# A procedure for quantitative characterisation of superparamagnetic minerals in

# environmental magnetism

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# ABSTRACT

Ultrafine grains of magnetic minerals provide reliable recordings of both naturally occurring and anthropogenically generated particulate matter in polluted air; magnetic data can be used to understand biogenic iron-cycling in anaerobic environments, as well as pedogenesis and paleoclimate studies of loess soils. The ultrafine fraction is produced under specific conditions and can be easily recognised by its superparamagnetic (SP) behaviour. Many proxies have been proposed to account for the SP contribution by measuring its susceptibility dependency with frequency (frequency effect) or the magnetization loss after removing an external inducing field. Here we introduce the Superparamagnetic Concentration and Dipole Moment (SPCDM) procedure for quantitative interpretation of SP magnetization. This procedure is well suited to SP carriers with a fast magnetization decay (<1s), as would be expected for magnetic minerals with a grain size distribution lying below the blocking volume for stable, single-domain (SD) magnetization. SPCDM requires a dedicated experimental procedure to isolate the SP response from the paramagnetic and remnant effects, as observed in samples with mixed contributions. The proposed technique was tested using synthetic, nanoparticles of magnetite and then to characterise the magnetic properties of air particulate matter (PM) sampled at Jânio Quadros tunnel in São Paulo, Brazil. For nano-sized magnetite, SPCDM estimates for dipole moment are invariable with mass concentration and consistent with the published results; estimates for particle concentration are strongly correlated with true mass concentration ( $R^2=0.96$ ). For air PM, SPCDM estimates a particle size with a diameter of 7.7±0.1 nm, a kind of ultrafine magnetic material not previously recognised in air pollutants.

**Keywords**: Magnetic properties; Environmental magnetism; Rock and mineral magnetism; Inverse theory.

#### **INTRODUCTION**

Fine and ultrafine magnetic minerals (<µm) found in rock, soils and air particulate matter are indicators of natural and anthropogenic processes affecting the iron cycling in shallow and deeper levels of the Earth's crust. Such magnetic mineral fractions are important for two reasons. Firstly, few geochemical and biogeochemical processes are able to produce or modify such small grains in soils and rocks (Taylor et al., 1987; Maher & Taylor, 1988; Maxbauer et al., 2016) and secondly, their characteristic superparamagnetic (SP) response can be recognised with common soil and rock magnetism procedures (Moskowitz et al., 1989; Moskowitz et al., 1993; Tadurno, 1995).

In general, the SP content can be recognised in the frequency domain by the susceptibility "frequency effect" (Dearing et al., 1996), from measurements achieved in at least two frequencies (470Hz and 4700Hz, for Bartington Instruments Ltd.). The susceptibility variation with frequency is minor (to null) in the absence of SP minerals and so no frequency effect is produced in such cases. The SP behaviour can also be identified in time domain measurements by measuring the magnetization decay ("viscous decay") after turning off an inducing magnetic field applied to the sample (Worm, 1999; Wang et al., 2010). Measurements in the time domain require an adequate time window and resolution tag to capture the magnetization decay waveform. A time window of 100 s is usually employed (Wang et al., 2010) and the decay rate is evaluated by the difference between magnetization at t=0 s and 100 s after the external field removal, normalised by the initial (t=0) magnetization. This quantitative proxy for recognising SP contents was introduced by Worm (1999) and improved by Machac et al. (2007) by introducing a set of intervals and field intensities. A close association between time and frequency domain percentage parameters was observed (Machac et al., 2007) despite the fact that both approaches only provide semiguantitative estimates for mass or volume concentration of SP minerals. It can be explained because both time and frequency percentage parameters (frequency effect and magnetization decay) result from mixed contributions of mineral type, grain-size and concentrations, therefore they are not simple indicators of concentration itself. These percentage proxies are partly conditioned by acquisition parameters, making the comparison of different datasets no simple matter. Magnetization decay, evaluated in time windows of 15 s (Worm, 1999) and 60 s (Machac et al., 2007) for example, are not necessarily correlated because decay rates are sensitive to minor variations in grain size. Wang et al. (2010) improved time-domain studies by using a J-meter coercivity spectrometer (Jasonov et al., 1998;

Wang et al., 2010) and measuring the magnetization immediately after the external field removal. There is also an extensive literature on using relaxation-based methods based on Néel theory for characterization of nanoparticle populations, under conditions for which the net magnetization is time-dependent over the measurement interval (e.g., Worm and Jackson, 1999; Shcherbakov and Fabian, 2005; Jackson et al, 2006; Egli, 2009; Kodama, 2013).

Previous works proposed different approaches to deal with magnetic grains exhibiting SP behaviour. Through the fitting of the Langevin function for a magnetization curve, they allow reconstructing the magnetic moment (or volume) distribution in synthetic samples. Berkov et al. (1999), using diluted ferrofluid samples propose fitting sums (or weighted integrals) through the singular value decomposition (SVD) technique and linear constraints to recover the distribution of magnetic moments. Woodward et al. (2007) compare measuring methods for the particle-size distribution of magnetic nanoparticles (transmission electron microscopy; Langevin fitting; and small-angle neutron scattering). The Langevin fitting was accomplished by least squares routines taking a priori assumptions about the distribution form. As developed in SPCDM, the Langevin fitting is applied after correcting IRM contributions, thus allowing the study of mixed samples as found in geological and environmental investigations. The SPCDM application to pure SP samples have much in common with previous work with synthetic materials.

A better characterisation of the SP fraction allows the investigation of a diversity of problems in environmental magnetism. SP minerals can be formed as a consequence of variable redox conditions during wet and dry cycles (Maxbauer et al., 2016) and these result in indicators that allow recovery environmental and depositional conditions in complex sedimentary basins, as well as helping us to understand records of climate change in paleosols and loess deposits (Maher & Thompson, 1991; Porter, 2001). SP particles are also generated during dissimilatory

iron reduction (DIR) in anoxic conditions, where oxidation of organic matter becomes coupled with microbial reduction of Fe(III) oxides, with extracellular precipitation of ultrafine magnetite (Moskowitz et al., 1989; Jimenez-Lopez et al., 2010; Li et al., 2013).

In addition to natural processes, ultrafine magnetic minerals are also generated by industrial and transportation systems (fossil fuel combustion, disk-breaks, pavement abrasion etc.) and these allow the application of magnetic measurements in pollutant provenance studies and air quality in urban areas (Sagnotti & Winkler, 2012). Magnetic fractions in air particulate matter also serve as tracers for associated pollutants with ultrafine grain size (Sagnotti et al., 2006), for which safe exposure limits are not well established (Donaldson, 2003; Bealey et al., 2007). Air particulate matter (PM) with aerodynamic dimensions below 0.1  $\mu$  m (PM<sub>0.10</sub>) has been a topic of concern in health sciences because of their capacity to reach deeper parts of the respiratory system, thereby enhancing the deleterious effects of associated hazardous substances (Morris et al., 1995; Pope et al., 2002; Calderón -Garcidueñas et al., 2008).

