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1 Superparamagnetic iron oxides nanoparticles from 2 municipal solid waste incinerators

3 FUNARI V.^{1,3}, MANTOVANI L.², VIGLIOTTI L.³, TRIBAUDINO M.², DINELLI E.¹, BRAGA R.¹

4 ¹Dipartimento di Scienze Biologiche Geologiche e Ambientali (BiGeA), Università di Bologna, Bologna, Italy

5 ²Dipartimento di Fisica e Scienze della Terra, Università degli Studi di Parma, Parma, Italy

6 ³Instituto di Scienze Marine, Consiglio Nazionale delle Ricerche, Bologna, Italy

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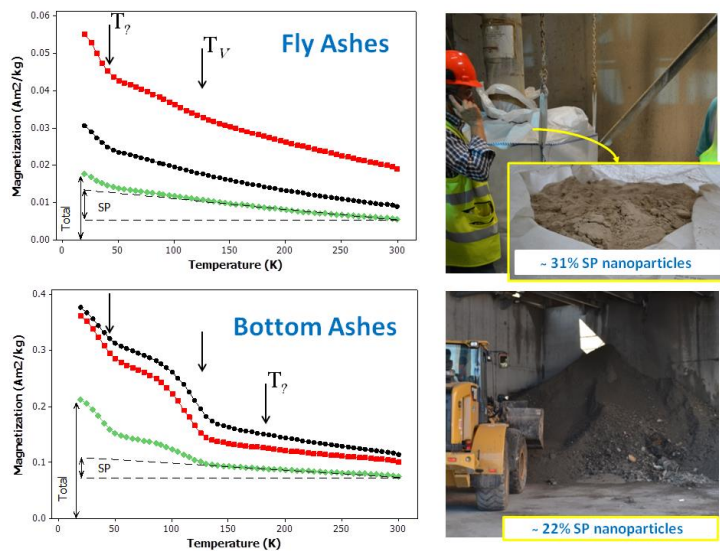
8 **Keywords:** Municipal Solid Waste Incineration (MSWI), fly ash and bottom ash, iron oxides,
9 superparamagnetic (SP) particles, anthropogenic pollution.

10 Highlights:

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

15

Graphical abstract



16

17 **ABSTRACT**

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

31 **1. INTRODUCTION**

32 Human exposure to nanoparticles pollution and environmental contamination related to Fe-
33 bearing phases has dramatically increased during the last 30 years. It is estimated that million tons
34 of toxic pollutants are released into the air each year [1]. Amongst these pollutants, iron- and
35 sulphur-rich nanoparticles are liable of a range of adverse health effects in the general population,
36 from subclinical chronic diseases to premature death [2]. Magnetite nanoparticles from particulate
37 matter are also found in human brain suggesting a connection between the presence of these
38 particles and neurodegenerative diseases such as Alzheimer's disease [3]. In this context,
39 environmental magnetic studies are beneficial to explore environmental media and characterise
40 therein contained iron minerals according to ferrimagnetic or antiferromagnetic properties [4].
41 Magnetic minerals can act as pollutant carriers through adsorption and structural incorporation.
42 Some studies reported a correlation between magnetic parameters and heavy metal contents in
43 different kinds of material, such as airborne particulate matter [5, 6], roadside pollution [7, 8], soils
44 [9-12] lake and river sediments [13, 14], and fly ashes [15-18]. Magnetic parameters are
45 successfully used as a tracer of a wide range of pollutants related to anthropogenic activities and
46 also to detect particulates that strictly represent a respiratory hazard. Magnetic properties are highly
47 sensitive to certain particle size ranges; conventional grain-size assignments (for magnetite) are:
48 superparamagnetic (SP: $d < 30$ nm); stable single domain (SD: 30 nm $< d < 84$ nm); pseudo-single

49 domain (PSD: $84 \text{ nm} < d < 17 \text{ }\mu\text{m}$); multi-domain (MD: $d > 17 \text{ }\mu\text{m}$) [19]. Particles formed by
50 combustion sources are usually fine or ultrafine [20], with a diameter in the submicron range, and
51 have the highest potential to endanger life [20, 21]. Heavy metal concentrations in the fine
52 particulate were found to be higher in industrial districts than in other areas [7], emphasising the
53 health risk associated with industrial emitters and industrial processes. The particles diameter and
54 the size distributions can vary in space and time due to differences in emission sources and
55 atmospheric processes [22, 23]. Therefore, dust and the finest fraction of ashes generated by
56 industrial processes gain increasing attention in environmental magnetic studies aimed to assess
57 anthropogenic alterations of air, soil, and water. Since coal combustion represents an important
58 world source of energy supply leading to the production of waste and dust, the iron minerals
59 occurring in raw materials, fuels, additives, or residues are carefully studied. During such a
60 technological process, the iron minerals are acknowledged to form highly magnetic particles with
61 the tendency to bind hazardous elements. An extensive literature on fly ashes and polluted soils
62 from coal-combustion power plants is available [15-18, 24]. Some works on Fe-smelters [14] and
63 on municipal landfill leachates [25] do exist. However, the assessment of the magnetic behaviour of
64 municipal solid waste incineration (MSWI) ashes remains largely overlooked despite their
65 recognised hazardous nature and the nanoparticles emission is acknowledged to occur [26]. The
66 municipal solid waste incineration (MSWI) is considered a good practice for reducing the waste
67 volume and recovering its energy to produce electricity. Nevertheless, the risk perceived by people
68 living near waste incinerators is very high and testified by a diffuse social response like the “*not in
69 my backyard*”. MSWI plants generate huge amounts of solid residues, around 10^4 t/a [27], and ca.
70 0.7 tons of gases and particulate vapour per tonne of input waste [28]. The bottom ash (BA) is the
71 largest fraction generated in the combustion chamber; after an approximate residence time of 30 to
72 45 minutes on the grate furnace (up to 1150° C), the BA is usually quenched in cold water.
73 Conversely, the particulate material from the combustion chamber is sparged to the Air Pollution
74 Control (APC) system equipped with some flue gas treatments devices, such as scrubbers, bag
75 filters, and electrostatic precipitators. Both MSWI ashes and MSWI emission at the stacks showed
76 particle diameters of recognised inhalable risk [26, 29], encompassing the risk of primary and
77 secondary pollution. The contribution of waste incinerators to the intake fraction is thought to be
78 negligible [30], but the limited number of studies coupled with the lack of standard protocols for the
79 risk assessment emphasises the need to further investigation.

80 This work aims at:

- 81
- investigating the magnetic properties of MSWI ashes from four Italian facilities;

- 82
- identifying the magnetic components liable of the strong magnetic signals observed in
- 83 prior start-point measurements [27, 31];
- evaluating whether a new pollution risk related to SP grains is significant.
- 84

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

89 2. SAMPLES AND METHODS

90 A collection of BA and FA samples was taken from four MSWI systems of northern Italy
91 following the sampling methodology as in Funari et al. [32]. The selected facilities are located in
92 four different municipalities and serve an area of about 10000 km² within the Po Valley. Each
93 incinerator equipped with a grate-furnace system operates at temperatures between 850-1100° C.
94 The solid waste input, which averages 1.5·10⁵ tons per year, consists of 90% household waste and
95 10% of special waste, i.e. processing waste from steel-making industries, scraps from ceramics,
96 automobile shredder residues, and hospital/pharmaceutical waste. The solid waste output averages
97 4.6·10⁴ BA and 4.1·10³ FA tons per year, respectively. The figure for BA does not include the
98 ferrous metal scraps (ranging 5-8·10³ tons per year) that are recovered by a rough magnetic
99 separation after quenching and re-melted for reuse in an integrated system; the ferrous metal
100 fraction is not taken in this study. The FA samples are further divided into different categories
101 depending on the APC technology. Where it was possible, FA were collected at the first recovery
102 phase without any treatment (untreated, FAU), after the electrostatic precipitator (FAE), and after
103 chemical bag filters, which involved the use of soda (FAS) or lime (FAL) additives. It is recognised
104 that samples of incinerated wastes cannot display the variability inherent in a given plant during the
105 time and changes of the feedstock materials. Nevertheless, each sample is representative of the
106 MSWI ash category of each MSWI plant, as determined by previous works focusing on the same
107 materials [27, 32, 33].

