Characterization of magnetic particulates in urban and industrial dusts

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Abstract

Morphology and mineralogy and magnetic parameters were analysed in atmospheric dust samples collected in 7 cities of Upper Silesia region (South Poland). The study was carried on by means of EDS spectroscopy, SEM technique, X-ray diffraction and Mössbauer spectroscopy. Special attention was paid to the magnetic fraction of studied dusts that is a potential carrier trace elements emitted to the environment. To assess the total content of magnetic fraction in bulk dust samples, mass specific magnetic susceptibility (χ) was measured using a MS2B "Bartington" sensor, then a physical separation of magnetic particles (mostly of technogenic origin) was conducted. The dusts revealed high diversity of χ value, which depended both on the sampling site and the prevailing direction of winds during the period of dust deposition on filters. In the case of atmospheric dusts, the χ value ranged from $10 \times 10^{-8} m^3kg^{-1}$ to $1577 \times 10^{-8} m^3kg^{-1}$. The highest values were detected in samples collected within the range of metallurgical dust emission. The morphological and mineralogical analyses showed that among the technogenic magnetic fraction ferrimagnetic spherules built of iron oxides from magnetite-maghemite series with admixtures of wustite, hematite, goethite and non-stoichiometric Fe-Zn oxides were the predominant structures. Significant differences in magnetic mineralogy of dusts coming from different branches of industry were observed. Magnetic fraction produced by the metallurgy and coke industry were mostly in forms of tightly compacted aggregates with well-formed crystal structure whereas in fly ashes from coal combustion spherical forms (typical ferromagnetic spherules) were mostly observed. Here the predominant magnetic minerals are: magnetite,

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maghemite, magnesioferrite and hematite that occurred among the silicates, aluminosilicates and amorphic phases. In coke and metallurgical dust distinctive mineral forms are metallic iron (α Fe) and iron sulphides.

Keywords: industrial dusts, magnetic particulates, iron minerals, ferromagnetic spherules.

1 Introduction

The early studies on mineralogy of atmospheric and industrial dusts in Poland were already carried out in the 1970s and 1980s [1–3]. The Upper Silesian atmospheric dust composition has been studied since the middle of the 1990s. The results have shown that the main mineralogical phases present in the atmospheric dusts of these areas were: quartz, various types of aluminosilicates (e.g. feldspars, clay minerals), carbonates (calcite, dolomite) [4–6], and various iron oxides [7]. While quartz and aluminosilicates can originate from natural sources, the occurrence of ferromagnetic iron oxides is mostly related to industrial emissions [5, 8, 9]. They occurred as a result of mineralogical transformations of iron bearing source minerals during high temperature technological processes (e.g. fuel combustion, metal ore processing, cement and ceramic production, etc.), so we call them technogenic particles [10]. Such minerals showing ferro- or ferrimagnetic properties were observed both in dust falling directly on the soil surface and in suspended dust (PM 10), which can be transported great distances, causing pollution of all the components of the natural environment [11, 12]. The suspended dust also includes particles of less than 2.5 μm in diameter (so called PM 2.5), which are a direct source of threat to people when inhaled into lungs, together with chemical substances, having a negative impact on people's health [13].

The presence of ferrimagnetic iron oxides can be easily detected using simple magnetic susceptibility (χ) measurements. In order to use magnetometry in industrial dust and aerosol analysis, it is crucial to become familiarized with the structure and form of occurrence of technogenic magnetic particles in different kinds of urban and industrial dusts. Firstly the anthropogenic origin of magnetic particles found in bottom sediments of the Mexican Bay was confirmed for the first time by Doyle et al. [14]. Later on, the presence of magnetic iron forms was also confirmed in industrial aerosols [15, 16].

