



EGUsphere, referee comment RC4  
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## Reply on AC2

Anonymous Referee #2

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Referee comment on "Magnetic fraction of the atmospheric dust in Kraków – physicochemical characteristics and possible environmental impact" by Jan M. Michalik et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-462-RC4>, 2022

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*We are grateful for the Referee's effort in reading our submission and his/her suggestions on improving the quality of the manuscript. We are addressing the questions/remarks/suggestions below. The changes will be included in the revised version of the manuscript and/or separate Supplementary Information document when we find it more adequate.*

- It is unclear what the purpose of the research presented was: whether the purpose of the manuscript is to present a novel way to sample the magnetic fraction or whether the purpose of the manuscript is to thoroughly characterize the magnetic fraction of dust found in the urban atmosphere. In the first case, the manuscript needs to be supplemented at least with a detailed description of the device's design and, finally, with an evaluation of its performance based on a comparison of the results with those from other methods as well as a recommendation for further research. Otherwise, it should be justified that this single sampling site is representative of the content and composition of magnetic fraction in the air.

The purpose of the work should be defined in the last paragraph of Introduction section, which is missing here.

*The aim of the study was to characterize magnetic fraction of aerosols in Kraków. Collection of the analytical material is very important in such study and the simple passive sampler was prepared and presented in the manuscript.*

*Single sample collected during nine months period gave a time averaged information. Sampling site was situated far from important sources of emission (e.g. industrial plant) and the sample can be considered as a "background" for the urban area. There are no indices of significant spatial variation in the aerosols composition (excluding close vicinity of individual sources of emission).*

*Testing the performance of the sampler was not the aim here, however we assume (which is supported by the discussions during seminar presentations of the results) that the way of sample collection we propose is interesting. On one hand it is cost effective (as compared to aspiration with cyclonic filters) and on the other all collected material is available for research (which is not the case when fibrous filters or membranes are used).*

*Suitable explanation related to the aim of the study will be added in the Supplementary*

information (see attached file).

**Thank you for explanation. Please include this explanation in the manuscript. Do not include the aim of the study in Supplementary information. Please amend the Introduction with properly edited last paragraph and include the information you have provided above. You can follow the good examples below which are taken randomly from the literature cited in your manuscript.**

Baker, A.R., French, M., Linge, K.L., 2006. Trends in aerosol nutrient solubility along a west–east transect of the Saharan dust plume. *Geophys. Res. Lett.* 33. <https://doi.org/10.1029/2005GL024764>

In this study we examine longitudinal variations in the solubility of aerosol Fe, P and Si using samples collected during Meteor cruise 55 (M55), a west – east transect of the tropical Atlantic Ocean in October/November 2002 [*Wallace and Bange, 2004*], and we include aerosol Al and Mn solubility data for comparison with our results from other regions of the Atlantic [*Baker et al., 2006*]. We use simple leaching protocols to investigate whether atmospheric processing has a significant effect on aerosol nutrient solubility over the spatial/temporal scales associated with transport of Saharan dust across the Atlantic Ocean. We emphasise however that these leaching protocols do not directly reproduce the solubility behaviour of aerosols on deposition to seawater, as discussed by *Baker et al.* [2006]. The M55 cruise track also crossed the Intertropical Convergence Zone (ITCZ) on a number of occasions and this enables us to compare nutrient solubility in Saharan dust aerosol with aerosols which originated in the southern hemisphere.

