

COMPOSITION AND SOURCES OF TOTAL SUSPENDED PARTICLES AT A COASTAL CITY IN FRANCE

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Abstract: The city of Dunkirk, like other cities where industrial sites are located, is likely to be exposed to air emissions that affect air quality.

In order to estimate the time variation of the composition of fine suspended particles in Dunkirk, we decided to undertake a daily sampling campaign at a fixed site and a sufficiently long period, ie 3 months, from February to May 2008.

Different weather conditions have been met during this period and samples have been collected under marine sea, industrial and urban influences.

The physicochemical analyses were focused on the inorganic fraction of the particles.

The interpretation of the origin of the particles was initially supported by local weather information. Secondly, we have tried to highlight the sources contributing the most in the explanation of the presence of elements and ions and their content at our receiver site. Based on the knowledge gained on steel works, we examined whether certain physicochemical parameters could be used to identify the influence of steel sources on the composition of atmospheric particles.

Keywords: Steel, TSP, SPUR, iron, coastal.

1. Introduction

In recent years, considerable amount of concerns have arisen on the extent of pollution, particularly the contribution of industrial emissions to particulate matter (PM) and metal levels in the neighboring residential areas [1], [2].

The town of Dunkirk (51°04'N; 2°38'E) was chosen as the study site because some of its specificities; it is located on the sea-side of Nord-Pas-de-Calais. Several industries of various fields were established: petrochemical, steel, cement, metallurgy. Therefore, the atmosphere of this site may well suffer from gaseous and particulate inputs of various origins: sea, industrial and vehicular.

The diverse sources of pollutants and the changing meteorological conditions make of Dunkirk an important case study of the effect of industrial and urban development on air quality under sea influence. In recent years, several studies have been conducted in order to characterize the particles and better understand their behavior in the atmosphere in the region of Nord-Pas-de-Calais and especially Dunkirk. [3]–[6]

Iron is the most anticipated element in particulate emissions of a steel plant. However, such a site cannot be considered as a single source from which a single type of particles would be emitted.

A steel plant includes all necessary facilities for the production of steel (raw materials ...) and each of these units should be seen as a source of particles by itself. As a consequence, each site unit may emit air particles whose physicochemical characteristics are different and depend on the materials used and the applied treatment. The origin tracers are not identical for each of the emission sources.

The aim of this work is to shed some light on the variations in the chemical composition of suspended particles at a local level, due either to weather conditions or to emission streams from natural and anthropogenic sources.

2. Experimental

TSP were sampled at the top of a 3 m mast implanted on the roof of the Research Institute that makes the sampling height of about 10 m above ground level.

The sampling point is directly under the influence of emissions of the industrial sector when the wind blows from direction 260 degrees to 320 degrees.

TSP were collected by global filtration on cleaned What mans 41 cellulose filters and mounted in a PVC holder, for a period of 12 h using a high capacity air aspiration device at a flow rate of $5 \text{ m}^3/\text{h}$, to which is connected a calibrated dry gas volume meter with a precision superior to 1%.

After sampling, filters were dried under laminar flow hood until constant mass and weighed with a precision of 0.01 mg. Meteorological conditions (wind direction and speed, rain falls, temperature, humidity, atmospheric pressure) have been recorded for each sample.

3. Analytical

Ion chromatography (IC) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were used to obtain the concentrations of different water soluble anions and elements respectively.

A Dionex DX100 chromatograph was used for the analysis of water soluble anions (Cl^- , NO_3^- , SO_4^{2-}) and a Dionex ICS900 for the analysis of ammonium ions (NH_4^+).

Water soluble anions were extracted (about 5 mg of particles) by leaching using an ultrasonic treatment for 30 min in 10 mL of ultra-pure water (MilliQ®, Millipore; resistivity = 18.2 M.cm). The leachate was filtered on a cellulose acetate membrane (porosity 0.45 μm) in a polyethylene flask and the volume adjusted to 20 mL, in each flask, by adding ultrapure water. The final solutions were conserved at 4 °C before injection in the analytical column. Elemental analysis was conducted using a Varian® Vista-Pro spectrometer. The list of elements that were analyzed was restricted to: Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Sn, Sb, Pb and Bi.

Analysis was done after acid digestion, considering about 5 mg of particles placed into a PTFE flask with $\text{HNO}_3/\text{HF}/\text{HClO}_4$ (4:1:0.5 v/v/v Suprapur®, Merck®) at 130 °C for 4 h. After evaporation at 170 °C and cooling, the solution was diluted with MilliQ water up to 10 mL and acidified up to 0.2% HNO_3 , prior to analysis. The quantification methodology was validated from the analysis of a certified aerosol sample from American NIST (Standard reference Materials, no.1648). Uncertainties in determining water soluble ions and elements concentrations were less than 3% (relative standard deviation from three analytical replicates).

4. Results and discussion

Averages of TSP concentrations obtained between February and May of 2008 are summarized in Table 1. The fourth column in this table refers to the % with respect to the total analyzed inorganic species.

Table 1: TSP average composition (ng/m^3)

	μ	σ	%
Al	311,9	309,2	1,3
Ca	1312,6	1523,7	5,4
Cr	12,0	31,6	0,1
Cu	14,6	20,4	0,1
Fe	769,9	929,0	3,1
K	378,4	406,9	1,5
Mg	291,7	213,2	1,2

Mn	75,3	141,7	0,3
Na	1622,8	1490,2	6,6
Ni	9,6	14,9	0,0
Pb	15,0	15,4	0,1
Sn	6,2	7,0	0,0
Ti	24,6	22,2	0,1
V	8,3	7,9	0,0
Zn	76,8	78,0	0,3
Cl ⁻	3700,4	3175,6	15,1
NO ₃ ⁻	8537,0	6622,3	34,8
SO ₄ ²⁻	3480,6	3474,5	14,2
NH ₄ ⁺	3861,0	2844,6	15,8
Total	24503,1		100,0

Of all the inorganic fraction, a strong contribution from nitrate species NO₃⁻, ammonium NH₄⁺, sulfates SO₄²⁻ and chlorides Cl⁻ is observed. These four species represent 79.9% of the average content of inorganic particles. Sodium ions Na⁺ (6.6%) and calcium element Ca (5.4%) also contribute strongly to the particulate filler, and then in descending order of contribution, Fe (3.1%), K (1.5%), Al (1.3%) and Mg (1.2%). The rest of the elements (Cr, Cu, Mn, Ni, Pb, Sn, Ti, V and Zn) represent an average proportion of 0.99%.