The anthropogenic magnetic particles contained in fly ashes from coal combustion are the best recognized and described in literature. During the process of combustion the iron present in coal (primarily in sulfides) is transformed into magnetic iron oxides (mostly magnetite and maghemite). According to Flanders [17] a 1% increase in the sulfide content of coal causes an increase in the iron oxides content of the ash of 7% (percentage by weight). Due to the significant height of power plant chimneys, the fly ashes are emitted into the atmosphere and can be transported long distances, and fine particles can remain in the air for a long period.

Studies on the morphology of magnetic particles show that they are of spherical shape (spherules) and measure from a few to several dozen micrometers. Sometimes their size may reach 20 nm [18–20]. Their surfaces may be smooth or corrugated. Some may form adhesions with the silicate phase (particularly the mullite or vitreous phase). Beside the morphological specification, the past investigations concentrated mostly on chemical analyses and were done on the basis of whole dust samples – not the individual separated mineral phases [21–23]. Separate silicate and magnetic phases in fly ashes coming from coal combustion in the USA were studied by Hulett et al. [24] and Hansen et al. [25]. These investigations showed that most of the elements, in particular those from the first row transition metals such as Pb, Zn, Cd, V, Cr, Co, Ni, and Cu, occurring in sulfide forms in coal, are related to magnetic minerals in fly ashes.

Apart from fly ashes, the correlation between the magnetic susceptibility on one hand and the Pb, Cu, Zn, and Cd content on the other hand was also found in atmospheric, urban, and roadside dusts by Hunt et al. [26]. A linear dependence between the occurrence of magnetic particles, expressed as an increase in the χ value and the content of such metals as Cu, Fe, Pb, and Zn in soils and sediments from the urban areas of London, was observed by Beckwith et al. [27].

In recent years the anthropogenic magnetic particles contained in suspended dusts and industrial aerosols have been studied with an increased frequency. These analyses were based mostly on magneto-mineralogical methods. They were carried out in a few large city agglomerations: Shanghai [27], Munich [28], Rome [12], Cologne [29], and Manchester [30]. In the last three agglomerations, plant materials such as needles, tree leaves, or roadside grass were used as bioindicators. These investigations revealed the presence of magnetic grains of ferrimagnetic minerals (multi-domain magnetite) and antiferrimagnetic minerals (hematite) as well as superparamagnetic particles in suspended dust and aerosol fractions. In some cases pyrrhotite also was found. The obtained results also showed that magnetic particles coming from various sources (metallurgy, solid fuels combustion, ceramic industry, traffic emission, soil erosion) have different magnetic characteristics.

Industrial plants located in the Upper-Silesian Industrial District are and were in the past a source of great amounts of anthropogenic dusts and aerosols emitted directly into the atmosphere. This matter has accumulated in the topsoil during the last decades and it is now revealed in numerous magneto-geochemical anomalies occurring in soils from this region [20]. Anthropogenic magnetic particles present in the uppermost soil horizons are relatively easy to distinguish from natural iron minerals occurring in soils [9, 20, 31]. However the variety of their forms is considerable and studies initiated in some European institutions indicate that there is a connection between the forms of anthropogenic minerals in soils and their sources of emission [32, 33]. In order to determine the genesis of the studied phases in detail, it is crucial to identify characteristics of the same types of particles occurring both in soils and in dusts from a given source.

The aim of this study is to investigate the mineral composition and the morphology of technogenic magnetic particles occurring in atmospheric dusts from Upper Silesia. Therefore, seven measuring points were chosen in the

Silesian province and one by its border (Olkusz – Little Poland province), where collectors of atmospheric dusts were installed.

2 Methods

Samples of atmospheric dusts were collected in polypropylene containers of 1 dm^3 volume installed on outriggers 2.5 m above the ground surface. Three containers were set up at every measuring point in order to collect the large amount of material necessary for a magnetic particles separation. The points were located in the following cities of the Silesian province: Katowice, Sosnowiec-E (eastern district), Sosnowiec-N (northern district), Siemianowice, Mysłowice, Dąbrowa Górnicza, Zabrze, and Olkusz (Little Poland province), fig. 1.

