Airborne Particulate Matter Characterization with Magnetic Methods, Mössbauer Spectrometry and Micro-weighing of Filters

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RADWAG BALANCES AND SCALES ADVANCED WEIGHING TECHNOLOGIES

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Scope of research

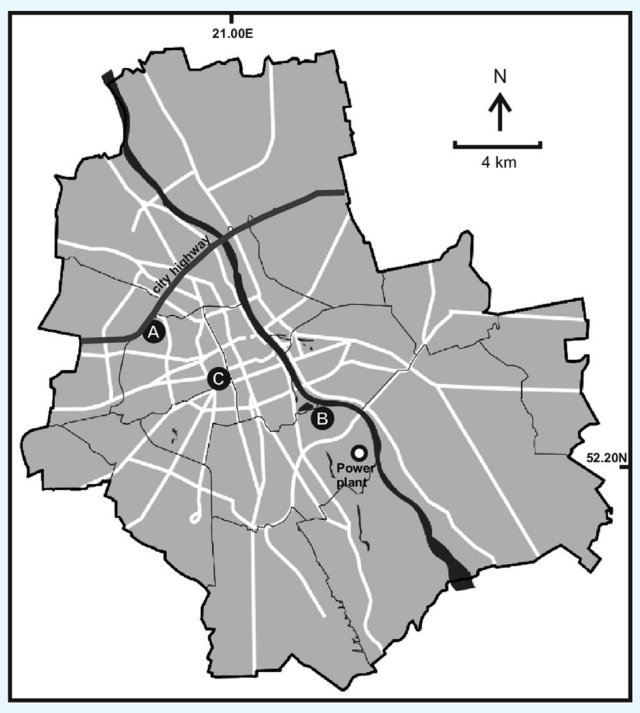
The **particulate matter (PM)** is collected on the borosilicite filters in the low-volume air samplers PNS-15 (Atmoservice, Poland) operating outside the three buildings in Warsaw (Poland) since 2014. The whole collection comprises of 407 filters. Each filter was exposed to total PM for 72 hours (3 days) with the effective air-flow volume of 2.32 m^3 per hour and accumulated the dust with grain-size significantly less than 100 µm. The mass of filters was precisely measured using a laboratory balance WAX 62 (RADWAG, Poland) with internal calibration and accuracy of $2\cdot 10^{-2}$ mg. In order to obtain the mass of PM, the mass of filter with PM was measured and then mass of the clean filter was subtracted. The PM masses were in the range of 2-15 mg. The concentration-dependent magnetic parameter – magnetic susceptibility (χ) was normalized on mass and calculated for individual filters. In order to identify mineralogical phases of PM (magnetically soft and hard) the variety of experimental methods [1] has been applied (thermomagnetic measurements, Day plot analysis of parameters of magnetic hysteresis loop and scanning electron microscopy). The Day plot [1], relating the ratio M_{rs}/M_s to the ratio H_{cr}/H_c, has allowed to estimate the average size of magnetic grains (M_s - saturation magnetization, M_{rs} - saturation remanence, H_c - coercivity and H_{cr} - remanence coercivity). Moreover, a speciation of Fe in the iron-bearing minerals has been determined with transmission Mössbauer spectrometry [2,3].