A comparison was then conducted between the average TSP concentrations collected and data reported in the literature at similar environments[7]–[11] (Figure 1). Despite the presence of an industrial density, the sum of the average concentrations of metals (Al, Ca, Cr, Cu, Fe, Mn, Mg, Na, K, Ni, Pb, Ti, Zn, and V) at Dunkirk was lower than other sites. In particular, the average content of Pb measured in 2008 was lower than on other sites. Zn content was less than the average measured on other sites to the exception of that measured at the coast of the Irish Sea. Fe, Cu and Ni contents were also lower except for those of the Irish Sea and Istanbul. In contrast, the average content of Mn in Dunkirk in 2008 was higher than the other sites.

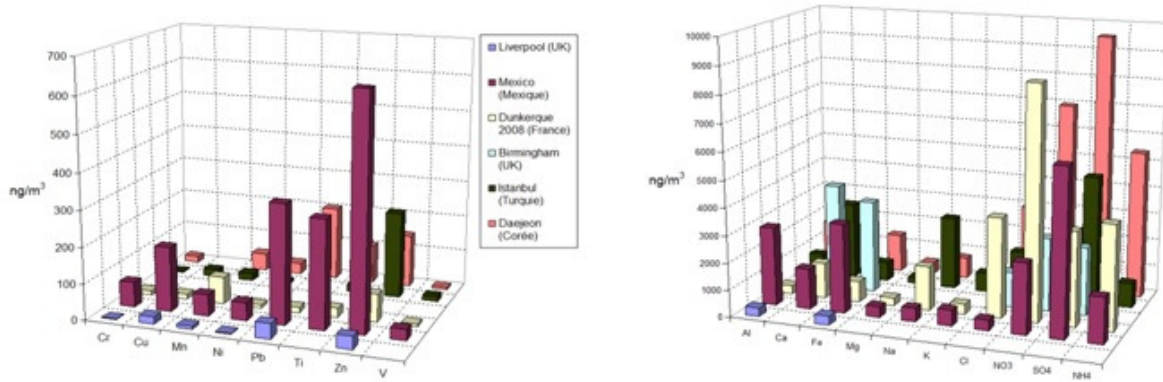


Figure1: Comparison of the average contents of elements with other sites in the world

The total inorganic content present a variation between a minimum of 5.4 g/m³ up to a maximum of 86.6 g/m³.

This evolution of total inorganic content shows peaks that correspond to increases in the content of NO₃⁻, NH₄⁺ and/or SO₄²⁻ species (figure2). However, there was no significant elevation of total inorganic when high levels of sodium and chloride ions were observed. It should be noted that when the proportions of NO₃⁻ and NH₄⁺ were high, those of Na⁺ and Cl⁻ were low, and vice versa. These species were therefore associated to different sources.

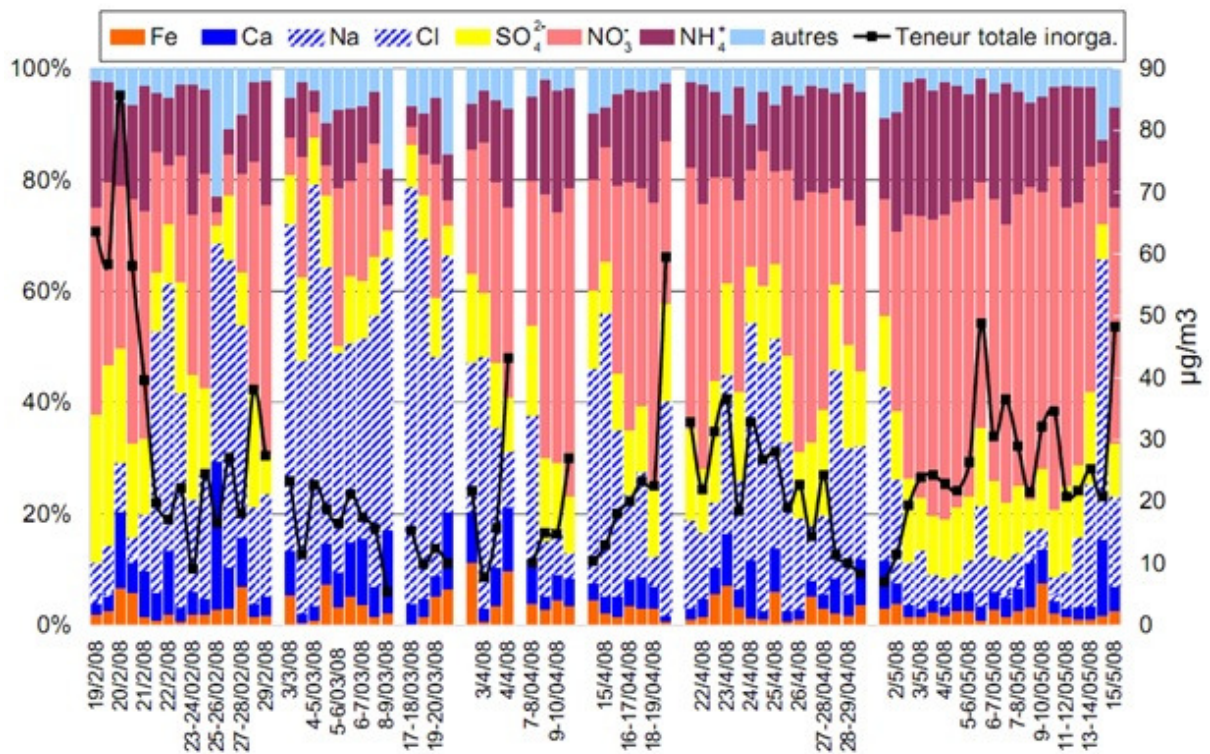


Figure 2: Time variations of TSP composition

We decided to show the temporal variation of Fe, Ca which are major components of fine particles due to their presence in soils and therefore were likely to be present in air through wind erosion. In addition, Fe and Ca could also originate from a steel industrial site. Similar trends were observed for the elements Ca and Fe.

The temporal variation of the levels of Na^+ and Cl^- showed episodes of elevated content for short periods especially with Cl^- . These episodes didn't occur at the same time as those observed for Fe, and Ca. Concerning NO_3^- and NH_4^+ trends, the magnitude of the levels was sometimes considerably greater than that of Fe, Ca, Na and Cl.