Despite their importance in environmental magnetism, the common techniques used to characterise SP fractions are not effective in answering key questions (Evans and Heller, 2003) about quantitative estimates for mass/volume concentration, grain size distribution, and mineral types, among others. Most techniques based on data acquisition proxies (frequency effect or decay rate, for example) can be regarded as not being effective in addressing such questions. We develop a quantitative procedure - SPCDM (Superparamagnetic Concentration and Dipole Moment) - to determine the concentration and the dipole moment of the magnetic carriers with SP behaviour. When the magnetic mineral is known (or assumed a priori), quantitative estimates of mean grain-size (though not of the size distribution) and particle concentration are obtained. An adequate database and processing scheme is required in order to isolate the SP response

before determining the unknown parameters in the Neel's model (magnetization of saturation and grain magnetic moment) with non-linear data inversion procedures. Particle concentration is then estimated from a basic, constitutive relationship relating the model parameters obtained from data inversion. SPCDM is validated by a control experiment, comprising samples with different concentrations of nano-sized synthetic magnetite within a narrow size distribution and then applied to analyse air particulate matter from air-quality monitoring stations installed in the Jânio Quadros tunnel in São Paulo, Brazil.

### **2. THEORY**

#### **2.1 Model construction**

Single-domain, ferromagnetic minerals exhibit an SP response when reduced to grain sizes down to a critical blocking volume that is able to sustain permanent magnetization at room temperature. Below this blocking volume, the orientation of the particles magnetic moments is disturbed by thermal fluctuations resulting in null bulk magnetization. When exposed to an external static field, the dipole moments are aligned with the inducing field sustaining a net magnetization as long as the inducing field is kept active, otherwise it vanishes. For an assemblage of uniform grains, this unstable magnetization decays according to the formula

$$M(t) = M_0 e^{\frac{-t}{\tau}},\qquad(1)$$

starting from magnetization  $M_0$  when t = 0 (when the inducing field is turned off). Magnetization M(t) decays according to a characteristic relaxation time  $\tau$  given by Néel (1955) and

$$\tau = \tau_0 e^{-\frac{E_M}{E_T}}, \quad (2)$$

where  $\tau_0$  is a time-factor varying from  $10^{-12}$ s to  $10^{-8}$ s (Dormann et al., 1996; Worm, 1998) and accounts for a characteristic time-lag between successive random thermal fluctuations (Berndt et

al., 2015).  $E_M = Kv$  represents the magnetostatic energy barrier required to switch the magnetic dipole direction, K [Jm<sup>-3</sup>] is the grain coefficient of anisotropy and v [m<sup>3</sup>] is its volume. Thermal energy ( $E_T = k_B T$ ) counteracts magnetic ordering by randomly flipping the grain dipole directions;  $k_B = 1,38 \times 10^{-23}$  [JK<sup>-1</sup>] is the Boltzmann constant and T is the temperature. The coefficient of anisotropy is given by the equation  $K = \mu_0 H_k \sigma_S/2$ , where  $H_k$  [Am<sup>-1</sup>] is the microscopic coercivity of the grain, such that  $H_k = 2.09H_c$  (Stoner &Wohlfarth, 1948). Term  $H_c$  is the sample macroscopic coercivity and  $\sigma_S$  is the saturation magnetization of the mineral species.

For measurements at a constant temperature, the relaxation time  $\tau$  is conditioned by grain size v and magnetic anisotropy K; both parameters express physical properties of the magnetic carriers. Figure1 illustrates the wide variation of relaxation times from minor changes in diameter that would be expected from spherical particles of magnetite (mineral specific saturation magnetization  $\sigma_s$ =480 kAm<sup>-1</sup>, K=2.31x10<sup>4</sup> Jm<sup>-3</sup>). The magnetization decay can be relatively fast ( $\tau$ =1.98x10<sup>-8</sup> s) for grains with diameters of 10 nm, in the 100 s time window for grains with diameters of 20 nm, and stable (9.4x10<sup>11</sup> years) for grains with diameters of about 28 nm. Experimental data shows that blocking volume for magnetite has a diameter between 25 nm and 30 nm (Dunlop & Özdemir, 2001) and approximately 17 nm for hematite (Jiang et al., 2014). Figure 1b is effective in showing how minor grain size variations may lead to substantial changes in the magnetization decay rate. This change is particularly sensitive in particles below a few nanometres in diameter with respect to a reference grain diameter for a blocking volume, sustaining stable magnetization in SD grains. It can be seen that a very narrow grain size distribution is associated with magnetization decay waveforms that are able to be captured in the 100s time-window, as have been observed in SP studies (e.g. Worm, 1999; Wang et al., 2010). For broader ranges of grain sizes below this limit fast decay rates (in milliseconds or microseconds) are expected. This faster decay behaviour may be within the time resolution interval of common equipment or in the range of transient coil induction fields, preventing further analysis based on modelling the magnetization waveform decay. Nevertheless, a "slow" decay rate (e.g. one captured in the 100s time-windows) is indicative of a coarser SP fraction nearing the characteristic blocking volume for SD grains.

For pure (non-mixed) ultrafine grains, the transient magnetization vanishes to zero within intervals of microseconds, henceforth termed 'fast SP decay'. This type of fast decay can be associated with particles of a grain size well below the critical volume for stable magnetization. For mixed SP-SD or SP-MD mineral fractions, the SP magnetization appears superimposed to stable magnetization. Figure 2 illustrates cases of fast decay rates observed for pure (Figures 2a and 2b) and mixed (Figures 2c and 2d) SP samples. Fast decay rates are observed in samples with nanoparticles of magnetite dispersed in wax (see Section 3) in a similar way to rates seen in air PM collected in the Jânio Quadros tunnel in São Paulo (Section 4). The air PM sample also exhibits IRM acquisition, according to the intensity of the inducing field and, as such, indicates a mixed contribution of magnetic carrier with grain sizes in the SP and SD-MD fractions.

Slower magnetization decay is observed in the sediments from the Jaraguá Cavern in São Paulo, as magnified in Figure 3 for samples exposed to an external field of 500 mT. Figures 3 illustrates that fast decay SP relaxation does occur in samples from air PM and are, therefore, indicative of ultrafine grain size distributions that have not been well accounted for in previous studies.

