Water-soluble components in PM$_{10}$ aerosols over an urban and a suburban site in the city of Sfax (Tunisia)

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RESUMEN

En este estudio se examinó la influencia de la fuente y de los factores meteorológicos en las características fisicoquímicas de los aerosoles atmosféricos recogidos en dos sitios, urbano y suburbano, de la ciudad de Sfax (Túnez) durante el año 2004. Los aerosoles atmosféricos se analizaron principalmente por su composición química y su evolución espacio-temporal. De acuerdo con la distribución del contenido de la partícula, las especies estudiadas fueron clasificadas en grupos distintos con diverso contenido y distribución temporal. Un análisis de componentes principales (PCA) reveló una relación clara entre el comportamiento de los componentes de cada grupo y sus correspondientes factores de la fuente y meteorológicos. Los resultados proporcionan una clara evidencia de un enriquecimiento desde el sitio que depende del estado del suelo, de la frecuencia de la exposición a los penachos industriales y de los fenómenos de transporte. La distribución de las fuentes reveló tres grandes grupos. El grupo I consistió de elementos de fuente natural incluyendo la marítima (Cl$^-$ y Na$^+$) y cortical (Ca^{++}, Mg^{++}, Fe$^{(2;3)+}$ y K$^+$). El grupo II se asocia con una "fuente primaria" antrópica atribuida al efecto local de los polvos radiactivos industriales del penacho que amenaza al sitio urbano. Esto se refiere principalmente al compuesto PO$_4^{3-}$. El tercer grupo se explica por una "fuente secundaria" antrópica que incluye NH$_4^+$, NO$_3^-$ y SO$_4^=$ compuestos resultantes del efecto de los procesos de conversión gas/partículas.

ABSTACT

This study examines the influence of source and meteorological factors on the physico-chemical characteristics of atmospheric aerosols collected at two sampling sites, urban and suburban, in the city of Sfax (Tunisia) during the year of 2004. Atmospheric aerosols were further analyzed for their chemical composition and spatio-temporal evolution was investigated. Based on particle content distribution, the species studied were classified into distinct groups with different content and temporal distribution. A principal component analysis (PCA) revealed a clear relationship between the behavior of the constituents of each group and their corresponding source and meteorological factors. The findings provide sheer evidence for a marked intra-site enrichment that depended on the soil state, the frequency of exposition to the industrial plumes and the transport phenomena. Source apportionment revealed three major groupings. Group I consisted of a natural source including maritime (Cl^- et Na^+) and crustal (Ca^{++}, Mg^{++}, $Fe^{(2;3)+}$ and K^+) elements. Group II is associated with a "primary" anthropic source attributed to the local effect of industrial plume fallouts which threatens the urban site. This mainly concerns the PO_4^{3-} compound. The third group is explained by a "secondary" anthropic source that included NH_4^+, NO_3^- and $SO_4^=$ compounds resulting from the effect of gas/particles conversion processes.

Keywords: Southern Mediterranean region, aerosol, source apportionment, meteorology, statistical analyses.

1. Introduction

Tropospheric aerosols have been the object of intensive research mainly because of their impact on health (Pope and Dockery, 2006), the Earth's climate (IPCC, 2007), visibility, ecosystems and building materials. Aerosol concentrations are influenced by meteorological factors, geographic conditions and particle emissions such as industrial emissions, traffic, agriculture activities and natural sources. The aerosol particles are of great importance in affecting atmospheric radiation, cloud formation as well as atmospheric photochemical reactions and the light extinction effect that influence global weather changes (Seinfeld and Pandis, 1998; Tsai *et al.*, 2003). The above characteristics of the aerosol particles are due to their water soluble components, e.g. magnesium, sodium, potassium, calcium, ammonium, nitrate, sulphate, chloride, etc. (Tang *et al.*, 1995; Tsai and Kuo, 2005).

Air quality degradation by particulate matter over polluted areas is often characterized by high levels of regional background aerosols on which intense episodes of their natural and or anthropogenic origins are superimposed. Such episodes are associated with synoptic and mesoscale meteorological conditions that favour formation and accumulation of aerosol pollutants at regional or even continental scales.

Numerous studies in Eastern and Western Mediterranean were focused on the inter-site (urban/suburban and urban/suburban/rural zones) enrichment of aerosol concentrations (Yatkin and Bayram, 2007; Türküm *et al.,* 2008; Pey *et al.*, 2009). Other studies were interested in the variability of regional background particulate matter levels (e.g. Rodríguez *et al.*, 2002, 2004; Pérez *et al.*, 2008, Dongarrà *et al.*, 2007; Gerasopoulos *et al.*, 2007; Querol *et al.*, 2008; Viana *et al.*, 2008a). However, only few studies dealt with the Southern Mediterranean region, characterized by arid and semi-arid climates. In this context, this work examines the temporal evolution of the principal soluble elements of aerosols sampled both in urban and suburban sites in Sfax City (Tunisia). It aims to identify, at the two particular sites, the behaviour of the aerosol constituents, particularly that of particulate sulphate, nitrate and ammonium. Furthermore, source apportionment of atmospheric particulate matter was investigated.

