EGUsphere, author comment AC2
https://doi.org/10.5194/egusphere-2022-462-AC2, 2022

Reply on RC2

Jan M. Michalik et al.

Author comment on "Magnetic fraction of the atmospheric dust in Kraków – physicochemical characteristics and possible environmental impact" by Jan M. Michalik et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-462-AC2, 2022

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.

A. 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 as 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 Supplementray information (see attached file).

B. 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.

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.

D. 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.

Specific comments:
Line 49 – chemical formula of SO2 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 month, 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.?

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.

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.

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.

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° of 2θ, which is much below widths of lines in samples. The data were collected with angular step of 0.016° of 2θ. The calibration measurements using NIST 660 revealed also instrumental broadening of the collected lines, which is essential to further analyses of reflections profiles.

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 SiO2 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.

Line 99: What was the total mass of material collected over a period of 9 months on the ... mm2 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.

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 Fe3O4 specimens which is smaller than 0.2% (The pure Fe3O4 specimen was also measured as a reference). The resulting broadening of the main reflections of the Fe3O4 (220 at 30.1° of 2θ and 311 at 35.5° of 2θ) can be noticed in the inserts to the Fig. 2.

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

Please also note the supplement to this comment:
https://egusphere.copernicus.org/preprints/2022/egusphere-2022-462/egusphere-2022-462-AC2-supplement.pdf