A satisfactory correlation between NH_4^+ and NO_3^- ($y = 1.49x$ and $r^2 = 0.85$) ions was obtained, showing that there was always an excess of ammonium over nitrate ions. It turns out that the neutralization of the ammonium ion is achieved also via combination with sulfate ions. (figure 3) [3]

According to literature [12], the majority of ammonium ions is in the form of ammonium nitrate NH_4NO_3 when the air mass in which they are formed were richer in NO_x than SO_x . The proportion of ammonium sulfate is higher in the case of an enriched air mass SO_x . For this reason, some authors distinguish the two ammonium nitrate and sulfate compounds.

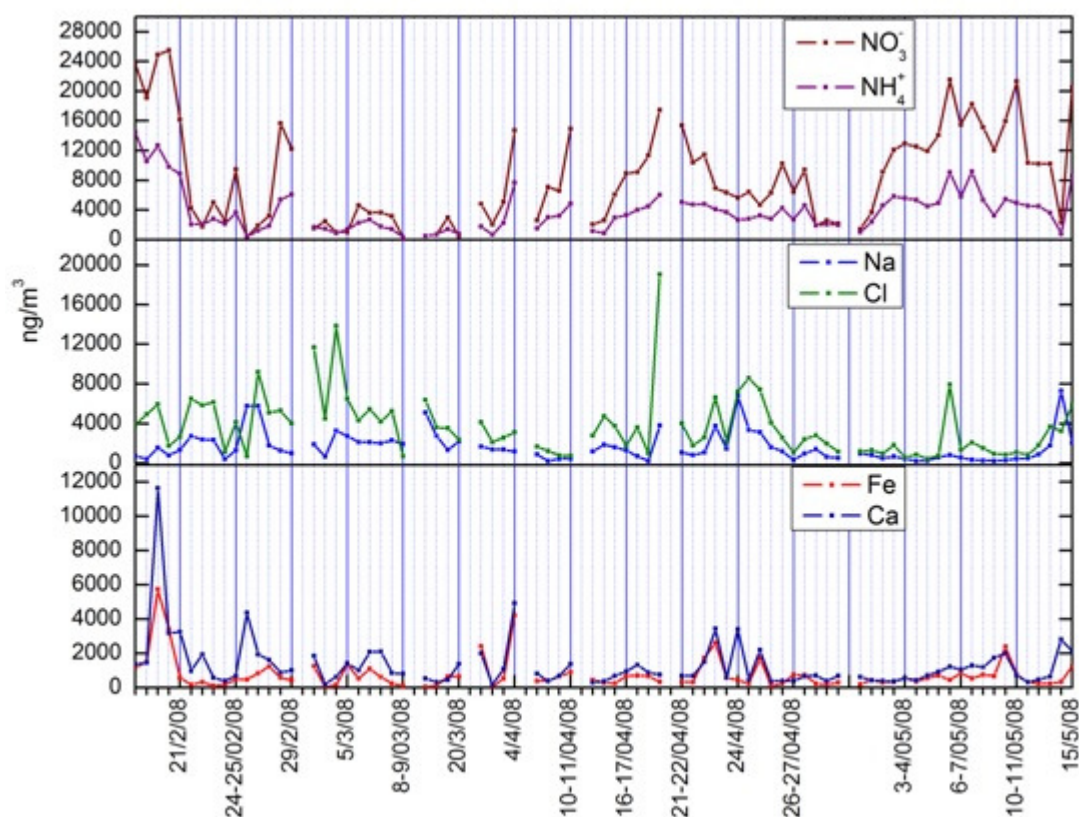
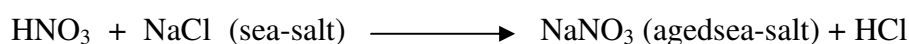


Figure 3: Time evolution of some representative elements and ions

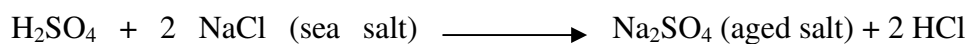
Nevertheless, our data showed that at Dunkirk, the proportion of ammonium nitrate form is higher than that of ammonium sulfate. It seems acceptable to include these two forms, under the term secondary inorganic aerosol, which are compounds of NH_4^+ , NO_3^- and SO_4^{2-} .

In parallel and as shown in figure 4, a satisfactory correlation "moderate" is obtained between Na^+ and Cl^- ions. This moderate correlation is understandable since there are two types of sea aerosols, those called fresh and those called aged sea aerosols.

It is well known that fresh sea aerosols possess a similar composition with that of sea water elements, while, aged sea aerosols lose part of their Cl^- ions as HCl , according to the reaction involving NO_x derivatives, represented below [13]:



Or, following the absorption of SO_2 in the droplets of sea salt, oxidized to H_2SO_4 [14]



this HNO_3 and H_2SO_4 reaction with sea salts intervenes permanently [15], [16]

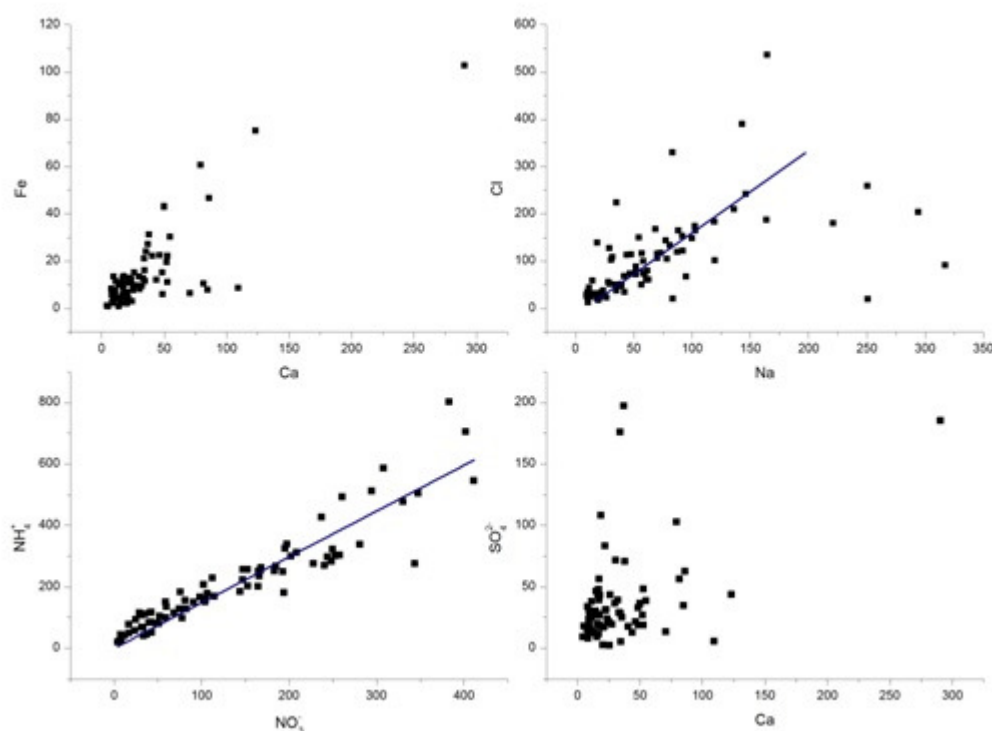


Figure 4: Correlation between: Fe and Ca, Na and Cl, NO_3^- and NH_4^+ , and Ca and SO_4^{2-}

