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Metal exposure in cows grazing pasture contaminated by iron industry: Insights from magnetic particles used as tracers☆

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ABSTRACT

Magnetic particles (MP) emitted by an iron smelter were used to investigate the exposure of cows grazing on a grassland polluted by these MP and by large amounts of potentially toxic elements (PTE). The morphology as well as the chemical composition of the MP separated from cow dung were studied. Large amounts of typical MP were found (1.1 g kg^{-1} dry weight) in the cow dung sampled from the exposed site, whereas these particles were absent from the reference unpolluted site. The ingested MP were mainly technogenic magnetic particles (TMP) emitted by the smelter. Considering the MP concentration in the grazed grass on the exposed site, it was concluded that cows absorb the MP not only from the grass but also from the soil surface. The results of a mild acidic leaching of the MP suggested that the particles were possibly submitted to a superficial dissolution in the abomasum, pointing at a potential route of transfer of the PTE originating from the TMP and leading into food chains. TMP were only a small part of the anthropogenic contamination having affected the soil and the dung. However, due to their unequivocal signature, TMP are a powerful tracer of the distribution of PTE in the different compartments constituting the food chains and the ecosystems. Furthermore, the measurement of the particle sizes gave evidence that a noticeable proportion of the MP could enter the respiratory tract.

1. Introduction

In developed countries such as those of the European Community, strict policies control the emission of anthropogenic contaminants into the atmosphere, through the measurement of air concentrations, mainly in densely populated areas, in order to avoid respiratory disorders in the population (European program CAFE "Clean Air For Europe", Pritchard et al., 1996; Costa and Dreher, 1997; Wilson and Suh, 1997; Haapala, 1998; Harrison and Yin, 2000; Dye et al., 2001; Kampa and Castanas, 2008; Suzuki, 2006). After their emission to the atmosphere, industrial organic or inorganic pollutants are submitted to a very complex deposition process, depending on the density of particles, the landscape morphology and meteorological events (Sabin et al., 2006; Uematsu et al., 2010). This deposition induces accumulation of poorly soluble compounds and of compounds having a high chemical stability in or on different matrices, among which the soil upper layer is one of the most contaminated (Kidd et al., 2000; Rapant et al., 2006; Laidlaw and Filippelli, 2008; Lestan et al., 2008; Bourennane et al., 2010). Such accumulation is in direct contact with living organismss, plants, animals and man included, which constitute the active part of anthropo-ecosystems. It represents a long term threat for their survival. The induced risk depends on the concentration levels of these potentially toxic substances in the ecosystem and on their specific toxicity which deeply varies from one living species to others (Simms et al., 2009; Lovett et al., 2009).

In most cases previously studying such deposition and accumulation of xenobiotics (e.g., Suzuki, 2006; Catinon et al., 2013; Aranzazu Revuelta et al., 2014), the deposits were composed of a

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mixture of a very large number of substances, elements or organic compounds which arose, from various sources (mines, smelting estates, other industries, car traffic, global urban emissions, etc). This mixture was generally so complex that it was not possible to evaluate accurately the role played by each source. In contrast, anthropogenic particles and the associated contaminants issued from several smelting activities have been shown to be emitted by intense, well-localized sources and have a readable signature (Szynkowska et al., 2008; Suzuki, 2006; Silva et al., 2009; Brown et al., 2011; Catinon et al., 2014; Miler and Gosar, 2015). Several recent studies have shown that technogenic magnetic particles (TMP), easily extractable from the deposit and having very recognisable shape and composition, are noteworthy markers of atmospheric transfer in several situations (e.g. Bucko et al., 2011; Catinon et al., 2014). Using these tracers, it seems possible to understand the distribution, concentration and ecological fate of the pollutants over longer periods of time and consequently evaluate their possible specific toxicological and ecotoxicological impacts. This is a first step in conceiving the possible ways of environmental management improvement (Kidd et al., 2000; Laidlaw and Filippelli, 2008; Lestan et al., 2008; Fränzle et al., 2012).

The purpose of the project partly reported here was to understand one step of the ecological contamination process, from the deposition of the elemental contaminants emitted by an industrial source to the uptake by living organisms. In the present study, we addressed the transfer of the elements to grazing animals through consumption of soil and herbage contaminated through aerial deposition. This transfer is an important step for accessing to the human food chain (Wilkinson et al., 2003; Gall et al., 2015). A herd of cows had been grazing consistently in a pasture located in the studied site, Chateauneuf (France), heavily contaminated by steel industry. The structure, composition, shape, size and rate of emission and of deposition of the corresponding TMP in this site had been studied previously over several years (Catinon et al., 2014). The current report shows how the anthropogenic elemental mixture containing TMP was acquired by cows through grazing and partly reemitted within the faeces, as an illustration of the incursion of anthropogenic elements into the food chain of a terrestrial ecosystem.

