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Statistical analysis of the concentrations of twelve metals in the Ligurian atmospheric aerosol

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Abstract – A correlation analysis based on the concept of singular-value decomposition of a matrix is applied here to an atmospheric aerosol data set, for twelve metals (Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Na, Ni, Pb and Zn) in the Ligurian Sea coastal environment. An iterative procedure allows atypical samples to be discarded, i.e. samples with characteristics significantly different to those of the whole data set. After five atypical samples have been objectively discarded, the general characteristics of the data set are better described and some features are enhanced according to a decreasing order of importance. For example, the mineral dust character of almost every metal is shown, which points out that the marine recycling component is negligible. Marine (Mg, Na) and anthropogenic (Cd, Cu, Pb, Zn) contributions are assessed as well. There is also evidence of some peculiar behaviours: among others, Fe clearly exhibits an anthropogenic component; the remainder of automotive Pb is still apparent; Ni exhibits a relatively high crustal component; Zn, despite its recognized anthropogenic character, is not clearly correlated with other anthropogenic metals. © 2000 Ifremer/CNRS/IRD/Éditions scientifiques et médicales Elsevier SAS

Ligurian Sea / atmospheric aerosol / trace metals / statistical analysis

Résumé – Analyse statistique des concentrations de douze métaux dans l'aérosol atmosphérique ligure. Une analyse de corrélation, basée sur le concept de décomposition d'une matrice en valeurs singulières, permet de décrire le comportement de douze métaux (Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Na, Ni, Pb et Zn) dans l'aérosol atmosphérique de la mer Ligure. Une procédure itérative permet d'écarter les échantillons atypiques, c'est-à-dire ceux dont les caractéristiques sont sensiblement différentes des tendances générales du lot de données. Après que cinq échantillons atypiques aient été écartés objectivement, les caractéristiques générales des échantillons sont décrites et quelques particularités sont mises en valeur, selon un ordre décroissant d'importance. Par exemple, le caractère crustal de chaque métal est mis en évidence, ce qui signifie que la composante de recyclage marin est négligeable. Les contributions à caractère marin (Mg, Na) et anthropique (Cd, Cu, Pb, Zn) sont également évaluées. Certains comportements particuliers sont mis en évidence : entre autres, il existe une composante anthropique de Fe ; le reliquat de Pb automobile est encore largement détectable ; Ni a un caractère détritique relativement fort ; Zn, bien que présentant un caractère anthropique marqué, n'est pas clairement corrélé avec les autres métaux liés aux activités humaines. © 2000 Ifremer/CNRS/IRD/Éditions scientifiques et médicales Elsevier SAS

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1. INTRODUCTION

Many elements are long-range transported by the atmosphere over marine areas. The western Mediterranean is influenced by anthropogenic activities because of numerous land-based emission sources [3]. Another significant source of metals to the western Mediterranean is the Sahara desert; strong, pulsed Saharan dust loads bring large amounts of crustal metals to the sea and the coastal regions [13, 15].

The climate of the Mediterranean Sea (i.e. wet winter and dry summer) is responsible for different removal rates for atmospheric particles [2]. The Mediterranean region is also characterized by strong meteorological events, by anthropogenic as well as by natural sources.

Nevertheless, apart from coarse particles which generally characterize short-term emissions, the residence time of airborne metals is long enough to enable them to spread over the marine areas and make the atmospheric aerosol relatively uniform in space. Despite the important role of meteorological parameters, the spatial variability of metal concentrations over the western Mediterranean Sea has been shown to be relatively low [25].

Thus, assuming that a mean behaviour can be defined for each metal, we attempt to highlight the main characteristics of a selection of twelve metals, discarding all atypical events.

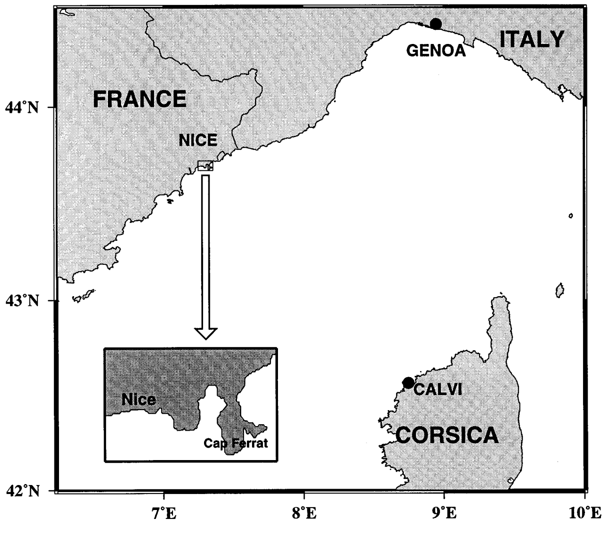

Figure 1. Location of the sampling site.