Then, we studied the correlation between the Ca component and sulfate ions SO_4^{2-} , because the form gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the most encountered form of calcium and sulfate ions in the particles. Figure 4 shows a huge disparity for Ca and SO_4^{2-} , which could be explained by the following: For calcium, it is known that calcium carbonate is also a major phase. It

represents a natural crustal and / or industrial origin (steel, cement). For the sulfate, it is predominantly under gypsum form, but as already mentioned, a portion is associated with ammonium ion. Finally, a part resulting from the conversion of SO₂ and adsorption phenomena can be associated with various metals, such as iron [4].

We were also interested in the existence of a dependency between the concentrations of Fe and Ca. Figure 5 shows at least two correlations: A first pattern emerges with Ca content approximately ten times higher than Fe, mainly in samples with almost no contribution of steel emissions. In contrast, the second trend certainly shows a majority of calcium, but this time with a much higher iron content. This correlation is most likely a reflection of the impact of steel plant emissions on the content and composition of atmospheric particles.

We have attempted to identify if specific weather conditions were encountered during certain episodes. For this purpose, we considered not only the local weather but also the back trajectories of air masses NOAA HYSPLIT [17].

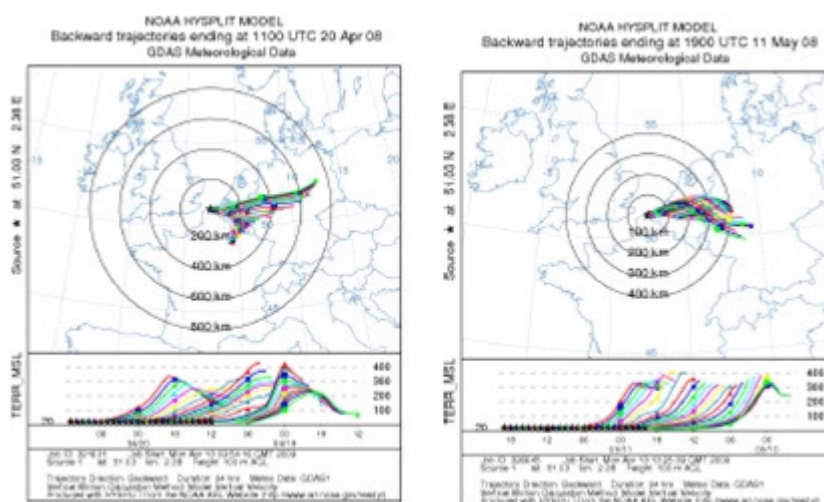


Figure 5: Back-trajectories recorded during peaks of NO₃⁻ and NH₄⁺

Figure 5 shows different back-trajectory, recorded when peaks were observed in the temporal variations of NO₃⁻ and NH₄⁺.

In the first two cases, the air mass has a continental origin. In the third case, which is rare, the air masses crossed the UK from North to South, before arriving to the North of France. In the last case, the air masses cross the French territory. All these cases have in common the crossing of a continental zone, which allows the air masses to charge in nitrate and ammonium.

It should be noted that in each of these cases, the weather was dry, which allowed the accumulation of nitrate and ammonium species in the atmosphere.

As discussed earlier, Sodium and chloride are the main components of sea aerosols. Back trajectories, when peaks of Na and Cl were recorded, show wind directions SSW to NE. (fig 6).

Under wind from W to NE, the site can be easily exposed to sea influences due to its proximity to the North Sea, located few kilometers from the sampling site. However, we see high content of Na and Cl in the sector WSW SSW. In this case, the back trajectories show high speed winds SW to SSW, the air masses were loaded in sea aerosols over the Atlantic Ocean and the English Channel when crossing the Northwest of France, before arriving at our sampling site.