108 We analysed BA and FA samples by a range of magnetic and mineralogical techniques. The
109 collected materials were oven dried at 40° C for one week. The biggest metallic fragments partially
110 melted or destroyed by the thermal treatment ($d > 1$ cm; mostly in BA samples) were hand-sorted
111 and removed before the measurements. For samples with abundant magnetic materials (i.e., BA),
112 magnetic extracts from dried and milled samples were obtained using a Nd hand magnet with a

113 plastic sleeve. Extracts from samples with sparse magnetic materials (i.e., FA), were collected using
114 a Frantz magnetic separator by imparting a 1.1 A current in the laminar isodynamic region and a
115 +15° side slope of the chute. A range of magnetic measurements was conducted on triplicate
116 samples at the Institute of Marine Sciences of the National Research Centre (CNR-ISMAR,
117 Bologna) and the Institute for Rock Magnetism (IRM, University of Minnesota). The chemical
118 composition, mineralogy, and morphology were investigated by non-magnetic technique, such as
119 XRF, SEM, XRD, at the BiGeA Department (University of Bologna) and the Department of
120 Physics and Earth Sciences (University of Parma). Furthermore, ⁵⁷Fe Mössbauer spectra were
121 measured at the IRM (University of Minnesota) on selected original samples and magnetic extracts.
122 Further details on analytical methods are in the Supporting Information (SI).

123 **3. RESULTS AND DISCUSSION**

124 ***3.1 XRD analysis and morphological observations***

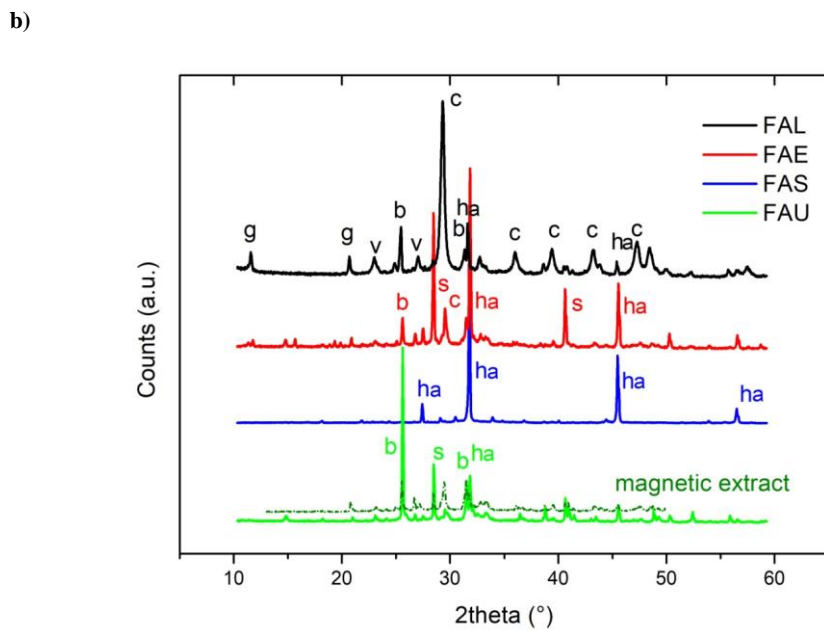
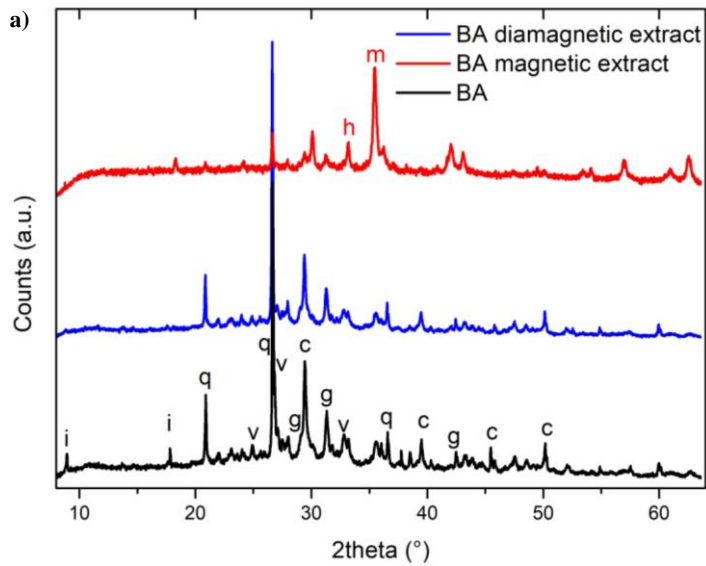
125 The BA and FA samples show complex X-ray diffraction patterns (Fig. 1), consisting of
126 crystalline phases and large amounts of amorphous/nanocrystalline materials. According to
127 numerous studies, the main phases in BA consists of solid phases with high melting points already
128 contained in the municipal solid waste feed and melt products such as glass, melilite- and spinel-
129 group minerals [34, 35]. Conversely, FA have a quite different mineralogy ascribed to the MSWI
130 technological process from the combustion to the subsequent flue-gas cleaning, i.e. vaporisation,
131 melting, crystallisation, vitrification, condensation and precipitation [36]. The main crystalline
132 phases are sulphates, carbonates, chlorides silicates, phosphates, and oxides. The phases identified
133 by XRD analysis and their semi-quantitative estimates are reported in Table S.1. On the XRD
134 analysis, the iron oxides result in lower amounts compared to other minerals. The XRD patterns for
135 all our specimens show a considerable amount of amorphous or nanocrystalline materials, which is
136 estimated around 50 wt. % BA and 15-20 wt. % FA (see SI for details).

137 Among the crystalline phases in BA samples, a few minerals such as quartz, gehlenite and
138 calcium carbonates (both calcite and vaterite) are easily identified (Fig. 1a). Other mineral phases
139 cannot be identified by a simple search-matching procedure due to a large number of overlapping
140 peaks and to the shift of peaks position because of solid solution members. For example, the
141 presence of plagioclase, feldspar, and pyroxene in BA is highly probable but estimating their
142 chemical composition is unrealistic due to solid solutions and substitutions of other metal ions in
143 the crystal lattice. Phyllosilicates (e.g., muscovite, illite), iron oxides, and a few peaks identifying

144 metallic aluminium are detectable as minor phases. This mineralogical assemblage is characteristic
145 of all BA samples. The magnetic extract of BA shows the presence of iron oxides such as hematite,
146 magnetite and wüstite. It is important to stress that the X-ray pattern diffraction of magnetite is the
147 same of a large number of oxides with a spinel-structure like Ca/Mg-ferrite, hercynite, chromite,
148 titanomagnetite and so on. Chemical substitutions and solid solutions in the spinel mineral are very
149 common, signifying the possible presence of impure Fe²⁺ and Fe³⁺oxides and iron vacancies.

150 Fig. 1b reports the XRD patterns of some FA categories, namely FAU, FAE, FAS and FAL
151 collected during different steps of filtration of the APC. All the FA have a lot of chlorides and
152 carbonates, whereas FAU, FAE and FAL also show a considerable amount of calcium sulphates,
153 both anhydrous and hydrated. Minor amounts of quartz and calcium alumina-silicates are also
154 detected. The FAS sample differs from FAU and FAE showing a large amount of NaCl, as a result
155 of the soda addition, and different mineralogical phases of carbonates (i.e., trona and nahcolite) and
156 sulphates (i.e., apththalite). Iron oxides are present in all FA samples, but they are relatively less
157 than those occurring in BA samples. The magnetic extract of the FAU sample doesn't help to
158 distinguish the magnetic mineral assemblage. As for BA, the presence of titanohematite or other
159 metals substituting in the spinel-like structures cannot be ruled out.