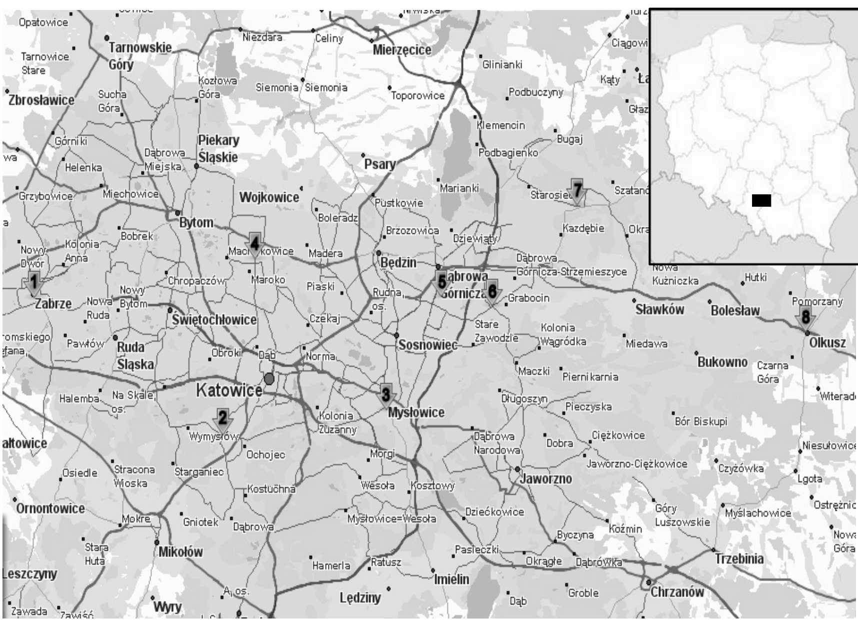

Figure 1: Location of sampling points of atmospheric dust collection.

The magnetic susceptibility measurements of dusts were conducted with the use of an MS2 "Bartington" laboratory magnetic susceptibility meter, equipped (depending on the amount of material) with an MS2B sensor, if the sample is large enough to fill the whole 10 cm^3 volume of the measuring cell (a constant volume of the measuring coil), or an MS2G, oriented on measurements of small amounts of the sample material, with an adjustable height of the measuring coil. The measurement of a dust sample with a given density was converted to specific magnetic susceptibility (mass susceptibility: χ) and displayed in m^3kg^{-1}.

From the averaged industrial dust samples a magnetic fraction separation was carried out. The separation was held in isopropanol, using an ultrasonic washer, which simplified the parting of individual grains.

Natural (unseparated) samples as well as magnetic concentrates and the residue from the separation were mineralogically and chemically analyzed with the use of the scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The SEM analysis was performed using an environmental scanning electron microscope, PHILIPS XL 30 ESEM/TMP, with an analytic EDS unit (EDAX detector, Sapphire type). The phase composition of samples was determined by means of standards, employing a PHILIPS PW 3710 X-ray diffractometer and X'PERT computer program.

In four cases (Siemianowice, Dąbrowa Górnicza, Sosnowiec N and S) where the amount of magnetic concentrate was also enough, Mössbauer spectrometry analysis was applied. Transmission Mössbauer spectrometry analysis was carried out on magnetically separated material using 57 Co:Cr source at room temperature in a constant acceleration mode that was calibrated by standard absorbents: sodium nitroprusside and metallic iron.