The distribution of a given element in the atmospheric aerosol is ruled by different parameters, among which the emission sources ostensibly play an important role. Therefore the different types of behaviour observed for a given metal essentially refer to its origin and transport mode.

2. EXPERIMENTAL

2.1. Sampling

The sampling station is located at the peninsula of Cap Ferrat (43° 41′ 10″ N, 7° 19′ 30″ E), on the southeastern French Ligurian coast (*figure 1*). Several previous works have stated that the Cap Ferrat sampling site is representative of the Ligurian coastal environment [13, 18, 19, 25]. The prevailing meteorological influences at Cap Ferrat are:

i) incoming air masses polluted by European emissions, generally from the north and the northeast, as observed as far away as Corsica [16];

ii) Atlantic oceanic air masses, especially in winter;

iii) Saharan dust episodes, occurring most commonly in spring and summer.

Due to its characteristics (a strip of land protruding into the sea), this site is also relatively sheltered from direct crustal sources and is under local marine influences: the average rainfall at Cap Ferrat is approximately 10 % lower than that observed at the neighbouring Nice airport, along the coast. Therefore, the sampling site is hardly subjected to local contamination; samples from Cap Ferrat were previously compared with offshore samples [21] and with samples from more sheltered coastal sites [25]: in both cases, the differences were small (always within a factor of 3). The sampling period extends from December 1994 to January 1996 with a sampling duration of approximately one week. Such a duration is longer than the short-term variability of coarse particles, but the contribution of coarse particles from close emission sources is presumed to be low. This sampling duration supposedly integrates short-term variations; for example, the diurnal variability of airborne metal concentrations cannot be assessed, but the aim of this work is to describe the average chemical composition of the coastal atmospheric aerosol.

Aerosols were collected by pumping surrounding air through a Sartorius membrane (SM 11106, cellulose acetate, porosity 0.45 μm, diameter 47 mm), placed on a filter holder connected to a low-volume pump (Reciprotor 406 G). This sampling apparatus was raised to the top of a 6-m-high mast. The average pumped volume was 128 ± 46 m^3, which collects enough particulate matter for elemental analysis. The standard deviation does not correspond here to any inaccuracy of the flow measurement, but only to the differences between the pumping duration, approximately based on the weekly scale.

2.2. Analysis

The aim here is to use the elemental concentrations in relation to the dust mass collected on the filter surface. The weighing of filters is a critical point in this protocol because the amount of matter is very low (2.8 ± 1.3 mg) compared to the weight of the filters themselves (approximately 70 mg), which varies with the relative humidity of the ambient air.

The accuracy of the balance (Sartorius MC 1) was 0.01 mg. Filters were weighed by series of 15, including five reference samples, and this operation was carried out on a dry day. Petri dishes containing the blank filters were left half-open close to the weighing machine for one hour, in order to be in equilibrium with ambient air. The reference samples were weighed twice, before and after measurement of atmospheric sample filters, in order to verify the lack of drift. The five reference samples were kept in the laboratory and the other ten were brought to the sampling site. At the end of the sampling campaign, the same methodology was used. A correcting factor was deduced from the evolution of the weight of the five reference samples in order to be applied to the atmospheric filters.

Aerosol samples were then dissolved by acid treatment by sets of twelve samples, including two blank filters. Each filter was folded into 4 and introduced into a Teflon bottle (15 mL) in which 900 μL HNO_3 65 % was added. The bottle was closed and put in a larger Teflon bottle (60 mL) and left at room temperature until complete dissolution. The apparatus was kept closed for one night in an oven at 150 °C. Bottles were cooled in a laminar airflow hood and left open until all the red smoke had evolved (which indicates that all HNO_3 has evaporated). The remainder was dissolved again with 200 μL HNO_3 65 % and 200 μL HF 40 % and left for 24 h (without evaporation) prior to being stored again in a drying oven for one night. The white residue was incorporated into 0.5 mL HNO_3 1M, ultrasonically agitated for two hours and made up to 5 mL with Milli-Q water. The solution was finally stored in a polypropylene bottle (8 mL) awaiting analysis. All reagents were provided by Merck (Suprapur quality).

