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Superparamagnetic iron oxides nanoparticles from municipal solid waste incinerators

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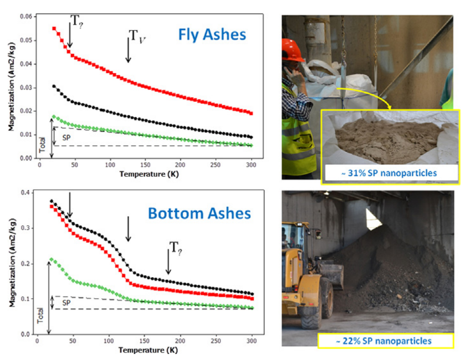
HIGHLIGHTS

- We interrogate risky SP and iron phases pollution originating from MSWI ashes.
- Magnetic techniques confirm a complex mineralogy with mixed iron oxides/sulphides.
- Magnetic domain states reveal particles (often aggregate) with varying grain sizes.
- Large amounts of SP grains may ensue during production/management of MSWI ashes.

GRAPHICAL ABSTRACT



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ABSTRACT

During their production, management, and landfilling, bottom (BA) and fly (FA) ashes from municipal solid waste incineration may liberate Fe-bearing, ultrafine particles and easily enter different environmental sinks of the biosphere. We aim to explore a collection of BA and FA samples from Italian incinerators to probe magnetic mineralogy and the fraction of harmful superparamagnetic (SP) nanoparticles (d < 30 nm). X-ray diffraction, electron microscopy observation, temperature- and frequency-dependent magnetometry, and Mossbauer analysis are performed. The integration of information from our rock magnetic and non-magnetic techniques leads us to conclude that the dominant magnetic carrier in our samples is magnetite and its intermediate/impure forms, while sulphides (i.e., monoclinic pyrrhotite) are important ancillary magnetic phases. The SP fraction fluxing from the BA and FA outputs of a single incinerator is detected and estimated in 10^3 tons/year. This work stresses the need to calibrate the current technologies towards a safer management of combustion ashes and certainly to inform the environmental impact assessment by using a combination of different methods.

1. Introduction

Human exposure to nanoparticles pollution and environmental contamination related to Fe-bearing phases has dramatically increased during the last 30 years. It is estimated that million tons of toxic pollutants are released into the air each year (W.H.O, 2013). Amongst these pollutants, iron- and sulphur-rich nanoparticles are liable of a range of

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adverse health effects in the general population, from subclinical chronic diseases to premature death (Pope et al., 2002). Magnetite nanoparticles from particulate matter are also found in human brain suggesting a connection between the presence of these particles and neurodegenerative diseases such as Alzheimer's disease (Maher et al., 2016). In this context, environmental magnetic studies are beneficial to explore environmental media and characterise therein contained iron minerals according to ferrimagnetic or antiferromagnetic properties (Thompson & Oldfield, n.d.). Magnetic minerals can act as pollutant carriers through adsorption and structural incorporation. Some studies reported a correlation between magnetic parameters and heavy metal contents in different kinds of material, such as airborne particulate matter (Muxworthy et al., 2002; Sagnotti & Winkler, 2012), roadside pollution (Hansard et al., 2012; Zhu et al., 2013), soils (Dearing et al., 1997; Fialová et al., 2006; Jordanova et al., 2003; Wang et al., 2010) lake and river sediments (Vigliotti et al., 1999; Zhang et al., 2011), and fly ashes (Jordanova et al., 2006; Lu et al., 2009; Magiera et al., 2011; Veneva et al., 2004). Magnetic parameters are successfully used as a tracer of a wide range of pollutants related to anthropogenic activities and also to detect particulates that strictly represent a respiratory hazard. Magnetic properties are highly sensitive to certain particle size ranges; conventional grain-size assignments (for magnetite) are: superparamagnetic (SP: $d < 30$ nm); stable single domain (SD: 30 nm $< d <$ 84 nm); pseudo-single domain (PSD: 84 nm $< d <$ 17 μm); multi-domain (MD: $d > 17$ μm) (Moskowitz et al., 2015). Particles formed by combustion sources are usually fine or ultrafine (Englert, 2004), with a diameter in the submicron range, and have the highest potential to endanger life (Englert, 2004; Solaimani et al., 2016). Heavy metal concentrations in the fine particulate were found to be higher in industrial districts than in other areas (Zhu et al., 2013), emphasising the health risk associated with industrial emitters and industrial processes. The particles diameter and the size distributions can vary in space and time due to differences in emission sources and atmospheric processes (Lamancusa et al., 2017; Levy et al., 2003). Therefore, dust and the finest fraction of ashes generated by industrial processes gain increasing attention in environmental magnetic studies aimed to assess anthropogenic alterations of air, soil, and water. Since coal combustion represents an important world source of energy supply leading to the production of waste and dust, the iron minerals occurring in raw materials, fuels, additives, or residues are carefully studied. During such a technological process, the iron minerals are acknowledged to form highly magnetic particles with the tendency to bind hazardous elements. An extensive literature on fly ashes and polluted soils from coal-combustion power plants is available (Jordanova et al., 2006; Lu et al., 2009; Magiera et al., 2011; Szuszkiewicz et al., 2015; Veneva et al., 2004). Some works on Fe-smelters (Zhang et al., 2011) and on municipal landfill leachates (Huliselan et al., 2010) do exist. However, the assessment of the magnetic behaviour of municipal solid waste incineration (MSWI) ashes remains largely overlooked despite their recognised hazardous nature and the nanoparticles emission is acknowledged to occur (Cernuschi et al., 2012). The municipal solid waste incineration (MSWI) is considered a good practice for reducing the waste volume and recovering its energy to produce electricity. Nevertheless, the risk perceived by people living near waste incinerators is very high and testified by a diffuse social response like the "*not in my backyard*". MSWI plants generate huge amounts of solid residues, around 10^4 t/a (Funari et al., 2016), and ca. 0.7 tons of gases and particulate vapour per tonne of input waste (C.P.P, 2004). The bottom ash (BA) is the largest fraction generated in the combustion chamber; after an approximate residence time of 30 to 45 min on the grate furnace (up to 1150 °C), the BA is usually quenched in cold water. Conversely, the particulate material from the combustion chamber is sparged to the Air Pollution Control (APC) system equipped with some flue gas treatments devices, such as scrubbers, bag filters, and electrostatic precipitators. Both MSWI ashes and MSWI emission at the stacks showed particle diameters of recognised inhalable risk (Cernuschi et al., 2012; De Boom & Degrez, 2012), encompassing the risk of primary and secondary pollution. The contribution of waste incinerators to the intake fraction is thought to be negligible (Buonanno & Morawska, 2015), but the limited number of studies coupled with the lack of standard protocols for the risk assessment emphasises the need to further investigation.