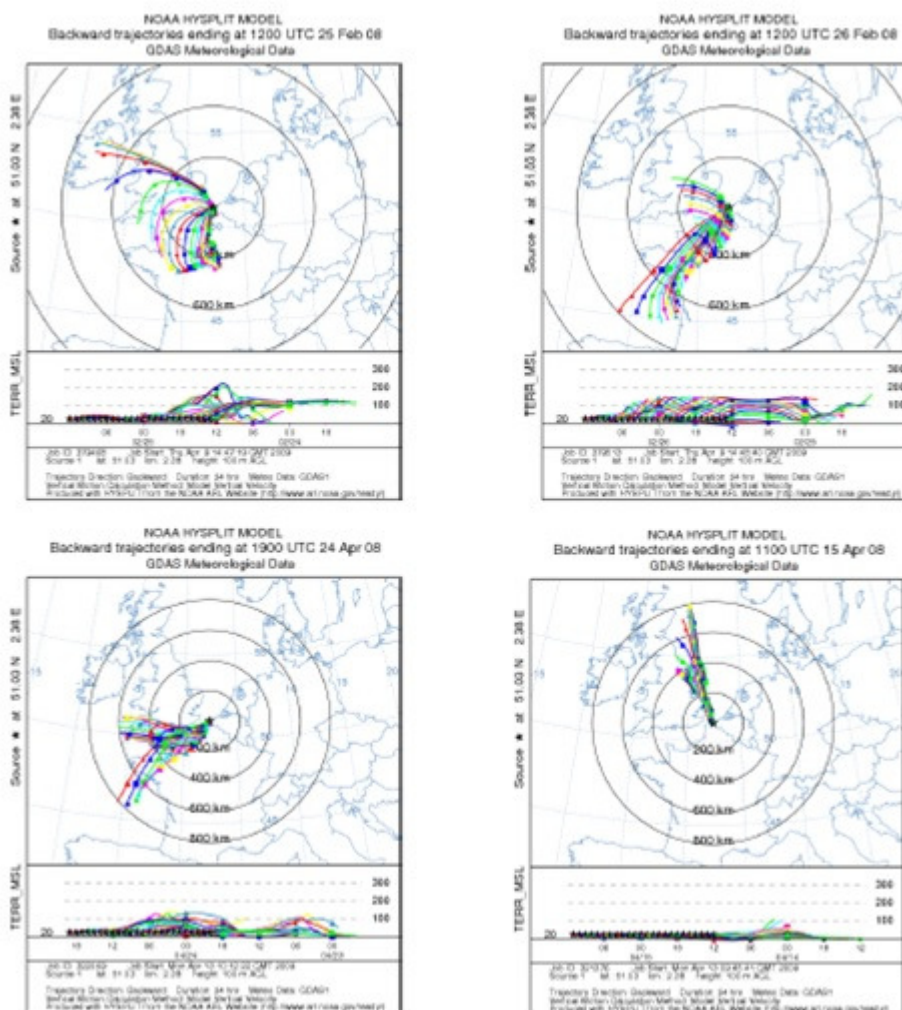


Figure 6: Back-trajectories recorded during peaks of Na and Cl

Several days of the sampling campaign were marked by high iron levels. This increase in the iron content is usually accompanied by an increase in Ca levels. Back trajectories show continental or sea air masses passing above the industrial area (fig. 7). In this case, the winds

are from SSW to NNE, and predominantly WNW (wind sectors covering the industrial area of Dunkirk)

The speed of the associated winds is relatively low, thus, favoring the accumulation of particulate matter.

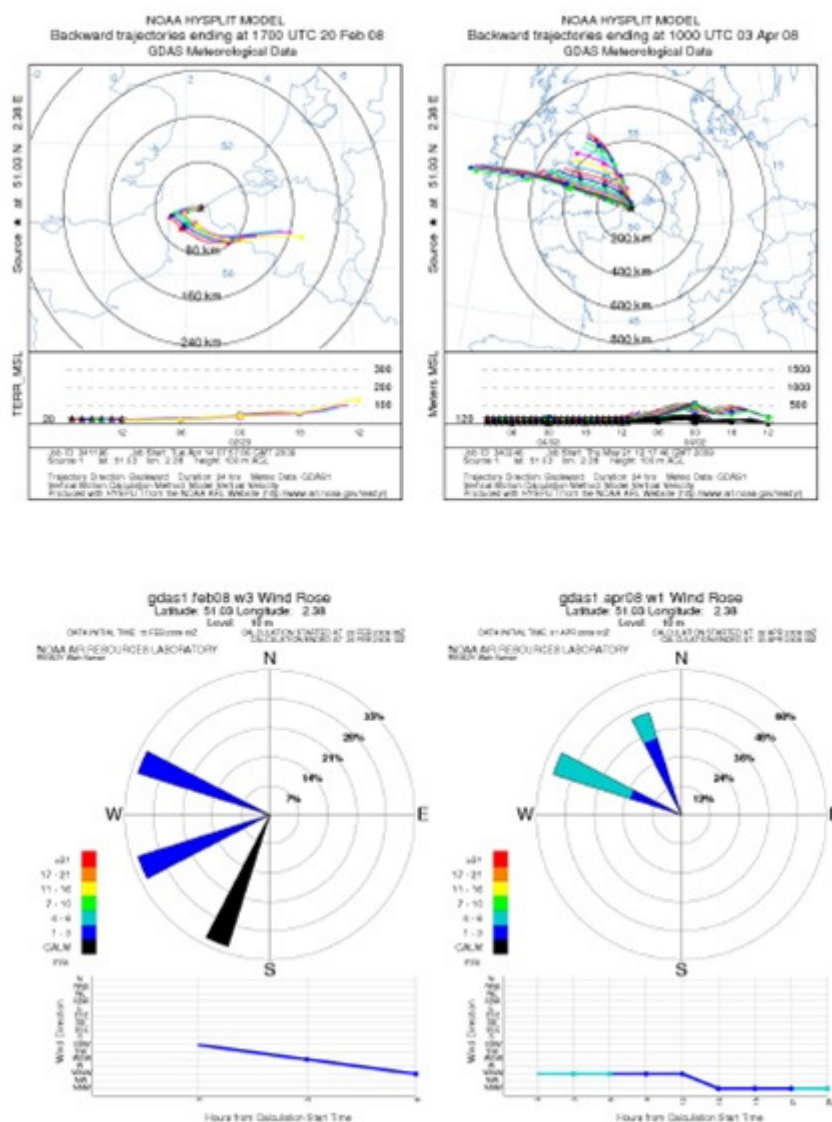


Figure 7: Back-trajectories and wind roses recorded during peaks of Fe and Ca

5. Concentrations roses

Figure 8 shows concentration roses for some elements and ions.

For Al, Fe, Ca, Mn, Pb, Sn, Ti and SO_4^{2-} , the highest content was observed with wind under the influence of the industrial sector ($250\text{--}345^\circ$). Al, Fe, Ca, Mn, Pb, Sn and SO_4^{2-} ion identify the intense industrial activity in this sector: metallurgy, steel, cement, combustion processes [18], [19].

In addition, Al, Ca, Sn and Pb show a high concentration for winds from the urban sector (60-250°). Al, Ca and Ti also have a crustal origin [20], [21]. Sn and Pb have an anthropogenic origin that cannot be attributed to local or distant contribution.