Sampling sites

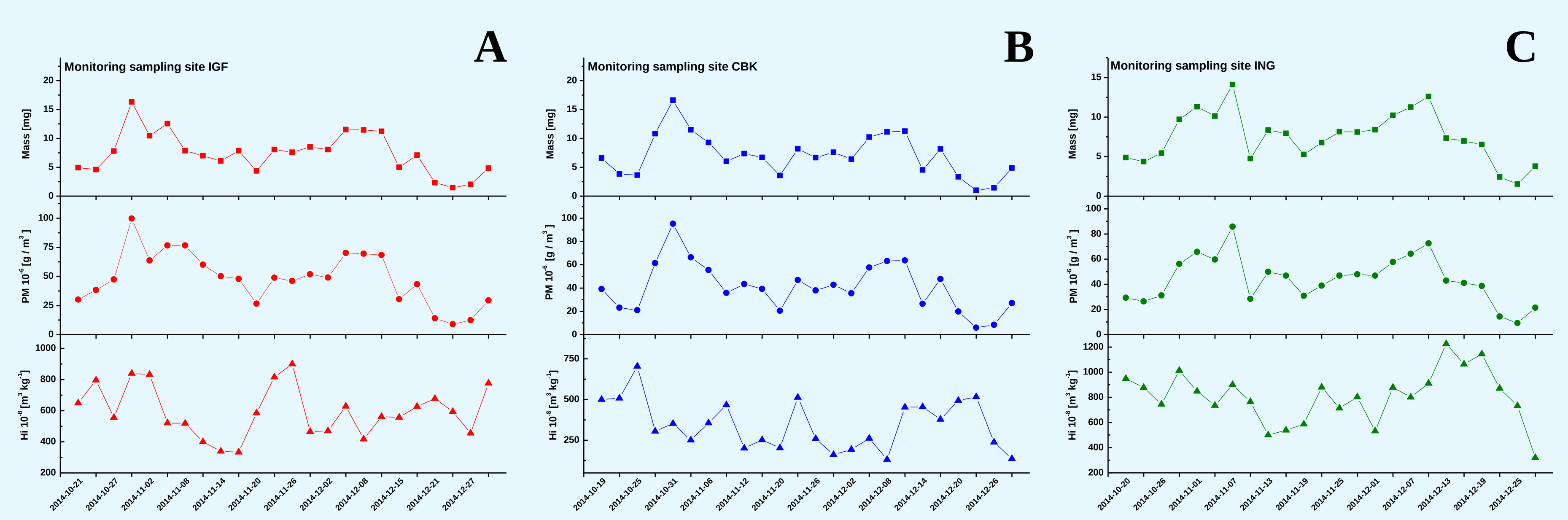
Warsaw, Poland, Polish Academy of Sciences (PAS)

A - Institute of Geophysics, PAS
B - Space Research Centre, PAS
C - Institute of Geological Sciences, PAS

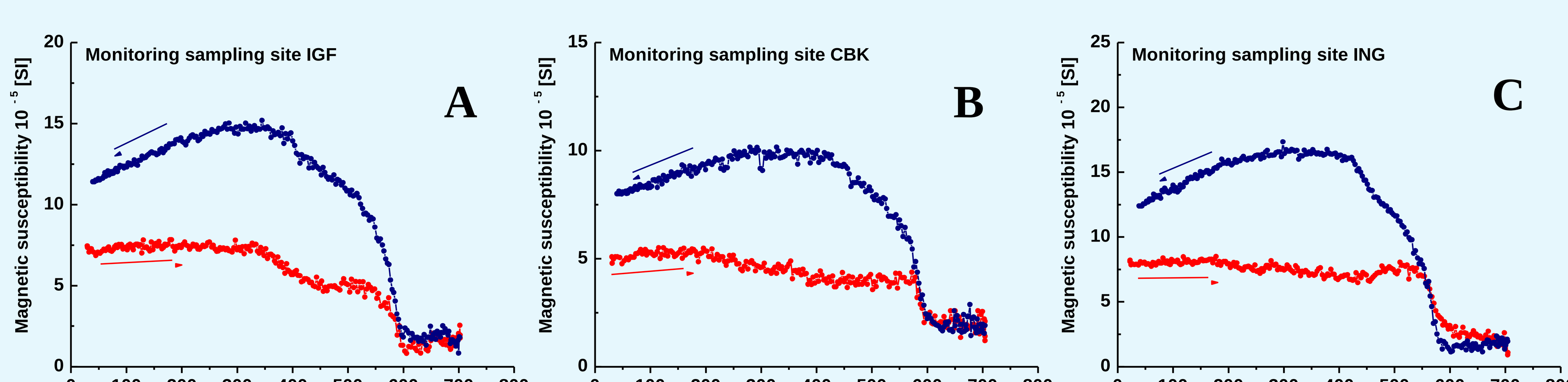
(the location of the city highway close to site A and the heat and power plant in the close distance to B site are also indicated).