For pure (non-mixed) ultrafine grains (e.g. Figures 2b and 2c), the transient magnetization vanishes to zero in microseconds; and is associated with particles of grain sizes well below the critical volume for stable magnetization. In exploration geophysics terms, this type of

magnetization is known as "induced magnetization" (Telford et al., 1990) and it appears superposed to stable magnetization in mixed SP-SD or SP-MD mineral fractions.

The SP contribution under the  $H_0$  [Am<sup>-1</sup>] external field is given by Equation 3 (Dunlop & Özdemir, 2001)

$$M(H_0, T) = M_S L(\alpha) \tag{3}$$

where

$$\alpha = \frac{\mu_0 v \sigma_S H_0}{k_B T} \tag{4}$$

and  $L(\alpha)$  is the Langevin function:

$$L(\alpha) \equiv \operatorname{coth}(\frac{\mu_0 v \sigma_S H_0}{k_B T}) - \frac{k_B T}{\mu_0 v \sigma_S H_0}.$$
(5)

In Equation 3,  $M_s$  is the sample specific saturation magnetisation and  $\mu_0 = 4\pi \times 10^{-7}$  [Hm<sup>-1</sup>] is the free space permeability. For hematite,  $\sigma_s$  is approximately 0.5% that of magnetite (Dunlop & Özdemir, 2001). The magnetic moment of the grain is  $\mu = v\sigma_s$  [Am<sup>2</sup>] and the sample saturation magnetization is  $M_s = n\mu$  [Am<sup>-1</sup>]. Term n [m<sup>-3</sup>] is the concentration (number of particles per volume) of the magnetic carriers. For a sample with density  $\rho$  [kgm<sup>-3</sup>], the mass-concentration of the magnetic carriers is obtained by  $n/\rho$ . The concentration of SP carriers (n) does not necessarily express the concentration of particulate matter, except under a very particular condition in which single magnetic particles are attached to single grains in the soil or particulate matter.

Under isothermal conditions, the SP magnetization dependence on the external field  $B = \mu_0 H_0$  is written as  $M(B) \equiv M(B,T)$ , such that

$$M(B) = M_S L(\frac{\mu B}{k_B T}). \quad (6)$$

From estimates of grain dipole moment  $\mu$ , and by assuming that the magnetization saturation  $\sigma_S$  is known, particle volume v can be determined by constitutive relationship  $\mu = v\sigma_S$ . By assuming particles with spherical shape, diameter estimates can be achieved.

#### 2.2 Inverse problem formulation

According to Equation 6, SP magnetization is described in terms of two unknown parameters:  $M_S$  and  $\mu$ . These parameters can be determined under an inverse problem formulation by considering a data set with N measurements of magnetization,  $M_i^o \equiv M(B_i)$ , when exposed to external fields  $B_i$ , i = 1:N. The unknown parameters can be determined by minimising a least-squares functional  $Q(M_S, \mu)$  such that

$$Q(M_S,\mu) = \sum_{i=1}^{N} [M_i^o - M^c(B_i, M_S,\mu)]^2 , \quad (7)$$

where the superscript o and c stand for 'observed' and 'calculated' magnetization values. According to inverse problem terminology (Aster et al., 2011), the minimisation of functional in Equation 7 configures a non-linear problem because one of the unknown parameters ( $\mu$ ) appears as an argument of a non-linear function. The determination of the unknown parameters then requires a non-linear optimisation procedure, usually converging with iterative steps, starting from an initial solution (or set of solutions) until reaching a data fitting criterion  $Q(M_S, \mu) \leq \varepsilon$  or stop condition. Parameter  $\varepsilon$  establishes the acceptability condition for data fitting, according to experimental error in the data.

The set of solutions minimising the functional Q can be accessed by mapping this function within a parameter space window and provide a visual representation of solutions satisfying  $Q \le \epsilon$  as well as possible alternative solutions (if they exist). This mapping is done by evaluating functional  $Q(M_S, \mu)$  for a mesh of values  $(M_S, \mu)$  in the parameter window  $M_{S,l} \le$  $M_S \le M_{S,u}$  and  $\mu_l \le \mu \le \mu_u$ , as defined by the lower (*l*) and upper (*u*) limits for the searched parameters. The solutions domain in this mapping appear below a contour level ("water level") which is established by threshold  $\varepsilon$ . Domain projection towards the coordinate axes  $M_S$  and  $\mu$  with the unknown parameters provides a visual representation for the uncertainty of the parameters in this modelled solution. Uncertainty analysis can also be carried out by finding multiple solutions or computing the parameters covariance for single solutions (Aster et al., 2011).

#### 2.3 Experimental aspects

An experimental procedure was devised to isolate the SP response in mixed carrier samples. The proposed procedure is well suited for samples with fast SP decay, as expected for ultrafine particles discussed in Section 2.2. For mixed SP-SD (or SP-MD) samples, the magnetization decays from magnetization  $M_0 \equiv M_0(B_i)$ , achieved under field  $B_i$ , at t=0s to isothermal, remnant magnetization  $M_q \equiv M_q(B_i)$ . Once corrected for paramagnetic effects, the difference  $M_0 - M_q$  can be regarded as isolating the SP response and, as such, well suited to be modelled according to Equation 6. For pure SP response, the magnetisation decay rate is represented as  $M(t)/M_0 = \exp(-t/\tau)$  (Equation 1) and for mixed SP-IRM contributions, by the expression  $[M(t) - M_q]/[M_0 - M_q] = \exp(-t/\tau)$ . The MicroMag3900-VSM measures the sample dipole moment  $S_D$  [Am<sup>2</sup>], and not the magnetization M [Am<sup>-1</sup>]. The relationship between the two is  $S_D = MV$  (Evans & Heller, 2003), where V is the volume [m<sup>3</sup>] of the sample. Thus, the sample dipole saturation  $S_{DS}$  [Am<sup>2</sup>] is given by  $S_{DS} = M_S V$ .