Blank filters were mineralised with the same protocol in order to constitute blank levels.

Analyses were carried out with differential pulse voltammetry for Cd, Zn, Cu, Pb, Ni, Co (EG&G Princeton Applied Research 264 A polarographic analyser in conjunction with a static mercury drop electrode and, for very low concentration levels, a glassy carbon electrode) and by inductively coupled plasma atomic emission spectrometry for Mn, Fe, Mg, Al, Ca and Na (Jobin-Yvon JY 138 Ultrace).

The detection limits and blank values are given in *table I.*

For further information, readers are referred to Migon and Caccia [18] for the sampling site characteristics, and to Migon et al. [20] for analytical details.

The mean concentration values in the atmospheric aerosol are given in *table I*, as well as minimum and maximum values.

3. DATA ANALYSIS

3.1. Method

The data consist of 67 samples from which the relationships between twelve elements (Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Na, Ni, Pb and Zn) are examined. The distribution of elemental concentrations in the atmospheric aerosol being log-normal [11, 18], the use of concentration logarithms is advocated here instead of concentration values themselves.

Table I. Geometric mean metal concentrations (with minimum and maximum values), logarithms of concentrations (with standard deviations), blank values, detection limits and total mass.

	Concentrations ($\mu g \cdot g^{-1}$)			Logarithms of concentrations			
	Geom. mean	Min.	Max.	Mean	Standard deviation	Blank values (ng)	Detection limits ($ng \cdot L^{-1}$)
Zn	1 003	306	3 547	3.001	0.171	12	20
Cd	11.61	3.40	51	1.063	0.206	0.2	1
Pb	1 013	323	1 917	3.006	0.127	2.8	20
Cu	166.3	13	692	2.220	0.247	24	2
Ni	103.8	36	313	2.015	0.184	16	3
Co	2.428	0.3	10	0.386	0.373	0.3	2
Mn	189.6	68	714	2.275	0.179	7.5	900
Fe	6 700	2 740	35 642	3.823	0.189	190	600
Mg	8 739	1 815	20 837	3.946	0.209	615	400
Ca	17 771	6 658	46 864	4.248	0.161	2 510	2 100
Al	5 357	1 373	61 985	3.725	0.285	350	1 500
Na	46 859	3 660	138 194	4.676	0.296	1 300	1 000
Total mass (mg)		0.49	7.04	2.799	1.295		

For the following, the word 'concentration' designates the concentration logarithm.

The analysis is based upon the mathematical concept of singular value decomposition (SVD) of a matrix.

Let A (12, 67) be the matrix of the present data set. The singular value decomposition breaks up A as a product of three matrices:

$$A = L(12, 12) \times S(12, 12) \times R(12, 67)$$

where L and R are the orthonormal matrixes of the left and right singular vectors (LSV and RSV respectively), and S is the diagonal matrix of the singular values, formed with positive real numbers.

This decomposition of the data set deserves its analysis insofar as:

i) it enables a good approximation of the data set with a small number of singular values (and associated LSVs and RSVs);

ii) these singular values are statistically significant;

iii) it is possible to identify underlying signals associated with these singular values.

The singular values are put in decreasing order, and thus the singular vectors are classified according to the decreasing percentage of the total variance that they represent. The analysis is thus reduced to singular vector analysis and it is made easier by the fact that, generally, a small number of singular vectors is sufficient to reconstitute the whole data set. Ultimately, these vectors are orthogonal and thus represent independent information.

In order to estimate the variations around the mean value for each element, the mean concentration is subtracted from each concentration value. Moreover, the concentrations of each element, which are of different orders of magnitude according to the element, are also divided by the standard deviation observed for that element.

An iterative procedure has been implemented in order to:

1. select significant singular vectors; this is achieved by operating a test called 'Rule *N*' [23]; it is based on a Monte Carlo procedure that simulates sampling data from normal independent populations with the same standard deviation, the null hypothesis being that the data matrix A has been drawn from such populations. By comparison of the singular values of the data set with the statistics of the singular values of the random data sets, it is possible to select the number of significant singular values. More precisely, for each singular value, a confidence interval is defined; only singular values that rise above the upper limit of the interval are significant, while singular values under the lower limit are not.