2. Material and methods

For the particular purposes of the current study, two sites were established in the city of Sfax during the year of 2004. The first was located in the urban center, 4 km from the industrial complex (Fig. 1). This site is exposed to industrial emissions from prevalent south-westerly winds. The second was 25 km from the urban center and situated in an area characterized by intensive agricultural activity and insignificant anthropic sources. It is, however, enormously exposed to the industrial emissions of the city along the north-eastern wind direction.
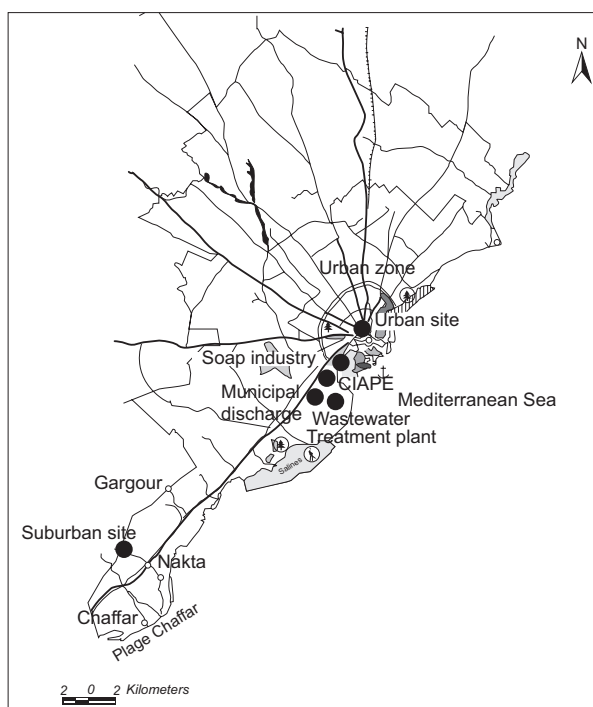

Fig. 1. Location map of Sfax City and the selected study sites.

At each site, aerosol sampling was carried out over a one year period (from January to December 2004). It was performed at three meters above the ground level by means of total air filtration using nuclepore filters, whose diameter was 4.7 cm and its porosity 0.45 μm. The threshold aerodynamic diameter of the aerosol sampler nozzle was 10 μm. Aerosol was sampled on a daily basis at an hourly rate of 180 litres. For the analysis of the particles, we proceeded by cumulative filters corresponding to sampling sequences of 7 days (168 h). The collected particulate matter was set into deionized water solution as follows: first, the filters were carefully removed from their supports and were placed in beakers. Then, 20 ml of deionized water were added to each sample. After three hours of vibration by an ultrasonic apparatus, each sample solution was analyzed by atomic absorption spectrometry (for Ca^{++}, Mg^{++}, Fe$^{(2;3)+}$, Na$^+$ and K$^+$) by ionic chromatography with a Shimadzu Hic-6A (for Cl$^-$, PO$_4^{3-}$, NO$_3^-$ and SO$_4^=$), and by colorimetry (for NH$_4^+$). Efficiencies of sodium extraction

were determined using pilot filters, which contained a well-determined quantity of sodium and which underwent the same treatment procedures that the studied samples were subjected to.

The average extraction output was found to be close to 98 %. Concentrations of the various chemical elements were calculated based on the following equation:

$$C = C' \cdot V_{H_2O} / V_{air} \tag{1}$$

where

C: Concentration of the chemical element in the aerosol in $\mu g/m^3$;

C':   Measured concentration in $\mu g/ml$;

V_{H_2O}: Volume of deionized water used to extract the particles by agitation with ultrasonic apparatus, in ml;

V_{air}:   Volume of the aspired air in m^3.

3. Climatic characteristics and urban activities of Sfax City

Sfax City is located in the south east of Tunisia on the Mediterranean Sea (Fig. 1). Its latitude and longitude are 34°43'N and 10º46'E, respectively. It is characterized by an original semi-arid Mediterranean climate, largely influenced by i) its mild and gentle topography and ii) its maritime exposure. It is one of the most industrialized and polluted cities in Tunisia. More details about the city and its air quality are presented elsewhere (Azri *et al.*, 2007).

4. Results and discussion

4.1 Spatial and temporal evolutions of the aerosol constituents

The descriptive study of the soluble elements (Ca^{++}, Mg^{++}, $Fe^{(2;3)+}$, Na^+, K^+, NH_4^+, Cl^-, NO_3^-, $SO_4^=$ and PO_4^{3-}) analyzed in the aerosols collected at the two selected sites showed three principal groups with distinct behaviors (Fig. 2). We can note, particularly: a first group made of Ca^{++}, Mg^{++}, $Fe^{(2;3)+}$, K^+ and PO_4^{3-}. In this group, curves representing content evolutions present minima during the spring and summer seasons (from March to August) and maxima during the fall and winter seasons (September to February).

A second group composed of Cl^- and Na^+. The evolution curves of the elements forming this group show a trend which is different from that of the elements of the first group. In fact, unlike the first group, fall and winter seasons are distinguished by low contents. Those of spring and summer are characterized by maxima values.