160 The SEM/EDS analysis on BA and FA (Fig. S.2) allows the observation of morphology and
161 grain-sizes, but the identification of potential substitutes/pollutants in the different mineral phases is
162 prevented. Both single crystals and glassy groundmass contain a significant amount of Si and Ca,
163 but also Fe, S, Ti, and other substituting/pollutant elements (e.g., Zn, Pb, etc.). Iron results in
164 association with Ca, Si, S, Ti, and other heavy metals. Some particles can be very small, with
165 diameters well below the micron range, overcoming the instrument resolution. Therefore: i)
166 pollutants may enter both crystalline and glassy phases, including those capable of a certain
167 magnetic response; ii) magnetic carriers are most probably minor phases, in form of impure oxides,
168 sulphates/sulphides (e.g., Fe₂(SO₄)₃, pyrrhotite, greigite), carbonates (e.g., siderite), alloys; iii) the
169 amorphous phase might be responsible for unaccounted magnetisation.



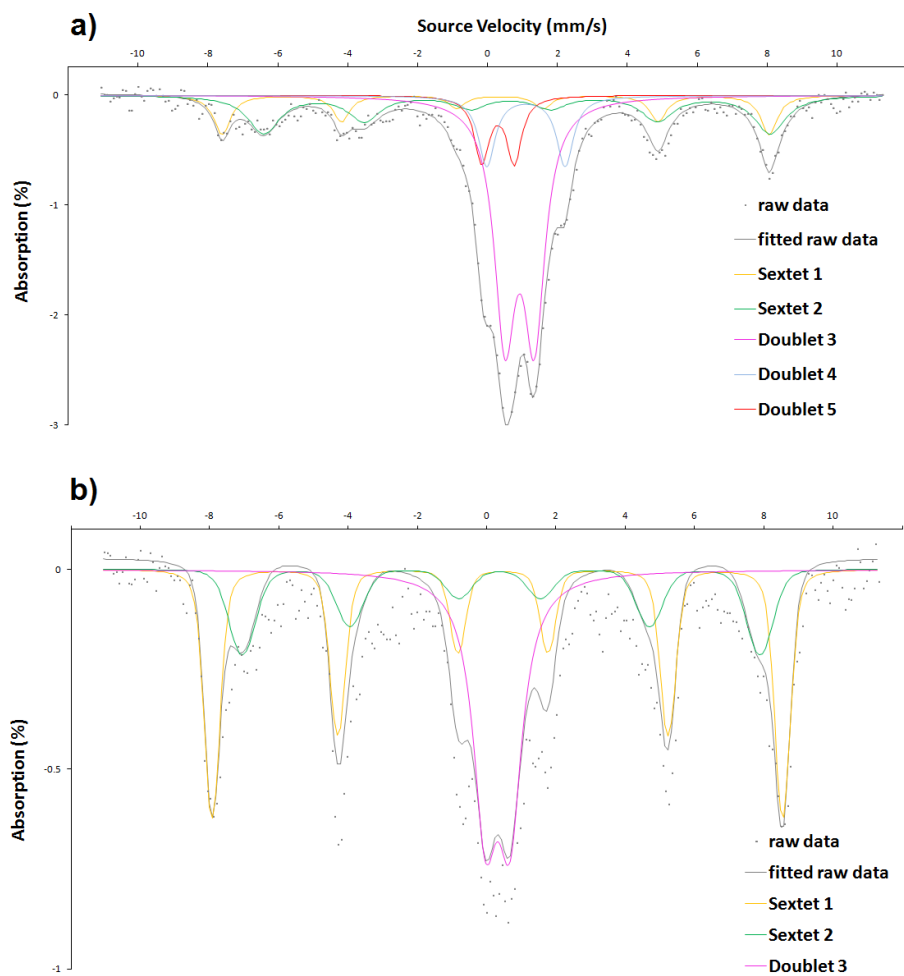
170 **Fig. 1** XRD spectra of representative samples of **a)** BA and **b)** different FA types, including magnetic
 171 extracts. For **a)**: *i* = illite, *q* = quartz, *v* = vaterite, *g* = gehlenite, *c* = calcite, *m* = magnetite, *h* =
 172 hematite; for **b)**: *g* = gypsum, *v* = vaterite, *b* = bassanite *c* = calcite, *ha* = halite, *s* = sylvite; FAL = bag
 173 filter fly ashes treated with lime; FAE = fly ashes from electrostatic precipitator; FAS = bag filter fly
 174 ashes treated with soda; FAU = untreated fly ashes.

175 3.2 Mössbauer spectroscopy

176 Mössbauer spectra (Fig. 2) and fitted parameters (Table S.2) for two selected samples of BA
177 and FA are reported. The Mössbauer spectrum of the FA sample has not displayed any signal, but
178 we were able to process the signal of a magnetic extract of the FA material. The obtained spectra of
179 BA and FA samples show considerable differences. In the BA sample (Fig. 2a), the sextets indicate
180 the two molecular geometries of magnetite (representing 34% of the whole spectrum) with their
181 characteristic parameters. However, the hyperfine field of Bhf for the sextets shows anomalies that
182 might relate to the presence of metallic iron, alloys, or magnetic sulphur minerals. The two central
183 doublets (i.e., 3 and 4 in Table S.2) with isomer shift close to 1 mm/s are characteristic of Fe²⁺ [37].
184 The high quadrupole splitting of doublets 3 and 4 might indicate either Al/Ti substitution in spinel-
185 like structures (i.e., FeAl₂O₄, TiFe₂O₄) or Fe²⁺ sulphides. The doublet 5 with a small isomer shift
186 may correspond to SP hematite, but the high quadrupole splitting might indicate Fe³⁺ ions in
187 carbonates/sulphates/silicates structures [5] as a superimposed signal. The FA sample (Fig. 2b) is
188 composed of two sextets with the characteristic Mössbauer parameters corresponding to magnetite.
189 The magnetite phase looks ferric (magnetization) due to the low IS and cation substitution may
190 account for the observed low Bhf. The doublet 3 corresponds to a Fe³⁺ phase, but its large line
191 width (0.85 mm/s) most likely points to a superposition of, at least, two Fe³⁺ doublets which cannot
192 be resolved. Noteworthy, the FA sample produced the so-called “intermediate relaxation” effect due
193 to SP grains, which translates in a collapse of the sextet in favour of a paramagnetic doublet or
194 singlet. The signal from this phenomenon was removed prior to fitting, so any contribution from
195 that material is not in the fitted spectra and might have reduced the number of recognised doublets.
196 To a lesser extent, the BA sample displayed an intermediate relaxation effect that, however, was not
197 so high to force changes in the standard fitting procedure. The cations distribution deduced from
198 these measurements is the following: Fe³⁺ and Fe²⁺ ions account for ~32% and ~68%, respectively,
199 of the total iron atoms in the BA sample; for the FAU sample, almost all the iron atoms are Fe³⁺ and
200 only 7% Fe²⁺ ions. These estimates assume that magnetite is stoichiometric (i.e., that 2/3 of the total
201 Fe in magnetite is Fe³⁺ and 1/3 is Fe²⁺) and thus possible errors may derive from the assumption of
202 perfect stoichiometry.

203 Observed spectra and iron states in our samples markedly differ from data of coal fly ashes
204 [38, 39] and other anthropogenic dust from industrial emitters [18] as well as from urban
205 atmospheric particulate matter [5]. Conversely, the obtained spectra are similar to those reported
206 earlier by Fermo et al. [40] for a FAE sample collected from a MSWI plant that probably adopted a

207 similar incineration technology. Fermo and co-workers recognised hematite, but they had
208 difficulties in identifying other lines probably due to SP-related effects.