2. discard atypical samples to prevent possible underlying signals (characteristic of the whole data set) from being masked; this is done by examining the RSVs; row j of matrix R contains the coefficients of sample j, used to multiply LSVs in order to reconstitute this sample; the removal of atypical samples is carried out as follows:

let N be the number of samples. For normal populations with the same standard deviation, a RSV has a average value of 0 and a standard deviation of $N^{-1/2}$. Let us fix a confidence interval, e.g. 99 %.

For each of the RSV qualified by 'rule *N*', let us say that samples that exhibit a value outside this confidence interval ($\pm 2.58\ N^{-1/2}$) are atypical and thus discarded.

Some samples may be atypical. Either they exhibit very peculiar characteristics that make them significantly different to the other samples, or they are contaminated or affected by technical problems. Such samples do not reflect the general trends of these concentrations and must therefore be discarded.

3.2. Specificity of the method

Given the present data set (elements × samples), a more classical method such as a principal component analysis would determine the principal components in the space of metals. That is, the diagonal matrix S would be associated with R (and not with L, which remains as it is). Conversely, the SVD formulation holds S and R as separate descriptive entities. The LSVs L (12, 12) are the principal components of the data set in the space of metals, while the RSVs R (12, 67) describe the behaviour of the various samples. Thus, the present method allows, by iterative examination of the singular values S and of the RSVs R, to objectively discard atypical samples and to select significant LSVs L.

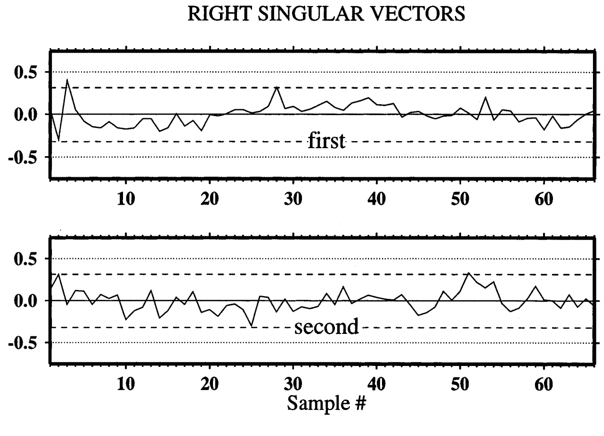

Figure 2. Two first RSVs (raw data). The abscissa is the number of sample; the ordinate is the vector component, each RSV being normal; the dotted lines represent the confidence interval at 99 % (see text).

The SVD technique holds the dimension of the elements and that of samples (which is, in the present case, that of time). The temporal variability, expressed in the RSVs, can thus be analysed separately.

4. CORRELATIONS AND GENERAL BEHAVIOUR

4.1. Atypical points (pointed out by the RSV)

The application of the procedure leads to the following iterations:

1. At the first iteration, SVD is operated on the 'raw' log-transformed data. The 'Rule *N*' test shows that only the two first singular values and associated singular vectors are statistically significant. *Figure 2* shows the first two RSVs. The two dotted lines represent the confidence interval at 99 %. Only some samples reach or exceed these limits: samples 2, 28, 51 and sample 3 which exhibits the highest coefficient (0.41, i.e. approximately 3.3 times the standard deviation).

It is then possible to discuss the reasons for which sample 3 (29 November–2 December 1994) may be chemically different: it exhibits very high concentration levels for Al and Fe (12 and 5.5 times the average concentration value, respectively) and, to a lesser extent, Co and Mn, which is characteristic of a crustal event. Although events from the Sahara generally reach the western Mediterranean regions in spring and summer [7, 15], sample 3 could be a Saharan input, as suggested by prevailing winds from the south (air mass back trajectories were not available). Enrichment factors (EFs) standardized to Al were calculated on the basis of upper Earth's crust data from Wedepohl [26]. EFs are very close to unity for Ca, Co, Fe, Mg, Mn and Na; a slight enrichment is observed for Cu (18) and Ni (12); higher EFs are found for Cd (195), Pb (114) and Zn (55). This does not contradict the crustal origin of this input: atmospheric inputs are generally mixed because of the contribution of different incoming air masses at different barometric levels. Chester et al. [5] and Guieu et al. [13] have previously stated that Mediterranean aerosols have a European anthropogenic background upon which Saharan inputs are episodically superimposed. As far as the very high Al, Co and Fe values are arguments for a Saharan signature, sample 3 is probably the result of the enrichment of a Saharan dust input during its transport over the Mediterranean Sea. Besides, this might also show the limits of the use of enrichment factors, apart from the fact that the concept of average soils (or rocks) used for such calculations is not very meaningful. Although Al is characterized by a high natural variability [8, 25], the concentration level of this sample is exceptionally high (61.985 $\mu g \cdot g^{-1}$ while the average Al value is 6.890 $\mu g \cdot g^{-1}$), with high Co, Fe and Mn values, too, and thus its chemical composition may be atypical.