Evolution in time of PM mass, concentration and mass-specific magnetic susceptibility



Thermomagnetic curves:



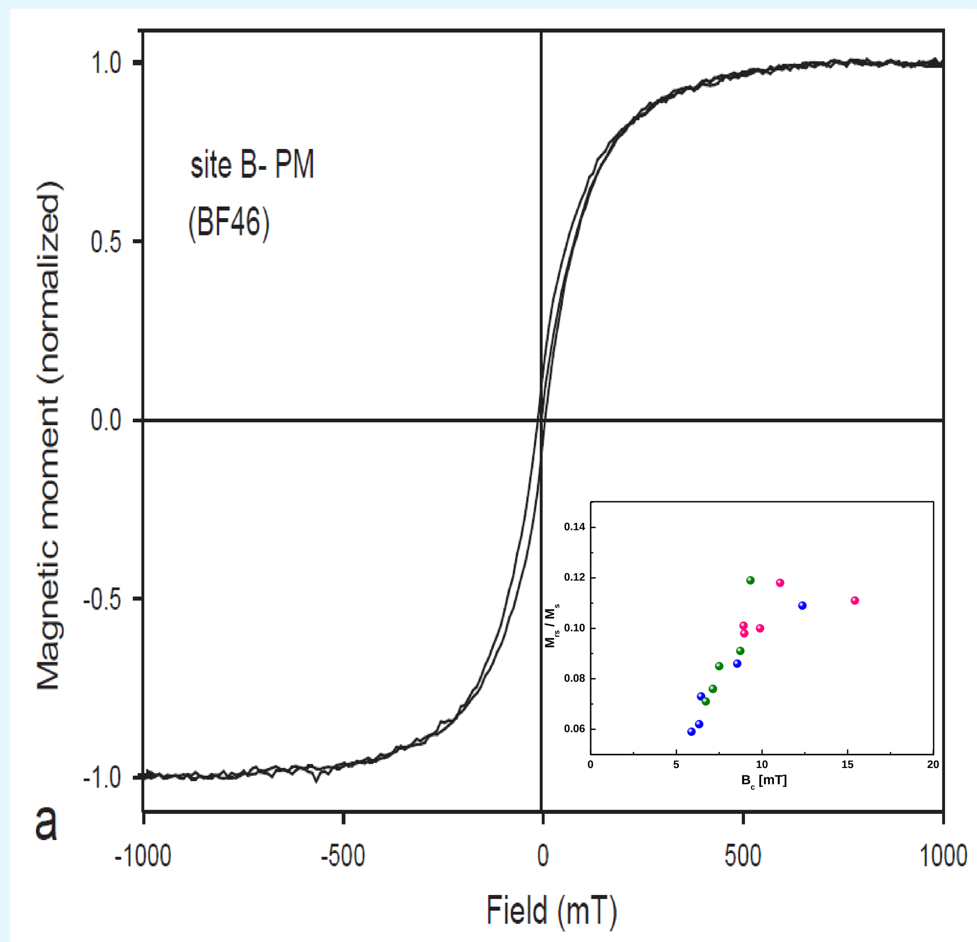
Heavy metals content in mg/kg (chemical analysis)