This differentiation of groups is related to the effect of the meteorology of the Sfax region, which is characterized by two antagonistic circulations of marine and continental winds (Fig. 3). During the fall and winter seasons, the increase in the contents of crustal elements is attributed to the effect of continental circulation, under the effect of SSW, SW and WSW winds. The frequency of these winds corresponds to 28 and 38% of the total observations registered during fall and winter seasons, respectively. On the other hand, during the spring and summer seasons,
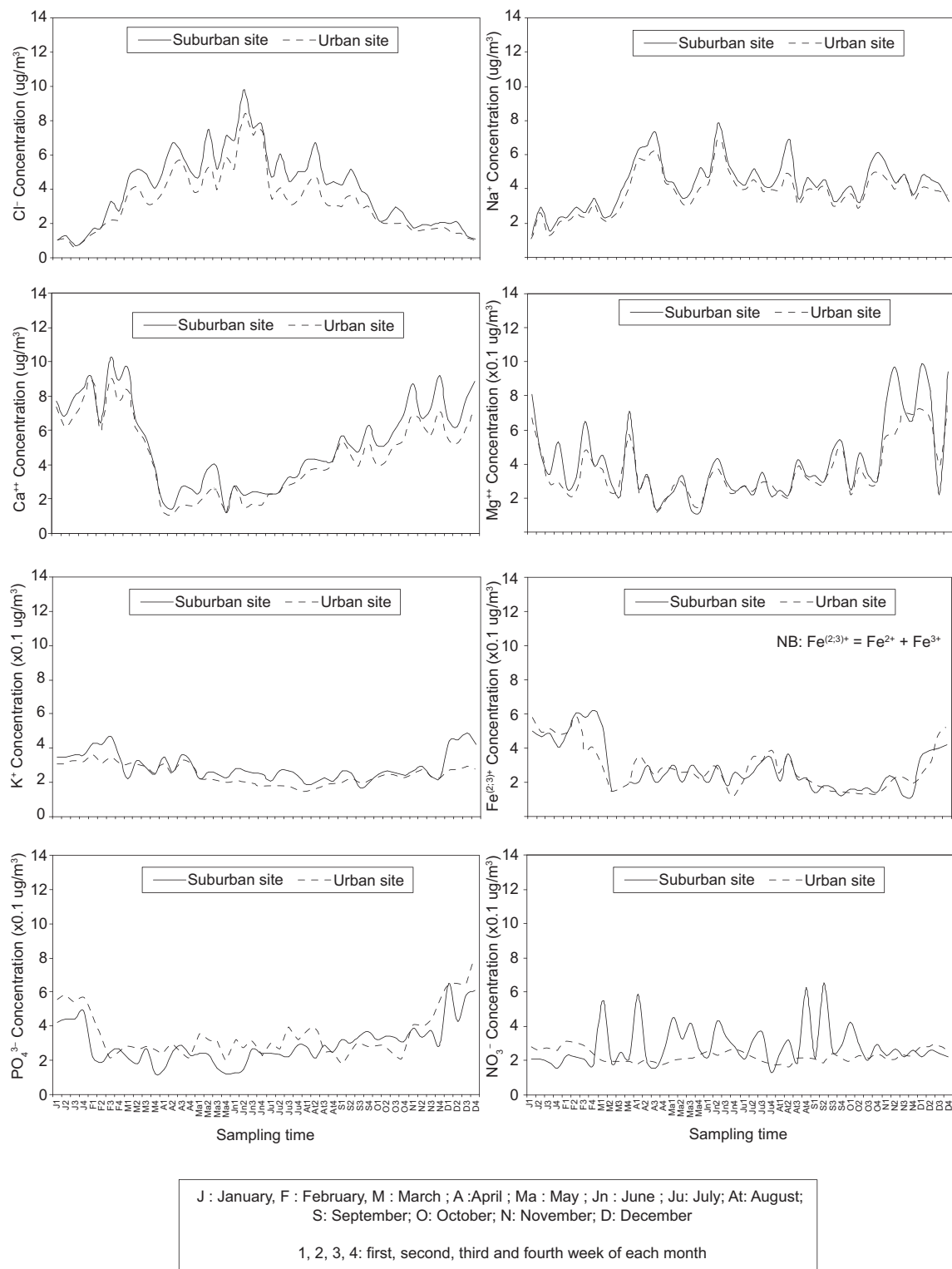
Fig. 2. Evolution of soluble elements of the aerosol sampled both in the urban and suburban sites (continues).
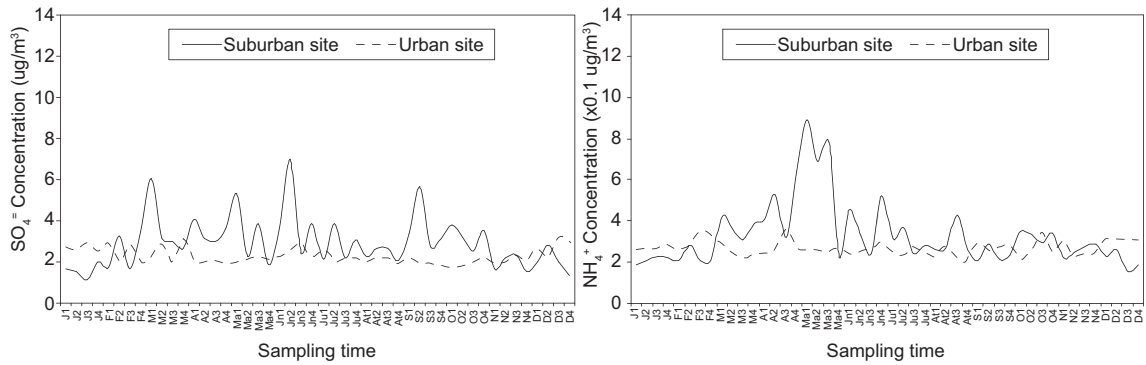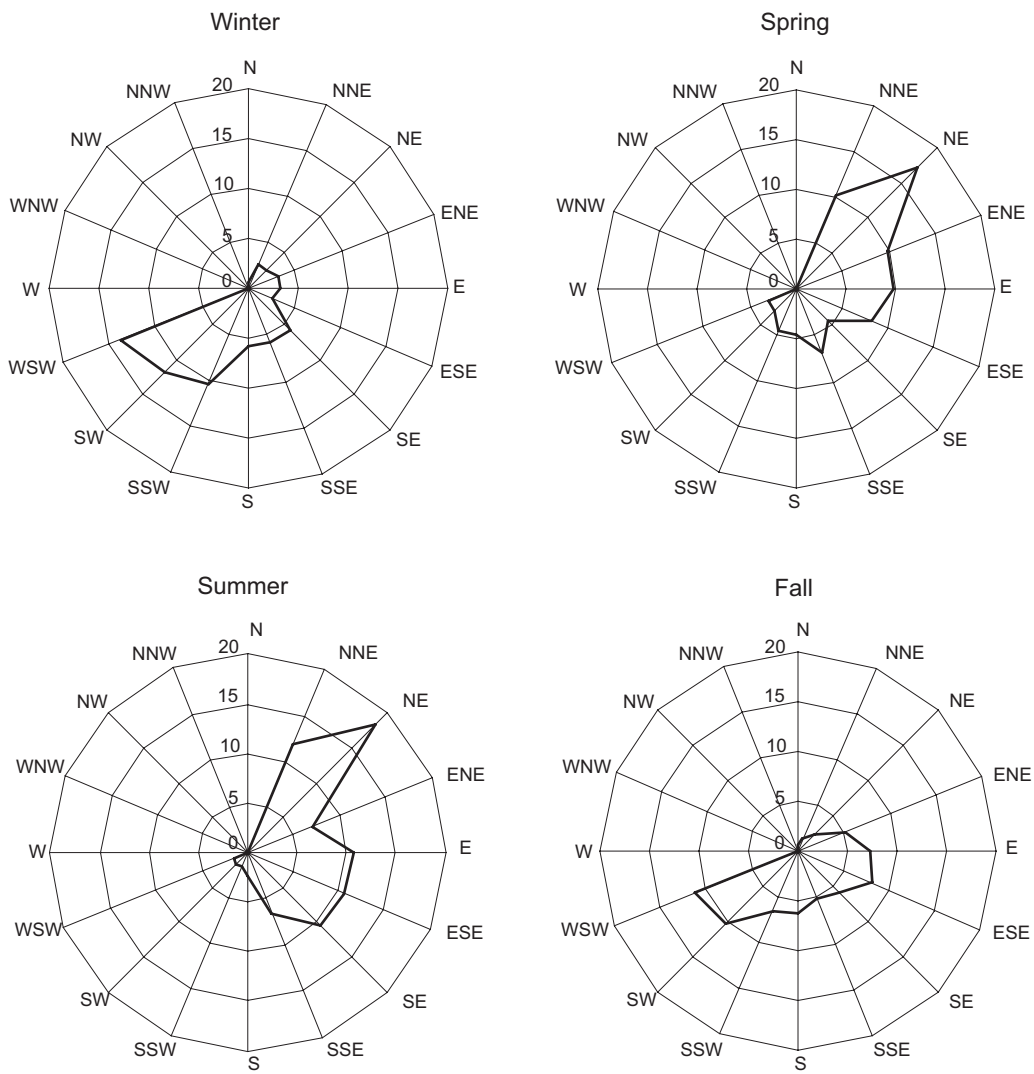
Fig. 2. Continued.