For samples 2 and 28, plugging of the membrane occurred during the aerosol collection. It is likely to affect the efficiency and the homogeneity of the air pumping, and thus to induce a discrimination of particles according to their size, i.e. according to their chemical composition.

During the collection of sample 51, a lawn was mown in the surroundings of the sampling site, which may have contaminated the sample. As a possible consequence, the total particle concentration is high (5.04 $mg \cdot g^{-1}$ for an average value of 2.8 ± 1.3 $mg \cdot g^{-1}$).

2. At the second iteration (after removal of samples 2, 3, 28, 51), SVD is operated on the remaining samples. Only the two first singular values are statistically significant, and the two first RSVs are examined. Sample 25 is out of the confidence interval and discarded. It is characterized by high Al, Ca, Na and, to a lesser extent, Mg concentration values, while Cd and Pb levels are relatively low. This sample may exhibit a marked crustal character. Indeed, for this sample, air mass back trajectories were available at 700 and 925 hPa, and they indicate that Saharan air masses reached Cap Ferrat in the first days of the sampling period [14].

At the third iteration (after removal of sample 25), once again only the first two singular values are statistically significant (*figure 3*) and the procedure stops because all the samples have coefficients within the limits. The resulting first two LSVs are used for the interpretation of the trace metal general behaviour in the atmospheric aerosol.

4.2. General trends (interpretation of the LSV)

The LSVs are presented in decreasing order of representativity of the variance. According to the validity test, only the two first LSVs can be taken into account. They are recorded in *figure 4.*

LSV 1: explains 35 % of the variation.

Except Na and Mg, all the components of the first LSV have the same sign, which means the concentrations vary jointly for all the selected elements. Indeed, most atmospheric matter loads originate from land-based sources. This is evident for elements with a significant crustal component (e.g., Al, Fe, Mn, Co and, to a lesser extent, Ni). On the one hand, Saharan material exhibits a significant content of Ni, as evidenced by relatively low enrichment factors normalized to aluminium in the aerosol [6]. On the other hand, European crustal aeolian dust samples can also exhibit a relatively high Ni content, perhaps due to the presence of serpentine (fairly abundant, for example, in north Corsica): soils formed on this mineral can contain from 100 to 7 000 $mg \cdot kg^{-1}$ Ni [4]. However, the anthropogenic component of Ni is substantial, too. In particular, oil combustion is responsible for the spreading of significant amounts of Ni [1]. This metal exhibits an intermediate character, as suggested by a correlation with Al less steady than that of Fe or Mn.

Anthropogenic emission sources are land-based, which can lead to a mediocre correlation between anthropogenic metals and crust-derived ones, despite an apparent antagonism. This may explain the slight covariance between Cu and metals of crustal origin, although the Cu crustal component is not negligible either [6, 12, 18].

Among anthropogenic metals, Pb is more steadily linked to crust-dominated metals. This may be due to a specific land-based anthropogenic activity, i.e. a

