

Iron apportionment in coastal aerosols: a SEM/EDX study

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1. Introduction

The atmosphere is the prevailing compartment for material transfer from land to sea, especially for trace elements such as iron to remote ocean surfaces (Jickells et al., 2005). Iron plays an important role in biogeochemical cycles (Watson et al., 2000). As it is an essential micro-nutrient for marine phytoplankton, iron can be regarded as a limiting factor for primary production (Boyd, 2000; Coale et al., 1996). Thus, characterization of iron species is of relevance, especially in coastal zones prone to up-welling.

The fate of atmospheric iron in the environment strongly rests on its solubility in natural waters (e.g. cloud droplets, seawater, lakes) and thus on its chemical form (Baker et al., 2006; Hoffmann et al., 1996; Hsu et al., 2005). The speciation of Fe-containing aerosols in the troposphere governs their solubility and thus the impact of both dissolved and particulate iron on phytoplanktonic growth, as well as their ability to serve as cloud condensation nuclei after formation of a soluble coating.

Natural emissions represent the predominant source (from 70 to 80% of atmospheric iron (Jickells et al., 2005)). However iron emitted by industrial activities is reported to be more soluble in aqueous media (Baker et al., 2006) and is seriously suspected of being a lot more bioavailable.

Our aim was to provide a detailed description of individual particles in order to determine the relative proportions of particle types and to distinguish different types of Fe-bearing particles so as to give an estimate of how large anthropogenic activities contribute to the total particulate iron in atmospheric aerosols in Western Europe.

2. Materials and Methods

Tropospheric aerosols were weekly sampled during a continuous campaign conducted at Cape Gris-Nez (eastern Channel: 50°52' N; 1°36' E) from June '00 to June '01. Atmospheric particulate matter was collected by bulk air filtration onto polycarbonate membranes (Nuclepore[®], AOX, 0.4 µm, 47 mm) at the top of a 14-m-high mast. The mean filtered volume was roughly 200 m³. The in-shore sampling site is located at the top of a 60-m-high cliff. Among the 52 samples collected during the one-year campaign, 12 were selected based on distinct geographical origins of aerosols determined by air-mass backward trajectories ending at 950 hPa.

Atmospheric particles were individually analyzed with a LEO 438VP scanning electron microscope, outfitted with a Gresham energy-dispersive X-ray detector. To obtain statistically relevant data, approximately 1000 particles per sample were examined. The net X-ray

intensities of 16 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni and Zn) were converted into apparent concentrations by applying Castaing's first approximation for quantitative analysis (Laskin and Cowin, 2001) and standardized up to 100%.

3. Results and discussion

3.1. Marine particles

Output results of ascending hierarchical analyses performed on SEM-EDX data are reported in Figure 1. Clusters partially composed of Na were grouped all together to form one large cluster (Figure 1, cluster E). Atmospheric sodium is principally derived from seawater, minerals and, in a lesser extent, from anthropogenic activities (Ooki et al., 2002). In our experiment, Na was never associated to Si or K, respectively tracer of Na-containing terrigenous and anthropogenic aerosols (Ooki et al., 2002) and can thus be regarded as totally derived from seawater. Na-containing particles, referred to as marine particles, were the major particle type representing on average 70% of particles. The overwhelming abundance of Na-rich particles is due to meteorological conditions specific to our coastal sampling site. Sea-salt particles are emitted prominently by breaking waves. They can be freshly-emitted sea-salt particles (arbitrarily designated as such when $\text{Na} + \text{Cl} > 90\%$) with no or low S content, or aged sea-salts ($\text{Na} + \text{S} + \text{Cl}$ or $\text{Na} + \text{S} > 90\%$), for which the atmospheric lifetime is long enough for effective conversion of chlorides into sulphates. The conversion of sea-salt particles by exchange of chlorides for sulphates and/or nitrates is documented in details elsewhere (Li and Okada, 1999; Roth and Okada, 1998).