Fig. 3. Seasonal wind distribution (%) during the study period.

the increase in the maritime component is attributed to the maritime air, which covers up the study sites, under the effect of NNE, NE, ENE, E, ESE, SE and SSE winds. The frequency of these winds fluctuates between 66 and 77 % of the total observations registered in spring and summer seasons, respectively.

During the four seasons, the mean wind velocity varied between 2 and 4.5 m/s, with a frequency of 92 %. Its evolution with time shows a trend which is completely different from those corresponding to the contents of the analyzed elements. According to Reydet (1984), the similarity between the wind speed and the load of natural elements becomes clear only starting from speeds higher than 7 m/s. It is also important to note that throughout the period of the study, the region was subjected only to weak rainfall. The degree of atmospheric leaching by precipitations was, therefore, insignificant.

A third group composed of NO_3^-, $SO_4^=$ and NH_4^+. The temporal evolutions of the elements of this group neither are in coincidence with those of the first group nor with those of the second group (Fig. 2). They are distinguished by the appearance of individualized maxima that can testify to the impact of anthropic sources. Above the suburban site, the marked peaks of NO_3^-, $SO_4^=$ and NH_4^+compounds are associated to the marine circulation. Their amplitudes double the recorded values above the urban site. The highest contents recorded above the latter were observed during the winter season and were under the effect of the continental circulation. The increase of the NO_3^-, $SO_4^=$ and NH_4^+ concentrations at suburban sites was also proved by Jurat and Romualdas (2005).

Due to their locations as to the industrial complex of the city (Fig. 1), these two sites appeared to be under the influence of the industrial emissions linked to the effect of the two predominantly NE and SW wind directions. Under the influence of the NE wind direction, the suburban site is exposed to the industrial plume with a frequency of 17 % of the total observations. The exposure frequency registered in spring was equal to that recorded in summer. Under the influence of the SW wind direction, the urban site, on the other hand, is exposed to the industrial plume with a relatively lower frequency of about 10 % of the total observations, which was registered equally in fall and winter seasons.

Figure 4 shows that the suburban site, compared to the urban site, is enriched by the majority of the analyzed elements except for PO_4^{3-}. The enrichment of this site in Cl^- and Na^+ could be explained by the fact that the aerosol was collected in an open area well exposed to maritime circulation. Its enrichment by the other crustal elements is possibly attributed to the dusts carried along to nearby agricultural soils. At this suburban site, in spite of the absence of nearby anthropic sources, its enrichment by compounds like NO_3^-, $SO_4^=$ and NH_4^+ could testify for their marked formation from gaseous precursors along the displacement of the urban plume under the effect of prevalently NE wind directions.

Still within the framework of the suburban site, the monthly conversion rate of SO_2 into $SO_4^=$ (GPC) was computed based on equation (2) (William *et al.*, 1980):

$$GPC\ (\%) = SO_4^=\ (\mu gS/m^3)/(SO_2 + SO_4^=)\ (\mu gS/m^3)\ 100 \qquad (2)$$

GPC: Gas/Particles conversion rate

The findings show that it is fluctuating between 15 and 40% for suburban site (Fig. 5). It is well pronounced during the spring and summer seasons (between 35 and 40%), still under the
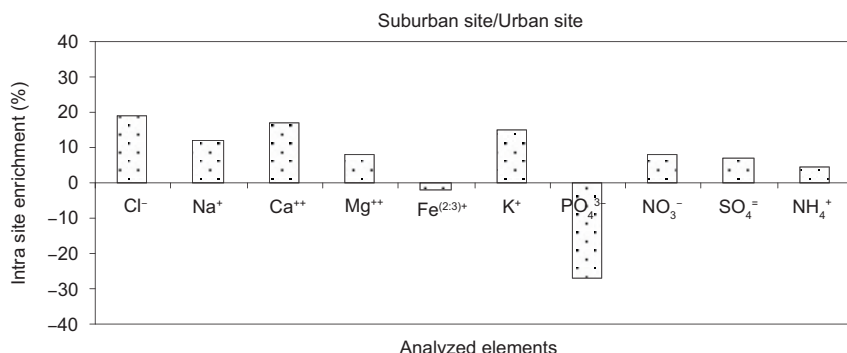
Fig. 4. Intra-site enrichment of the aerosol constituents.

effect of predominantly NE winds. It is highly correlated with the frequency of the north-eastern winds ($r = 0.726$). It exceeds the monthly conversion rate calculated for the urban site, which fluctuated between 5 and 16%. This relatively marked suburban increase is possibly attributed to the importance of oxidation processes during the displacement of the urban plume. This result is in congruence with the findings reached by Acker *et al*. (2005) and Horng *et al*. (2007) for south of France and Taiwan.
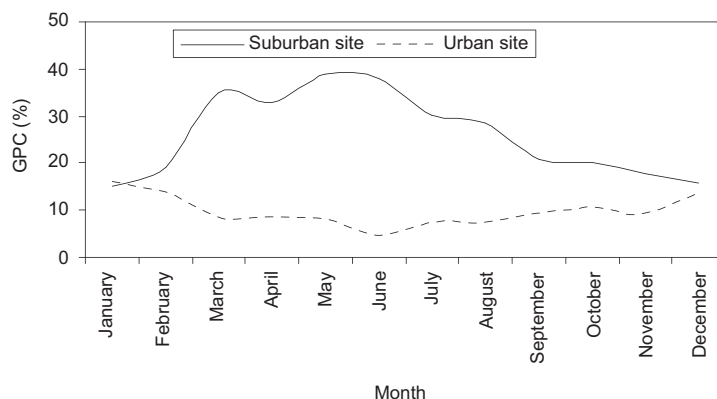

Fig. 5. Monthly conversion rate of SO_2 into $SO_4^=$.

Compared to the suburban site, the urban site, which is found to be less enriched in natural elements, is conditioned by stand soils and buildings that reduce the transportation of dust particles and intensify impaction phenomena. The reduced enrichment in NO_3^-, $SO_4^=$ and NH_4^+ could testify that the gas/particles conversion processes are relatively limited in the areas closer to the anthropic sources. The pronounced PO_4^{3-} enrichment of the urban site testifies to the importance of the local effect of industrial plume fallouts, particularly those from the SIAPE factory (Fig. 1). This factory, which processes phosphate for the manufacture of phosphoric acid was shown to be a locally potential source for the emission of dust particles highly enriched in terms of the aforementioned compound (Azri *et al*., 2000).