The procedure devised to provide a database for the proposed technique followed the following steps. Initially, the sample was AF-demagnetised (120 Hz, from 1T to zero in 2% increments) and then subjected to external fields  $B_i$  of 5, 10, 15, 20, 25, 30, 40, 60, 80, 100, 120, 140, 180, 220, 260, 300, and 340 mT, where i = 1:17 during 10 s intervals. Longer exposures of

20 s and 40 s were tested but this gave equivalent results. The magnetization  $M_0$  is measured when the external field is on, setting t=0s when this field is turned off. Magnetization decay M(t)is then recorded and averaged between 2s and 4s to obtain equilibrium magnetization  $M_q$ . In general, a flat baseline for magnetization was achieved as fast as 10 to 20 ms after the external field was turned off, within coil inductive effects. For the tested samples, the averaging window from 2 s to 4 s was unaffected by such effects, thus giving a baseline equilibrium for magnetization  $M_q$ . The differences  $M_i^o \equiv M_0(B_i) - M_q(B_i)$  were then computed for external fields  $B_{i}$ , to isolate the sample SP response. Magnetization decay of SD and MD grains occurs at time lengths above 100 s (Fabian, 2003; Williams and Muxworthy, 2006) and tends to be cancelled when computing  $M_0 - M_q$ . This is strictly true when viscous decay is not observed in the time-window in which  $M_q$  is averaged and this difference computed. Errors were estimated by repeating the acquisition procedure for the calibrator sample (2853 YIG Sphere) 15 times. The percentage error was then evaluated and applied to measurements with tested samples. Paramagnetic correction was carried out by the approach to saturation method, developed by Jackson and Sølheid, (2010). This correction was implemented through the scripts introduced by Paterson et al. (2018), using the estimated paramagnetic susceptibility  $\chi$  and calculated it for each field Bi as  $\chi B_i$  to remove the paramagnetic response from  $M_i^0$  estimates.

#### 2.4 Computational aspects

The SPCDM codes were implemented in two main steps. Data files from MicroMag3900 were processed according to the procedures described in Section 2.3, to isolate the SP response. An inverse procedure (as described in Section 2.2) was then applied to minimise  $Q(S_{DS}, \mu)$ . The minimisation of this function was achieved with the FMINCON function of the Matlab Optimisation Toolbox, based on the interior point algorithm of Byrd et al. (2000). As an iterative procedure, FMINCON requires an initial solution, which, in SPCDM, was chosen randomly within a feasibility interval, guaranteeing the parameters positivity. The optimisation procedure was applied 10 times for each data set, starting from random initial solutions in order to probe alternative solutions and uncertainty. The set of resulting solutions were then used to evaluate mean  $\hat{S}_{DS}$  and  $\hat{\mu}$  model parameters and their respective standard deviations. These mean-solution values were used to check data fitting and evaluate SP concentration according to  $\hat{n} = \hat{S}_{DS}/\hat{\mu}$ . It is worth noting that SPCDM estimates for concentration did not necessarily give the particulate matter concentration, except under very particular situations in which single magnetic carriers were attached to single particles in the particulate matter. A factor expressing how many magnetic particles are attached to air PM grains is required to better evaluate air PM concentration from SPCDM estimates.

## 2.5 Quantifying SP contribution in total magnetization

In order to evaluate the contribution of the SP fraction in total magnetization we apply the parameter

$$\% SP = \left(\frac{M_{SP,1T}}{M_{H,1T}}\right) * 100 ,$$
 (8)

which relates SP magnetization  $M_{SP,1T} \equiv M(\hat{\mu}, \hat{S}_{DS}, B_{1T})$  calculated from Equation 6 and total magnetization  $M_{H,1T}$  as measured in the hysteresis curve. This parameter can be evaluated under other external field intensities but the value of 1T is advised to take into account contributions from high coercivity (hematite-like) minerals, as well as to saturate SP and IRM magnetization. Parameter %SP is not related to data acquisition parameters (frequency range, time intervals or field intensity), especially considering that it varies little, when evaluating for external fields high enough to saturate both SP and IRM magnetizations.

#### **3. SPCDM APPLICATIONS**

## 3.1 Nanoparticles of synthetic magnetite

The first set of samples to test the SPMDM procedure comprised nanoparticles of synthetic magnetite with a mean diameter of 8 nm. These nanoparticles were synthesised according to a thermo-decomposition process reducing a Fe(III) solution under boiling temperature (>200°C) in the presence of stabilising agents, controlling the growth of the magnetite precipitates. A common aliquot of nanoparticles was used to prepare 0.2%, 1.0%, 1.9%, 3.2%, 4.4% and 5.0% of mass concentration by mixing with wax. As illustrated in Figure 2b for a 5% concentration sample, the nanoparticles have a pure SP behaviour at room temperature, as expressed by null coercivity in the hysteresis curve and fast magnetization decay. Its fast SP decay rate is compatible with the analysis based on Figure 1. Figure 4 shows SPCDM results with inverted model parameters and respective data fitting for a sample with a concentration of 5%. Figure 4b shows the objective function mapping, centred at the solution model obtained from data inversion. The narrow domain of alternative solutions and the absence of alternative local minima, guarantees the uniqueness for the inverted parameters.

Table 1 presents SPCDM results for the samples tested, with nanoparticles of magnetite at different concentrations. For each sample, the inversion procedure was repeated ten times, starting with a randomly chosen solution to determine the spreading range for the inverted solutions.

The results in Table 1 show that, independent of sample concentration, the grain dipole moment estimated for the magnetic carrier is practically the same. This gives consistency to SPCDM results regarding that all tested samples were prepared with particles sharing common specifications, in terms of grain size and composition. As suggested by this test, the SPCDM estimates for grain dipole moment are not distorted by particle concentration, thus recovering an important property of magnetic carriers. The mean grain dipole moment of  $1.07 \times 10^{-19} \pm 0.01$  Am<sup>2</sup> was estimated for the grains, which is in agreement with previous estimates of ( $0.85 \times 10^{-19}$  Am<sup>2</sup>) for grains of magnetite with 8 nm diameter, as presented by Ge et al. (2007).

Figure 5 shows the SPCDM estimate for the mean dipole moment for nanoparticles of magnetite, in addition to published results for magnetite with different grain sizes (Goya et al., 2003; Ge et al., 2007; Sievers et al., 2012). Also in Figure 5, is a reference to curve for model  $\mu = v\sigma_s$ , assuming  $\sigma_s$ =480 kAm<sup>-1</sup> (saturation magnetization for magnetite) and spherical particles when evaluating volume *v*. Despite a paucity of dipole moment data for nano-sized magnetite, one can observe a good agreement between data and model predictions, suggesting that dipole moment estimates can be used for preliminary inferences about the particle diameter of magnetite-like minerals with fast SP decay. For the nanoparticles of magnetite tested here, a mean diameter of 7.5±0.2 nm was estimated, in agreement with diameter determination from the TEM image (Figure 5), which points to real diameters of 8.0±0.7 nm. It should be stressed that this is a preliminary inference but, in principle, it promises to be useful in environmental studies where pollutant provenance for distinctive grain sizes can be indicative of specific sources.

SPCDM estimates for mass-concentration (parameter  $n_m$ ) from Table 1 were plotted in Figure 6 with respect to true mass concentration, producing a clear linear dependence (R<sup>2</sup>=0.96). This result validates the SPCDM procedure as a quantitative technique to determine concentrations of magnetic fractions in fine and ultrafine grain sizes.

