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Trend in total atmospheric deposition fluxes of aluminium, iron, and trace metals in the northwestern Mediterranean over the past decade (1985-1997)

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Abstract. The total atmospheric deposition of aluminium (Al), cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) on the northwestern coast of Corsica (Pirio) was sampled for two years, and their respective concentrations were measured during that period. The sampling station was chosen for its isolation from any local and regional sources of contamination. The year-to-year variability of the total atmospheric deposition was found to be high (up to a factor of 2). Using Al as the crustal reference indicates that Pb, Cd, and Zn are mainly associated with man-made aerosols (> 85%), and Fe is mainly associated with crustal aerosols (> 70 %). However, our results indicate that Saharan dust is a potential source of "natural" lead, especially in the case of a major input of dust to the northwestern Mediterranean. To determine the spatiotemporal variability of the trace metals over the northwestern Mediterranean Sea, the observed fluxes were compared to those found in the past decade using the same methodology. The comparison indicated a relative homogeneity of Cu and Ni fluxes over the northwestern Mediterranean and over the past decade. The decrease found in Al and Fe since 1985 (by a factor of 4 to 6) can be related to the decrease in Saharan dust fallout. The limitation in the use of lead additives in gasoline may have resulted in a decrease in the European atmospheric lead emissions by a factor of about 6 since 1985 and in a maximum decrease in the total atmospheric flux by a factor of 12 at most if the natural interannual variability of atmospheric deposition in this region is taken into account. So the recorded decrease in the atmospheric lead flux since 1985 (by a factor of ~30) reveals a slight local contamination at the earlier Corsican station. In the case of Cd and Zn, there was a decrease by a factor of 30 and 23, respectively, between the data obtained at La Tour du Valat (July 1988 to June 1989) and those at Pirio (March 1996 to March 1997); such a decrease cannot be the consequence of either a reduction in emissions in Europe as a whole (the factor being at most 4), or the distance from the emission sources. Hence, we can confirm that Zn and Cd fluxes at La Tour du Valat and Zn fluxes at Cap Ferrat were not representative of a long-range transport to the Mediterranean but the result of a local/regional contamination. The large decrease observed for metals (Cd, Zn, and Pb) mainly mobilized by human activities, results from a combination of the actual diminution of the concentrations due to a reduction in the emissions and the occurrence of local/regional contamination for some elements at some sampling sites.

1. Introduction

In recent years, several studies have shown that the atmosphere is the main transport pathway for trace metals to marine waters [Patterson and Settle, 1987; Martin et al., 1989; Bergametti et al., 1989; Duce et al., 1991; Jickells, 1995]. The atmospheric input of these components has an impact on biological processes in the sea [see, for example, Fitzwater et al., 1982; Duce and Tindale, 1991] and on marine biogeochemical cycles.

The input of trace metals from the atmosphere to the water column is particularly important in a semi-enclosed sea like

the Mediterranean [Bergametti et al., 1989; Chester et al., 1981, 1993; Dulac et al., 1987; Guieu et al., 1991, 1993, 1997; Martin et al., 1989; Migon et al., 1991, 1997]. The northwestern Mediterranean Sea, in particular, is a very interesting case study as regards the atmospheric input, because the atmospheric chemistry is dominated by the antagonistic influences of natural (mainly from the south of the basin: the Sahara) and human (mainly from the north of the basin) sources [see, for example, Dulac et al., 1987; Bergametti et al., 1988, 1989; Chester et al., 1981, 1984, 1993; Guerzoni et al., 1988; Loÿe-Pilot and Morelli 1988; Loÿe-Pilot et al., 1986, 1990; Migon and Caccia 1990; Guieu et al., 1997]. In fact, the composition of the atmosphere in the northwestern Mediterranean is dominated by the human signature upon which are superimposed different Saharan inputs [Martin et al., 1989; Chester et al., 1993; Guieu et al., 1997]. The Mediterranean Sea also receives a substantial quantity of pollutant trace metals from rivers, but the impact of riverine discharge is limited to the coastal areas [Martin et al., 1989; Migon, 1993; Guieu et al., 1993, 1997].

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In the last decade, several studies have been undertaken at coastal sites in the northwestern Mediterranean, covering various periods and using various methods to characterize the atmospheric fluxes of trace metals to the marine environment [Bergametti, 1987; Migon, 1988; Chester *et al.*, 1990; Guieu, 1991; Remoudaki, 1990; Migon *et al.*, 1997]. The comparison of the data from four Mediterranean stations has shown a relative homogeneity in the average aerosol concentrations over the northwestern Mediterranean Sea, but high spatial variations in the total deposition flux were found for some metals, such as Zn and Cd [Guieu *et al.*, 1997]. This suggests a specific local or regional contamination by cadmium and zinc at the sites having the highest fluxes. The choice of a remote site is therefore mandatory in order to determine actual fluxes of trace metals to the open waters of the northwestern Mediterranean.

The different aims of this study are to evaluate, at a remote station, the total atmospheric fluxes of trace metals, in particular, Zn, Cd, and Pb, and to determine the spatiotemporal variability of these mean fluxes in the northwestern Mediterranean Sea by comparing our results with previously published data over the past decade.

2. Material and Methods

2.1. Sampling Station

The sampling site was established at Pirio (42°21' N, 8°44' E, 350 m above sea level) on the northwestern coast of Corsica (Figure 1). This station was chosen because of its isolation from any contamination sources (road, wire fencing, smoke, automobile traffic) and because it was far away from any industrialized area or intensive agriculture zone. The site, which is 9 km from the sea, is under marine influence. The marine fraction makes up 65% of the major element inputs [Loÿe-Pilot, 1995]. The soil surface consists of hard rocks (rhyolite) or is covered by vegetation; hence local dust from the resuspension on soil particles in the atmosphere is negligible. Pirio represents a quite good observatory for air quality in the northwestern Mediterranean Sea [Loÿe-Pilot, 1995].

2.2. Collection

The total atmospheric deposition (bulk deposition) was collected continuously from January 27, 1995, to March 18, 1997, in 12 samples representing time periods ranging from 28 to 132 days. The collector was made of a 4 L polyethylene bottle placed on a 1.7-m-high wood stack. A polyethylene funnel was placed on top of the bottle (surface: 113 cm²). A nylon mesh (porosity: 40 µm) covered the funnel in order to prevent insects and organic debris from falling inside the bottle. For each sample, the funnel was rinsed at the end of the sampling period with ultrapure water before a new bottle was set up.

From aerodynamic considerations, it might seem that the dry deposition could be underestimated by such a collector. However, the intercomparison between such a device and other bulk collectors used at other sites (Tour du Valat, Capo Cavallo) indicated that the efficiency was the same in both cases [Remoudaki *et al.*, 1991]. Our conclusions on the spatial and temporal trends are therefore valid in spite of a probable slight underestimation of the total fluxes reported here.

2.2.1. Conservation. After collection, the samples were carried back to the laboratory in Montrouge, where they were transferred to a clean room and weighed. Samples were acidified to pH~2 (HNO₃ suprapur-Merck) to desorb metals that might have stuck on the bottle walls and to avoid algal development.

2.2.2. Field blank. A field blank was made to estimate possible contamination introduced during transport and/or generated by the reagents and/or by the operator. In the field, a given volume of ultrapure water was poured into a clean collector. The same protocol as for the other samples was then followed. The metal content was found to be negligible, representing only 10% of the lowest value measured in the samples.