4.2 Study of enrichment factors and multivariable analysis

In order to refine the findings from the descriptive analysis, we proceeded to conduct an analytical approach based on three major tools, namely the enrichment factors, the principal component analysis (PCA) and the multiple linear regressions. This will be elaborated on in the sections below.

4.2.1 Enrichment factors

Computed enrichment factors were based on Ca and Cl selected as crustal and marine references, respectively. The enrichment factors of a selected element (X) are determined by equations (3) and (4) and may be subdivided into three classes.

$$EF_{crust}\left(X\right) = \frac{\left(\left[X\right]\left[Ca\right]^{-1}\right)_{aerosol}}{\left(\left[X\right]\left[Ca\right]^{-1}\right)_{crust}} \tag{3}$$

$$EF_{sea\,water}\left(X\right) = \frac{\left(\left[X\right]\left[Cl\right]^{-1}\right)_{aerosol}}{\left(\left[X\right]\left[Cl\right]^{-1}\right)_{sea\,water}} \tag{4}$$

EF_{crust} (X): Enrichment factor of the compound X with respect to the crust

$EF_{sea\,water}$ (X): Enrichment factor of the compound X with respect to the sea water

[X]: Concentration of the compound X

[Ca]: Concentration of Ca

([X][Ca]$^{-1}$)$_{aerosol}$: Concentration of the compound X with respect to that of Ca in the aerosol

([X][Ca]$^{-1}$)$_{crust}$: Concentration of the compound X with respect to that of Ca in the crust

[Cl]: Concentration of Cl

([X][Cl]$^{-1}$)$_{aerosol}$: Concentration of the compound X with respect to that of Cl in the aerosol

([X][Cl]$^{-1}$)$_{sea\,water}$: Concentration of the compound X with respect to that of Cl in the sea water

Slightly enriched: EF<10;

Enriched: 10<EF<1000;

Highly enriched: EF>1000.

Based on the computation of the enrichment factors (EF) of the chemical elements in the aerosols with respect to calcium and chlorine (Table I), two major points were noted: (i) first, with respect to the urban site, Ca^{++} and Fe$^{(2;3)+}$ are essentially of crustal origin. They are slightly enriched compared to the crust (EF < 10), and enriched to highly enriched compared to the sea water (64 < EF < 8.3 x 10^6). Cl$^-$ is typically marine; it is not enriched compared to the sea water (EF<10) and is enriched compared to the crust (EF > 10). Na$^+$ and K$^+$ are slightly enriched compared to both the

crust and the sea water. They present a mixed origin related to these two sources. $SO_4^=$ and PO_4^{3-} are enriched compared to the crust and to the sea water ($10 < EF < 69$). They result from sources other than the sea and the earth crust; ii) second, at the suburban site, PO_4^{3-} is characterized by a particular behavior. It has a dominantly crustal origin.

Table I. Enrichment factors of analyzed elements with respect to calcium and chlorine.

		Ca^{++}	$Fe^{(2;3)+}$ *	K^+	Na^+	Cl^-	$SO_4^=$	PO_4^{3-}
Urban site	Crust	1	0.45	0.76	1.07	198.5	62.74	27.89
	Sea water	64.18	8.3×10^6	7.71	2.05	1	13.13	3.5×10^5
Subrban site	Crust	1	0.04	0.08	1.03	211.58	69	1.92
	Sea water	60.22	6.7×10^5	3.57	1.85	1	15.04	2.3×10^4

* $Fe^{(2;3)+} = Fe^{2+} + Fe^{3+}$

4.2.2 Statistical data processing by PCA

Source identification for atmospheric aerosol is important for developing effective strategy to reduce their emissions. One of the methods for source identification is principal components analysis (PCA). Our attention was drawn to this method first through a review article about methods and results for aerosol source apportionment over European region and then through the article published by Viana *et al.* (2008b). The statistical processing of the data by such method proves that at each site, the distribution of the various analyzed elements falls into distinguished groups (Figs. 6 and 7). Indeed, at the level of the urban site, three principal groups can be distinguished (Fig. 6). They are typical of three aerosol sources, where the first set of elements (Ca^{++}, Mg^{++}, $Fe^{(2;3)+}$, K^+ and to a less degree PO_4^{3-}) is of a dominantly crustal origin, the second set (Cl^- and Na^+) is of a dominantly marine source, and the third set ($SO_4^=$, NH_4^+, NO_3^- and to a less degree PO_4^{3-}) is highly associated with anthropic activities. As far as the suburban site is concerned, the classification of the aerosol constituents also showed three distinct groups (Fig. 7): the first has a dominantly crustal origin and is composed by Ca^{++}, Mg^{++}, $Fe^{(2;3)+}$, K^+ and PO_4^{3-}; the second has a dominantly marine origin and is comprised of Cl^- and Na^+; and the third group has a prevalently anthropic origin and is formed by $SO_4^=$, NH_4^+ and NO_3^-.