Estimates for parameter %SP (Table 1), representing the contribution of SP magnetization in total magnetization under the 1T field, reach 98.5%. This result confirms that magnetization of nano-sized magnetite keeps no IRM, holding magnetization only (~100%) from

the SP contribution. The  $\sim 1.5\%$  difference may be due to accuracy limits in retrieving model parameters from the inversion of noisy data and experimental errors or measuring total field magnetization.

## 3.2 Air PM in the Jânio Quadros tunnel

Samples of air PM were collected from air quality monitoring stations in the Jânio Quadros tunnel in São Paulo, from 23 to 25 March, 2004. These samples were analysed by Martins et al. (2006) and Sanchez-Ccoyllo et al. (2009) and then stored in the Laboratory of Paleomagnetism and Rock Magnetism of IAG-USP. Each sampling day was divided into five intervals of two hours, from 08:00 AM to 18:00 PM. The air PM samples were acquired using a Mini-VoITM Air Sampler (Airmetrics Eugene, OR, USA), with a flow volume of 7 L min<sup>-1</sup> (Baldauf et al., 2001; Sanchez-Ccoylloet al., 2009). The particulate was sieved through a sequence of 10 filters, using a MOUDITM (micro-orifice uniform deposit impactor, MSP Corporation, Shoreview, MN, USA). As well as being analysed by the SPCDM procedure, the air PM samples were subjected to magnetic susceptibility measurements using a Multifunction Kappabridge MKF1-FA (Agico). SPCDM data were measured with a MicroMag3900-VSM (Lake Shore Cryotonics). To enhance the magnetic response, the set of 10 filtered fractions was grouped into pairs, according to adjacent grain size specifications, and then measured as a single sample.

As illustrated in Figure 2c, the magnetic relaxation of the air PM collected in the Jânio Quadros tunnel has a fast SP behaviour and growing IRM acquisition with increasing external fields, which is indicative of samples of mixed carriers with different properties (grain size and/or composition). A magnetic response indicating mixed contributions in air PM was also observed by Maher (2009). In the Jânio Quadros tunnel, the finer-grained minerals exhibit fast SP decay (Figure 3b) and the coarser ones show low coercivity (1.93 to 4.55mT) in the hysteresis curve; this is indicative of magnetite as a contributor in the IRM response.

SPCDM results for air PM in the Jânio Quadros tunnel are presented in Table 2. The grain magnetic moment for these samples has a mean value of  $1.14 \times 10^{-19} \pm 0.05$  Am<sup>2</sup>, which does not significantly change in the time intervals in which the samples were collected. This result suggests that the magnetic properties of the air PM in the tunnel atmosphere are practically invariant, in terms of the carrier magnetic properties (size and composition) despite variable traffic conditions being observed during the test period. This result could be indicative of a uniform atmosphere in the tunnel (at least in terms of its ultrafine content properties) but it could also result from bias introduced by the filtering procedure, possibly through selecting specific grain fractions along the chain of filters. A better evaluation is required to allow continuity of this study. The mean value of the air PM gran magnetic moment is  $1.14 \times 10^{-19} \pm 0.05$  Am<sup>2</sup>, which, by applying the constitutive model  $\mu = \nu \sigma_s$  as previously discussed, gives a mean diameter of  $7.7 \pm 0.1$  nm for air PM in the tunnel. The estimate of such ultrafine content in the air particulate can probably be representative of a set of substances with common aerodynamic properties. From this point of view, the magnetic content in air PM may serve as a surrogate for hazardous substances (heavy metals, organics, etc.) that are also present in air PM but possibly deserving of more attention in air quality policies.

Although the magnetic carrier that comprises the air PM is rather homogeneous, its concentration covers a broad variation range. The sample dipole saturation varies from 1.76  $\pm 0.06 \times 10^{-7} \text{ Am}^2$  to  $6.05 \pm 0.08 \times 10^{-7} \text{ Am}^2$  and corresponds to volume-concentrations from 1.84  $\pm 0.18 \times 10^{12} \text{ m}^{-3}$  to  $6.46 \pm 0.26 \times 10^{12} \text{ m}^{-3}$ . Despite a 3-fold variation, there was no clear association with traffic density, which may suggest a dependency on sources not related to engine-

combustion and contributions from sources like disk-brakes or suspended matter from pavement abrasion, among others. The %SP parameter varies from 88.9% to 98.7%, suggesting that contributions from stable magnetization (in the coarser fractions) varies from day-to-day. This result was unexpected, especially regarding the uniformity of the SP content. For all samples, the magnetization from SP contribution was prevalent.

The concentration of Fe for air PM in the Jânio Ouadros tunnel (Sanchez-Ccovllo et al., 2009) varies between 0.73 and 3.21  $\mu$ gm<sup>-3</sup> (~4x), which is a range comparable to variations (~3x) in sample dipole saturation ( $R^2$ =-0.57, in Figure 7d) and particle concentration ( $R^2$ =-0.61 in Figure 7e). The correlation between true Fe concentration and inverted particle concentration is an inverse one, suggesting that the SP mineral fraction decreases as Fe content increases. This kind of behaviour can be explained by assuming that the higher Fe content comprises nonferromagnetic minerals and, therefore, has only a minor contribution to SP properties. Such incursions of high Fe content could, for example, be hosted by paramagnetic or hematite-like minerals, with secondary contributions to the SP response often being modulated by magnetitelike minerals. The possibility of a second mineral phase could also explain the minor variations in magnetic susceptibility (Figure 7a), as all samples showed susceptibility within the error margin 2.03±0.33 SI. No correlation between Fe content and the grain dipole moment (Figure 7b) and particle diameter (Figure 7c) can be inferred due to the uniformity of the magnetic fraction in the particulate matter of the tunnel atmosphere. The negative correlation between Fe content and IRM suggests that high iron content is not forming ferromagnetic minerals in the SD-MD fractions with stable magnetization.

#### **4. CONCLUSION**

We have presented the SPCDM procedure to enable quantitative interpretation of SP magnetization for particles with grain sizes below the characteristic diameter for stable SD grains (at least by 1 or 2 nm). This condition encompasses a wide range of fine and ultrafine particles that can be characterised using the Néel model parameters for superparamagnetism, in terms of its dipole moment, magnetization saturation and, from both parameters, quantitative inferences about particle concentration. A constitutive model for the grain dipole moment (in terms of grain volume and magnetization saturation) allows estimation of the grain size diameter by assuming spherical shaped particles and magnetite-like carriers. Testing by the SPCDM procedure, using synthetic samples with nanoparticles of magnetite of different concentrations, produced a clear linear dependency between inverted and true concentrations as well as correct estimates for the grain dipole moment, estimated as  $7.5\pm0.2$  nm for a true distribution (TEM image) of  $8.0\pm0.7$  nm. Grain dipole moment (and, therefore, grain diameter) did not vary with concentration, thus validating the proposed procedure.