Rutkowski, R., Białowicz, J.S., Rachwał, M., Rogula-Kozłowska, W., Rybak, J., 2020. Magnetic Susceptibility of Spider Webs and Dust: Preliminary Study in Wrocław, Poland. *Minerals* 10. <https://doi.org/10.3390/min10111018>

The application of spider silk in the magnetic monitoring of urban road dust has never been directly compared to conventional methods. This study aims to report the magnetic susceptibility of urban road dust settled in indoor and outdoor environments, and to compare the data with results obtained from spider webs exposed to indoor and outdoor pollutants. The research hypothesis states that spider webs are appropriate substrates for monitoring environmental pollution due to their good entrapment of aeolian particulate pollution, and thus, they can be employed in studies of urban pollution pathways and human exposure to pollutants. Additionally, road dust represents an equilibrium of deposition and erosion since the last rain, wind, or storm event. Thus, we can assume that spider webs can re-disperse aeolian dusts in a linear and proportionate way, similar to stratigraphic layers of sediment on a road, allowing relationships to be established between webs and road dust and between indoor and outdoor sediments.

Moteki, N., Adachi, K., Ohata, S., Yoshida, A., Harigaya, T., Koike, M., Kondo, Y., 2017. Anthropogenic iron oxide aerosols enhance atmospheric heating. *Nat. Commun.* 8. <https://doi.org/10.1038/ncomms15329>

In this study, *in situ* aircraft measurements using a modified single-particle soot photometer (SP2)<sup>25</sup> and electron microscopy are performed to show that anthropogenic FeO<sub>x</sub> particles, particularly aggregated magnetite nanoparticles, are ubiquitous in the continental outflows from East Asia. We then evaluate their contribution to atmospheric shortwave absorption on the basis of the observed size-resolved mass concentrations and

particle morphologies. Our results indicate that the absorption by anthropogenic FeO<sub>x</sub> is at least 4–7% of the BC absorption over East Asia.

#### ▪ Introduction

The Introduction lacks a final paragraph stating the goals/objectives of the work. Also, the Introduction lacks a paragraph discussing potential sources of magnetic particles (which is discussed in the Results section, among others).

The paragraph related to the main goals will be added to the text.

I suggest rewriting the Introduction section providing the information in the following order: characteristics of magnetic fraction in air dust, known sources, known health effects, known environmental effect, various methods of sampling, and then the "last paragraph of Introduction".

*The Introduction contains information related to approaches used in magnetic fraction of aerosols studies (lines 23-38), health (lines 39-43) and environmental effects (lines 49-55). Sources are not discussed in the Introduction. Discussion is included in the chapter Results and discussion to avoid repetitions of data and citations.*

#### **No comments.**

#### C. Conclusions

Please comment on the novelty of the sampling method proposed. Would you suggest wide application of this design and methodology? What are pros and cons?

*Sampling method used in the study is relatively simple and inexpensive. It is possible to collect a sample significantly enriched in magnetic components. Relatively high content of non-magnetic particles is most probably related to the presence of complex aggregates of various particles in the atmosphere. Simplicity of the sampling method can be considered as suggestion for its wide application. On the other hand it would be interesting to test other samplers of magnetic fraction. Also, it is worth mentioning that in contrast to other commonly used "active" methods is that only the particles really suspended in the air are stuck on the magnet surface. We are of course aware that strong wind conditions can affect the efficiency of the sampler and change the composition of the samples. However long collection time, and elimination of rain induced deposition are certainly an advantage.*

**Please include this explanation in the manuscript in Conclusion section.**

- The characterization and discussion of the results is strongly biased toward spherical particles. Please acknowledge the presence of angular particles derived simply from rust. The word "rust" is not even used in the text. Rust is probably the main source of Fe-rich particles in urban environment. What is their relation to the magnetic fraction? Are you sure no hematite or goethite particles accompany the magnetic fraction? Please supplement the text with relevant observations, comments, and literature data.