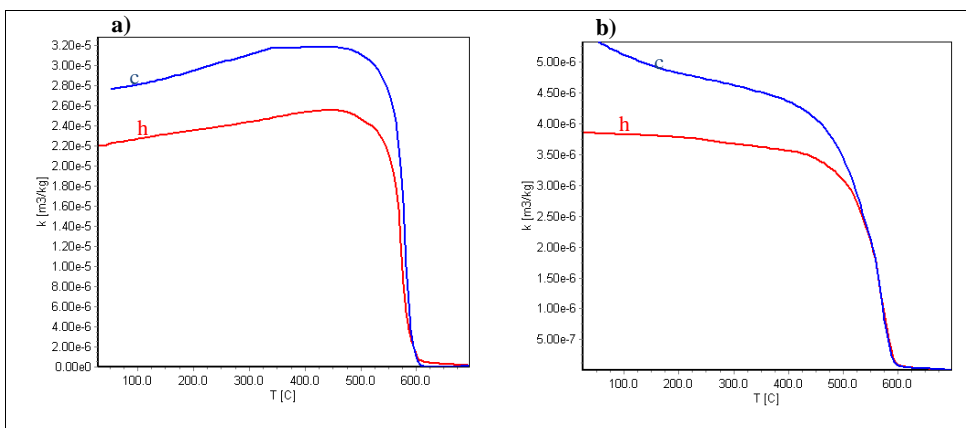


209

210 **Fig. 2** Mössbauer spectra of representative BA (a) and FA (b) samples, recorded at ~85 K. Deconvolution
211 fits using Lorentzian line shapes algorithm are provided. Fitting reliability can be assessed by comparing the
212 raw data points (dots). The spectrum in b results from a FAU magnetic extract since original material
213 produced a very weak signal. Further details on experimental conditions are provided in SI.

214 **3.3 Thermomagnetic analysis**

215 The analysis of the thermomagnetic curves of BA and FA samples indicates that magnetite
216 with its characteristic Curie temperature (T_C) of $\sim 580^\circ\text{C}$ is the main ferrimagnetic phase (Fig. 3).
217 The T_C of the FA sample (Fig. 3b) is slightly below 580°C likely due to a higher presence of
218 impure magnetite than in BA. The first derivative of the heating-cooling lines for the BA sample
219 also shows peaks at $\sim 300^\circ\text{C}$, unlike FA, that might represent the contribution of other carriers of
220 magnetic signal such as sulphides or native metals (e.g., Ni). In many cases, the first derivative of
221 the thermomagnetic curves for FA samples reveals a slight decrease of the heating curve near
222 temperatures between $500\text{--}550^\circ\text{C}$, which can be related to magnetite with a variable composition
223 (cation substitution). These peaks might reflect the presence of Ca/Mg-ferrite [18] that is likely
224 sourced from the lime/dolomite addition. Heating and cooling curves show that no significant
225 mineralogical changes occur during heating, while a certain proportion of weak magnetic minerals
226 may turn into stronger ones at high temperature, so susceptibility is higher during cooling. Evidence
227 of maghemitization is also found in BA samples in the first part (up to 500°C) of the
228 thermomagnetic lines where a susceptibility gain occurs (Fig. 3a). The hypothesis of a contribution
229 of maghemite transforming to hematite cannot be rejected especially in the BA sample, where the
230 susceptibility is not zero after 580°C . However, the diagnostic feature of maghemite (which T_C is
231 ca. 650°C) is not observed. During cooling of both samples, the magnetisation is almost completely
232 reversible until the T_C and then shows an increase in κ at the end of the run. Unlike the BA
233 thermomagnetic curves that display the characteristic shape of ferrimagnetic components, the
234 heating-cooling curves of all the FA samples reach the maximum of κ at room temperature. This
235 feature points to a contribution of paramagnetic phases that adds to the ferrimagnetic components.



236 **Fig. 3** Thermomagnetic curves of selected BA (a) and FA (b) samples in an air atmosphere. κ = magnetic
237 susceptibility, T = temperature, h = heating line, c = cooling line.

238 **3.4 Hysteresis properties**

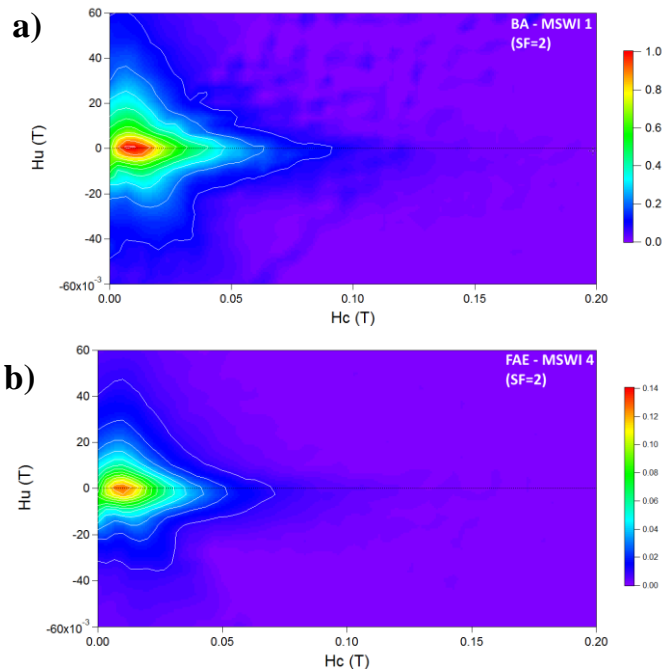
239 The MSWI samples are characterised by narrow hysteresis curves (SI) that saturate below
240 ~200 mT and low coercivity (B_C range: 7.2 – 14.1 mT), indicating the predominant contribution of
241 low coercivity ferromagnetic minerals such as magnetite. Both MSWI samples produce tall, thin
242 hysteresis loops typical of pure magnetite with a significant reversible component of the
243 magnetisation [4]. The uncorrected loops (Fig. S.3) indicate a higher contribution of
244 paramagnetic/diamagnetic components in FA than in BA. Moreover, the hysteresis curves resemble
245 the typical loop of SP grains, showing a steep magnetisation versus field curve which saturates at
246 low fields [19]. Variations in grain-size play a major role in determining the shape of the curve [4];
247 we hypothesise that the shape of the overall loops is the combination of MD and SP magnetite
248 grains, with a larger contribution of pure MD magnetite in BA sample than in other FA [19]. The
249 BA samples show a slightly larger B_C than FA samples, averaging 10.5 mT and 8.6 mT,
250 respectively. The relatively high values of coercivity of remanence (B_{0CR}), ranging 24 – 52 mT,
251 confirm the presence of strong ferro(i)magnetic components. These differences in the mean values
252 of B_C and B_{0CR} also confirm that the magnetic grain-sizes in FA are finer than those in BA.
253 Hematite, which usually results in flat, fat loops, often not saturated, seems absent or, at least,
254 occurs at low concentrations that do not affect the shape of hysteresis curves. The fact that hematite
255 is 200 times less susceptible to magnetisation further supports this observation.

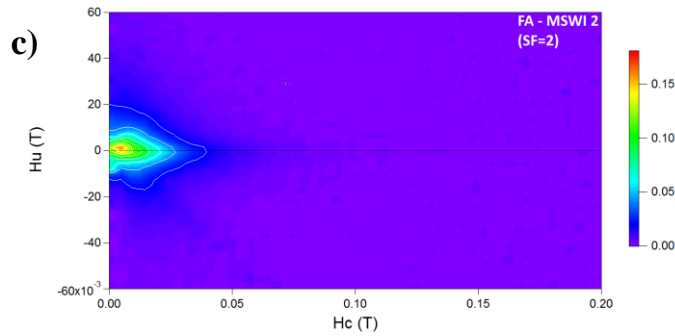
256 **3.4.1 Analysis of FORC distribution**

257 First order reversal curve (FORC) diagrams provide further information from hysteresis loops
258 that is unavailable from standard measurements. A FORC diagram is calculated from a suite of
259 partial hysteresis curves, which are measured by saturating a sample with a large positive field
260 followed by a step-wise decreasing reversal field [41]. FORC diagrams for both BA and FA
261 samples (Fig. 4) show a strong coercivity peak around 10 mT and a strong interaction fields (H_u)
262 spreading asymmetrically to high coercivities (± 80 mT BA; ± 40 mT FA), signifying a prevalent
263 ferro(i)magnetic component. A broad, not well-defined, central ridge with a long tail along the H_c
264 axis up to 100-150 mT characterises BA and FA samples and is indicative of the coexistence of
265 hard magnetic phases. Former studies indicated that traffic related ferrimagnetic grains consist of
266 partially oxidized magnetite particles, in the form of a magnetite-like core covered by an oxidized
267 cation-deficient maghemite-like coating (Muxworthy et al., 2003; Sagnotti et al., 2009). This
268 oxidized coating may be responsible of the coercivity tail extending beyond the typical range for