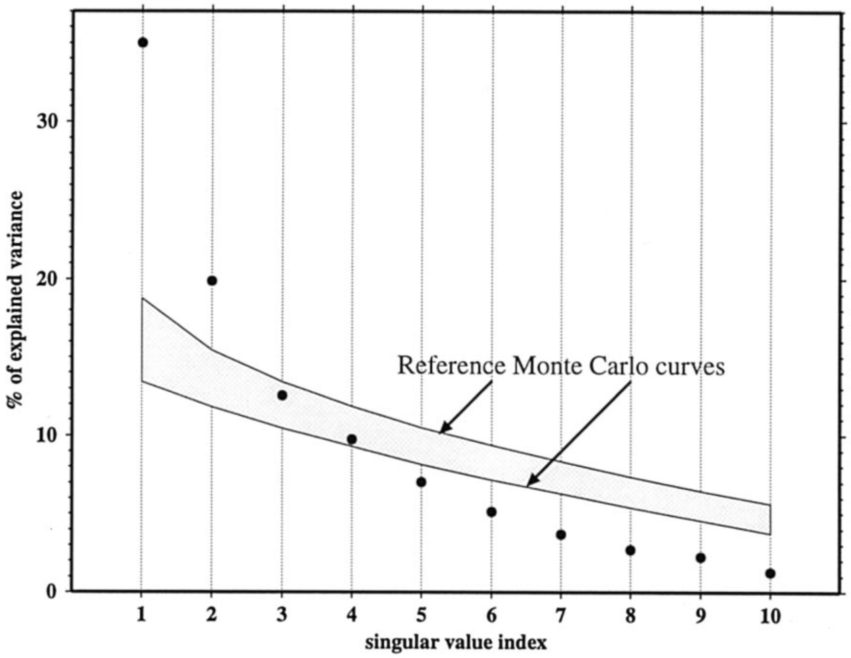

Figure 3. Geometry for 'rule *N*': the shaded segment indicates the 99 % confidence interval along the singular value index axis. Singular values 1 and 2 rise above this segment, which means they are significant. 3rd and 4th singular values are in the intermediate band, where the noisy singular values are. We took into account only the two first singular vectors for the discussion.

remainder of the continuously decreasing automotive exhaust [10, 17]. This specific behaviour was more marked when the contribution of automotive exhaust was great [19].

On the other hand, for Cd and Zn, the strong anthropogenic character dominates the crustal one [18], and there is no observed covariance between these metals and crustal elements. For the case of Cd, this may be also due to its accumulation in the marine surface microlayer, which is relatively efficient in the Ligurian Sea, and the Cd marine recycling component is very significant, if compared with that of Cu, Pb or Zn [22].

Na and Mg mostly originate from sea-salt particles, and this specificity appears here. Ca is abundant in sea-salt particles, but also exhibits a non-negligible crustal component, with amounts of calcite in windblown dust [7, 15]. This mixed origin may explain the fact this element is not correlated with Na and Mg.

LSV 2: explains 20 % of the variance.

Elements of natural origin (crustal + marine) are plotted here against those associated with anthropogenic inputs. Indeed, an anticorrelation appears between Na, Mg, Ca, Al, Fe, Co and Ni (natural), and Cd, Cu, Pb (anthropogenic). The relationship between Ca and Mg is particularly strong, and may be the signature of late spring and summer Saharan influences, i.e. inputs characterized by high calcite content and alkaline properties [9]. Although Fe is unquestionably a crust-dominated metal, the relative weakness of its relation with other elements of natural origin may indicate that Fe anthropogenic component

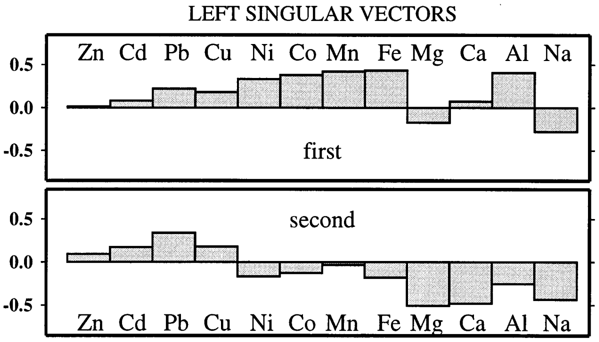

Figure 4. Two first LSVs. The ordinate is the value of the LSV component.