*Spherical particles are really an important point of the discussion of electron microscope study. It is related to the anthropogenic, high temperature origin.*

*Rust is commonly occurring (on rails, cars and other vehicles construction elements, urban infrastructure, etc.). It can be considered as a source of Fe-rich particles (e.g. hematite particles). This interpretation will be added to the text. Goethite has not been identified in our sample.*

**Please include this explanation in the manuscript.**

Specific comments:

Line 49 – chemical formula of SO<sub>2</sub> needs correction

Line 57: Magnetic fraction collection

- please expand and rephrase the description by stating, among other things, what size the individual magnets were, how many of them, what the total collecting area was, why the sampler was placed in such a way (vertically, at a height of 1.5-1.7m), why the sampler was placed in such a location (whether the location was chosen deliberately because of existing knowledge of air pollution in the city or because of convenience), why collection lasted 9 months, which part of the year (seasons), whether the surface was protected from precipitation from above, whether the direction of the vertical collecting surface was directed in the direction of the most common wind direction, how far the grass-covered ground surface reached, whether there are potential sources of magnetic particles in the area, how far away were potential close-range sources (e.g. streets, streetcar lines) and long-range sources, etc. Is it possible to show a photo of the sampler or installation?

*Data will be added in Supplementary Materials (see SI\_1).*

- The information provided in Figure 1 is not discussed or explained in the text. Why were magnetic field measurements and simulations performed, how do they compare, what is their relevance to the predicted performance of the sampler design, how do these measurements and simulations support the predicted performance of the sampler, to what extent was this confirmed by the observed distribution of magnetic particles on the PVC film (Fig. 1 D and E), etc.?

**Please answer these questions. Please include the answers in the manuscript. Please use the information provided in Figure 1 in the text.**

Line 83

The powdered samples were placed on single-crystalline silicon no-background holders.

Does this mean that the sample was ground before analysis, or was it analysed as is?

The sample was ground prior to the analysis.

**Please include this explanation in the manuscript.**

Lines 85 – 87

This separation process, for obtaining a laboratory concentrate of the magnetic fraction, is no different from obtaining the magnetic fraction from dust samples collected with classical samplers. Please include such a comment in the text, here or in Conclusions, so that it is clear that for this analytical method the proposed way of sampling atmospheric dust did not give positive effect.

*Separation of magnetic components from significantly enriched in magnetic particles sample is very effective. It is possible to consider two "classical" methods of aerosols collection. Separation of magnetic fraction from filters (e.g. quartz filter) in sampling using aspirators is difficult. Samples obtained using this method are very rich in combustion products (soot, tar balls). Samples collected by sedimentation (dust fall samples) contain material from dry and wet deposition. Samples of dust fall contain often big quartz grains. Magnetic fraction is a very minor component in dust fall by weight and its separation is much more difficult.*

**Please include this explanation in the manuscript.**

Line 87

The collected diffraction patterns were analysed in terms of the Rietveld method using the FullProf Suite Package (Rodríguez-Carvajal, 1993).

What does it mean: phase identification or quantitative analysis, or both? Please add in the text.

*FullProf suite was solely used for Rietveld refinement, which resulted in quantification of observed crystalline phases. The phase identification was a multistep process, which involved: analyses of chemical composition followed by trial refinements of the most apparent, common phases; usage of automatic phase recognition software (eg. Panalytical HighScore 3.0) for search of secondary phases and confirming the main phases.*

**Please include this explanation in the Methods section.**

What was the resolution of the collected diffraction pattern? Was it sufficient for proper analysis by the Rietveld method? Please add in the text.

*The resolution of the instrument calibrated using NIST 660 standard is  $0.065^\circ$  of  $2\theta$ , which is much below widths of lines in samples. The data were collected with angular step of  $0.016^\circ$  of  $2\theta$ . The calibration measurements using NIST 660 revealed also instrumental broadening of the collected lines, which is essential to further analyses of reflections profiles.*

**Please include this explanation in the manuscript.**

Lines 90 – 96

Please provide the following information in the text:

Did you use a separate subsample of the material collected on the PVC film, different from the sample used for XRD?