From these distributions, we noted that PO_4^{3-}, $SO_4^=$, NH_4^+ and NO_3^- compounds underwent a change of positions (Figs. 6 and 7). This fact is possibly explained by the following reasons: The PO_4^{3-} belonging to the anthropic group of the urban aerosol proves that the effect of the industrial plume fallouts in the nearby urban areas is restricted. Furthermore, its individualized behavior with regards to the group of secondary compounds ($SO_4^=$, NH_4^+ and NO_3^-) confirms that it does not result from the atmospheric transformations of phosphoric compounds.

At the level of the suburban site, the secondary compounds $SO_4^=$, NH_4^+ and NO_3^- present an affinity with those of the second group (Na^+ and Cl^-). They present fairly significant correlation coefficients with chlorine (0.524; 0.450 and 0.300; threshold of significance = 0.300 for $p < 0.05$ and $n = 48$). They are possibly related to the effect of the maritime circulation, which can drain the urban pollution of the city up to the suburban site by north-eastern winds. This observation is confirmed by a significantly positive correlation between the total mass of the secondary compounds ($SO_4^=$, NH_4^+ and NO_3^-) and the frequency of the north-eastern dominant winds ($r = 0.646$).
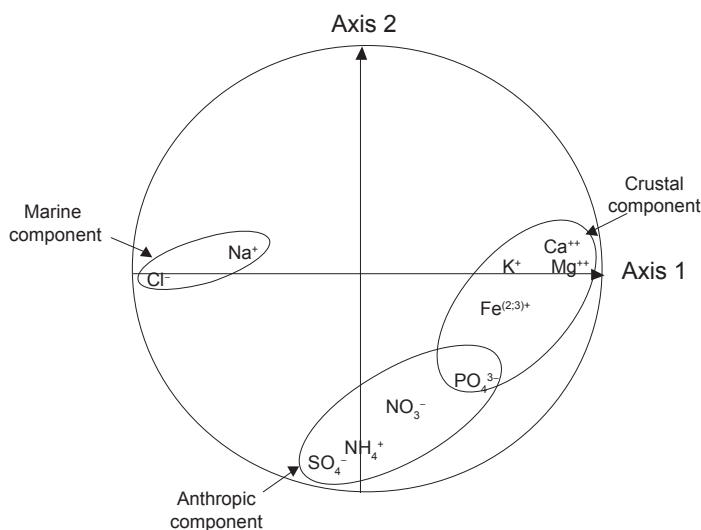
Fig. 6. Distribution of the analyzed elements in the correlation circle
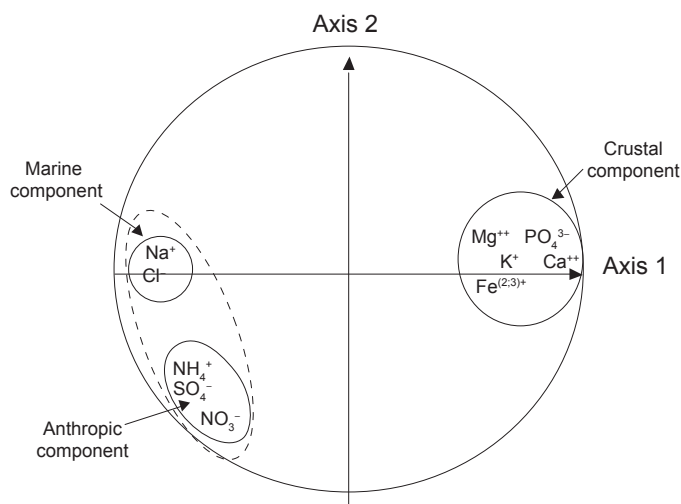(case of the urban site).

Fig. 7. Distribution of the analyzed elements in the correlation
circle (case of the suburban site).

4.2.3 Multiple linear regressions

Multiple linear regressions were used to estimate the relative contributions of the crustal, marine and anthropic sources revealed by PCA analysis. A characteristic explanatory variable was assigned to each natural source. The mass of Cl^- and Na^+ was chosen for the marine source and the mass of Ca^{++}, K^+, Mg^{++} and $Fe^{(2;3)+}$ for the earth crust source. The general relationship for each element X is given by equation (5) below:

$$X = a_1 \cdot \text{Mass}_{\text{Marine elements}} + a_2 \cdot \text{Mass}_{\text{Crustal elements}} + a_3 \qquad (5)$$

where a_1 and a_2 represent the coefficients of regression and the relative contributions of the marine and crustal sources; a_3 represents the residue and expresses the anthropic contribution.