3 Results and discussion

The magnetic susceptibility of urban dusts collected from cities located in the Silesian province revealed a significant diversification. The highest χ values were recorded for the samples from Dąbrowa Górnicza located in close vicinity to the Metallurgical Complex "Katowice Steelworks" including also large coke plant "Przyjaźń". The χ values in this area averaged $457 \times 10^{-8}\ m^3kg^{-1}$; however in the individual samples collected from this site a significant diversification occurred. Some samples showed values only slightly above $50 \times 10^{-8}\ m^3kg^{-1}$, while the maximum measured value amounted to $1577 \times 10^{-8}\ m^3kg^{-1}$. This is most likely a result of diversification in wind direction in the sampling point area. Winds blowing from the site of large industrial or urban sources of dust emission carry much greater loads of technogenic magnetic particles than prevalent winds blowing from the site of large forest areas lacking significant emission sources. The second largest values were recorded in Siemianowice (point located in the southern part of the city not far from Katowice centre). The values in this region averaged $233 \times 10^{-8}\ m^3kg^{-1}$, while the highest values reached $600 \times 10^{-8}\ m^3kg^{-1}$, with the median estimated at $201 \times 10^{-8}\ m^3kg^{-1}$, which shows a much lower diversity in χ values among particular samples collected from this point. The measuring point is surrounded on all sides by urban and industrial areas (Siemianowice and Katowice), causing a lesser dependence of the measured parameter on the wind direction. Average χ values > $100 \times 10^{-8}\ m^3kg^{-1}$ were also recorded in Zabrze ($172 \times 10^{-8}\ m^3kg^{-1}$) and in Sosnowiec–N ($108 \times 10^{-8}\ m^3kg^{-1}$). The lowest χ values were observed in Olkusz and in the eastern and southern districts of Sosnowiec and Katowice. Here, some of the χ values decreased to below $20 \times 10^{-8}\ m^3kg^{-1}$, practically indicating the lack of magnetic particles in the samples, which means that in some periods (most likely when the winds blow from the south) the dusts in this region do not contain technogenic magnetic particles. The average χ values in this area range from 60 to $80 \times 10^{-8}\ m^3kg^{-1}$, tab. 1.

Table 1: Mass specific magnetic susceptibility (χ) of atmospheric dusts collected in some cities of Upper Silesia.

City	magnetic susceptibility χ [$\times 10^{-8} m^3 kg^{-1}$]			
	mean	median	min.	max
Zabrze	172	78	28	112
Katowice	77	45	9	191
Siemianowice	233	201	47	600
Mysłowice	95	91	43	194
Sosnowiec N	108	122	51	153
Sosnowiec E	68	41	14	323
Dąbrowa Górnicza	457	312	54	1577
Olkusz	59	57	21	99

The analyses of X-ray diffractograms for crude samples (unseparated) show that the dominant components of atmospheric dusts at all points were quartz, feldspars, clay minerals (kaolinite, illite), dolomite, and calcite. Moreover, the presence of secondary minerals such as anthropogenic calcium sulfate (showing a different hydration state than natural gypsum) and gypsum was observed in the samples. Among the magnetic fraction, which amounts to only a few percent, the presence of magnetite accompanied by hematite was observed. For most samples goethite and wustite were also identified on X-ray patterns, fig. 2.

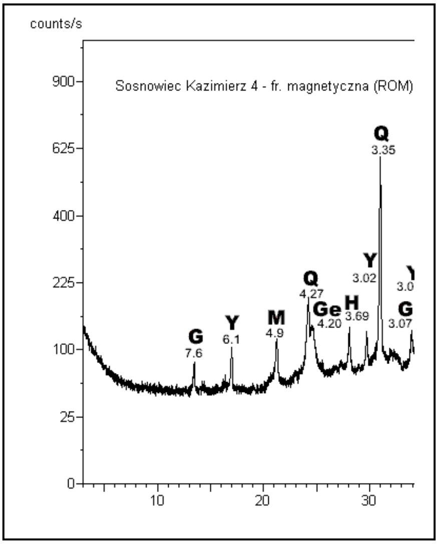

Figure 2: X-ray diffraction pattern of magnetic concentrate obtained from sample of atmospheric dust from Sosnowca E: G – gypsum, Y – $CaSO_4$ of anthropogenic origin, M – magnetite, Q – quartz, Ge – goethite, H –hematite, W – wustite.