2.2.3. Cleaning procedure. All the plastic used was of high-density polyethylene (Nalgene); the material was prepared inside a clean room: the bottles and funnels were soaked in a Decon bath for one week, then they were soaked for two weeks in a 50% HCl bath, then they were rinsed with ultrapure water. For the transport to and from the sampling station, the bottles were kept inside a double plastic bag.

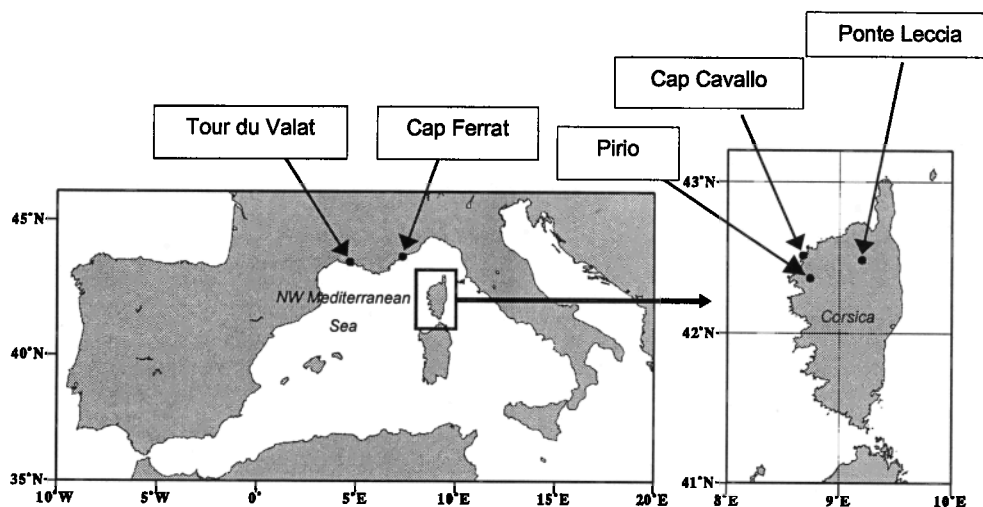


Figure 1. Map of the northwestern Mediterranean showing the location of the Pirio sampling site along with those of the other sites discussed in the present paper.

Table 1. Characteristics of the Sampling and Analytical Procedures Used at the Different Sites in the Northwestern Mediterranean

| | Type of Device | Surface, cm ² | Analysis | Duration of One Sample, days |
|-------------------|---|--------------------------|---|------------------------------|
| Capo Cavallo (1) | "Crapal" acidified to pH 1 | 1020 | acid soluble fraction + insoluble fraction*, AAS + SFX | 4 to 75 |
| Tour du Valat (2) | "Crapal" acidified to pH 1 | 1020 | evaporation of an aliquot, digestion, AAS | 30 |
| Cap Ferrat (3) | Filtration kit filled-up with acidified seawater | 50 | acid-soluble fraction, AAS | 7 |
| Pirio This Study | 4-l bottle with funnel | 113 | total evaporation/digestion, AAS | 28 to 132 |

(1) *Bergametti* [1987] and *Remoudaki* [1990]. (2) *Guieu* [1991]. (3) *Migon et al.* [1997]. AAS, atomic absorption spectrometry; SFX, fluorescence X spectrometry. Crapal: device used originally by the French Commissariat à l'Energie Atomique, made of plexiglass.

* Acid-soluble fraction for Pb only.

2.3. Preparation of the Samples and Analysis

To solubilize the particulate phase before analysis by atomic absorption spectrometry (AAS), the samples were entirely evaporated inside a 1 L Teflon beaker on a hot plate ($T \approx 220^\circ\text{C}$) and then acid digested (inside a Milestone 1200 Mega microwave oven). The evaporation procedure and the acid digestion are fully described by *Ridame* [1997]. SLRS-3 reference material (National Council of Canada) was used to evaluate the reliability of the evaporation phase; recovery was satisfactory and reproducible. Eight aliquots (17.4 to 41.5 mg) of MESS-2 reference material (National Council of Canada) were digested in the microwave oven to test the reliability of the acid digestion. Five reagent blanks were performed to test the contaminant effect of the nitric acid used for the digestion. The samples were analyzed by graphite-furnace atomic-absorption spectrometer (Varian AAS 800 Spectra) in order to determine the metal concentrations. A standard addition method was used for Cd, Cu, Mn, Al, and Ni; for Fe, Zn, and Pb, the concentrations were calculated from the calibration curve. Triplicate measurements were performed, and the reproducibility was found to be between 0 and 5% for all the metals analyzed.

Results obtained on the certified reference material indicate the high accuracy of the analyses: the mean recoveries for Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn were, 93 ± 8 , 100 ± 5 , 90 ± 9 , 87 ± 7 , 91 ± 10 , 106 ± 11 , 88 ± 6 , and $97 \pm 9\%$, respectively. The low standard deviations (within about $\pm 10\%$) demonstrate good reproducibility of results. The blank values were below the detection limit.

2.4. Selection of Comparable Data

To assess the spatial and the temporal variability of the metal fluxes in the northwestern Mediterranean Sea, the fluxes obtained during a two-year survey at our remote sampling site will be compared, in section 3, with the surveys previously carried out for various Mediterranean sites (Tables 1 and 4). In this discussion, we shall consider only data sets obtained for a representative sampling period and for comparable sampling procedures. Similar fluxes have been determined since 1985 at only three coastal stations: Cap Cavallo [*Bergametti*, 1987; *Remoudaki*, 1990; *Remoudaki et al.*, 1991], Cap Ferrat [*Migon et al.*, 1997] and Tour du Valat [*Guieu*, 1991, *Guieu et al.*, 1993, 1997] (Figure 1). The characteristics of the various devices used and the sampling protocol at each site are detailed in Table 1.

In the discussion of the terrigenous elements (Al, Fe), data from the Pirio station will be compared with the Saharan dust input recorded at another Corsican station, Ponte Leccia ($42^\circ 21' \text{N}$, $9^\circ 12' \text{E}$) (Figure 1). The procedure used for the determination of the Saharan dust input at this site is described by *Loÿe-Pilot et al.* [1986] and *Loÿe-Pilot and Martin* [1996].

3. Results and Discussion

The total deposition fluxes for each sample measured for 26 months are given in Table 2 and are expressed in $\text{mg} \cdot \text{m}^{-2}$. To compare our results with those previously published and to discuss the temporal evolution, it was necessary to consider the fluxes for a one-year period. For this reason, two annual fluxes were derived from the present data (annual flux year 1: samples P2→P6 (March 14, 1995, March 13, 1996); annual flux year 2: samples P7→P12 (March 13, 1996, March 18, 1997)). Fluxes recorded at the other sites were also recast in one-year periods (see Table 4).

3.1. Variability of the Fluxes Measured at Pirio

The mean fluxes of Pb, Cu, and Ni (year 1 - year 2) were very similar: 1.1-0.7, 1.4-0.7, and 0.4-0.4 $\text{kg} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$, respectively (Table 2). The lowest flux was observed for Cd: 0.07-0.04 $\text{kg} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$; this metal has been shown, on the global scale, to have the lowest values of man-made and crustal emissions in comparison to other metals [*Nriagu*, 1989]. The mean fluxes of Zn and Mn are similar: 6.1-4.2 and 6.5-6.3 $\text{kg} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$, respectively. The terrigenous elements, Al and Fe, present the highest values of mean fluxes: 171-270 and 118-156 $\text{kg} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$, respectively. The maximum interannual difference is found to be a factor of 2 at Pirio, as at other sites.

