, As, Cd and Ni were lower than the proposed assessment thresholds.

- Source apportionment first results of a PMF receptor model shown: a) Kozani (S1) the identified main sources were coal combustion and road-traffic emissions, b) Ptolemaida (S2*)* the main sources were coal combustion, road-traffic emissions and soil dust transferred from open pit mines, c) Eratyra (S3) the main PM10 sources were the crustal dust and the biomass-wood burning.

However the source apportionment study is particularly challenging due to a large number of urban and industrial sources presenting similar elemental profiles and therefore it is imperative further investigation of the PM10 source contribution at the specific receptor sites.

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