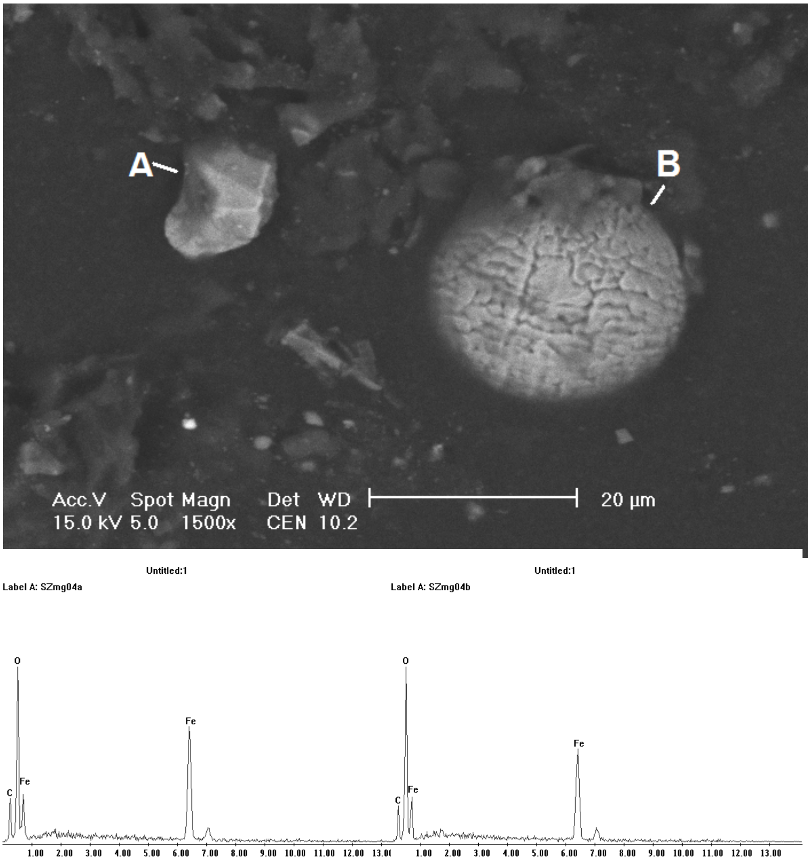

Figure 3: Different forms of iron oxides from atmospheric dust collected in Sosnowiec N (A – magnetite probably of natural origin, B – maghemite technogenic spherule).

Microscopic photographs taken of atmospheric dust preparations using the SEM show both the morphology and the size of the particles. The majority of magnetic phase particles are of spherical (so called magnetic spherules) or oval form with diameters ranging from a few dozen micrometers to a few tenths of a micrometer. Their surfaces are smooth or corrugated; some of them (especially the ones with smooth surfaces) have superficial holes indicating that they are empty inside, figs. 3 and 5. Some form incrustations on aluminosilicates, fig. 5. Besides the spherical forms, angular forms also occur, fig. 3. The last group was found primarily in samples from the Siemianowice and Dąbrowa Górnicza areas. A very interesting magnetic particle in a skeletal form was found in atmospheric dusts from Siemianowice, fig. 4.

It was observed that a considerable number of particles occurred in a fraction < 10 µm, which is a fraction of suspended dust. This fraction had a significant