Histograms representing the temporal variation in the fluxes are presented in Figure 2 (monthly fluxes in $\mu\text{g} \cdot \text{m}^{-2}$ for each sample). Because the samples were not all collected during the same sampling period, the variability of the total atmospheric fluxes can be calculated only on the limited set of five samples having similar sampling durations (about 55 days): P4→P8 (September 27, 1995, June 30, 1996). The coefficient of variation calculated for the corresponding fluxes was high: Al→86%; Zn→85%; Cu→73%; Fe→70%; Cd→67%; Mn→58%; Ni→56%; and Pb→41%. A similar range for this coefficient was already established by *Guieu et*

Table 2. Bulk Atmospheric Fallout of Metals Corresponding to Each Sample and Annual Fluxes for Two Yearly Periods

| | Sampling Period (Number of Days) | Al, mg. m ⁻² | Fe, mg. m ⁻² | Mn, mg. m ⁻² | Zn, mg. m ⁻² | Cu, mg. m ⁻² | Pb, mg. m ⁻² | Ni, mg. m ⁻² | Cd, mg. m ⁻² |
|---|---|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| P1 | Jan. 27 to March 14, 1995 (46) | 17.6 | 8.4 | 0.3 | 0.31 | 0.20 | - | 0.05 | 0.007 |
| P2 | March 14 to July 24, 1995 (132) | 38.8 | 28.7 | 2.8 | 3.38 | 0.91 | 0.31 | 0.12 | 0.017 |
| P3 | July 24 to Sept. 27, 1995 (64) | 39.8 | 29.4 | 1.9 | 1.37 | 0.30 | 0.23 | 0.09 | 0.014 |
| P4 | Sept. 27 to Nov. 20, 1995 (54) | 30.9 | 18.5 | 0.6 | 0.24 | 0.03 | 0.14 | 0.04 | 0.004 |
| P5 | Nov. 20, 1995, to Jan. 18, 1996 (59) | 46.1 | 29.6 | 0.8 | 0.52 | 0.05 | 0.15 | 0.08 | 0.021 |
| P6 | Jan. 18 to March 13, 1996 (54) | 14.5 | 10.8 | 0.4 | 0.53 | 0.07 | 0.24 | 0.06 | 0.011 |
| P7 | March 13 to May 4, 1996 (52) | 96.6 | 50.6 | 1.6 | 0.39 | 0.06 | 0.24 | 0.14 | 0.007 |
| P8 | May 4 to June 30, 1996 (57) | 17.6 | 14.1 | 1.4 | 1.72 | 0.19 | 0.09 | 0.05 | 0.005 |
| P9 | June 30 to Sept. 14, 1996 (76) | 113.9 | 63.9 | 2.0 | 0.80 | 0.25 | 0.08 | 0.14 | 0.010 |
| P10 | Sept. 14 to Dec. 5, 1996 (82) | 11.2 | 6.7 | 0.8 | 0.90 | 0.16 | 0.12 | 0.05 | 0.015 |
| P11 | Dec. 5, 1996, to Feb. 18, 1997 (75) | 32.3 | 22.1 | 0.5 | 0.35 | 0.06 | 0.19 | 0.06 | 0.005 |
| P12 | Feb. 18 to March 18, 1997 (28) | 2.3 | 0.5 | 0.1 | 0.07 | 0.01 | 0.01 | 0.01 | 0.001 |
| Annual fluxes kg km ⁻² y ⁻¹ | | | | | | | | | |
| P2 → P6 | annual flux year 1 (363) | 171 | 118 | 6.5 | 6.1 | 1.4 | 1.1 | 0.4 | 0.07 |
| P7 → P12 | annual flux year 2 (370) | 270 | 156 | 6.3 | 4.2 | 0.7 | 0.7 | 0.4 | 0.04 |

al. [1991] from the La Tour du Valat data set. In that study, since the wet deposition was found to be more variable than the dry deposition, the authors suggested that part of the variability of atmospheric deposition may be attributed to rainfall fluctuations. Although some correlation between the ratio of dry to total flux and rainfall was observed for Cu, no general satisfactory correlation could be clearly established for the other elements.

3.2. Sources of the Metals

Each sample represents an integration of the total atmospheric fallout for periods of various duration (from 28 to 132 days). In these conditions, a single sample represents the mixing of fallout from air masses of different origins, with different loads of pollutants and natural aerosols. To identify the main sources of metals, aluminium is used as a tracer of the crustal particles. However, in this study, we do not use the mean crustal Al content as the crustal reference, since it is not representative of surface soils which are the source of atmospheric terrigenous components [Schütz and Rahn, 1982; Hong et al., 1996]. In Corsica, as in the open northwestern Mediterranean, the terrigenous component is mostly made up of Saharan dust, which represents 90% of the total particulate input [Loÿe-Pilot and Martin, 1996].

The choice of a representative range of concentration for a given element in the crustal material is an important question. In fact, few data are available in the literature concerning the concentrations or the metal/Al ratio in the Saharan end-member. Furthermore, it was shown by Guieu and Thomas [1996] that the so-called "Saharan aerosols" collected in the

northern part of the Mediterranean Sea can easily be contaminated by man-made aerosols locally or during their transport over the Mediterranean [see also Chester et al., 1984]. This finding limits the choice of references and the range that we have chosen, since it may not exactly be representative of the Saharan end-member. On top of this approximation, these Saharan aerosols are not homogeneous over the source regions. Five different references were chosen (see Table 3): three of them were the concentrations established for the erodible or upper crust [Masson, 1982; Martin and Whitfield, 1983; Wedepohl, 1995]; one of them was a "typical" Saharan end-member [Guieu and Thomas, 1996]; and one of them was the particulate phase of a major Saharan rain [Guieu, 1991]. The metal/Al ratio was calculated for each reference. Figure 3 and Figures 4a and 4b show the upper and lower range of the ratio obtained from these references, hence possibly delimiting the "area" in which the "Saharan end-member" may be located.