For air PM samples collected in the Jânio Quadros tunnel, SPCDM provided useful information about particle diameter ( $7.7\pm0.1$  nm), which was well below the critical volume for stable magnetization. To our knowledge, the existence of such ultrafine particles in air PM had not previously been identified. This is a promising result, when considering better assessment of air quality related to pollutants in the fine and ultrafine fractions because magnetic particulates can serve as a surrogate for other particulate fractions exhibiting the same aerodynamic behaviour, but with deeper concerns to public health or environmental pollution. The quantitative evaluation of grain properties may also be useful in studies of provenance or proxies to evaluate assimilation of particulate pollutants by living beings. As proposed, SPCDM is well suited for

ultrafine SP fractions when the equilibrium magnetization after the external field removal, is observed in a few seconds. This procedure must be revised when handling samples with slower magnetization decay as this is indicative of coarser SP fractions. SPCDM works well however, for mixed samples with fast SP decay and stable IRM associated with low-coercivity (magnetitelike) minerals, as is characteristic of the samples analysed.

The SPCDM procedure has limitations that should be pointed out to the reader. Firstly, since based on Langevin data fitting, the SPCDM method is well suited for SP fractions with "fast" magnetization decay (as such, for grain-size distributions well below the thermally stable volume grains in room temperature). It is unsuited for mineral fractions with "viscous" decays (grain volumes nearing the blocking volume) for which the relaxation times are comparable to measurement timescale. Secondly, it is assumed that the grain-size of the "fast" decay SP fraction is narrow enough (or unimodal) to be represented by a uniform grain-size, as in the Néel model. Real estimates for grain-size distribution may require observations with variable time scales (e.g., temperature, frequency) to reconstruct the distribution of size-dependent activation energy (Worm and Jackson, 1999; Shcherbakov and Fabian, 2005; Jackson et al, 2006; Egli, 2009; Kodama, 2013), which are not implemented in SPCDM. Thirdly, the magnetization saturation of the mineral SP fraction must to be known a priori to evaluate grain volume. It is not required, however, to obtain concentration estimates, which are provided by rationing two independent parameters obtained from data inversion.

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#### References

Aster, R. C., Borchers, B., & Thurber, C. H. (2011). Parameter estimation and inverse problems (Vol. 90). *Academic Press*.

Baldauf, R. W., Lane, D. D., Marotz, G. A. & Wiener, R. W. (2001). Performance evaluation of the portable minivol particulate matter sampler, *Atmospheric Environment* 35(35), 6087–6091.

Bealey W.J., McDonald A.G., Nemitz E., Donovan R., Dragosits U., Duffy T.R. & Fowler D. (2007). Estimating the reduction of urban PM<sub>10</sub> concentrations by trees within an environmental information system for planners. *Journal of Environmental Management* 85: 44-58.

Berndt, T., Muxworthy, A. R., & Paterson, G. A. (2015). Determining the magnetic attempt time  $\tau_0$ , its temperature dependence, and the grain size distribution from magnetic viscosity measurements, *J. Geophys. Res. Solid Earth*, 120, 7322–7336.

Berkov, D. V., Görnert, P., Buske, N., Gansau, C., Mueller, J., Giersig, M., ... & Su, D. (2000). New method for the determination of the particle magnetic moment distribution in a ferrofluid. *Journal of Physics D: Applied Physics*, 33(4), 331. Byrd, R. H., Gilbert, J. C. & Nocedal, J. (2000). A trust region method based on interior point techniques for nonlinear programming, *Mathematical Programming* 89(1), 149–185.

Calderón-Garcidueñas L. and 14 coauthors (2008). Long-term air pollution exposure is associated with neuro inflammation, an altered innate immune response, disruption of the bloodbrain barrier, ultra ne particulate deposition, and accumulation of amyloid  $\beta$ -42 and  $\alpha$ -synuclein in children and young adults. *Toxicologic Pathology* 36: 289-310

Dearing, J. A., Dann, R. J. L., Hay, K., Lees, J. A., Loveland, P. J., Maher, B. A., & O'grady, K. (1996). Frequency-dependent susceptibility measurements of environmental materials. *Geophysical Journal International*, 124(1), 228-240.

Donaldson, K. (2003). The biological effects of coarse and fine particulate matter.

Dormann, J. L., D'Orazio, F., Lucari, F., Tronc, E., Prené, P., Jolivet, J. P., ... & Nogues, M. (1996). Thermal variation of the relaxation time of the magnetic moment of  $\gamma$ -Fe 2 O 3 nanoparticles with interparticle interactions of various strengths. *Physical Review B*, 53(21), 14291.

Dunlop, D. J., & Özdemir, Ö. (2001). *Rock magnetism: fundamentals and frontiers (Vol. 3)*. Cambridge universitypress.

Egli, R. (2009). Magnetic susceptibility measurements as a function of temperature and frequency I: inversion theory. *Geophysical Journal International*, 177(2), 395-420.

Evans, M. E., & Heller, F. (2003). Environmental Magnetism: Principles and Applications of Enviromagnetics, Academic, San Diego, California.

Fabian, K. (2003). Some additional parameters to estimate domain state from isothermal magnetization measurements. *Earth and Planetary Science Letters*, 213(3-4), 337-345.

Fabian, K. (2006). Approach to saturation analysis of hysteresis measurements in rock magnetism and evidence for stress dominated magnetic anisotropy in young mid-ocean ridge basalt. *Physics of the Earth and Planetary Interiors*, 154(3-4), 299-307.

Ge, J., Hu, Y., Biasini, M., Beyermann, W. P. & Yin, Y. (2007). Superparamagnetic magnetite colloidal nanocrystal clusters, *Angewandte Chemie International Edition* 46(23), 4342–4345.

Goya, G., Berquo, T., Fonseca, F. & Morales, M. (2003). Static and dynamic magnetic properties of spherical magnetite nanoparticles, *Journal of Applied Physics* 94(5), 3520–3528.

Jackson, M., Carter-Stiglitz, B., Egli, R., & Solheid, P. (2006). Characterizing the superparamagnetic grain distribution f (V, Hk) by thermal fluctuation tomography. *Journal of Geophysical Research: Solid Earth*, 111(B12).

Jackson, M., & Solheid, P. (2010). On the quantitative analysis and evaluation of magnetic hysteresis data. *Geochemistry, Geophysics, Geosystems*, 11(4).