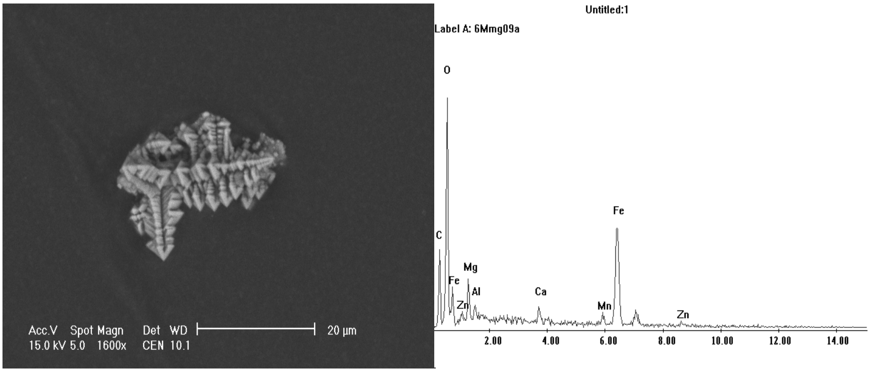

Figure 4: Skeletal form of iron oxide with admixtures of Mg, Al., Ca, Mn and Zn, occurring in atmospheric dust from Siemianowice.

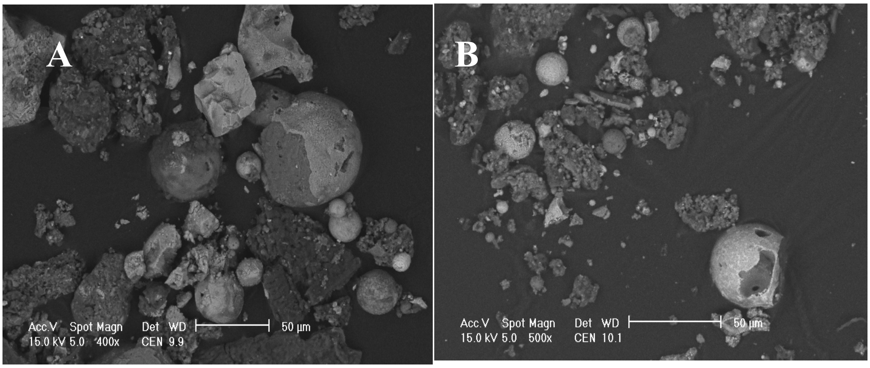

Figure 5: Iron oxides incrustations on aluminosilicate spherules (A – sample Olkusz, B – sample Siemianowice).

contribution in all the measured samples from which the microscopic preparations were made. Within this fraction both silicate forms and iron oxides having ferrimagnetic properties were present.

Due to the application of EDS and SEM it was possible to determine the chemical composition of individual magnetic particles. The EDS analysis showed that the chemical composition of highly magnetic spherical particles occurring in the atmospheric dusts from deposition differs in the iron content. Among the iron oxides, the intermediate phases such as magnetite-maghemite and hematite were the most common. In some samples magnesioferrite was identified. The rest of the iron oxides were present in lower quantities in various sampling sites; thus maghemite was found in Siemianowice, and wustite was present in Dąbrowa Górnicza, Sosnowiec E and N, and Katowice, fig. 2. Metallic iron (α-Fe) was identified rarely, fig. 6, mostly in the iron and steel industry regions. It was observed in the samples from Sosnowiec-E and Katowice Steelworks (Dąbrowa Górnicza). Iron sulfide forms were observed in the dusts collected from the eastern part of the Silesian Province. Pyrrhotite was found in Dąbrowa Górnicza and can be related to the emissions of the “Przyjaźń” coking plant located in the vicinity of the steelworks. The more common paramagnetic iron sulfides such as pyrite and marcasite were identified in the atmospheric dust samples from Olkusz. Furthermore, technogenic Fe-Zn oxides with a non-stoichiometric composition were observed in Siemianowice and Sosnowiec-N. Goethite occurred quite commonly in the samples from Siemianowice, Sosnowiec-N, and Olkusz.