The average Fe/Al flux ratio in the atmospheric samples was similar to that of the Saharan end-member (Figure 3, solid line), indicating that iron is mainly associated with crustal particles originating from the Sahara desert in the samples collected in Corsica. For all the samples, Mn, Ni and Cu have a metal/Al ratio higher than that of the Saharan end-member, indicating that these metals are partly associated with a different type of particle, probably produced by human activities. The metal/Al ratio for Pb, Cd, and Zn is much higher than that found in the Saharan end-member, indicating that they may be borne by aerosols generated by human activities. Nevertheless, for one sample, the Pb/Al ratio is

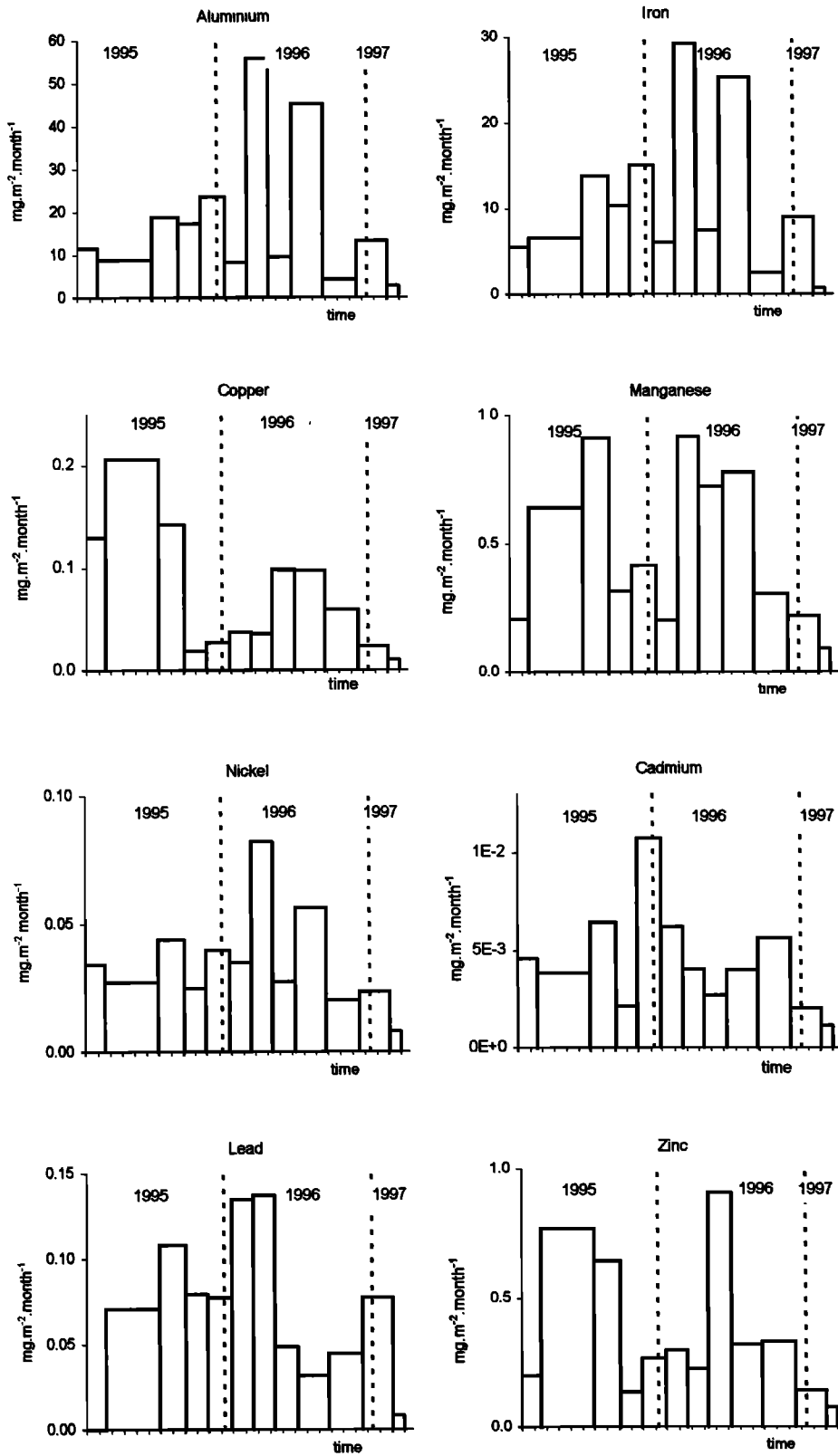


Figure 2. Temporal variation in of the total atmospheric fluxes mg. m⁻² per month measured at the Pirió station from 27 January 1995 to 18 March 1997. Each histogram bar represents a month.

Table 3. Five Different Crustal References and the Minimum and Maximum Associated Values of the Metal/Aluminium ratio

| | Reference | | | | | (Me/Al) min | (Me/Al) max |
|---------|-----------|------|------|-------|------|-------------|-------------|
| | [1] | [2] | [3] | [4] | [5] | | |
| Al, % | 8.13 | 6.93 | 7.3 | 7.74 | 7.4 | - | - |
| Fe, % | 5 | 3.59 | 5.04 | 3.089 | 4.6 | 0.399 | 0.690 |
| Cu, ppm | 55 | 32 | 30 | 14.3 | 23 | 1.85E-4 | 6.77E-4 |
| Mn, ppm | 950 | 720 | 502 | 527 | 880 | 6.81E-3 | 1.19E-2 |
| Ni, ppm | 75 | 49 | 50 | 18.6 | 30 | 2.40E-4 | 9.23E-4 |
| Cd, ppm | 0.2 | 0.2 | - | 0.102 | 0.13 | 1.32E-6 | 2.89E-6 |
| Pb, ppm | 13 | 16 | - | 17 | 25 | 1.60E-4 | 3.38E-4 |
| Zn, ppm | 70 | 127 | - | 52 | 76 | 6.72E-4 | 1.83E-3 |

Read $1.85E^{-4}$ as 1.85×10^{-4} . [1] upper crust *Masson* [1982]; [2] erodible crust *Martin and Withfield* [1983]; [3] composition of the particulate phase of a typical Saharan rain collected at la Tour du Valat *Guieu* [1991]; [4] upper crust *Wedepohl* [1995]; [5] elemental composition in the fine fraction ($<50\mu\text{m}$) of Saharan soils (average of 5 samples) *Guieu and Thomas* [1996].

close to the Pb/Al ratio found in the Saharan end-member; this finding is explained below.

In an attempt to quantify the contribution of the man-mobilized fraction for each metal, the enrichment factors and the excess fraction were calculated. The various metal/aluminium ratios (Me/Al) determined in the above-mentioned studies were used in the calculation. The enrichment factor is given by

$$EF_{Al} = \frac{\left(\frac{Me}{Al}\right)_{\text{sample}}}{\left(\frac{Me}{Al}\right)_{\text{Saharan or crustal reference}}} \quad (1)$$

The excess fraction derived from this calculation represents the fraction (percentage) of nonterrigenous origin and is given by the following formula:

$$X_s = \frac{100}{Me_{\text{sample}}} \times \left[Me_{\text{sample}} - \left(Al_{\text{sample}} \times \left(\frac{Me}{Al}\right)_{\text{Saharan or crustal reference}} \right) \right] \quad (2)$$

The enrichment factor and the excess fraction were calculated for Cd, Cu, Fe, Mn, Ni, Pb, and Zn over the whole sampling period and are given in Figures 4a and 4b. A percentage ranging from 75 to 100% of iron flux was associated with crustal aerosols. At least 50% of Mn is associated with noncrustal aerosols; this number varied highly from one sample to the other, indicating the high variability of the human Mn input. Metals such as Cu and Ni are mainly associated with noncrustal particles (excess fractions of 71-92% and 58-89%, respectively) even though the crustal fraction is not negligible. The coefficients of variation were relatively low for Cd and Zn (1% and 5-13%), and were typically associated with noncrustal aerosols with an excess fraction of 99% and 87-95%, respectively.