269 stoichiometric magnetite. Asymmetry and negative regions are commonly seen in FORC diagrams
270 of MSWI ashes. The origin of asymmetry and negative regions is ascribable to an artefact of the
271 fitting procedure, the presence of hard magnetic phases (hematite, sulphates/sulphides, and
272 carbonates), or magnetostatic interactions. This observation suggests that a hard phase is well mixed
273 with a softer phase like magnetite: the overall FORC distributions are likely a result of
274 homogeneous mixtures of different mineralogical phases, which overlap and combine to give a
275 single distribution [42]. All the FORC distributions are representative of a PSD magnetic
276 assemblage, therefore with transitional behaviour between true MD and SD grains. The presence of
277 closed contours near the maximum distribution peaks further points to fine SD and PSD grains as
278 the prevalent magnetic fraction. The FORC diagram representative for BA materials (Fig. 4a) is
279 typical of PSD materials and approaches the reference diagrams for synthetic aluminous iron oxides
280 and those for natural sulphidic sediments [43]. The FA materials express a similar FORC
281 distribution which is, however, transitional towards SP materials (compare FORC distribution for
282 SP greigite [43]).

Commentato [VF1]: Suggerimento di un revisore ma non aggiunge molto a mio avviso.... Non so se metterlo

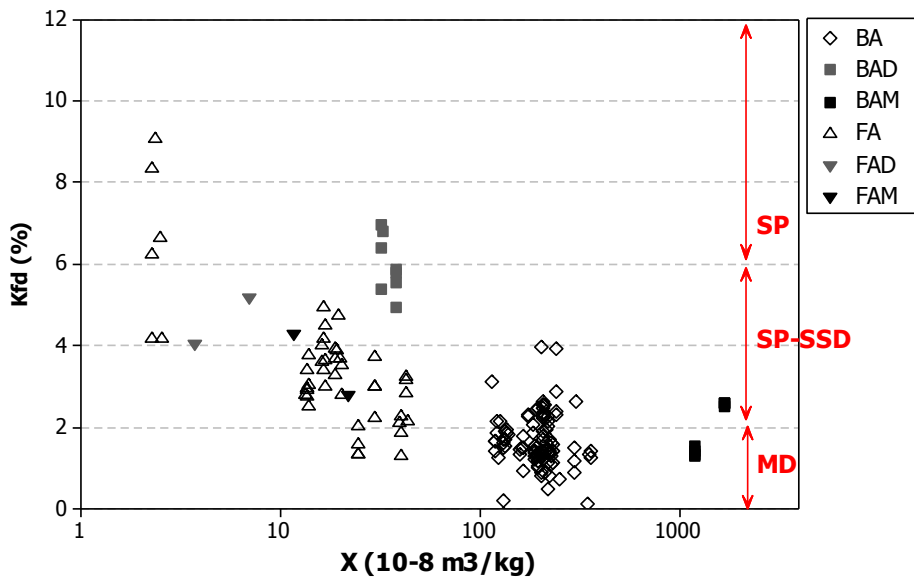




283 **Fig. 4** - First-order reversal curve (FORC) diagrams for representative samples of BA (a), FAE (b), and FAU
 284 (c). The FORC diagrams are computed using FORCinel software [44] that allowed the processing with
 285 optimum smoothing factor (SF), magnetic drift and first point artefact corrections.

286 3.5 Magnetic susceptibility of MSWI ashes

287 Fig. 5 plots the mass specific magnetic susceptibility (χ) and its frequency dependence (κ_{fd})
 288 (see SI). The susceptibilities clearly cluster BA and FA samples. The magnetic extracts (closed
 289 symbols in Fig. 5) are also separated accordingly, even though the magnetic separation is less
 290 efficient for FA than BA as suggested by the spread in the χ ranges. The average χ values of BA
 291 samples range $179\text{--}226 \times 10^{-8} \text{ m}^3/\text{kg}$, being the highest χ value $362 \times 10^{-8} \text{ m}^3/\text{kg}$. The FA samples
 292 show χ values about one order of magnitude lower than those for BA, averaging $20.2 \times 10^{-8} \text{ m}^3/\text{kg}$.
 293 These data are in agreement with previous magnetic measurements on MSWI ashes [27] and partly
 294 lie within the range of χ values for MSW landfill leachates ($64\text{--}970 \times 10^{-8} \text{ m}^3/\text{kg}$) [25] and other
 295 incineration residues such as coal fly ashes ($306\text{--}4804 \times 10^{-8} \text{ m}^3/\text{kg}$) [17, 18]. The χ measurements
 296 of MSWI ashes reported here are consistent with those of sediments near Fe-smelters ($200\text{--}600 \times$
 297 $10^{-8} \text{ m}^3/\text{kg}$) [14] as well as they closely agree with the χ values of residues after lignite burning,
 298 cement dust, and coke dust ($579, 146, 356 \times 10^{-8} \text{ m}^3/\text{kg}$ on average, respectively) [18]. The FA
 299 samples from bag filters, especially FAS, experience low susceptibilities ($2.3\text{--}14 \times 10^{-8} \text{ m}^3/\text{kg}$) as a
 300 likely consequence of low iron contents in those materials. The intensities of the measured
 301 susceptibility are proportional to the average iron contents determined by XRF (Table S.4),
 302 indicating Fe-bearing minerals are chief carriers of the magnetic signal. Also, the lower
 303 susceptibilities are ascribable to a higher proportion of total iron contained in paramagnetic
 304 minerals (this mainly pertains the FA samples).



305

306 **Fig. 5** Frequency dependent susceptibility (κ_{fd} %) vs. mass specific magnetic susceptibility (χ) for BA and FA
 307 samples, including their magnetic extracts (where the suffix M= magnetic; D= (more) diamagnetic).
 308 Magnetic state domains boundaries as defined by Dearing et al. [9].

309 A characteristic feature of MSWI ashes is the relatively high percentages of κ_{fd} , exceeding the
 310 2% in most of the measures and reaching peaks greater than 8% for a few samples, in agreement
 311 with the first measures of magnetic susceptibility on MSWI ashes [27]. The BA samples (1.7 κ_{fd} %
 312 on average) show lower κ_{fd} values with respect to the FA ones (3.6 κ_{fd} % on average) whence
 313 maxima are recorded for the samples that belong to the FAS category. Values of κ_{fd} % similar to
 314 those observed for MSWI samples are quite uncommon amongst anthropogenic materials. For
 315 example, magnetic measurements on solid industrial end-products from thermoelectric power plants
 316 and steelworks resulted in κ_{fd} % averages narrowly at, or below, the 2% threshold [16]. Coal fly
 317 ashes despite high χ averages, experience lower κ_{fd} % values compared to those from MSWI FA
 318 [45]. Nonetheless, a wide range of materials of both geogenic and anthropogenic origin such as
 319 Chinese loess, pedogenetic soil horizons, urban topsoils, street dust, and urban particulate matter,
 320 have levels of κ_{fd} comparable to MSWI samples [7, 12, 46]. Many authors reported that these
 321 materials characterised by a high κ_{fd} parameter have abundant SP-sized grains. Fig. 5 shows that
 322 more than 50% BA samples are MD-dominated, while the remaining BA lie within the SP-SSD
 323 region. It is worth noting that the BA (more) diamagnetic extracts experience higher κ_{fd} % than the

324 magnetic ones, indicating a potential contribution of SP grains in the BA materials. Conversely, the
325 most of FA is in the SP-SSD region, and some are in a SP state. According to the semi-quantitative
326 model by Dearing et al. [9], MSWI samples result in relatively high contents (>10% on mass
327 weight) of SP particles overreaching the 2% κ_{fd} threshold in the majority of samples. Anthropogenic
328 magnetic minerals are usually large magnetic grains in a MD state, but the χ_{fd} parameter for MSWI
329 ashes likely indicates admixtures of SP and coarser non-SP grains, being the latter component
330 MD/PSD-dominated.