2. Material and methods

2.1. Sampling sites

Since 1865, an intense steel industry has been developing in the Giers River valley between St Chamond and Givors cities (S.E. of France). The large metallurgic plant is located at the bottom of the valley (alt. 221 m.a.s.l.) in the small town of Chateauneuf (Loire department, France) close to the Rive-de-Giers city. The average production of this plant is from 55,000 tons to 80,000 tons of steel per year.

The main sampling place for atmospheric deposits stands on the top of a hill (alt. 335 m.a.s.l.) which looks down onto the Chateauneuf village (alt. 221 m.a.s.l.) and onto the important smelting plant located 0.5 km away. An enclosed 3 ha pasture is located on the top of the hill and adjacent to the graveyard where deposit sampling was carried out from tombstones (Catinon et al., 2014). In this pasture, cow dungs were sampled periodically. Another herd was grazing in a pasture located in Longes, 5 km away from Chateauneuf. The cow dung from this site was sampled once, for comparison. In both sites, the vegetation was dominated by grass (Poaceae).

2.2. Cow dung sampling

The cow herd (10–20 cows) grazed three to four months each year in spring (April to June) and in autumn (September to November). Dungs of different ages, fresh to completely dry, were sampled in 3 L polyethylene bags without taking the bottom part to avoid soil contamination. Their dry weight (DW) content was measured on a 10 g aliquot after 48 h drying at 40 °C. An aliquot of each sample (from 100 to 500 mg) was heated at 550 °C overnight under controlled conditions (Saarela et al., 2005; Reimann et al., 2008) to calculate the organic matter content.

2.3. Magnetic particles isolation and concentration measurement

Dung (~1000 g) was dispersed in water with a Wareing blendor and the magnetic particles were extracted repeatedly as previously described for soil (Catinon et al., 2014), using a ferrite magnet (Walker Braillon magnetics) wrapped in a double polyethylene bag. After several washings and sonication (2 × 1 min), the magnetic particles (MP) pellet was air dried at 60 °C, weighed and the ratio magnetic particles to total dry weight calculated. The same protocol was applied to soil and grass.

2.4. SEM-EDX studies

Particle imaging and microanalysis were performed using a ZEISS SUPRA 55 VP Scanning Electron Microscope (SEM), allowing a spatial resolution down to 1.0 nm, coupled to an Energy Dispersive X-ray (EDX) microanalysis system (SAHARA Silicon Drift Detector with Spirit Software of PGT) allowing high counting rates (Catinon et al., 2013, 2014). SEM photographs were used for size measurement, volume and weight gross estimations. A ZAF semi-quantitative evaluation of concentrations (>5 g kg^{-1}) was carried out on 1 mm^2 large samples corresponding to a 3–5 mg of material. This allowed a comparison between samples, especially for the ratio Si/Al.

2.5. ICP-MS: determination of elemental content

The total digestion of the dung (~100 mg) after extraction of the MP fraction and the MP fraction (~50 mg) was conducted in PTFE closed flasks, on a digestion plate (Digiprep, SCP Science) using ultrapure reagents (HNO_3 Normatom grade, VWR; HCL, HF, $HClO_4$: TraceMetal grade, FisherScientific). HCl (5 mL) was added (100 °C for 10 h). After evaporation, 5 mL HF and HNO_3 were added (100 °C, 10 h). After evaporation, 5 mL of $HClO_4$ and HNO_3 were added (120 °C, 20 h). The solutions that contained no residue were evaporated to dryness, retaken 3 times in 2 mL of HNO_3 and then diluted to 50 mL with HNO_3 0.5 M. The elemental content was determined by inductively coupled plasma – mass spectrometry ICP-MS (X^{II+} CCT series, Thermo). The data quality was controlled with the certified reference material sediment-SL1 (International Atomic Energy Agency, Vienna). The concentration values obtained agreed within the certified or information values within 10% for all except Na and K (20 and 25% lower than the information values, respectively). Analytical uncertainties were lower than 8%, except for Ag and Cd (12 and 16%, respectively).

2.6. MP acidic attack

A sample of dung purified MP fraction (50 mg) was dispersed in HNO_3 1 M (Rotipuran ultra from Roth) for 24 h at laboratory temperature. After centrifugation at 5000 rpm, the pellet was discarded and the solution evaporated to dryness was submitted to SEM-EDX analysis.