On average, 89-95% of the Pb was associated with man-mobilized aerosol. However, as mentioned earlier, one sample (P9) where the excess fraction was lower (51-77%) indicated that up to 50% of Pb in this sample was associated with aerosols of crustal origin. Indeed, during the P9 sampling period, a major Saharan event was recorded at the Ponte

Leccia sampling station. This rain event lasted for two days; it carried a dust flux of 1.7 g. m^{-2} . The high aluminium flux in P9 (114 mg. m^{-2}) can be entirely attributed to this "red rain". The Sahara desert is thus a potential source of "natural" lead in the event of a major input of dust to the northwestern Mediterranean. Assuming that the Saharan dust had a Pb concentration ranging from 13 to 25 ppm (Table 3), the calculation indicated that the Saharan event recorded during P9 provided a natural Pb input of 22-43 $\mu\text{g. m}^{-2}$, which represented 30-55% of the total atmospheric lead flux established for the P9 sample. For the two years considered, with an Al flux of $171\text{-}270 \text{ kg. km}^{-2} \cdot \text{y}^{-1}$ and an Al content in the Saharan end-member ranging from 6.93 to 8.13%, the flux of natural lead originating from the Saharan source can be roughly estimated to be within 3-10% of the total atmospheric lead flux. However, the excess fractions of Cd and Zn for this sample P9 (97-98% and 74-90%, respectively) indicated that, even with an important Saharan event during the sampling period, these elements were still predominantly man-mobilized.

These results are in good agreement with the inventories of human sources of metals [*Nriagu*, 1989; *Pacyna*, 1984, 1998] and with previous results from various coastal sites of the northwestern Mediterranean [*Guieu et al.*, 1997]. The present results confirmed that Mediterranean aerosols have an important man-made background [*Martin et al.*, 1989; *Chester et al.*, 1993; *Guieu et al.*, 1997].

3.3. Evolution of the Fluxes Over the Past Decade

To assess the spatial and temporal variability of the metal fluxes in the northwestern Mediterranean Sea, the two annual fluxes measured at our remote site were compared with those previously observed at selected Mediterranean sites (see section 2). Considering the whole data set (Table 4), the mean fluxes for Ni and Cu were quite similar, indicating little spatial and temporal variability of the total atmospheric flux over the studied area during the past decade. For other trace metals, important variations were observed from one site to another. We shall discuss the cases of (1) the terrigenous components (Al and Fe) and (2) the man-mobilized components (Cd, Zn, and Pb).

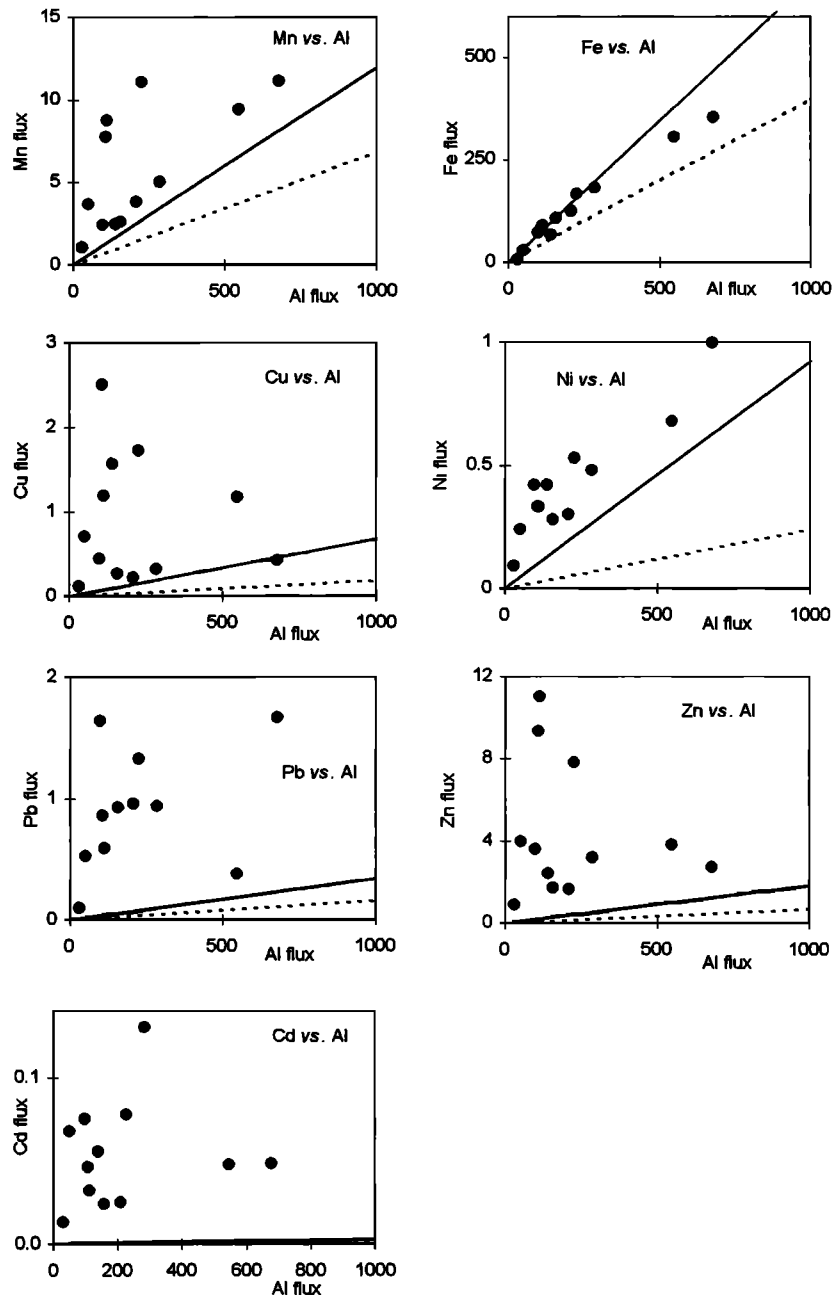


Figure 3. Metal versus aluminium in the total atmospheric deposition. The lines indicate the minimum (.....) and maximum (—) metal / aluminium ratio in the various Saharan or crustal references (Table 3).

3.3.1. Terrigenous components: Al and Fe. The annual flux of Al (171-270 kg. km⁻². y⁻¹) obtained in this study was similar to the measured mean flux at Cap Ferrat for 1995: 283 ± 520 kg. km⁻². y⁻¹ reported by *Journel* [1998]. The annual fluxes at the Pirio station were lower by a factor of 4-6 when compared to the average fluxes established at the other stations (Cap Cavallo and Tour du Valat) since 1985 (Figure 7a). Since a spatial difference in the Saharan fluxes between the two Corsican sites (Cap Cavallo and Pirio; same elevation; distance between the sites: ~25 km) and even between Corsica and the French coast is not likely, this trend corresponds to a decrease in the Saharan dust input in the past decade [*Loÿe-Pilot and Martin, 1996*] (Figure 5). A dust flux was calculated

from the Al fluxes established at the Pirio station for 1995 (P1 → P5) and 1996 (P6 → P11) assuming an Al concentration of 6.93-8.13% in the Saharan dust. This computed flux for 1995 and 1996 was in good agreement with the values measured at Ponte Leccia during the same time period (Figure 5). The measured and calculated fluxes of dust for 1995 and 1996 confirm the decrease in the Saharan dust fallout recorded since 1987 [*Loÿe-Pilot and Martin, 1996*]. Accordingly, the flux of Fe at the Pirio station (118-156 kg. km⁻². y⁻¹) is lower by a factor of 4-6 compared to 1987.