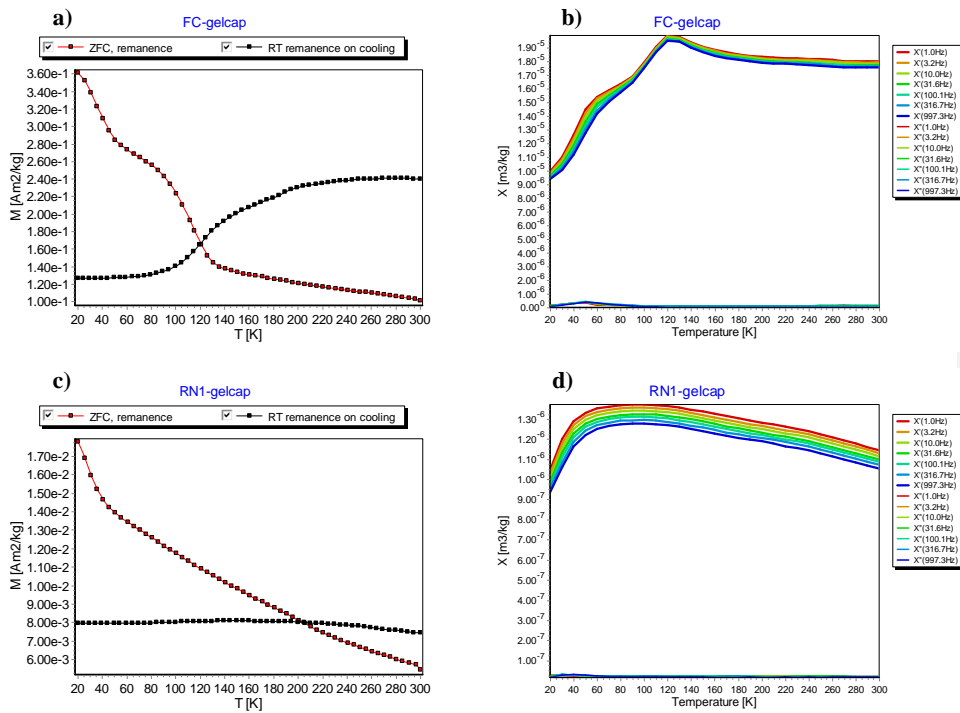
331 A contribution of the SP fraction derived from the κ_{fd} parameter can be misinterpreted for
332 rather varying mineralogical assemblages and needs to be further supported by more robust means,
333 for example by temperature-dependent data. We attempt to quantify the SP fraction of MSWI ashes
334 in a section sotto, where a comparison with other techniques such as low-temperature
335 remanence/susceptibility measurements [47, 48] is provided.

336 **3.6 Magnetic Properties Measurement System (MPMS)**

337 Selected BA and FA samples were measured using the MPMS to probe in detail magnetic
338 mineralogy and eventual SP behaviour. In Fig. 6, low-temperature remanence curves are obtained
339 by first imparting a 2.5 T SIRM at room temperature (RTSIRM) and measuring during zero-field
340 cooling (ZFC) to 20 K (RT remanence on cooling), and then imparting a 2.5 T SIRM at low
341 temperature (LTSIRM) and measuring while zero-field heating back to room temperature from 20
342 K (ZFC, remanence). Further details regarding the acquisition procedure are provided elsewhere
343 [49]. The measured sequences show magnetite-like shapes for most of MSWI samples.
344 Nonetheless, the low-temperature remanence curves of BA and FA samples have distinct shapes in
345 agreement with the preliminary observation reported in [31]. The BA samples systematically show
346 a dramatic loss of remanence between 100 K and 130 K during zero-field cooling (Fig. 6a). This
347 drop, associated with the isotropic point and the Verwey transition, confirms that magnetite is the
348 main remanence carrier in BA material. This feature is recognisable for the reference curves of
349 coarse-grained magnetite albeit the drop of remanence in pure MD magnetite is very sharp and
350 narrower at 120 K. Most probably, the observed curves for BA samples are characteristic of
351 mixtures of coarse (e.g., MD) and fine (e.g., SD/PSD/SP) grains and adhere, for example, to
352 reference curves of pozzolanic materials [50]. BA curves display an additional small drop on
353 cooling at about 190 K (Fig. S.4) that may be due to nano-hematite [51]. Conversely, the ZFC
354 LTSIRM warming curves of FA samples show a steep decrease at very low temperatures and
355 monotonically decrease after ~40 K. The room-temperature remanence shows a flat trend, which is
356 expressed by 90% of the FA samples in this study (the remaining 10% shows almost the same

357 behaviour of BA samples). The Verwey transition in FA samples is not clear probably due to the
358 presence of oxidised/impure magnetite or unblocking of SP grains. Overall, the behaviour of the
359 remanence for FA samples suggests the presence of finer grains than those occurring in BA
360 materials as well as a crowd of minerals much more oxidised (or hydrated). The measured curves of
361 FA samples resemble those of maghemite or pozzolanic ash.

362 The Verwey transition typically occurs at ~120 K in stoichiometric magnetite, but the
363 observed Verwey transitions for MSWI ashes occur over a broad temperature range (i.e., 110-130
364 K), indicating nonstoichiometry (see also Fig. 6) and the presence of grains partly oxidised (i.e.,
365 maghemitization). According to the first derivatives of the ZFC-FT curves (Fig. S.4) and the
366 remanence changes associated with the Verwey transitions, it is clear that magnetite is less oxidised
367 in BA than FA. Other phase transitions occur in BA and FA samples over characteristic temperature
368 ranges, which are liable of the remanence carried by different minerals. Phase transitions of FA
369 samples are less clear than those of BA samples, but still present (Fig. 6a and c). A phase transition
370 at about 30 K on ZFC curves is always present and visible both in BA and FA samples. This might
371 indicate either i) the presence of siderite (FeCO_3) that experiences a magnetic transition at ~38 K or
372 ii) the Besnus transition (30-34 K) diagnostic of monoclinic pyrrhotite, despite it is not visible in the
373 RTSIRM cooling curves, or iii) most likely, an effect due to a poorly-understood electronic
374 relaxation phenomenon in pure and oxidised magnetite at that T. The RT curves of both BA and FA
375 sample reveal weak magnetic transitions at ~260 K and ~190 K (see also Fig. S.4) probably
376 corresponding to the Morin transition for $\alpha\text{-Fe}_2\text{O}_3$ hematite and nano hematite, respectively.
377 Measurements of AC susceptibility by MPMS (Fig. 6b and d) support a significant contribution of
378 SP grains especially in FA materials. FA samples show larger frequency dependence than BA and
379 the temperature of the peak in both in-phase and out-of-phase susceptibility (X' and X'' in Fig. 6),
380 which corresponds to the blocking temperature, is shifted towards lower temperature (~30 K for
381 FA; ~50 K for BA). Both in-phase (X') and out-of-phase (X'') susceptibilities are one order of
382 magnitude higher in BA than in FA. The increased amplitudes in BA samples can be due to either
383 one or a combination of the following factors: i) conductive eddy currents, indicating the presence
384 of native metals or graphite; ii) high contents of pyrrhotite, hematite, iron or titanomagnetite; iii)
385 significant SP/SD presence [19]. The MPMS measurements confirm the presence of a significant
386 population of SP grains in FA samples, and a less significant but still detectable SP population in
387 BA samples. In general, mixed mineral assemblages encompassing impure (titano)magnetite,
388 (titano)hematite, ilmenite, pyrrhotite, and native metals are characteristic of these anthropogenic
389 materials and may conceal the real SP contribution.