	Mn	Fe	Mg	Cd	Cu	Pb	Zn	Al.	P	Ti	Co	Cr	Mo	Ni	As	Ba	Sr
AF-39 23-26.11.2014	251.77	17321.76	1227.48	9.09	486.16	258.67	1527.31	2412.20	587.23	128.14	6.39	42.05	25.82	49.50	25.89	203.35	61.94
AF-43 05-08.12.2014	162.26	10001.50		15.33	365.51	386.73	2087.19	1006.52	408.37	58.07	4.48	15.84	15.92	23.55	34.19	177.73	27.62
Average	207.01	13661.63		12.21	425.84	322.70	1807.25	1709.36	497.80	93.10	5.44	28.95	20.87	36.52	30.04	190.54	44.78
BF-18 23-26.11.2014	113.65	5708.39		11.52	216.31	331.49	1438.09	772.64	443.84	82.96	4.04	10.62	11.06	24.85	37.61	91.55	33.89
BF-23 08-11.12.2014	148.44	9361.08		17.20	568.89	585.98	2193.05	722.98	472.07	53.77	5.61	26.03	17.75	24.03	55.94	198.08	37.61
Average	131.05	7534.74		14.36	392.60	458.74	1815.57	747.81	457.95	68.36	4.82	18.33	14.40	24.44	46.77	144.81	35.75
CF-14 22-25.11.2014	267.25	18279.82	249.99	10.69	508.52	345.68	1592.19	1868.57	528.08	120.31	5.28	54.78	17.63	41.20	21.26	326.20	51.67
CF-18 04-07.12.2014	303.40	21901.72	761.16	12.93	624.37	367.92	1604.00	2571.38	535.68	125.51	5.59	51.82	21.13	32.03	27.28	339.81	56.71
Average	285.33	20090.77	505.58	11.81	566.44	356.80	1598.10	2219.97	531.88	122.91	5.44	53.30	19.38	36.61	24.27	333.00	54.19