3.3.2. Man-mobilized components. Zn, Cd and Pb. The annual fluxes of Zn (6.1-4.2 kg. km⁻². y⁻¹) and Cd (0.07-0.04 kg. km⁻². y⁻¹) at the Pirio station were among the lowest values

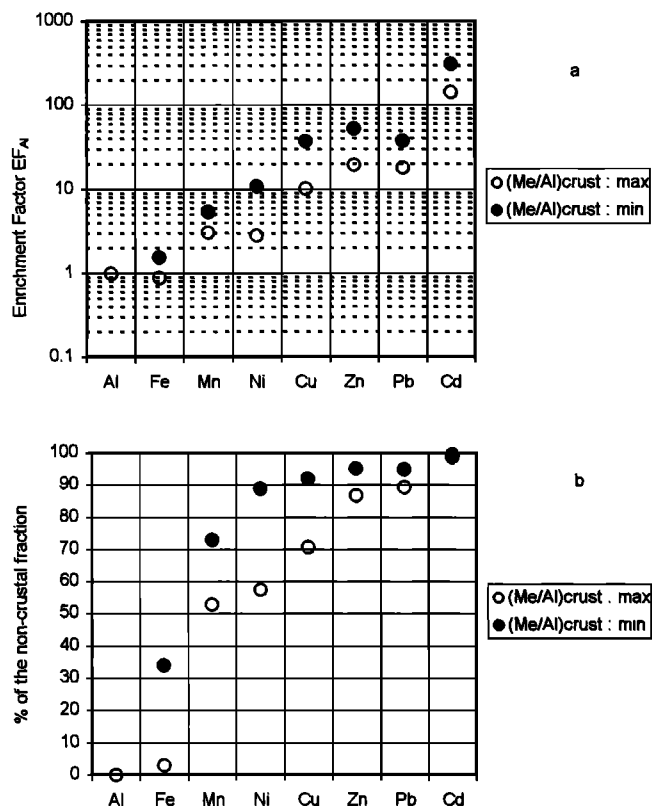


Figure 4. (a) The average enrichment factor EF_{Ai} and (b) the average excess fraction Xs , as defined in the text, calculated for the whole data set. Open circles: calculation using the minimum $(Me/Al)_{crust}$; solid circles: calculation using the maximum $(Me/Al)_{crust}$ (from Table 3).

published for this region (Table 4). For Cd, the flux was lower than, but similar to, that found at the Cap Ferrat site (no data are available for the Cap Cavallo site). The flux at Tour du Valat was 20–40 times higher than that at the Pirio site (Figure 7b). For Zn, the fluxes at Tour du Valat and Cap Ferrat were similar and about 20 times higher than that at Pirio (Figure 7e) (no data were available for Cap Cavallo).

The observed differences can be related to (1) the spatial variability, (2) the temporal variability related to rainfall fluctuations over time and/or (3) the temporal variability related to the actual evolution of the concentrations in the atmosphere over the past decade, and (4) the possible contamination of the samples from the earlier stations.

3.3.2.1. Spatial variability: The hypothesis of a spatial variation in the fluxes between the different regions is not supported by the results of an intercomparison that took place during a 1 month period simultaneously at three sites: Tour du Valat, Cap Ferrat, and a site near Ajaccio in Corsica. This intercomparison showed that the total atmospheric fluxes measured were the same [Guieu *et al.*, 1997]. Moreover, the fact that the Ni, Cu, and Cd fluxes were similar at Cap Ferrat and Pirio indicated that there was no clearly decreasing trend in metal fluxes with respect to the distance of the sampling site from the continental pollution sources between the French coast and Corsica.

The two annual Pb fluxes measured at the Pirio station were 1.1 and 0.7 $kg \cdot km^{-2} \cdot y^{-1}$ and appear to be lower than the fluxes recorded at the other Mediterranean sites (Table 4). The recorded decrease in the annual atmospheric flux of Pb from 1985 (Cap Cavallo) up to the present time (Pirio) (Figure 7c) was about 30 $kg \cdot km^{-2} \cdot y^{-1}$, at most. Since the two sites are quite close to each other (~25 km), a difference due to spatial variability is not a realistic hypothesis and should be attributed to the temporal variability, related to meteorological fluctuations and/or to the reduction of emissions, or partly to a possible contamination of the Cap Cavallo site.

3.3.2.2. Temporal variability related to rainfall fluctuations over time: The interannual variability of atmospheric fluxes could be explained by meteorological factors such as rainfall and synoptic pattern. It is well known that, other things being equal, a greater amount of rain triggers greater fluxes; this hypothesis was, for example, verified for major elements in the Fango valley, where the Pirio site is located [Loÿe-Pilot, 1995; Loÿe-Pilot *et al.*, 1998]. According to Remoudaki *et al.* [1991], the rainfall amount and the rainfall frequency are the most important factors of the flux variability. The annual rainfall for the different sampling periods and stations is shown in Figure 6. The historical average annual rainfall at Pirio was the highest, whereas that

Table 4. Comparison of Annual Bulk Fluxes of Metals in $kg \cdot km^{-2} \cdot y^{-1}$ With Other Published Values for the Northwestern Mediterranean Sea

| | Cap Cavallo | | Tour du Valat | | Cap Ferrat | Pirio | |
|----|---------------------------------|---------------------------------|--------------------------------|--------------------------------|---------------------------------|--|--|
| | 3/25/85 to 3/22/86 ^a | 3/22/86 to 4/16/87 ^b | 5/11/88 to 5/6/89 ^c | 7/1/88 to 6/19/89 ^c | 10/1/92 to 9/30/93 ^d | 3/14/95 to 3/13/96 (This Study) annual flux year 1 | 3/13/96 to 3/18/97 (This Study) annual flux year 2 |
| Al | 1036 | 516 | 990 | 845 | | 171 | 270 |
| Cd | | | 1.6 | 1.2 | 0.07 | 0.07 | 0.04 |
| Cu | | | 2.3 | 1.9 | 2.2 | 1.4 | 0.7 |
| Fe | 679 | 325 | 945 | 851 | | 118 | 156 |
| Mn | 24 | 8.7 | 15.9 | 14.8 | | 6.5 | 6.3 |
| Ni | | | 1.6 | 1.4 | 1.4 | 0.4 | 0.4 |
| Pb | 31 | 15 | 3.5 | 3.4 | 3.1 | 1.1 | 0.7 |
| Zn | | | 115.5 | 96.1 | 80.3 | 6.1 | 4.2 |

Read 3/25/85 as March 25, 1985.

^a Bergametti [1987] and Remoudaki *et al.* [1991] (the latter in the case of Pb).

^b Remoudaki [1990] and Remoudaki *et al.* [1991] (the latter in the case of Pb).