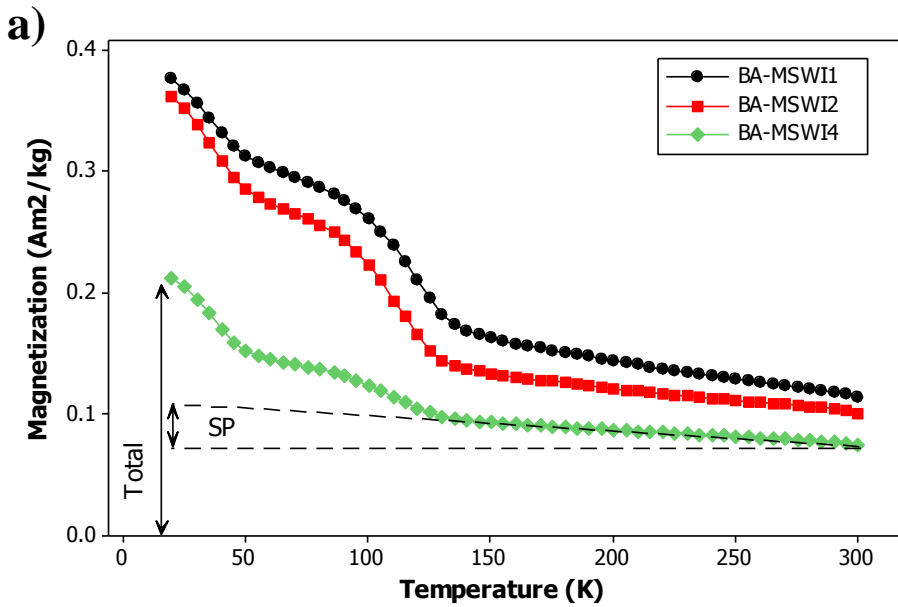
390 **Fig. 6** MPMS measurements of representative BA sample (above) and FA sample (below). Low-temperature
 391 remanence curves (a, c) during zero-field cooling to 20 K (RT remanence on cooling) and on heating
 392 back to room temperature (ZFC, remanence). AC susceptibility (b, d) is measured at 7 different
 393 frequencies and in fixed field amplitude as a function of temperature; both in-phase (X') and out-of-
 394 phase (X'') susceptibility are displayed.

395 3.6.1 Estimation of the SP fraction

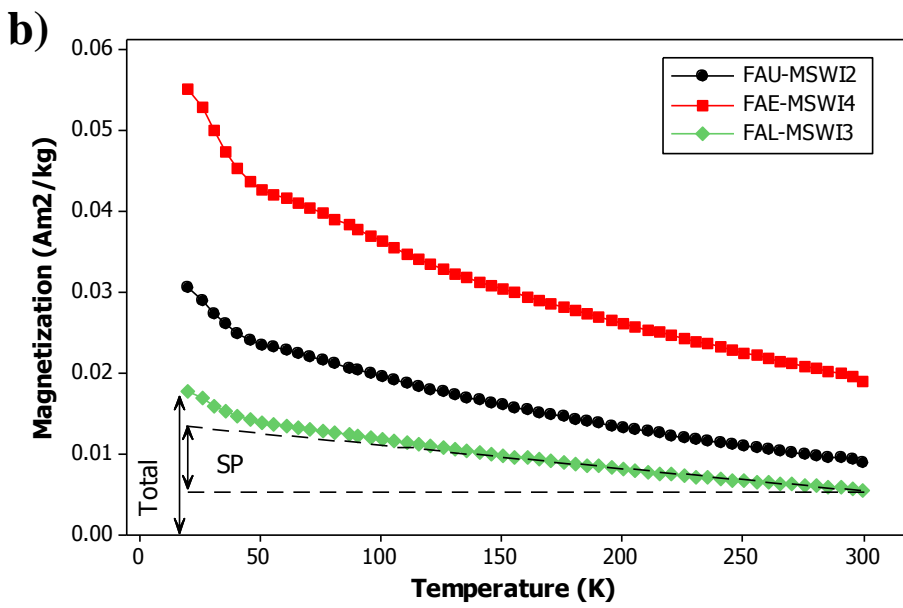
396 The low-temperature remanence curves in Fig. 6 display a steep decay between 20 and 40 K
 397 for both samples and another steep drop between 100 and 120 K for the BA sample, superimposed
 398 on a smooth monotonic decrease towards ambient temperatures, which may be attributed to the
 399 progressive unblocking of the SP population. Other evidence of a SP contribution in both BA and
 400 FA obtained from previous sections (e.g., the χ_{fd} parameter, the hysteresis properties) adds to this
 401 observation. Although a magnetic method that provides a quantitative measure of the amount of SP
 402 grains in environmental or anthropogenic sample materials doesn't exist, Banerjee *et al.* (1993)
 403 proposed a method based on thermal unblocking of LTSIRM for a quantitative estimate of the SP
 404 fraction ($d < 30$ nm) of magnetite. By using the same approach, we tried to measure the real
 405 contribution of SP grains on the magnetic response. The Fig. 7 attempts to compare low-
 406 temperature thermal demagnetization of the SIRM for several BA and FA samples and to apply the

Eliminato: Fig. 7

408 graphical interpretation technique. The general loss of remanence between 20 K and 300 K
409 indicates a significant presence of SP nanoparticles; while the slightly different slope amongst the
410 samples in [Fig. 7](#) suggests a small variation in grain-size distribution of magnetic particles. The
411 contribution to the remanence of SP grains can be determined by subtracting both the value of the
412 thermally-stable 300 K remanence (from the whole curve) and the remanence lost during the T_V
413 (the specific temperature value of T_V was extrapolated from the first derivative of the remanence
414 curve for each sample). The values for SP content obtained using the graphical method point to a SP
415 fraction in the range of 16-22% in BA samples and a 25-31% SP fraction is found in FA samples.
416 Although [Fig. 7a](#) and [b](#) show the simultaneous presence of large and small grains in both BA and
417 FA samples, the contribution of SP grains is considerable and relatively higher in FA rather than
418 BA as argued before. Very interesting observations are the following: i) since the BA samples have
419 a lower SP fraction compared to FA samples, most of the SP grains are probably carried from the
420 combustion chamber to the APC system; ii) the largest content of SP grains is estimated in FAU,
421 which represents the material recovered from the first section of filtration [33], suggesting that most
422 of the SP grains are not caught by the subsequent steps and are thus released in the atmosphere. In
423 addition, the values for SP content obtained exploiting the ratio χ to SIRM [48] compare favourably
424 with the more reliable thermal demagnetization of low-temperature SIRM technique: SP fractions
425 lie in the range 10-35% and 26-58% for BA and FA, respectively. In this case, the increases of
426 χ /SIRM (assumed to be due to SP grains) are measured with reference to a baseline, which was
427 selected to be the lowest measured χ /SIRM value. These estimates are conservative because we
428 measured, with all probabilities, only a fraction of SP grains that survives to preserve this signal.
429 Moreover, diverse oxidation levels in BA and FA magnetic minerals translates in an artificial
430 lowering of SP/total ratio [52] and the probable presence of iron oxyhydroxides (e.g., the RT-ZFC
431 curves likely contain a signal from ferrihydrite) could result in a further underestimate of the SP
432 fraction using the low-temperature technique [48].



433



434

435 **Fig. 7** Low-temperature thermal demagnetisation of a SIRM imparted at 20 K, for representative samples of
 436 BA (a) and FA (b). Ashes deriving from different MSWI plant and different FA categories are also
 437 indicated. Note the graphical analysis according to the method of Banerjee et al. (1993).

438 4. CONCLUDING REMARKS

439 *4.1 Disentangling mixed magnetic mineral assemblages of Fe-bearing phases*

440 The high values of magnetic susceptibility (χ) of MSWI ashes (Fig. 5) and their direct relation
441 to the total iron contents (Table S.4) suggest that iron oxides are the dominant magnetic carriers,
442 irrespective of the MSWI combustor designs and heterogeneous waste feed. All the magnetic
443 measurements verified the chief role of magnetite-like phases in both BA and FA samples.
444 According to the Mössbauer analysis, the magnetite to hematite ratio is higher in BA than in FA
445 samples. The low content of magnetite in FA results in lower χ values compared to those of BA. A
446 large amount of hematite in FA reasonably depends on the lower temperature profile and the
447 different oxygen pressure within the APC system. A contribution of hard magnetic phases and
448 paramagnetic minerals has been proven for both BA and FA samples, but the ferro(i)magnetic
449 component of BA is found to be overwhelming. The strong magnetic signal of BA samples likely
450 depends on iron oxides sourced from waste metal fragments that were assimilated by melting and
451 later re-crystallized during incineration and quenching. Conversely, the chemical additives used in
452 the APC system virtually dilute the ferro(i)magnetic component of FA. The magnetic spinels found
453 in MSWI ashes, especially those occurring in FA, are ferrite according to the temperature-
454 dependent data. Ferrimagnetic intermediate titanohematite and titanomagnetite can occur in FA and
455 BA, respectively (FeO-TiO₂-Fe₂O₃ ternary diagram in Fig. S.5), and add to the overall magnetic
456 response.