3.2. Continental particles

All particles with no Na were assigned to continental – including both natural and anthropogenic – origins. As reported by authors taking an interest in the North Sea (De Bock et al., 1994; de Hoog et al., 2005; Injuk et al., 1993; Rojas and Van Grieken, 1992), only a small variety of particle types is statistically found whatever the meteorological conditions are. Ca-S-rich particles (on average $\text{Ca} + \text{S} = 91\%$), identified as gypsum, represented on average 17% of particles (Figure 1, cluster A). They can be the product of fractional crystallization of marine aerosols. They may also result from the reaction of marine CaCO_3 with atmospheric anthropogenic sulphur compounds or with DMSO/DMS (an end-product of algal protein material breakdown) (Xhoffer et al., 1991). However, Hoornaert et al. (1996) pointed out that these marine sources are only of little importance. They suggested that a large fraction of gypsum particles comes from anthropogenic sources, including the reaction between land-derived CaCO_3 and atmospheric sulphur compounds. Several industrial sources (e.g. dust from gypsum quarries, metal plants, combustion processes and desulfurizing processes in fossil fuel power plants) may also explain the presence of gypsum particles in the low troposphere. Therefore, Ebert et al. (2000) attributed gypsum particles to natural and anthropogenic sources in equal proportions. Al-Si-rich particles (on average $\text{Al} + \text{Si} = 70\%$), identified as aluminosilicates, represented roughly 8% of particles (Figure 1, cluster B). They comprise a large variety of minerals. Thus, the ratio Al/Si widely varies depending on the other minor associated elements (Ca, K, Mg, Na, S and Fe). These particles can be of crustal origin (e.g. windblown soil dusts), or of anthropogenic origin (e.g. fly ashes produced by burning fossil fuels) (Van Malderen et al., 1992; Xhoffer et al., 1991). These two distinct sources emit particles of similar chemical composition.

3.3. Fe-bearing aerosols

Fe-rich particles (on average Fe mass concentration = 69%) represented on average 4% of particles (Figure 1, cluster D). Fe-rich particles are thought to be more likely of anthropogenic origin, even though they could also be of crustal origin (Chester et al., 1996; Moore et al.,

1984; Prospero et al., 2001). Considering the large extent of industrial activities in northern France – located approximately 50 km away from the east of the sampling site – strongly influencing the local apportionment of inorganic aerosol pollutants (Véron et al., 1999), Fe-rich particles are usually attributed to industrial emissions. Regional contamination of air masses by industrial aerosols was confidently witnessed by the presence of spherical Fe-rich particles similar to those emitted by steel works (Kopcewicz and Kopcewicz, 2001; Xhoffer et al., 1991).

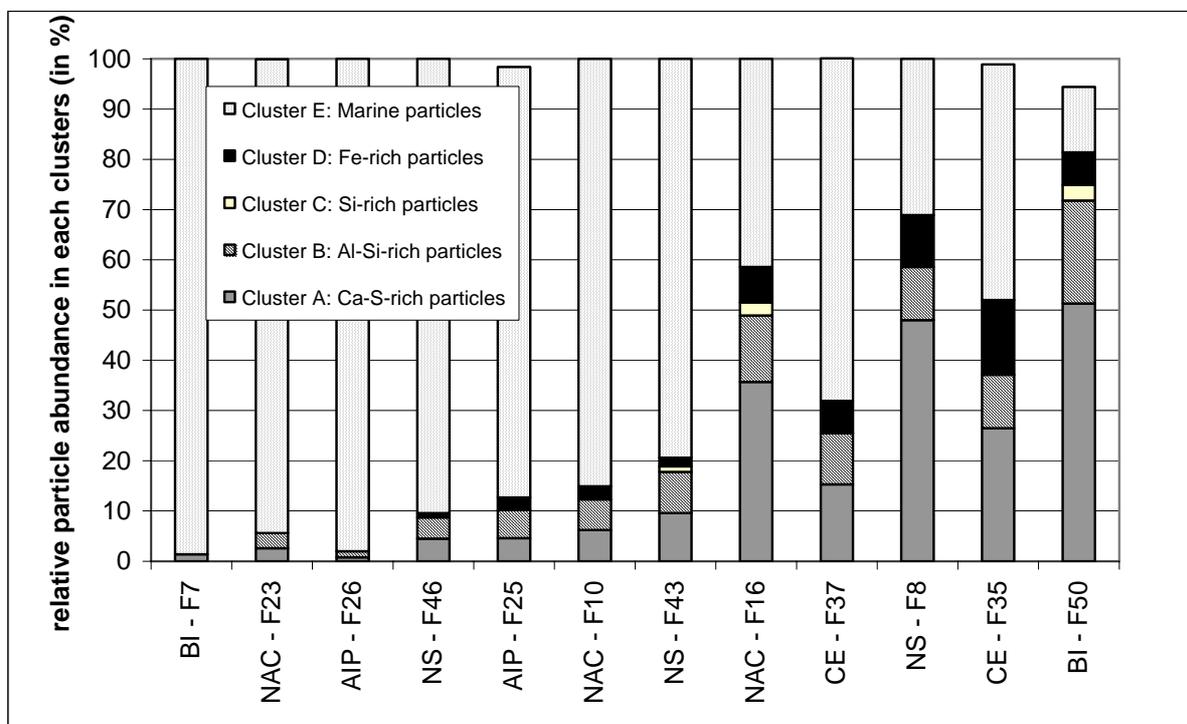


Figure 1: Results of the ascending hierarchical analysis of the atmospheric aerosol samples (the geographic classification is named behind the filter number)