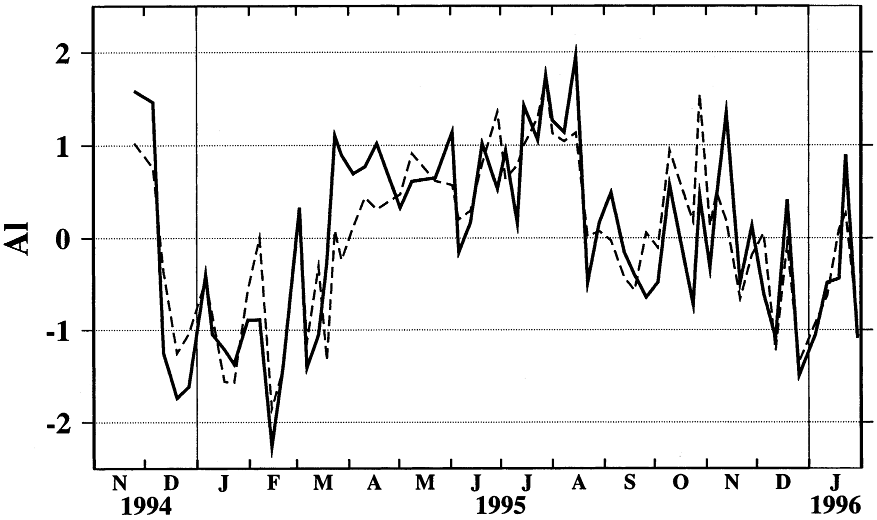

Figure 5. Seasonal variability of Al atmospheric concentrations (logarithms), plotted with the RSV 1, drawn after the removal of atypical samples. The full line is Al data (62 samples) and the dotted line is the first RSV (by a multiplicative factor).

is not negligible [24]. This also applies to Co and Ni.

Mn is really an 'intermediate' element and is not linked with the other metals. Among the urban-dominated elements (Cd, Cu, Pb, Zn), Pb exhibits the strongest anticorrelation with elements of natural origin. Indeed, its natural component is very low, if compared, for example, to that of Cu. Nevertheless, a comparable behaviour was expected for Cd [18]. The lower coefficient associated to Cd may also reflect the marine recycling component observed for this metal.

Surprisingly, Zn is not anticorrelated with metals of natural origin.

It is noteworthy that the profiles of the RSVs are likely to provide an indication of the temporal variability of the main trends that are drawn by the associated LSVs. For example, Al inputs lay out the variability of crustal inputs; the seasonal variability of Al atmospheric inputs is plotted in *figure 5*, in parallel with RSV 1 drawn after the removal of atypical samples. The behaviour underlined by the first LSV ('crustal *versus* marine') exhibits a seasonal variability, which appears in the RSV 1. This variability seems to be governed by climatic and meteorologic constraints. Al inputs (i.e. crustal loadings, including pulsed Saharan events) are mostly brought by southern air masses, in spring and summer essentially [7, 15].

It is more difficult to see a seasonal pattern in the second RSV ('natural *versus* anthropogenic'), probably because most of pollutants are continuously emitted along the northwestern Mediterranean shores. This erratic behaviour might be found in the temporal variability of typically anthropogenic elements such as Cd, Pb or Zn.

5. CONCLUSION

The method used here shows relationships at various levels of representativity of the variance, i.e. relationships of decreasing statistical importance.

The study of RSVs indicates that some events are too rare to be characteristic of the ostensibly homogeneous Ligurian atmosphere. For example, Saharan events may be considered as chemically atypical events, at least when they are not significantly mixed with other air masses. The occurrence of such events cannot be neglected for budget calculations or impact studies (e.g. a couple of Saharan events may represent almost the total annual input of some elements such as Al or Fe), but they should not be taken into account for any description of the chemical background of a given marine aerosol.

In other respects, some correlations may not be linked to similarities between the emission sources.

Other processes occurring during the transport of trace metals in the atmosphere, which involves other parameters (e.g. mean particle size, chemical reactivity, hygrophilia, etc…) may induce another type of covariance. This may be expected at more sheltered sampling sites, but it was not observed at Cap Ferrat, probably because it is relatively close to the emission sources (at least for anthropogenic elements), and it is probably not significantly influenced by the transport processes of the incoming air masses.

Acknowledgements

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REFERENCES

[1] Anwari M.A., Tuncel G., Ataman O.Y., Lead and nickel levels in Black Sea aerosols by ETA-AAS, Intern. J. Environ. Anal. Chem. 47 (1992) 227–237.

[2] Bergametti G., Dutot A.L., Buat-Ménard P., Losno R., Remoudaki E., Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean, Tellus 41B (1989) 353–361.

[3] Béthoux J.P., Courau P., Nicolas E., Ruiz-Pino D., Trace metal pollution in the Mediterranean Sea, Oceanol. Acta 13 (4) (1990) 481–488.

[4] Brooks R.R., Serpentine and its vegetation, Croom Helm, London, 1987.