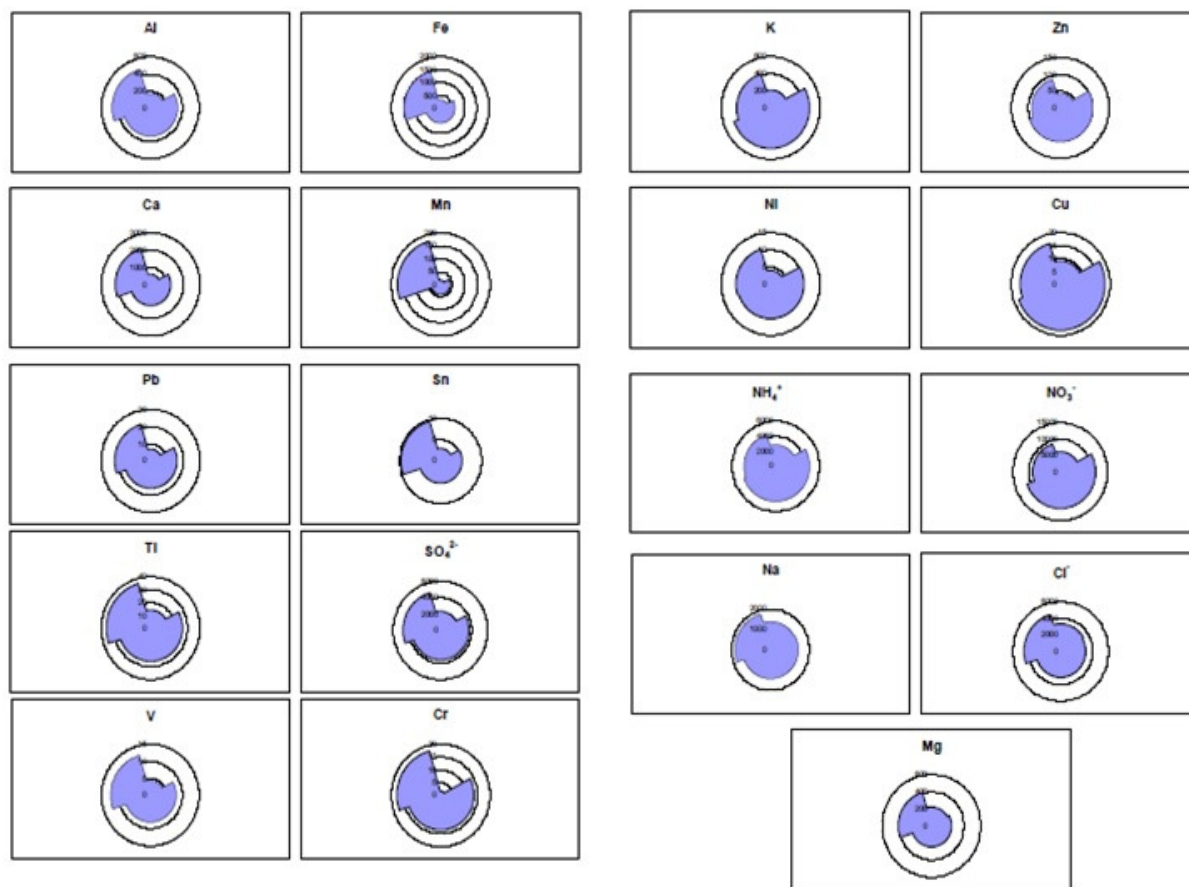


Figure 8: Concentrations roses of different elements and ions

The industrial origin of vanadium could be explained by its presence in steel and in petrochemical emissions [22]. Vanadium could also be found in car related emissions.

As for chromium, its origin in the industrial sector is mainly explained by the steel emissions. The significant contribution in the urban sector could come from the emissions due to the wear of mechanical parts used in car brakes [23].

The water-soluble species Na^+ , Cl^- and Mg^{2+} are major constituents of seawater. Concentrations rose of Na and Cl have the highest average content under the influence of industrial-sector "(250° -345°), which is in alignment with the North Sea influence. Concentration levels under the sea-sector (345° -60°) appear relatively low, due to weakly charged air masses. Species Na^+ , Cl^- and Mg^{2+} are mainly related to marine origin. Nevertheless, we previously showed that sodium and chloride were emitted by the task of the steel plant [24]. Therefore, industrial contributions are not to be excluded in this sector.

Finally, we find that the concentration levels in the urban sector are relatively high, mainly due to resuspension of sea aerosols, crustal and anthropogenic origins of sodium that could not be excluded [25].

In the case of Mg, we found that the maximum concentration is pronounced under the industrial sector (250-345°). Recall that the Mg element is relatively concentrated in diffuse emissions of the steel plant. This observation is interesting, implying that this element could be considered in combination with other characteristic elements to identify industrial contributions in atmospheric samples.

K, Zn, Ni and Cu. These elements presented the higher contents under the urban than under the industrial sector. Although there is no known relationship between K and Zn, they showed a similar concentration rose. In general, Zn present an exclusively anthropogenic origin, while the presence of K can be explained in part by crustal contribution [22]. In agreement with literature data [26], it is proposed that intakes of Zn in the urban sector are connected to road traffic, particularly to the fine particle resuspension from tire wear. Under the industrial sector, the presence of Zn is explained by emissions from the steel industry.

As for the element K, besides its crustal origin, its strong contribution in the urban sector could be explained by emissions related to domestic heating coal [27]. Moreover, a traffic contribution is not to be excluded. Some additives used as lead substitutes in gasoline engines, contain potassium. It is to be noted that the stack emissions of the agglomeration unit contains a high proportion of K and is considered the largest emitter of particles in the steel plant.[28]

The concentration of Ni present similar trends for industrial and urban sectors. Ni is considered a good marker for the activity related to the burning of oil and derivatives (fuel, heavy fuel oil) [22]. The crustal contribution is extremely low [29]. Ni concentration rose could be explained by the emissions related to burning fossil fuels. Under the urban sector, it corresponds to emissions from road traffic (cars and trucks) and under the industrial sector, it could be appended to emissions from petrochemical industry, without the exclusion of probable emissions related to the activity of the steelwork plant [6].

The Cu element has a maximum concentration under the urban sector. Its origin is identical to that of chromium. It could be generated by the wear of the mechanical parts used for braking the vehicle [23].

As for NO_3^- ion and NH_4^+ concentrations roses, they present high contributions in all sectors but with a maximum oriented towards sector (60-250°). These species result from the conversion of gaseous compounds (NO_x , NH_3) stable in the particulate form (NO_3^- , NH_4^+). Moreover, the air masses back trajectories showed continental origin, mainly from Eastern Europe or France.

6. Source Attribution

Previous studies reported the difficulty in the separation between the influence of two sources: sources mixing soil, sea, vehicle and secondary aerosols[29], or industrial sources and vehicle emissions [30].

In order to identify industrial sources having an impact on the content and composition of atmospheric particles, we applied the source profiles technique single report (SPUR), proposed by H. Annegarn [31] for the identification of steel emission sources [32]. Using this technique, the episodes during which a source is dominant could be identified by examining plots of $[A] / [B] = f ([B])$, where A and B are elements of interest for the follow-up of a source.

The emissions of the sintering unit have a different chemical composition than the other facilities.