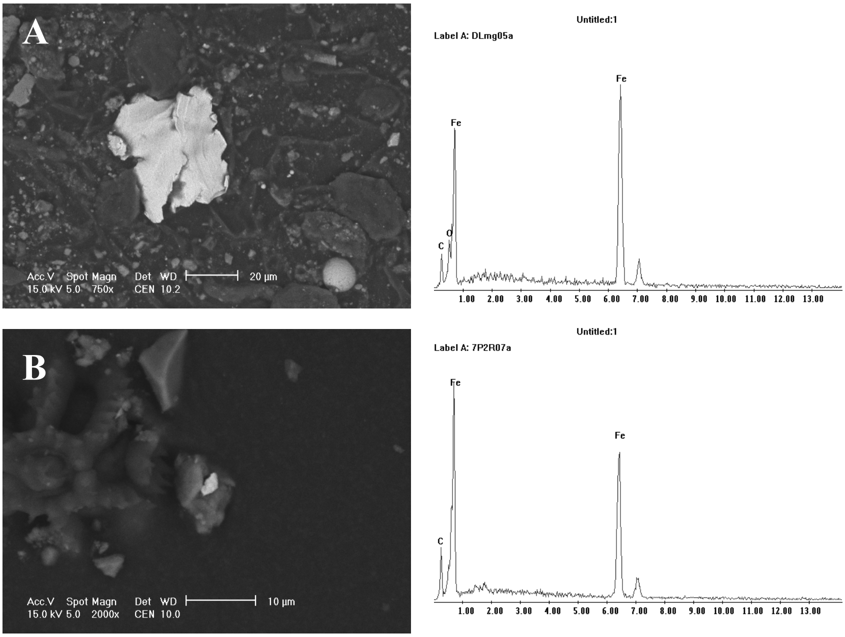

Figure 6: Angular particles of metallic iron (α Fe) in atmospheric dust from: A - Dąbrowa Górnicza; B Siemianowice.

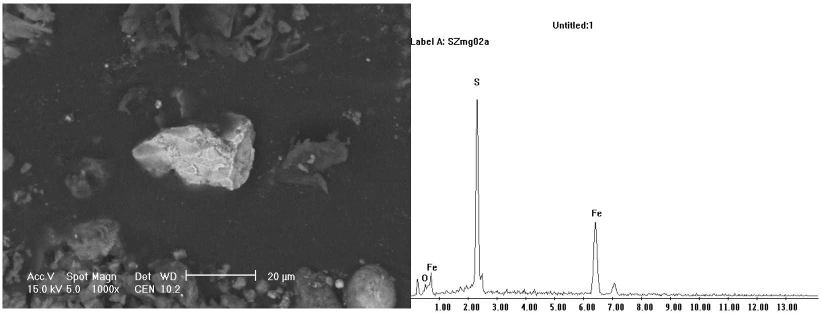

Figure 7: Magnetic particle of iron sulphide from atmospheric dust collected from Sosnowiec N.

Table 2: Percentage quantitative assessment of mineral forms of iron calculated on the base of Mössbauer spectroscopy and X-ray diffractograms.

City	Quantitative assessment of mineral forms of iron [%].				
	Fe aluminosilicate	magnetite	$Fe_{1\pm x}S$	FeS_{2-x}	α Fe
Siemianowice	39	55	0	0	9
Sosnowiec N	70	27	0	3	
Sosnowiec E	29	52	19	0	0
Dąbrowa Górnicza	34	60	3	0	3

Analyses carried out with the use of Mössbauer spectroscopy (tab. 2) confirmed the presence of such phases as magnetite, metallic iron, and hematite in dusts and revealed the occurrence of two sulfide forms of FeS_{2-X} (probably pyrite with paramagnetic properties) and $Fe_{1\pm X}S$ (probably ferromagnetic pyrrhotite), paramagnetic iron aluminosilicates, and ferroalloys with ferrimagnetic properties. The percentage quantitative assessment of mineral forms of iron minerals was presented in table 2. The amount of magnetite in dusts from Dabrowa Górnicza, Siemianowice, and Sosnowiec E was between 50 and 60%, whereas in Sosnowiec N it was only 27%. In the last sample, iron aluminosilicates forms were predominant. In dust samples located close to metallurgical plants, metallic iron or magnetic ferroalloys were also detected. Also sulfides with the formula $Fe_{1\pm X}S$ (probably pyrrhotite) were present mostly in dusts from localities influenced by iron metallurgy and/or the coke industry.