Tables II and III summarize, for each of the analyzed elements, the regression coefficients a_1, a_2 and a_3, the percentage corresponding to each source and the correlation coefficients R^2. The aerosol constituents are shown to be divided into five groups:

i) a first group containing Cl^-, which is fully characterized by a marine contribution, and thereby testifying its purely marine origin;

ii) a second group gathering the elements Ca^{++}, $Fe^{(2;3)+}$, Mg^{++} and K^+ that has null or relatively low marine contributions but very high earth contributions that exceed 100%. This group does not show any contribution of anthropic sources and proves the significance of crustal source influence. The selective disintegration of the crustal particles provides the ground that may justify the excess of 100%. This result is in accordance with Azri *et al.* (2000);

iii) a third group containing PO_4^{3-} which is characterized by no maritime contribution rates and considerable crustal and anthropic contribution rates;

iv) a fourth group containing Na^+, NH_4^+ and $SO_4^=$, which is characterized by significant contributions from various sources. This confirms the existence of multiple sources (marine, crustal and anthropic) for these elements. The third source represented by a_3 is very significant and explains the persistence of residual concentrations, particularly those of NH_4^+ and $SO_4^=$. This is probably explained by the contribution of the atmospheric transformations of sulphur compounds (as secondary aerosol);

v) a fifth group, containing NO_3^-, which actually presents a weak marine contribution (10%), a null earth contribution and a very significant anthropic contribution (113 and 114%). The latter, characterized by a very high residue, provides evidence for the contribution of the atmospheric transformations of nitrogen compounds.

Table II. Coefficient values and contributions of marine, crustal and anthropic sources computed by multiple linear regressions (case of the urban site).

	a_1	% Marine	a_2	% Crustal	a_3	% Anthropic	R_2
Cl^-	0.4328	97	−0.1162	-	−0.0102		0.989
Na^+	0.3821	79	0.0734	14	0.1289	7	0.776
Ca^{++}	−0.1066	-	0.8225	108	−0.0411	-	0.982
Mg^{++}	−0.0029	-	0.0646	104	−0.0168	-	0.714
$Fe^{(2;3)+}$	−0.0201	-	0.1422	311	−0.6716	-	0.852
K^+	0.0033	17	0.0544	132	−0.5804	-	0.873
PO_4^{3-}	−0.0112	-	0.0477	88	−0.1331	42	0.649
NO_3^-	0.0052	8	−0.0212	-	0.0928	114	0.438
$SO_4^=$	0.0869	19	0.0431	12	0.5478	69	0.366
NH_4^+	0.0082	22	0.0048	7	0.0616	71	0.331

Table III. Coefficient values and contributions of marine, crustal and anthropic sources computed by multiple linear regressions (case of the suburban site).

	a$_1$	% Marine	a$_2$	% Crustal	a$_3$	% Anthropic	R$_2$
Cl$^-$	0.4759	98	−0.1031	-	−0.0114		0.993
Na$^+$	0.3909	76	0.0775	12	0.1329	11	0.762
Ca^{++}	−0.1027	-	0.8457	105	−0.0428	-	0.975
Mg^{++}	−0.0034	-	0.0663	102	−0.0157	-	0.739
Fe$^{(2;3)+}$	−0.0193	-	0.1483	341	−0.6721	-	0.821
K$^+$	0.0035	10	0.0569	129	−0.5817	-	0.884
PO$_4^{3-}$	−0.0143	-	0.0484	108	−0.1328	-	0.627
NO$_3^-$	0.0041	12	−0.0236	-	0.0909	113	0.421
SO$_4^=$	0.0879	25	0.0442	10	0.5454	66	0.348
NH$_4^+$	0.0079	20	0.0059	12	0.0633	68	0.346

5. Conclusions and recommendations

The study of the soluble constituents (Ca^{++}, Mg^{++}, Fe$^{(2;3)+}$, Na$^+$, K$^+$, NH$_4^+$, Cl$^-$, NO$_3^-$, SO$_4^=$ and PO$_4^{3-}$) of the aerosol collected at both urban and suburban sites revealed an evident influence emanating from various sources and meteorological factors. It showed that the natural component (marine and crustal) of the aerosol is conditioned by the effect of two antagonistic wind circulations. The contribution of the marine source, in terms of chlorine and sodium, was proved to be marked during spring and summer seasons. On the other hand, the contribution of the continental source, in terms of Ca^{++}, Mg^{++}, Fe$^{(2;3)+}$ and K$^+$, was found to be important during the fall and winter seasons. The contribution of the anthropic sources, in terms of NH$_4^+$, NO$_3^-$, SO$_4^=$ and PO$_4^{3-}$, was demonstrated to be dependent on two prevalent wind directions, namely north-east and south-west, which drain the industrial plume from the city to the studied sites. The current study's statistical approach, which is based on the computation of enrichment factors, on the principal component analysis and on the multiple linear regressions, proved the existence of three principal sources:

i) a natural source including maritime (Cl$^-$ and Na$^+$) and crustal (Ca^{++}, Mg^{++}, Fe$^{(2;3)+}$ and K$^+$) elements;

ii) a "primary" athropic source which threatens the urban site and which is attributed to the local effect of industrial plume fallouts. It concerns the PO$_4^{3-}$ compound in particular;

iii) a "secondary" anthropic source that included NH$_4^+$, NO$_3^-$ and SO$_4^=$ compounds and that resulted from the effect of gas/particles conversion processes. The impact of this source has been proven to be more pronounced on the suburban site than on the urban one. This is probably attributed to the combined effect of the prevalent north-east wind and the course duration of the industrial plume which are relatively more marked in the suburban site.

It is hoped that these findings will encourage further research on atmospheric aerosols. Some of the research areas prompted by our study would include the study of the dry deposition and aerosol size distribution in downtown Sfax and the examined suburban site. The extended monitoring (over many years) of air quality is also required to ensure a better understanding of the geochemical behaviour of secondary aerosols.

Acknowledgement

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