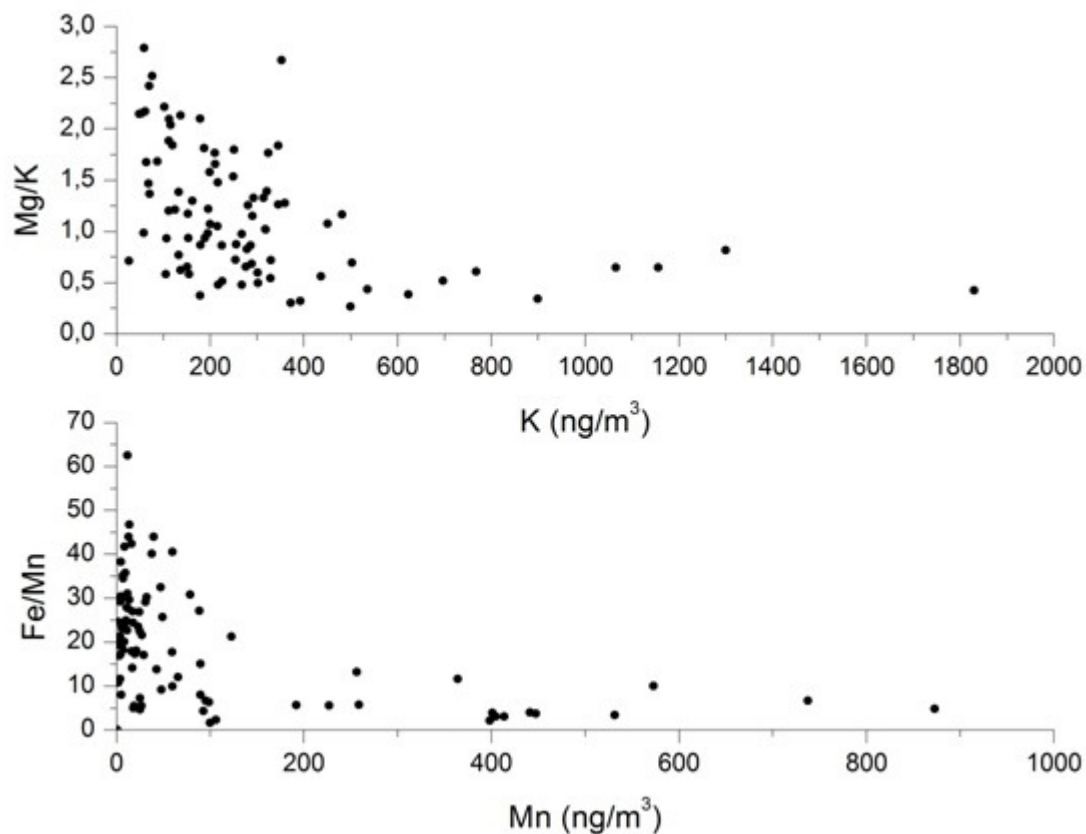


Figure 9: Plots $Mg/K = f(K)$, and $Fe/Mn = f(Mn)$

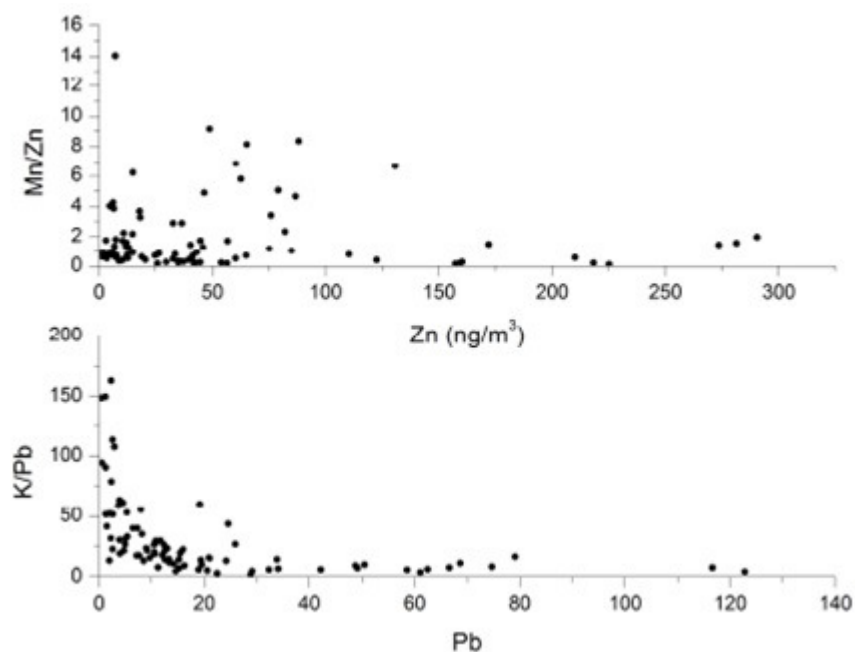


Figure 10: Plots of $Mn/Zn = f(Zn)$ and $K/Pb = f(Pb)$

Cooking chimney emissions are rich in K, Cl and NH_4^+ and also possess relatively high levels of Fe, Ca and Mg. This abundance of K element appears to be an interesting feature to identify the impact of sintering on the composition of the particles in the environment.

In addition, for samples collected in the sea and industry sectors, Mg concentration rose showed that this element mainly originated from these areas. It should be mentioned that the sea aerosols are always characterized by a Mg content higher than that of K, with a Mg / K ratio of about 3.2 [33]. In contrast, K levels were higher in the industrial sector with respect to sea-sector, showing a ratio Mg / K <1 in sintering emissions (table 1).

We propose to check if the Mg / K ratio can be used to identify the influence of sintering unit on the composition of atmospheric particles.

The value of Mg / K as a function of K content is shown in Figure 9. We note that several samples follow a value significantly greater than 1. Moreover, we could verify that the corresponding samples had a strong sea contribution, in terms of their Na and Cl content.

Several samples are characterized by Mg / K ratios <1, in particular when the K contents in the samples are high. This result highlights the influence of the sintering unit.

We retained the value Mg / K <1 as the threshold value to estimate qualitatively when the influence of the sintering chimney was detected. We found that 43% of the samples would be likely influenced by this source. The more the ratio of Mg / K was low, while having high levels of K, the greater is the importance of the contribution of this source.

We should mention that Mg / K ratios <1 were also found at the blast furnaces source. The influence of this source could therefore explain the low value of Mg / K ratio. However, this source contains low levels in both K and Mg suggesting a minor contribution to the Mg / K ratio in the atmosphere.

In some peaks characterized by high contents of Fe, the levels of Mn, Zn and Pb were also high.