The majority of magnetic particles are of a spherical shape, which is typical of the particles originating from the processes of solid fuel combustion [20, 34]. These are the so called ferrimagnetic spherules which are formed during the coal combustion. Their sizes range from a few to several dozen micrometers. Some of them have smooth surfaces, while others have corrugated surfaces; some form adhesions with the silicate phase (in particular mullite or vitreous phase). The internal structure of spherules is dual. The ones with smaller diameters are full and have a magnetic core, which is likely to be either a non-stoichiometric spinel from the magnetite-maghemite series ($Fe_{3-X}Me_XO_4$) or a mineral with the structure of ferrite, $MeFe_2O_3$, where a part of the iron ions may be substituted by other metals (Mn, Ni, Co, Zn, Mg, Cd, and Cu) [9].They are most usually coated with a thin silicate, aluminosilicates, or calcareous crust. Magnetic spherules of another type are empty inside and their crust consists in most part of magnetite or an intermediate magnetite-maghemite phase. On the surface of these spherules the gas escape holes are visible. They were formed during a fast solidification of iron oxides and silica at high temperature. This can be concluded from the large quantity of vitreous silicate phase and mullite. According to the results of research, the technogenic magnetic particles, as a carrier of increased magnetic susceptibility values (χ) of atmospheric dusts, frequently also contain significant quantities of other elements, including heavy metals (Mn, Zn, Cr, and Ni). They can be bound either by the spinel's crystalline structure or by the forces of surface adsorption. In the latter case, after deposition on the soil surface, particularly in forested areas where the soils have an acid reaction, these metals can be relatively easily released to the environment, being a potential ecological threat. The analysis of the results of SEM-EDS measurements shows that differences in the metal types bound with the magnetic particles were observed in different sampling sites. In the Dąbrowa Górnicza area that is within the range of Katowice Steelworks' impact, but particularly in the region of Siemianowice in close vicinity to still active steelworks and a few other old plants of the central part of the Upper-Silesian Industrial District, some relations between the magnetic particles and characteristic metals of the processes of ferrous metallurgy such as nickel and chromium were observed. In this region also larger amounts of angular particles were found. Their presence in soil organic horizons had been confirmed earlier in the regions of the iron and steel industry, particularly in proximity to the old steel plants [20, 35].

From the analysis of the data in table 1 it can be inferred that the atmospheric dusts collected in these areas reveal much higher χ values. This is not only a result of the higher concentration of technogenic magnetite-maghemite spherules but also the effect of the presence of metallic iron, which occurs in the form of angular particles, in these dusts. Metallic iron is the strongest ferromagnetic material and its magnetic susceptibility is about 400 times higher than that of a stoichiometric magnetite.

4 Conclusions

- Magnetic susceptibility of the atmospheric dusts in Upper Silesia is spatially diversified. The highest χ values occur in the areas surrounded on all sides by urban-industrial regions, especially in the areas of direct impact of the metallurgical plants (Siemianowice and Dąbrowa Górnicza).
- The magnetic susceptibility of dusts collected from the same site shows high variation over time even during a one month period. This results from variable meteorological conditions, where the main role is played by the altering directions of winds transporting the pollutants. It is particularly visible in the regions adjacent on one side to large forested areas, where no local pollution sources are present. The wind direction determines the type and amount of magnetic particles contained in the dust fall.
- Regarding the morphological structure of the magnetic particles separated from atmospheric dusts from Upper Silesia, the prevailing morphological forms are the magnetic spherules built of ferrimagnetic iron oxides from the magnetite-maghemite series with an admixture of wustite, hematite, goethite, and Fe-Zn non-stoichiometric oxides.
- Angular particles, composed of either iron oxides or metallic iron, prevail in atmospheric dusts from the regions of direct impact of the metallurgical plants (Siemianowice and Dąbrowa Górnicza). The metallic iron present in these dusts causes a significant increase in χ values.

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