This work aims at:

- investigating the magnetic properties of MSWI ashes from four Italian facilities;
- identifying the magnetic components liable of the strong magnetic signals observed in prior start-point measurements (Funari, 2016; Funari et al., 2016);
- evaluating whether a new pollution risk related to SP grains is significant.

Spatiotemporal variations of MSWI pollution patterns are not assessed in this work. Here we provide magnetic reference data of a particular combustion product to inform pollution-related environmental magnetic studies and to assess potential health risks triggered by urban waste incineration.

2. Samples and methods

A collection of BA and FA samples was taken from four MSWI systems of northern Italy following the sampling methodology as in Funari et al. (2016). The selected facilities are located in four different municipalities and serve an area of about 10,000 km^2 within the Po Valley. Each incinerator equipped with a grate-furnace system operates at temperatures between 850 and 1100 °C. The solid waste input, which averages $1.5 \cdot 10^5$ tons per year, consists of 90% household waste and 10% of special waste, i.e. processing waste from steel-making industries, scraps from ceramics, automobile shredder residues, and hospital/pharmaceutical waste. The solid waste output averages $4.6 \cdot 10^4$ BA and $4.1 \cdot 10^3$ FA tons per year, respectively. The figure for BA does not include the ferrous metal scraps (ranging $5–8 \cdot 10^3$ tons per year) that are recovered by a rough magnetic separation after quenching and re-melted for reuse in an integrated system; the ferrous metal fraction is not taken in this study. The FA samples are further divided into different categories depending on the APC technology. Where it was possible, FA were collected at the first recovery phase without any treatment (untreated, FAU), after the electrostatic precipitator (FAE), and after chemical bag filters, which involved the use of soda (FAS) or lime (FAL) additives. It is recognised that samples of incinerated wastes cannot display the variability inherent in a given plant during the time and changes of the feedstock materials. Nevertheless, each sample is representative of the MSWI ash category of each MSWI plant, as determined by previous works focusing on the same materials (Funari et al., 2015; Funari et al., 2016; Funari et al., 2016).

We analysed BA and FA samples by a range of magnetic and mineralogical techniques. The collected materials were oven dried at 40 °C for one week. The biggest metallic fragments partially melted or destroyed by the thermal treatment ($d > 1$ cm; mostly in BA samples) were hand-sorted and removed before the measurements. For samples with abundant magnetic materials (i.e., BA), magnetic extracts from dried and milled samples were obtained using a Nd hand magnet with a plastic sleeve. Extracts from samples with sparse magnetic materials (i.e., FA), were collected using a Frantz magnetic separator by imparting a 1.1 A current in the laminar isodynamic region and a + 15° side slope of the chute. A range of magnetic measurements was conducted on triplicate samples at the Institute of Marine Sciences of the National Research Centre (CNR-ISMAR, Bologna) and the Institute for Rock Magnetism (IRM, University of Minnesota). The chemical composition, mineralogy, and morphology were investigated by non-magnetic technique, such as XRF, SEM, XRD, at the BiGeA Department (University of Bologna) and the Department of Physics and Earth Sciences (University of Parma).