^c Guieu [1991]

^d Migon *et al.* [1997]

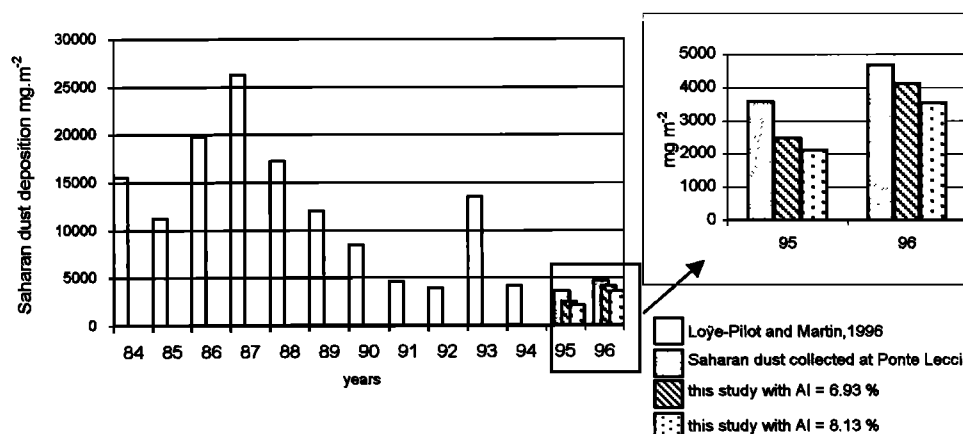


Figure 5. Evolution of the Saharan dust flux (mg. m^{-2}) in Corsica. 1984-1994: measured [from *Loje-Pilot and Martin*, 1996]; for 1994-1996: (1) measured at the Ponte Leccia site and (2) calculated from the Al fluxes determined at Pirió using Al concentrations 6.93-8.13%.

at Tour du Valat was the lowest. If the amount of rainfall is an important factor in atmospheric flux variability, those fluxes measured at Pirió should be the highest and those measured at Tour du Valat, should be the lowest. Unexpectedly, however, the fluxes measured at Pirió were lower than those measured at the other stations, and, consequently, the decreasing trend observed for Cd, Pb, and Zn (Figure 7) cannot be related to a decreasing trend in rainfall.

The frequency of the precipitation periods F_p (as defined by *Remoudaki et al.* [1991]: F_p is the number of groups of precipitation events during a period divided by the duration of the period in days; the groups of precipitation events are separated from each other by at least 4 dry days) has also been quoted as a relevant parameter to explain interseasonal and interannual variability of trace metal fluxes. F_p was calculated for the sampling periods at Cap Cavallo and Pirió. At these two sites, the synoptic pattern is strictly the same, but the annual rainfall is systematically higher at Pirió. The F_p and mean annual rainfall were, respectively, 0.065 d^{-1} and 1082 mm for the whole sampling period at Pirió (March 14, 1995 to March 18, 1997) and 0.051 d^{-1} and 569 mm at Cap Cavallo (March 25, 1985, to April 16, 1987). According to *Remoudaki et al.* [1991], the F_p value for Pirió would perhaps correspond

to slightly lower fluxes, but the difference in the amount of rainfall would certainly lead to higher fluxes at Pirió. Therefore, the meteorological factors cannot explain the temporal variability between the fluxes observed at Cap Cavallo in the years 1985-1987 and at Pirió in the years 1995-1997.

Considering the interannual difference in the fluxes at Pirió, some decrease was observed between year 1 and year 2 (see Table 2) for Zn, Cu, Pb, and Cd. This decrease could be partly attributed to the decrease in rainfall (year 1: 799 mm; year 2: 700 mm), but not to the frequency of the precipitation periods, which is within the same range ($F_{p_{\text{year}1}} = 0.063$ and $F_{p_{\text{year}2}} = 0.068$). However, the very low input of metals during the last month of sampling (a very dry period) had a strong influence on the flux in the second year.

3.3.2.3. Temporal variability relative to the actual evolution of the concentrations in the atmosphere over the past decade: In the following discussion, we seek to determine whether the sharp decrease observed between the fluxes of Cd, Zn, and Pb over the past decade could be the result of a reduction in metal emissions.

Pb. The important decrease in Pb in the atmospheric flux could be a consequence of the limitation in the use of lead

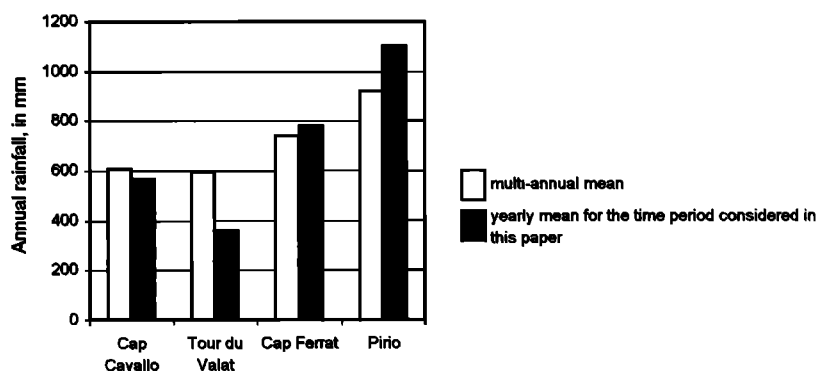


Figure 6. Annual rainfall (mm) recorded at each Mediterranean site for the time period considered, along with the multi-annual mean (Cap Cavallo: 1954-1987; Tour du Valat: 1944-1986; Cap Ferrat: 1948-1988; Pirió: 1974-1994).