Jasonov, P., Nourgaliev, D., Burov, B. & Heller, F. (1998). A modernized coercivity spectrometer, *Geologica Carpathica* 49(3), 224–226.

Jiang, Z., Liu, Q., Dekkers, M. J., Colombo, C., Yu, Y., Barrón, V., & Torrent, J. (2014). Ferro and antiferromagnetism of ultrafine-grained hematite. *Geochemistry, Geophysics, Geosystems*, 15(6), 2699-2712.

Jimenez-Lopez, C., Romanek, C. S. & Bazylinski, D. A. (2010). Magnetite as a prokaryotic biomarker: a review, *Journal of Geophysical Research: Biogeosciences* 115(G2).

Kodama, K. (2013). Application of broadband alternating current magnetic susceptibility to the characterization of magnetic nanoparticles in natural materials. *Journal of Geophysical Research: Solid Earth*, 118(1), 1-12.

Li, J., Benzerara, K., Bernard, S., & Beyssac, O. (2013). The link between biomineralization and fossilization of bacteria: Insights from field and experimental studies. *Chemical Geology*, 359, 49-69.

Machac, T. A., Zanner, C. W. & Geiss, C. E. (2007). Time dependent irm acquisition as a tool to quantify the abundance of ultrafine superparamagnetic magnetite in loessic soils, *Geophysical Journal International* 169(2), 483–489.

Maher, B. A. (2009). Rain and dust: magnetic records of climate and pollution. *Elements*, 5(4), 229-234.

Maher, B. A. & Taylor, R. M. (1988). Formation of ultrafine-grained magnetite in soils, *Nature* 336(6197), 368–370.

Maher, B. A. & Thompson, R. (1991). Mineral magnetic record of the chinese loess and paleosols, *Geology* 19(1), 3–6

Martins, L., Andrade, M. F., Freitas, E. D., Pretto, A., Gatti, L. V., Albuquerque, E. L., Tomaz, E., Guardani, M. L., Martins, M. H., & Junior, O. M. (2006). Emission factors for gas-powered vehicles traveling through road tunnels in São Paulo, Brazil, *Environ. Sci. Technol.*, 40, 6722–6729.

Maxbauer, D. P., Feinberg, J. M., & Fox, D. L. (2016). Magnetic mineral assemblages in soils and paleosols as the basis for paleoprecipitation proxies: A review of magnetic methods and challenges, *Earth-Science Reviews* 155, 28–48.

Morris W.A., Versteeg J.K., Bryant D.W., Legzdins A.E., McCarry B.E., & Marvin C.H. (1995). Preliminary comparisons between mutagenicity and magnetic susceptibility of respirable airborne particulates. *Atmospheric Environment* 29: 3441-3450

Moskowitz, B. M., Frankel, R. B., Bazylinski, D. A., Jannasch, H. W. & Lovley, D. R. (1989). A comparison of magnetite particles produced anaerobically by magnetotactic and dissimilatory iron-reducing bacteria, *Geophysical Research Letters* 16(7), 665–668.

Moskowitz, B. M., Frankel, R. B., & Bazylinski, D. A. (1993). Rock magnetic criteria for the detection of biogenic magnetite. *Earth and Planetary Science Letters*, 120(3-4), 283-300.

Néel, L. (1955). Some theoretical aspects of rock-magnetism, *Advances in physics* 4.14 (1955): 191-243.

Paterson, G. A., Zhao, X., Jackson, M., & Heslop, D. (2018). Measuring, processing, and analyzing hysteresis data. *Geochemistry, Geophysics, Geosystems*.

Pope III, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K. & Thurston, G. D., (2002). Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution, *Jama* 287(9), 1132–1141.

Porter, S. C. (2001). Chinese loess record of monsoon climate during the last glacial–interglacial cycle, *Earth-Science Reviews* 54(1-3), 115–128.

Sagnotti, L., Macri, P., Egli, R. & Mondino, M. (2006). Magnetic properties of atmospheric particulate matter from automatic air sampler stations in Latium (Italy): toward a definition of magnetic fingerprints for natural and anthropogenic PM<sub>10</sub> sources, *Journal of Geophysical Research: Solid Earth* 111(B12).

Sagnotti, L., & Winkler, A. (2012). On the magnetic characterization and quantification of the superparamagnetic fraction of traffic-related urban airborne PM in Rome, Italy. *Atmospheric environment*, 59, 131-140.

Sánchez-Ccoyllo, O. R., Ynoue, R. Y., Martins, L. D., Astolfo, R., Miranda, R. M., Freitas, E. D., ... & Andrade, M. F. (2009). Vehicular particulate matter emissions in road tunnels in Sao Paulo, Brazil. *Environmental monitoring and assessment*, 149(1-4), 241-249.

Shcherbakov, V. P., & Fabian, K. (2005). On the determination of magnetic grain-size distributions of superparamagnetic particle ensembles using the frequency dependence of susceptibility at different temperatures. *Geophysical Journal International*, 162(3), 736-746.

Sievers, S., Braun, K.-F., Eberbeck, D., Gustafsson, S., Olsson, E., Schumacher, H. W. & Siegner, U. (2012). Quantitative measurement of the magnetic moment of individual magnetic nanoparticles by magnetic force microscopy, *Small* 8(17), 2675–2679.

Stoner, E. C., &Wohlfarth, E. P. (1948). A mechanism of magnetic hysteresis in heterogeneous alloys. *Philosophical Transactions of the Royal Society of London*. Series A. Mathematical and Physical Sciences, 599-642.

Tarduno, J. A. (1995). Superparamagnetism and reduction diagenesis in pelagic sediments: enhancement or depletion?. *Geophysical Research Letters*, 22(11), 1337-1340.

Taylor, R., Maher, B. & Self, P. (1987). Magnetite in soils: I. the synthesis of single-domain and superparamagnetic magnetite, *Clay minerals* 22(4), 411–422.

Telford, W. M., Telford, W. M., Geldart, L. P., & Sheriff, R. E. (1990). *Applied geophysics (Vol. 1)*. Cambridge University Press.

Wang, X., Løvlie, R., Zhao, X., Yang, Z., Jiang, F., & Wang, S. (2010). Quantifying ultrafine pedogenic magnetic particles in Chinese loess by monitoring viscous decay of superparamagnetism. *Geochemistry, Geophysics, Geosystems*, 11(10).

Williams, W., & Muxworthy, A. R. (2006). Understanding viscous magnetization of multidomain magnetite. *Journal of Geophysical Research: Solid Earth*, 111(B2).

Woodward, R. C., Heeris, J., St Pierre, T. G., Saunders, M., Gilbert, E. P., Rutnakornpituk, M., ... & Riffle, J. S. (2007). A comparison of methods for the measurement of the particle-size distribution of magnetic nanoparticles. *Journal of Applied Crystallography*, 40(s1), s495-s500.