To deepen our interpretations, a statistical reanalysis was performed only with Fe-bearing particles (863 particles with detectable Fe in their spectra), extracted from the whole dataset (11 842 particles). Among the nine output clusters (Table 1), only 3 clusters (clusters 2, 3 and 5) have high Fe contents ($\text{Fe} > 60\%$) accounting for 54.9% of Fe-bearing particles. These clusters probably gather together iron ((oxy)hydr)oxides. Iron oxides are usually interpreted as goethite, hematite or magnetite in atmospheric aerosols (Hoffmann et al., 1996; Kopcewicz and Kopcewicz, 2003). They are typically perfect spherules formed during industrial high-temperature processes such as those operated in steelworks and coal-fired power plants, although anthropogenic irregularly-shaped iron oxide particles can also be encountered (Seames, 2003; Zhang et al., 2005). Iron oxides were sometimes enriched in Zn (see Table 1, cluster 5) or Cr and Ni (Table 1, cluster 2) as reported in other works (Chen et al., 2006; Ledoux et al., 2004). These particles are likely formed during the re-melting/refining of scrap steel which already contains these metals as alloy components. Other clusters comprise mixtures like cluster 1 (probably mixed NaCl and Fe-rich particles) or cluster 8 (supposedly gypsum and Fe-rich particles), as well as larger particles of aluminosilicates (see Table 1, clusters 6-7) accounting for 34.2% of Fe-bearing particles. The aqueous solubility of aluminosilicates is slightly higher than that of iron oxides (Martin, 2005; Sofikitis, 2004), although the solubility likelihood depends above all on the natural or

anthropogenic origin of particles (Deguillaume et al., 2005; Hoffmann et al., 1996; Hsu et al., 2005). 1.3 % of Fe-bearing particles were mixed with titanium oxides (Table 1, cluster 9), which are often observed in atmospheric aerosols (Chen et al., 2006; Ebert et al., 2000; Murr and Bang, 2003).

Previous works (Machemer, 2004; Moreno et al., 2004) demonstrated how large steel works emissions impact on the atmospheric abundance of iron oxide particles. The impact at a regional scale of the steel metallurgy plant – located approximately 50 km away from the east of the sampling site – on the concentration of atmospheric pollutants was also demonstrated using lead isotopic tracers (Deboudt et al., 1999; Flament et al., 2002; Véron et al., 1999). It is in fact strongly linked to regional meteorological conditions (Ledoux et al., 2004). A regional contamination by Fe-rich particles emitted during steel works operations is suggested here.

	Relative abundance (in %)	Mean of relative elemental concentrations for each cluster (in wt.%)	Mean diameter (in μm)
Cluster 1	4.0	Cl(35%) Fe(33%) Na(21%)	0.87
Cluster 2	8.1	Fe(64%) Cr(19%) Ni(6%)	0.92
Cluster 3	42.5	Fe(87%)	0.90
Cluster 4	4.2	Fe(34%) S(25%) Na(23%) P(6%)	0.93
Cluster 5	4.3	Fe(61%) Zn(33%)	0.90
Cluster 6	22.6	Si(47%) Al(25%) Fe(11%)	1.62
Cluster 7	11.6	Si(32%) Fe(22%) Al(13%) Na(10%) Cl(6%)	1.63
Cluster 8	1.4	Ca(32%) S(32%) Fe(11%) Si(11%)	2.35
Cluster 9	1.3	Ti(67%) Fe(12%)	1.37

Table 1: Hierarchical clustering analysis of particles containing iron, extracted from all analysed samples. Only elements with a relative elemental concentration superior to 5% are reported in the table.

4. Conclusion

This work was devoted to characterizing Fe-bearing particles in coastal aerosols. Our specific in-shore sampling situation induced observing multi-disperse aerosols from distinct geographical origins. Single-particle analysis by SEM-EDX is demonstrated here to be particularly well-suited to revealing the relative proportions of Fe-bearing particles. A large variety of iron species encountered during the one-year campaign is attributed here to the mixing of crustal, industrial and marine-originating aerosols. ((Oxy)hydr)oxides and aluminosilicates are the main Fe-containing chemical forms, accounting respectively for 55% and 34% of particles.

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6. References

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