*We first used the sample for Mossbauer spectroscopy. Then the filler (sucrose) was removed and the sample was measured with x-ray diffraction. As the SiO<sub>2</sub> peaks dominated over other reflections we opted for separating the magnetic species once more. This allowed removal of silicon oxide matrix embedding iron compounds that were of the main interest.*

How did you split the sample to ensure its representativeness?

Did you use a method of concentrating the magnetic fraction similar to that used in XRD measurements? What was the size/mass of the sample used for magnetization measurements? Was it sufficient to make the measurement? Was it a separate subsample, or material previously used for other measurements? Please provide this information in the text.

*All of the collected material (apart from a small amount used for SEM/EDX) was used for magnetization measurements. We could have used some subsample but assuring representativeness would be difficult and the measurements could have taken much longer time.*

**Please include all these explanations in the manuscript to clarify the methods. Apparently, this is important information in case someone tries to duplicate this approach, since the order of analysis is crucial to success.**

Line 99: What was the total mass of material collected over a period of 9 months on the ... mm<sup>2</sup> of the sampler?

*The sample was not weighted. In fact the amount was so small the Mossbauer spectroscopy analysis seemed impossible without adding a filler. Even though the measurements lasted longer than usual until reasonable statistics were achieved especially at liquid nitrogen temperature.*

**Please include this explanation in the manuscript to explain why it was not possible to estimate the amount of magnetic dust fallout.**

Line 104

Instead for:

The results of the XRD studies (Fig. 2) suggest that the separated fraction

There should be:

The XRD results (Fig. 2) suggest that the magnetic fraction separated from the collected sample

Lines 106 - 107

Precise analysis of the profile of magnetite reflexions in the XRD pattern suggest the distribution of various elements at the Fe-sites (e.g. Cr, Mn, Co, Zn) as typical of naturally abundant ferrites (Fig. 2).

Please elaborate, it is not clear from this sentence which part of the curve and which observation or which part of Fig. 2 leads to this conclusion.

*This remark was based on evidenced strain in the profile of this phase. The strain could be extracted from instrumental broadening (thanks to calibration measurements), therefore Rietveld refinement revealed strains for all phases. The residual strains are related to static defects of the structure e.g. atomic disorder on Wyckoff positions originating from substitution of different types of atoms into specific sites. The refined strain was found to be about 0.75%, which is significantly higher than typical values for pure Fe<sub>3</sub>O<sub>4</sub> specimens which is smaller than 0.2% (The pure Fe<sub>3</sub>O<sub>4</sub> specimen was also measured as a reference). The resulting broadening of the main reflections of the Fe<sub>3</sub>O<sub>4</sub> (220 at 30.1° of 2θ and 311 at 35.5° of 2θ) can be noticed in the inserts to the Fig. 2.*

**Please include all these explanations in the manuscript.**

Lines 112 – 114

Please move this part of the text (discussion of SEM results, grain size and morphology) to line 103, so that SEM results are together, followed by XRD results.

The paragraph was organized according to material discussed (not according to method applied). Form of occurrence of non-magnetic components was discussed after information about their identification using XRD. The paragraph will be re-organized.

Line 215

Instead for Fe- rich particle It should be Fe- rich particles

Line 236

Domains with the magnetite ordering reach the size of 10 nm (Fig. 5G, H).

Please elaborate and explain what information relevant to the topic of this study was gained from HRTEM analysis and results presented in Fig. 5H? magnetite was identified already using several other methods.

*HRTEM imaging allows for proving the existence of the ferrous nanoparticles: 10 nm and smaller on one hand and bigger - up to 200 nm on the other. The former are small enough to cross human body barriers and the latter ones are more difficult to be removed from the human body. Moreover we show crystallinity of those smallest particles proving their chemical composition what is important form the point of view of the assessment of the health impact.*

**Please edit and then include all these comments in the manuscript (here or in the Methods section) to explain what information relevant to the topic of this study was gained from HRTEM analysis and results presented in Fig. 5H.**

Please move Figure 5 to a place below the text discussing its content.