[5] Chester R., Nimmo M., Alarcon M., Corcoran P., The chemical character of the Northwestern Mediterranean aerosol, EROS 2000 3rd Workshop, October 1991, Texel, The Netherlands, Wat. Pollut. Res. Report 28 (1992) 495–504.

[6] Chester R., Sharples E.J., Sanders G.S., Saydam A.C., Saharan dust incursion over the Tyrrhenian Sea, Atmos. Environ. 18 (5) (1984) 929–935.

[7] De Angelis M., Gaudichet A., Saharan dust deposition over Mont Blanc (French Alps) during the last 30 years, Tellus 43B (1991) 61–75.

[8] Dulac F., Buat-Ménard P., Arnold M., Ezat U., Martin D., Atmospheric input of trace metals to the western Mediterranean Sea: 1, Factors controlling the variability of atmospheric concentrations, J. Geophys. Res. 92 (D7) (1987) 8437–8453.

[9] Durand P., Neal C., Lelong F., Anthropogenic and natural contributions to the rainfall chemistry of a mountainous area in the Cevennes National Park (Mont-Lozere, southern France), J. Hydrol. 130 (1992) 71–85.

[10] Flament P., Deboudt K., Bertho M.L., Puskaric E., Changes in the lead content of atmospheric aerosols above the Eastern Channel between 1982–83 and 1994, Sci. Total Environ. 192 (1996) 193–206.

[11] Georgopoulos P., Seinfeld J., Statistical distributions of air pollutant concentrations, Environ. Sci. Technol. 16 (1982) 27–35.

[12] Grousset F., Buat-Ménard P., Boust D., Tian R.C., Baudel S., Pujol C., Vergnaud-Grazzini C., Temporal changes of aeolian Saharan input in the Cape Verde abyssal plain since the last Glacial period, Oceanol. Acta 12 (2) (1989) 177–185.

[13] Guieu C., Chester R., Nimmo M., Martin J.M., Guerzoni S., Nicolas E., Mateu J., Keyse S., Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean, Deep-Sea Res. II 44 (3–4) (1997) 655–674.

[14] Journel B., Apports atmosphériques de métaux en mer Ligure : caractérisation géochimique et devenir dans la colonne d'eau (site Dyfamed), PhD Thesis, univ. Aix-Marseille, 1998, 275 p.

[15] Loÿe-Pilot M.D., Martin J.M., Morelli J., Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean, Nature 321, 6068 (1986) 427–428.

[16] Loÿe-Pilot M.D., Morelli J., Fluctuations of ionic composition of precipitations collected in Corsica related to changes in the origin of incoming air masses, J. Aerosol Sci. 19 (5) (1988) 577–585.

[17] Migon C., Alleman L., Leblond N., Nicolas E., Evolution of atmospheric lead over the northwestern Mediterranean between 1986 and 1992, Atmos. Environ. 27A (14) (1993) 2161–2167.

[18] Migon C., Caccia J.L., Separation of anthropogenic and natural emissions of particulate heavy metals in the western Mediterranean atmosphere, Atmos. Environ. 24A (2) (1990) 399–405.

[19] Migon C., Gentili B., Application of objective analysis to metallic traces in the atmospheric aerosol, J. Atmos. Chem. 16 (1993) 277–284.

[20] Migon C., Journel B., Nicolas E., Measurement of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea, Atmos. Environ. 31 (6) (1997) 889–896.

[21] Migon C., Morelli J., Nicolas E., Copin-Montégut G., Evaluation of total atmospheric deposition of Pb, Cd, Cu and Zn to the Ligurian Sea, Sci. Total Environ. 105 (1991) 135–148.

[22] Migon C., Nicolas E., The trace metal recycling component in the northwestern Mediterranean, Mar. Pollut. Bull. 36 (4) (1998) 273–277.

[23] Preisendorfer R.W., in: Mobley C.D. (Ed.), Principal component analysis in meteorology and oceanography, Elsevier, Amsterdam, 1988.

[24] Remoudaki E., Étude des processus contrôlant la variabilité temporelle des flux atmosphériques de polluants et de poussières minérales en Méditerranée occidentale, PhD Thesis, univ. Paris-7, 1990, 224 p.

[25] Sandroni V., Migon C., Significance of trace metal medium-range transport in the western Mediterranean, Sci. Total Environ. 196 (1997) 83–89.

[26] Wedepohl K.H., The composition of the continental crust, Geochim. Cosmochim. Acta 59 (7) (1995) 1217–1232.