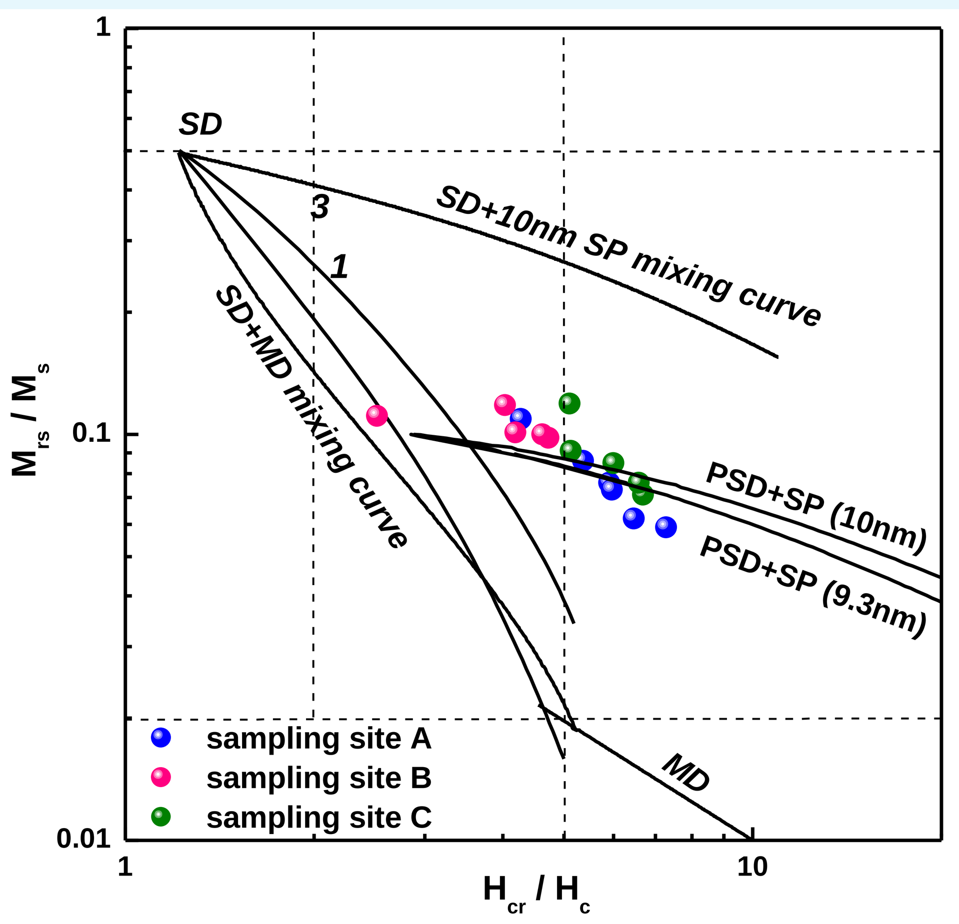
SEM images of filters with PM

SEM AF-39(23-26.11.2014) SEM BF-18 (23-26.11.2014) SEM CF-14 (22-25.11.2014)

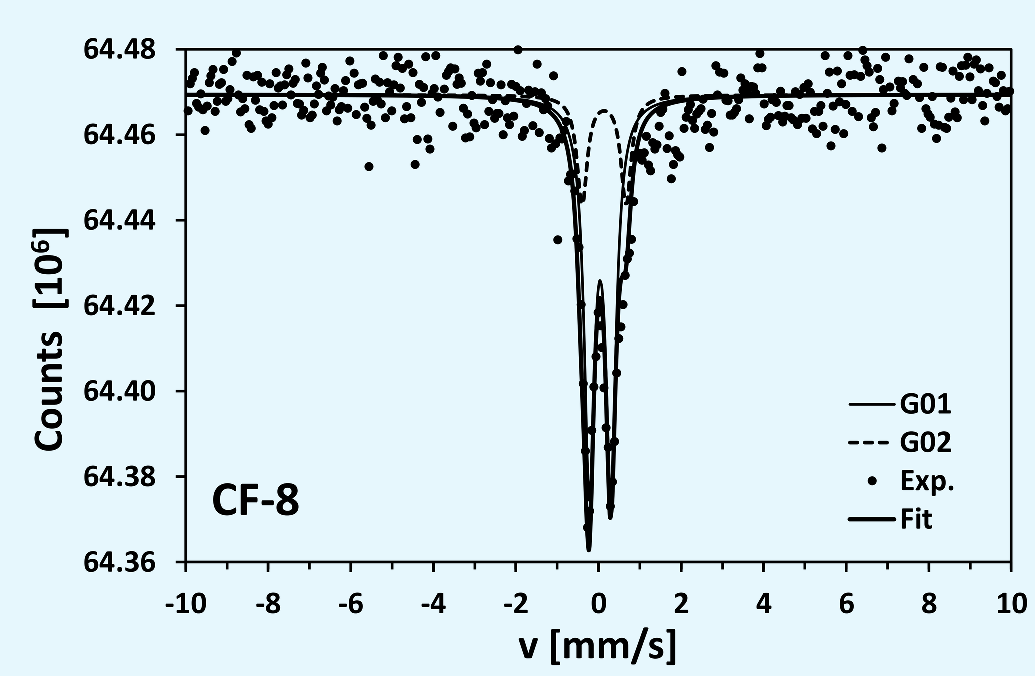
Exemplary magnetic hysteresis parameters:



Day-Dunlop plot:



Transmission Mössbauer spectra at room temperature for the filter of the highest susceptibility



		[mm/s]	[mm/s]	[mm/s]
No.	P [%]	IS*	QS	γ/2
G01	77.6	0.144	0.525	0.150
G02	22.4	0.239	1.065	0.150

$\chi_{CF8} = 1598\cdot 10^{-8}$ m³/kg = $= 1.598\cdot 10^{-5}$ m³/kg

P – Fe percentage contribution
IS* – isomer shift (rel. to α-Fe)
QS – quadrupole splitting
γ/2 – line half-width

G01 – doublet corresponding to traces of paramagnetic Fe in Be windows of γ quanta counter (diluted alloy addition) / P_{FeBe} contribution /