Worm, H. U. (1998). On the superparamagnetic—stable single domain transition for magnetite, and frequency dependence of susceptibility. *Geophysical Journal International*, *133*(1), 201-206.

Worm, H. U. (1999). Time - dependent IRM: A new technique for magnetic granulometry. *Geophysical Research Letters*, 26(16), 2557-2560.

Worm, H. U., & Jackson, M. (1999). The superparamagnetism of Yucca Mountain tuff. *Journal* of Geophysical Research: Solid Earth, 104(B11), 25415-25425.

Table 1 - SPCDM results for synthetic samples of nanoparticles of magnetite with variable massconcentration (%) in paraffin;  $\mu$  and  $S_{DS}$  are the grain dipole moment and sample dipole saturation, respectively;  $n_m$  is mass-concentration of magnetic carriers (number of magnetic carriers per sample mass); %SP is the contribution of SP magnetization in total magnetization under external field of 1 T.  $S_{DS} = M_S V$  where  $M_S$  is sample saturation magnetization and V is sample volume.

Conc. (%)	μ (10 <sup>-19</sup> Am <sup>2</sup> )	S <sub>DS</sub> (10 <sup>-5</sup> Am <sup>2</sup> )	$n_{\rm m}$ (10 <sup>15</sup> g <sup>-1</sup> )	% SP
0.2	$1.07 \pm 0.01$	0.39±0.00	0.99±0.03	98.5
1.0	$1.06 \pm 0.00$	1.39±0.01	4.38±0.15	98.7
1.9	$1.06 \pm 0.01$	2.99±0.01	8.78±0.31	98.9
3.2	$1.07 \pm 0.01$	4.30±0.00	12.50±0.40	98.6
4.4	$1.08 \pm 0.01$	6.71±0.02	15.20±0.50	98.6
5.0	1.06±0.00	4.13±0.00	15.60±0.60	98.9

Table 2 – SPCDM results for particulate matter in the Jânio Quadros tunnel in São Paulo, Brazil;  $\mu$  and  $S_{DS}$  are the grain dipole moment and sample dipole saturation;  $n_v$  is volumeconcentration of magnetic carriers (number of magnetic carrier per air flow volume in each sampling interval), and %SP the contribution of SP magnetization under external field of 1T.

Dav	Sampling	u	Sds	n <sub>v</sub>	% SP
5	Interval	$(10^{-19} \text{ Am}^2)$	$(10^{-7} \mathrm{Am^2})$	$(10^{12} \mathrm{m}^{-3})$	/0 ==
1	08:00-10:00	1.14±0.09	1.76±0.06	1.84±0.18	98.7
	10:00-12:00	1.11±0.03	1.94±0.01	2.08±0.06	96.5
	12:00-14:00	1.20±0.07	2.20±0.06	2.19±0.16	95.6
	14:00-16:00	1.22±0.02	2.13±0.20	2.08±0.03	88,9
	16:00-18:00	1.22±0.05	2.83±0.04	2.77±0.69	96.4
2	08:00-10:00	1.11±0.04	6.05±0.08	6.46±0.26	79.1
	10:00-12:00	1.11±0.05	4.49±0.07	4.82±0.23	96.8
	12:00-14:00	1.18±0.02	5.12±0.04	5.16±0.11	97.4
3	08:00-10:00	1.14±0.03	3.08±0.04	3.23±0.10	97.5
	10:00-12:00	1.13±0.05	4.58±0.08	4.84±0.27	98.7
	12:00-14:00	1.22±0.09	1.84±0.04	1.81±0.16	93.5
	14:00-16:00	1.14±0.01	4.48±0.03	4.66±0.79	97.6



Figure 1: a) Variations of relaxation time with diameter of spherical magnetite-like minerals and b) corresponding magnetization decay normalized by initial magnetization  $M_0$ . Blocking volume with stable magnetization (blue), thermally active particles with viscous (green and magenta) and fast (red) magnetic relaxation as expected in 100s window.



Figure 2: Hysteresis curves (left) normalize by high-field magnetization  $M_{hf}$  (magnetization expressed in fields of 1 and 0.5 T) and magnetization decay curves (right) normalized by in field magnetization  $M_0$  (magnetization measured during external fields applications); a) calibrator 2853 YIG Sphere with pure SP behaviour; b) nanoparticles of synthetic magnetite with 8 nm diameter; c) air particulate matter collected in Jânio Quadros tunnel, São Paulo; d) sediments from Jaraguá Cave, São Paulo with subtle magnetic decay in 100s window. Pure SP response is observed in sample a),b); combined SP and IRM responses observed in samples c and d. Zerocrossing in hysteresis curves for sample b is consistent with pure SP composition; low coercivity in samples c and d is indicative of magnetite-like minerals comprising a coarser fraction with IRM response. The decay curves for in fields of 10, 25, 60, 120, 220, 340 mT. SPCDM data have 17 in field inductions, for illustration only 6 are presented.



Figure 3: Magnetization relaxation after applying a 500mT normalized by in field magnetization  $M_0$ ; a) nanoparticle of synthetic magnetite with fast relaxation; b) air particulate matter with same behaviour; c) sediments from Jaraguá Cave with slower magnetization decay, suggestive of coarser SP minerals.



Figure 4: Inversion products of the SPCDM procedure; a) data fitting and estimated parameters grain dipole moment  $\mu$  [Am<sup>2</sup>]; sample dipole saturation  $S_{DS}$  [Am<sup>2</sup>] and number of magnetic carriers *N*. Measured data (black circles) and fitting curve (red) from the inverted model parameters. b) Objective function with inverted model solution (white cross). For the sake of graphical representation the value of 10 $\varepsilon$  is contoured (black) for a threshold data fitting  $\varepsilon$  equal to 5.0E-8, with stop criterion  $Q_{min} < \varepsilon$ .



Figure 5: SPCDM estimate for the moment dipole (red cross) for nanoparticles of magnetite with particle size distribution diameters centred at 8(1) nm (inset histogram) and published values from previous studies. Dashed curve evaluated from constitutive equation  $\mu = \sigma_s v$  for  $\sigma_s$ =480 kAm<sup>-1</sup> (saturation magnetization of magnetite). Samples with nanoparticles of magnetite and Transmission Electron Microscopy (TEM) picture (inset) provided by D. G. da Silva, S. H. Toma and K. Araki.



Figure 6: SPCDM estimates for particle concentration versus true mass-concentration.



Figure 7: SPCDM results and magnetic properties for air PM collected in Jânio Quadros tunnel in São Paulo.