Following our data, the Mn content showed interesting values exceeding 100 ng/m^3 with a maximum value reaching 880 ng/m^3 . These peaks appeared to be isolated. In order to realize whether these Mn peaks could be associated with the steel site emissions, we compared the Fe/Mn ratio obtained for the atmospheric samples with those determined for steel sources studied on the steelworks of Arcelor Mittal [24]. All have Fe / Mn ratio > 50, corresponding to the minimum value obtained in the emissions of the sintering unit. These ratios are high because of high Fe levels, not necessarily because of low levels of Mn.

Furthermore, we wanted to have an idea about the values of Fe / Mn from literature. Interestingly, we found at Dunkirk, the lowest Fe / Mn ratio. This is explained by the high levels of Mn.(table 2)

Table 2: Ratio Fe/Mn recorded at different sites

Site	Gênes (Italie)	Mexico (Mexique)	Liverpool (UK)	Istanbul (Turquie)	Daejeon (Corée)	Dunkerque (France)
Fe/Mn	125	50	38	35	29	9
Mn/Zn	-	0,09	0,25	0,08	0,33	1,8
K/Pb	1,7	1,8	-	10,1	4,1	8,3
Reference	[32]	[34]	[11]	[8]	[9]	[3]

For samples with low Mn content, Fe / Mn ratio fluctuated between 1 and 64. Many points comply with the Fe / Mn ratio encountered on other sites worldwide.

Furthermore, we observed samples characterized by low Fe / Mn ratio with high levels of Mn. They clearly correspond to wind sectors from the industrial area, with parallel elevations of the contents of other characteristic elements of industrial emission Fe, Ca, Zn, Pb.

The influence of a ferromanganese alloys production site, present also in the industrial area, should not be neglected. This observation is confirmed after analyzing two particulate samples taken near the ferromanganese plant and under its influence.

Indeed, the ferromanganese plant emissions have relatively low Fe / Mn ratio ($0.25 < \text{Fe} / \text{Mn} < 0.7$) due to high Mn contents. Relative high concentration levels of Fe, Ca, Zn and Pb were also identified in the corresponding samples. In descending order of their atmospheric content: $[\text{Mn}] > [\text{Fe}] > [\text{Ca}] > [\text{Al}] > [\text{Zn}] > [\text{Pb}] > [\text{Ti}] \dots$

We then investigated the elevation in Zn content. As discussed earlier, zinc does not have a dominant industrial influence. Non-industrial influences may explain its presence.

Based on our knowledge of the sources, we know that zinc is emitted both at Arcelor Mittal facilities (particularly the steel mill) and at the ferromanganese production site.

We remarked similar Fe / Zn ratio ($30 < \text{Fe} / \text{Zn} < 40$) for these two industrial sites. However, Mn / Zn ratio provided significant differences: Site Arcelor Mn / Zn ≈ 6 and RDME Mn / Zn ≈ 100 .

We therefore proposed a Mn / Zn representation as a function of Zn for all samples (figure 10).

Mn/Zn ratio had a random distribution when Zn levels were low. Mn / Zn high values surely reflect the influence of ferromanganese alloy production site. At this stage, we were unable to exclude a contribution of Arcelor Mittal site. However, this representation showed several points with Mn / Zn close to 1, with high levels of Zn in the atmosphere. This result suggested the exclusion of a dominant steel or metallurgical (ferromanganese) origin.

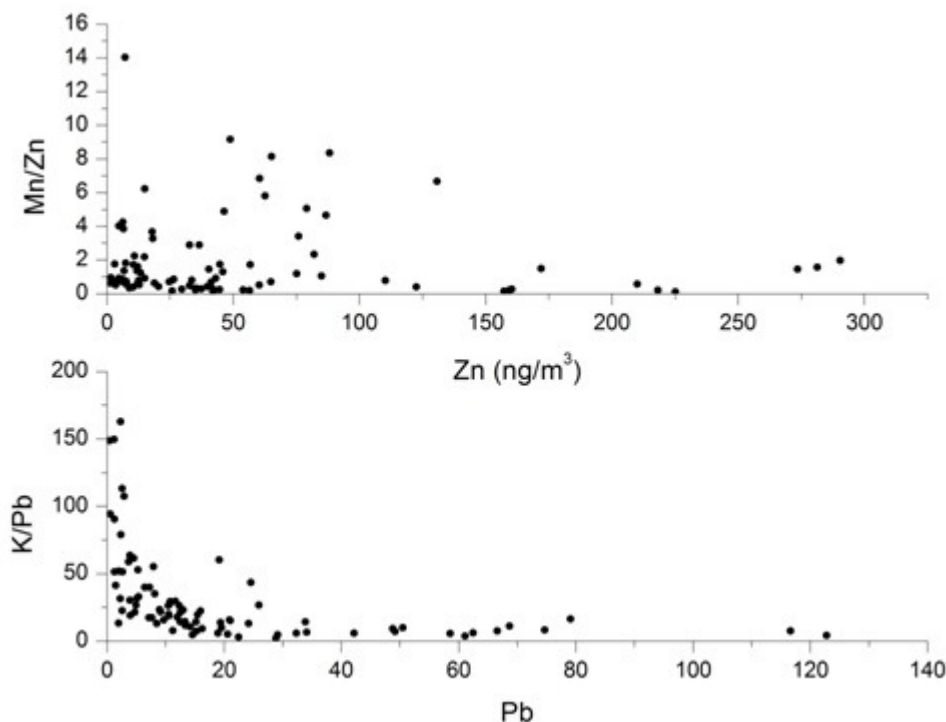


Figure 11: Plots of $Mn/Zn = f(Zn)$, and $K/Pb = f(Pb)$

Finally, we focused our attention on the origin of lead in particles. Given the characteristics of the main sources of lead emissions, we plotted the K / Pb ratio as a function of Pb content. For low Pb content, a random distribution was also observed. For high Pb contents, several items tend to show a K / Pb ratio, fairly constant.

Its value is close to that encountered in both emissions from sintering unit of the steel plant and the ferromanganese plant. This observation shows that Pb peaks are well correlated to emissions from both sources.

In summary, the study of the change in the concentration of elements and relationships between elements (K / Mg, Mn / Fe) allowed us to identify qualitatively the influence of a particular industrial source in atmospheric samples.

However, it was not always possible to distinguish the dominant source using the SPUR model. The situation became more complex when multiple sources were present in the same industrial field.

Acknowledgements

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