G02 – doublet attributed to paramagnetic Fe^{3+} ions – presumable in dominating **aluminosicate phase** in PM on deposited in filter (or in **glassy phase** – eg. in fly ashes from power plant [4]). / P_{AlSi} contribution /

$\rho_{Fe3O4} = 5.2$ g/cm³

$\kappa_{Fe3O4\ MD} = 2.8$

$\chi_{Fe3O4\ MD} = \kappa_{Fe3O4\ MD} / \rho_{Fe3O4} = 5.38\cdot 10^{-4}$ m³/kg

Main results and conclusions:

- **The thermomagnetic analysis supplemented by SEM observations demonstrated the in PM the spherical and irregular-shaped magnetite particles in size of a few µm are present. No metallic iron is visible for any site (A, B, C) in PM.**
- **On Day-Dunlop diagram PM data are located in the area for PSD (pseudo-single-domain) magnetite and ultra-fine SP (superparamagnetic) grains. The magnetically hardest PM is observed for B site.**
- **The fluctuations of PM mass are strong (~ 50%; weather conditions) - not correlated with smaller susceptibility changes (~ 30%; human activity).**
- **The temporal variations of magnetic susceptibility differ between the localities, with the lowest for site B and higher for sites A and C (apparently, not a vicinity of power plant but a road traffic increases the magnetic susceptibility).**
- **The application of the Mössbauer spectroscopy faces a lot of problems due to a small amount of PM in filter ($\sigma_{PM} \sim 1$ mg/cm²). The traces of Fe in Be windows of counter ($d_{Be} \approx 200$ µm) is visible (absorption $A_{BeFe} \approx 0.16\%$). Comparing this with α-Fe callibration foil ($d_{Fe} \approx 20$ µm, and absorption $A_{Fe} \approx 20\%$) the content of iron in beryllium has been estimated as $Cp_{FeInBe} = (A_{BeFe}/d_{Be})/(A_{Fe}/d_{Fe}) \approx 0.08\%$ (like in high purity technical Be). The estimation of Fe amount of in aluminosilicates dominating phase can be done as follows: $\sigma_{Fe\_AlSi}/\sigma_{Fe} = (A_{BeFe} / A_{Fe}) * (P_{AlSi}/P_{FeBe}) \approx 0.2\%$ (where $\sigma_{Fe} = 16$ mg/cm²). Thus $\sigma_{Fe\_AlSi} \approx 32$ µg/cm² and $\sigma_{Fe\_AlSi} / \sigma_{PM} \approx 3\%$ (in good agreement with the results of chemical elem. analysis ~ 2 %).**
- **In the Mössbauer spectra no magnetite is visible (because of small relative content, like in [2]) although it has been detected with magnetic methods (due to high susceptibility an magnetization values). The simple calculation of magnetite content $m_{Fe3O4}/m_{PM} \approx \chi_{PM}/\chi_{Fe3O4} \approx 3\%$ probably leads to significant overestimation (due to the mixture of phases). On the other hand, the G02 component can originate not only from aluminosilicates but also from very fine particles of magnetite of significantly reduced hyperfine field due to the superparamagnetic effects and surface defects.**

References

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Expanded UYA 4Y and MYA 4Y functionality - filter weighing - RADWAG Balances And Scales

UYA 2.4Y Ultra-Microbalance

Maximum capacity [Max]: 2.1g
Readability [d]: 0.1µg

MYF chamber for filter weighing

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Thanks to an innovative mechanical design , the functionality of the UYA 4Y ultra-microbalance and MYA 4Y microbalance has been expanded by filter weighing option. This new operation is possible to be carried out due to easy disassembly of the regular weighing chamber and replacing it with a custom-design chamber for filter weighing.

The filter weighing chamber is characterized by high ingress protection. Large open-work weighing pan allows precise weighing of filters of various dimensions (max ø100). The chamber is made of stainless steel which makes it resistant to influence of chemicals, prevents colour change and scratches.