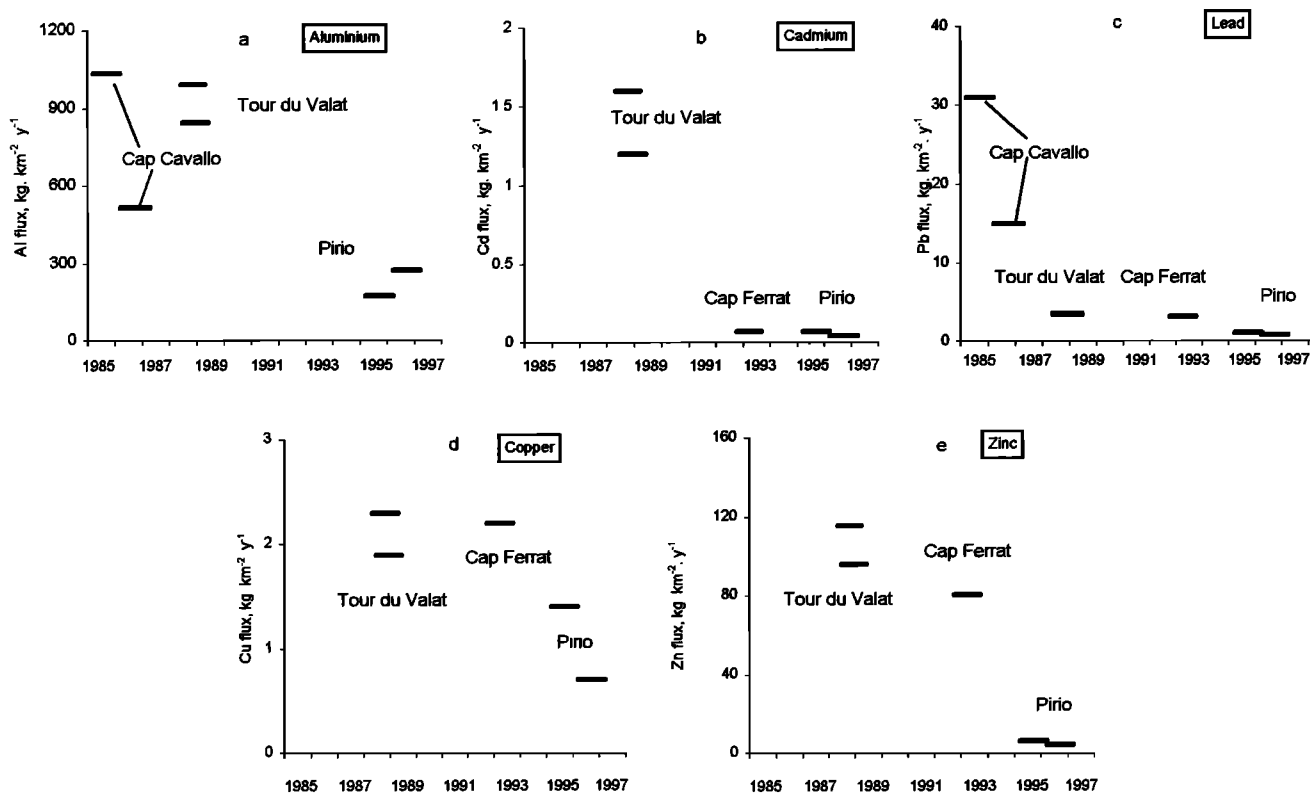


Figure 7. Evolution of the total atmospheric flux of metals between 1985 and 1997 in the northwestern Mediterranean. (a) aluminium; (b) cadmium; (c) lead; (d) copper and (e) zinc. References: Cap Cavallo (March 1985 to March 1986): *Bergametti* [1987]; Cap Cavallo (March 1986 to March 1987): *Remoudaki* [1990]; Tour du Valat (May 1988 to June 1989): *Guieu* [1991]; Cap Ferrat (October 1992 to September 1993): *Migon et al.* [1997].

additives in gasoline. As a consequence of this limitation (in effect in France since 1988), a decrease in the atmospheric Pb concentrations by factors of 1.3 and 1.4 in aerosols and rainwater, respectively, was observed between 1986 and 1992 at Cap Ferrat [*Migon et al.*, 1994]. Marine Pb concentrations measured in the northwestern Mediterranean basin from 1983 to 1992 decreased by a factor of 2 in the surface waters [*Nicolas et al.*, 1994]. In 1990, although northern Europe had already started to use unleaded gasoline intensively, 72% of atmospheric Pb was still coming from the use of leaded gasoline throughout Europe [*Pacyna*, 1998]. Between 1985 and 1990, the decrease in Pb emissions was highly variable depending on the country considered: on the European scale, the decrease was by a factor of 1.6, whereas in France, it was by a factor of 2.9; and in Eastern Europe, emissions remain constant or are increasing slightly. This trend means that, between 1985 and 1990, the maximum diminution that could be recorded at the coastal French sites could only be by a factor of about 3. The diminution recorded in 1985-1987 (Cap Cavallo) and 1990 (Tour du Valat) indicated a factor of 4 to 9; consequently, this decrease cannot be explained by the reduced use of leaded gasoline alone. Other human sources of atmospheric Pb (stationary emissions) decreased by a factor of 2.2 between 1985 and 1995 in Germany [*Karl et al.*, 1997], where environmental policies are the most stringent; thus the evolution of these sources cannot explain the measured decrease either. In France, for example, the cutting-down of

Pb emission by the use of unleaded gasoline and the increase in the number of diesel-powered cars led to a diminution by a factor of 6.2 between 1985 and 1995 [*Comité Professionnel du Pétrole*, 1997]. This reduction is still much smaller than the factor (14-44) between Cap Cavallo (1985-1987) and Piro (Figure 7). Hence only part of the observed decrease in the total atmospheric flux of Pb since 1985 in the northwestern Mediterranean can actually be attributed to the decrease in the consumption of leaded gasoline and stationary emissions. The other part of the decrease is probably due to a local contamination of the previous Corsican sampling station.

Zn and Cd. The Cd and Zn emissions in Europe between 1955 and 1990 are known [*Pacyna*, 1997, 1998]; there are no recent data (after 1990) available for Europe as a whole. From the available data and for the period 1985-1990, a diminution by a factor of 1.12 was recorded for Cd; this value results from the averaging of emissions from European countries with a serious reduction policy (Germany: decrease x 1.8) and European countries where emissions are still increasing (Spain: increase x 3.4). For Germany, where data on emissions are available up to 1995 and reduction policies are effective, a diminution by a factor of 3.3 was recorded between 1985 and 1995 [*Karl et al.*, 1997]; hence a decrease by a factor of 4 represents a maximum for Europe overall. The decrease by a factor of 30 or more found between Tour du Valat and Piro are thus totally unrealistic, given the knowledge of the evolution of the emissions in Europe. This

fact confirms the existence of a local or regional source of Cd at the Tour du Valat site.

As the evolution of the Zn emissions are similar to those for Cd [Pacyna, 1998], decreases by factors of 16 and 23 between Cap Ferrat and Tour du Valat and Pirio have to be explained by a local or regional source of contamination at the two continental sites. This finding demonstrates that the Cd and Zn fluxes measured at La Tour du Valat cannot be extrapolated to the northwestern Mediterranean. For this reason, these data were not taken into account in the global budget presented by Guieu *et al.* [1997]. For the same reason, the Zn flux measured at the Cap Ferrat station may not be representative of the long-range transport of this metal in the northwestern Mediterranean.

4. Conclusions

A 2 year data set on atmospheric deposition of trace elements in Corsica permits a reassessment of the total atmospheric fluxes over the northwestern Mediterranean. Comparison with the previous data obtained in the same area with the same methods allows an interpretation of the possible changes in composition or intensity of the deposition over the past decade.

Considering the whole data set, the mean fluxes for Ni and Cu are quite similar, indicating little spatial and temporal variability of the total atmospheric flux over the northwestern Mediterranean during the last decade.

For the terrigenous components, Al and Fe, the mean flux at the Pirio station is lower by a factor of 4-6 when compared to the average fluxes established at the other stations since 1985. These metals originate mainly from the Sahara. The observed decrease corresponds to a decrease in the Saharan dust fallout. The 1995 and 1996 Saharan dust fluxes (measured and derived from aluminium measurements) confirm the decreasing trend in the Saharan dust fallout recorded since 1987 in Corsica.

When considering the elements mobilized by human activities, the mean fluxes of Zn and Cd at the Pirio station are among the lowest values published for this region (data available since 1988). For Cd, the flux is lower than but similar to that at the Cap Ferrat site. The flux at Tour du Valat is 20-40 times higher than at Pirio. For Zn, the fluxes at Tour du Valat and Cap Ferrat are similar, but about 20 times higher than that at Pirio. The recorded fall in the atmospheric flux of Pb from 1985 (Cap Cavallo) to the present time (Pirio) shows a decrease by a factor of about 30. The deposition fluxes of the man-mobilized elements seem thus to have dramatically decreased over the past decade.

No clear downward trend in metal fluxes as a function of the distance of the sampling site from the continental pollution sources between the French coast and Corsica is suspected. Meteorological factors (such as the amount of rainfall and the frequency of precipitation periods) also could not explain the downward trend in the fluxes over the decade. Even considering the evolution of the emissions of pollutants, the observed decrease in deposition fluxes exceeded European emission reductions.

While a great part of the observed decrease in the total atmospheric fluxes of these metals over the past decade in the northwestern Mediterranean is actually attributable to the decrease in European Pb emissions, contamination at the earlier sampling stations explains the high fluxes reported for

Zn at Tour du Valat and Cap Ferrat and for Cd at Tour du Valat. In the case of Pb, a slight contamination of earlier samples by local sources is suspected for Cap Cavallo.

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