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Characterization of iron and manganese species in atmospheric aerosols from anthropogenic sources

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Abstract

Electron paramagnetic resonance (EPR) was used to study the chemical form of iron, manganese and other paramagnetic species in airborne particles collected on southern coastal part of the North Sea, located in France. In parallel, chemical analysis was performed to obtain the metal concentrations in samples whereas an individual analysis of particles was provided by scanning electron microscopy coupled to an energy-dispersive X-ray spectrometer (SEM-EDX). EPR spectra have evidenced Fe^{3+} and Mn^{2+} ions in the form of isolated or agglomerated species, as well as carbonaceous products with variable signal intensities according to the wind direction. The monitoring of a signal of isolated Mn^{2+} ions on a distance close to 90 km was proposed as tracer of particles from a Mn local emission source. Fe^{3+} signals are relative to agglomerated species and differences in the type of interaction between these species were evidenced following the wind direction. Fe^{3+} EPR signals parameters revealing antiferromagnetic contribution in Fe-rich particles were found for an industrial origin at Dunkerque.

Keywords: Mn^{2+}; Fe^{3+}; EPR; SEM-EDX; Tracer; Chemical form

1. Introduction

In recent years, considerable concerns have arisen on the extent of the pollution, particularly by the presence of metals in airborne particles. These observations lead to investigation of their origin with the development of characterization or speciation studies, using, for example, particle-induced X-ray emission (PIXE) (Dutta et al., 1998), Mössbauer spectroscopy and X-ray fluorescence (Hoffmann et al., 1996; Weber et al., 2000). The southern coast of the North Sea is particularly concerned by this form of pollution and atmospheric particles collected in cities in this area contain non-negligible amounts of as Fe, Mn, Cu and Cr (Baeyens and Dedeurwaerder, 1991; Injuk et al., 1998; Ebert et al., 2000). For this reason, it can be supposed that electron paramagnetic resonance could give an interesting contribution to the identification of the chemical environment of some metal ions, which are paramagnetic following their oxidation degree (Fe^{3+}, Mn^{2+}, Cu^{2+}, Cr^{3+}). Electron

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paramagnetic resonance (EPR) spectroscopy remains a technique as yet rarely applied for the study of atmospheric particles (Yordanov et al., 1996; Ledoux et al., 2002). Due to its high sensitivity, this non-destructive technique can be used for the analysis of particles collected on filters. EPR can confirm the presence of paramagnetic species having one or more unpaired electrons and permit in some cases to describe the environment of the species in its matrix.

In this work, chemical analysis, scanning electron microscopy coupled to an energy-dispersive X-ray spectrometer (SEM-EDX) and electron paramagnetic resonance (EPR) were used to study manganese and iron species. The aim of this study is to illustrate the contribution of EPR and SEM-EDX for the characterization and the investigation of the origin of Mn^{2+} and Fe^{3+} ions, following their chemical environment and their concentration in atmospheric particles.

2. Experimental methods

2.1. Sampling and sample processing

Aerosol samples were collected on the southern coast of the North Sea between Wimereux and Dunkerque (Nord-Pas de Calais region) (Fig. 1). The Wimereux and Cape Gris-Nez sites were affected by S-SW winds directly by the emissions of an important ferromanganese metallurgy plant until the end of 2003 (10% of the world production) situated in the Boulogne-sur-Mer agglomeration (120,000 inhabitants) at a distance of 5 km from Wimereux and 20 km from Cape Gris-Nez. Aerosols were sampled there between November 1998 and June 1999. Dunkerque is an industrial city (210,000 inhabitants) where particle emissions (handling of ores, steel plant, petrochemistry) from industries are estimated to 4200 t/year (DRIRE, 2004). Particles were sampled there in June–July 2000 and January–February 2001. In both cases, the sampling was performed at the top of a mast at about 10 m high above ground level. Particles were collected simultaneously by global filtration on cleaned Whatman 41 cellulose filters and polycarbonate filters with respective porosities 0.04 and 0.45 μm. Samples were collected for a period of 12 h using a 5 m^3/h pumping device. At the source point, a six-stage high-volume cascade impactor (Sierra 235, 68 m^3/h) was used in parallel in order to obtain size-segregated particles. The cut-off diameters (D_{p50}) of the different impactor stages are 5.08, 2.10, 1.04, 0.64, 0.33 and 0.04 μm. In this area, the climate is dominated by W-SW winds. Meteorological conditions have been recorded by an automatic weather station, DAVIS weather monitor II, implanted on the sampling site.

2.2. Aerosols analysis

Inductively coupled plasma–atomic emission spectrometry (ICP-AES, Varian Liberty II) was used to quantify Al, Ba, Cr, Fe, Mn, Sr and Zn, whereas Cu and Pb concentrations were determined with the graphite furnace atomic absorption spectrometry (GFAAS) technique (Perkin Elmer, AAnalyst 600, Zeeman background correction). Automated single particle analysis was performed on a 438 VP microscope (LEO, Cambridge, UK) equipped with an energy-dispersive X-ray spectrometer (IXRF, USA) (SEM-EDX). Typical working parameters were an accelerating voltage of 25 kV, a beam current of 300 pA and a magnification of 3500×. In these conditions, particles taken into account are in the size range of 0.2–10 μm (geometric diameter). 600 randomly selected particles for each sample were analysed. In fact, according to

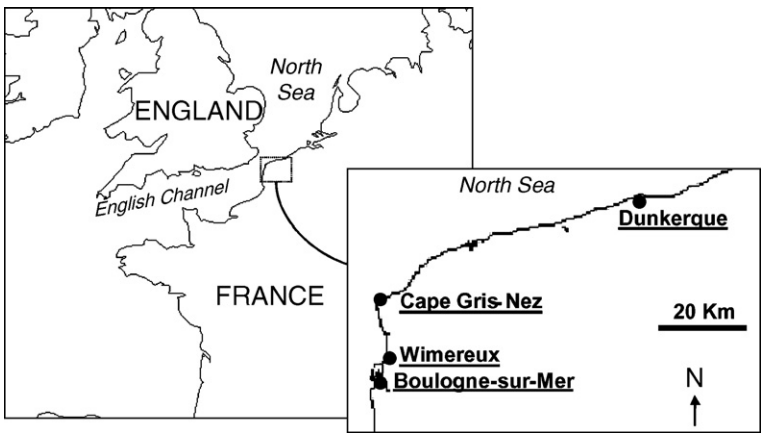

Fig. 1. Sampling location.