457 Nonstoichiometry is pervasive for minerals in MSWI ashes as suggested by the MPMS
458 transition temperatures. The simultaneous presence of magnetite, maghemite, and hematite
459 confirmed by rock magnetic measurements and wüstite inferred by the XRD analysis, emphasises
460 complex pathways of mineral formation. Intermediate phases with iron vacancies and substitution
461 of di- and tri-valent metals occur in BA and FA sample from MSWI, as argued for other
462 anthropogenic materials [15, 45]. Many magnetic measurements may infer hard magnetic phases
463 such as greigite, monoclinic pyrrhotite, antiferromagnetic oxides, and siderite, but they are hardly
464 confirmed. The Mossbauer analysis apparently detects magnetite and hematite alone, but the
465 following factors may have concealed other Fe-bearing minerals: the thermal relaxation effect,
466 overlaps of (sub)doublets, anomalies of the hyperfine field of Bhf, and a considerable amorphous
467 phase. The coarse resolution of the XRD analyses coupled with the presence of many mineralogical
468 phases at elevated concentrations prevented a comprehensive identification of minerals in our
469 samples. Hysteresis properties and temperature-dependent phase transitions ought to represent,
470 other than magnetite, maghemite or sulphur minerals; sulphides and sulphates are naturally

471 incompatible minerals, but they may coexist in MSWI residues in complex phase equilibrium or
472 perhaps disequilibrium. For example, pyrrhotite is an intermediate product of the chemical pathway
473 to pyrite formation and arises in reductive conditions in a wide temperature window (ca. 300-1100°
474 C; [18]) which roughly corresponds to that encountered in different stages of a MSWI system.
475 Sulphide minerals, especially those of the pyrite group, may end up in the municipal solid waste
476 feed as they are essential for various applications such as, cathode material in Li-batteries,
477 semiconductors, and photovoltaic solar panels. Besides iron oxides, care should also be given to
478 sulphur-related pollution which is an important factor of risk associated with lung cancer and
479 cardiopulmonary mortality [2].

480 In summary, the integration of information from our magnetic and non-magnetic techniques
481 leads us to conclude that the dominant magnetic carrier in our samples is magnetite and its
482 intermediate/impure forms (e.g., titanomagnetite, maghemite, titanohematite, and ferrite), while
483 sulphates/sulphides (monoclinic pyrrhotite, magnetic Fe³⁺ sulphate) and carbonates are important
484 ancillary magnetic carriers. This might strongly affect the magnetic properties of MSWI ashes and,
485 in turn, prevent an efficient use of many fundamental magnetic plots that have to be regarded with
486 caution.

487 ***4.2 Anthropogenic pollution and SP nanoparticles***

488 A distinct magnetic signature characterises BA and FA generated in MSWI plants as it was
489 predicted in a preliminary study [31]. Relatively high values of χ and κ_{FD} are characteristic
490 parameters of MSWI ashes. Measurements of the field- and temperature-dependence of induced and
491 remanent magnetisation show discernable differences between BA and FA samples. It has been
492 proven that BA and FA's magnetic properties notably differ from those of loess, sediments, or soil
493 resulting from natural processes [11] as well as other anthropogenic sources of pollution, such as
494 coal fly ashes, dust from power stations or Fe-smelters, and landfill leachates [18]. The present
495 study thus provides reference data for discriminating anthropogenic ferrimagnetic particles
496 originated from MSWI systems.

497 The most important finding is the observed SP behaviour of BA and FA materials. The κ_{FD}
498 parameter readily detected a contribution of SP particles and can be a reliable indicator for the
499 preliminary assessment of the SP potential of MSWI ashes. Indeed, measurements of frequency-
500 dependent susceptibility performed on-site can serve as a fast and cost-effective tool for monitoring
501 SP nanoparticles. The SP fraction of BA and FA materials was confirmed and semi-quantitatively
502 determined by temperature-dependent measures. The results presented above for SP concentrations

503 (Fig. 7), which provide output predictions for four national MSWI facilities, were obtained using
504 representative samples from the first half-year of waste production. A SP amount of up to 31% (for
505 FA) is alarming, but the dusty nature of MSWI ashes is well-known and routinely complicates their
506 safe management. The estimated amounts of ultrafine particles are consistent with other works that
507 revealed more than half of the FA material is submicron-sized, according to laser grain-size analysis
508 [29]. SP-sized grains in MSWI ashes are unlikely to be detected by non-magnetic techniques; in
509 fact, we suppose that the SP fraction, being associated with a population of large ferrimagnetic MD
510 particles, either occurs as a coating of MD particles, as argued for traffic-related particulate matter
511 [6], or agglomerates during re-deposition [53]. As such, SP magnetic state does not mean ultrafine
512 particles readily available to mobilization and transport. The different analytical sensitivities to
513 grain-size and mineralogy highlight the importance of combined approaches to assess the nano-
514 pollution related to SP grains in MSWI ashes. The following estimates assume the SP fraction is
515 made of discrete grains and are intended to raise awareness about potential risks and to further our
516 understanding on this particular kind of anthropogenic material. Taking the average of MSWI BA
517 and FA outputs ($3.5 \cdot 10^4$ t/a and $4.1 \cdot 10^3$ t/a, respectively [33]) and the estimated SP concentrations
518 according to Banerjee's graphical method on low-temperature demagnetization curves, we obtain a
519 SP fraction ranging 5.6-7.7 (BA) and 1.0-1.3 (FA) kilo tons/year. These figures are indicative of the
520 SP annual flow from solid ashes of a typical MSWI system and translate to $\sim 45 \cdot 10^4$ tons/year SP
521 grains (as a maximum range value) discharged every year by a medium-sized country running 50
522 MSWI plants. The overall SP contribution is likely underestimated and does not include the SP
523 fraction that is not retained by the MSWI filters and escapes in the atmosphere. Buonanno et al.
524 concluded that the ultrafine particle emission from waste incinerators is negligible and that the
525 efficiency of the filtration devices is relatively high [30]. However, their review relies on a limited
526 number of studies based on non-magnetic methods. Considering an average of $1.03 \cdot 10^5$ t/a of
527 particulate vapour escaping from the smokestack of a typical MSWI plant [33] and a conservative
528 10% SP estimate included in this particulate emission, a resulting SP fraction in the order of 10^4 t/a
529 is realistic and significant in a long-term view. We can surmise that agglomeration and clumping of
530 smaller SP grains with larger ones favour the filtration efficiency and decrease the inhalation risk.
531 Nonetheless, the SP fraction estimates stress the risk related to re-suspended dust during handling
532 and recycling processes. It was not in the scope of this study to assess the SP particulate emissions
533 via air-quality monitoring systems or whether our estimates on solid outputs are directly related to
534 the size of the MSWI facilities, system designs, or waste feed compositions, but certainly, that
535 would be the objective of future research.

536 Given these premises, it is logical that the numerous MSWI facilities producing huge amounts
537 of solid residues and particulate vapour have a significant impact on urban areas. The inhalation risk
538 related to nanoparticles from MSWI hot spots may have a severe effect locally (within 50 km
539 distance) although sulphur species could overcome larger distances [23]. As such, ultrafine
540 pollution from waste incineration may add to the general particulate pollution from a range of
541 outdoor sources (e.g., traffic) to which people are exposed. So, there is a need to calibrate the
542 current technologies towards the safer management of incineration waste and plan new monitoring
543 strategies that consider the use of magnetic methods. Alterations to the combustion process or the
544 implementation of secondary treatment technologies may render the MSWI systems more
545 environmentally secure and the MSWI ashes better suited for handling, reuse, or long-term
546 landfilling.

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