Chemical, magnetic and Mössbauer effect analysis of road dust from expressway

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Abstract. Environmental dusts of urban and industrial origin are one of the most important factors responsible for air and soil pollution – mainly because of heavy metals content. In this work a dust collected from the acoustic barriers of E-77 expressway (Poland) has been investigated. Chemical analysis was performed by means of atomic absorption spectrometer with flame atomization (F-AAS). Fe, Al and Zn metals dominate in the investigated road dusts. Mössbauer spectra collected at room temperature enabled the identification of several iron-containing phases in the dust. Some traces of hematite and magnetite have been found as well as α-Fe phase in ferromagnetic state. A significant component could be interpreted as pure iron in paramagnetic state. The dominating doublet in the spectrum of high quadrupole splitting could correspond to iron carbonates. Complementary measurements of low-field AC magnetic susceptibility confirmed a different metal content in the road dust samples collected from different altitudes of acoustic barriers.

Key words: road dusts • environmental dusts • flame spectrometry • Mössbauer spectrometry • magnetic susceptibility

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Introduction

Road dust is commonly used as an indicator of heavy metal pollution of the environment. Concentrations of metals in road dusts, particularly trapped by acoustic barrier, make it possible to determine the importance of basic processes responsible for emission of metals from means of transport, including brake wear, tyre wear, road abrasion and fuel combustion [14]. Road dust emitted from the E-77 dual carriageway has been analysed. The road consisted of two carriageways with two lanes each and two shoulders with an asphalt surface. Double guard rails separate the carriageways and single guard rails run along the right edge of each carriageway. The average year traffic density on the investigated sites of the E-77 dual carriageway was 24 089 ± 1401 veh/h [6]. The research area was located in a typically agricultural region in Poland away from industrial sources of trace metals. In order to investigate the composition of environmental dust, various experimental methods are commonly used like HRTEM, EDX, SEM techniques [1, 10, 16], magnetic susceptibility and remanence measurements [1, 2, 4, 5, 11, 12] as well as Mössbauer spectrometry [7–9, 11, 13]. The main goal of the present work was to determine chemical elements content in road dusts and to find Fe-rich phases.

Experimental and samples

The examined samples (ca. 20 g) have been collected by means of a vacuum cleaner from acoustic barriers on two surfaces: the 0.0–0.6 m × 20 m bottom section, and the 1.8–2.4 m × 20 m upper section (road dust samples are denoted as P-1 and P-2, respectively).

The collected samples have been dried in air at room temperature under laboratory conditions to constant weight, and then sieved through a nylon 1 mm screen and stored in hermetically sealed plastic containers. The samples have been thoroughly mixed before each use.

The content of metals in the road dust samples was determined via microwave-assisted digestion of the samples according to the manufacturer's protocol (Millestone, 1992). The weighed amounts of 0.5 g have been placed in 100 mL Teflon vessels with 5 mL of 65% HNO_3 (GR, Merck) and 1 mL of 30% H_2O_2 (GR, Lach-Ner). Then, the samples were digested in a microwave oven (MLS 1200 MEGA), according to the program: 1) 6 min, 250 W; 2) 1 min, 0 W; 3) 6 min, 400 W; 4) 6 min, 650 W; 5) 6 min, 250 W; 6) 5 min, ventilation. After cooling, the digests were transferred to polypropylene standard flasks and diluted to 50.0 mL with water. For each sample, three subsamples were digested simultaneously.

The values of concentration of Al, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the eluates after the microwave--assisted digestion were determined using an atomic absorption spectrophotometer AAS – Agilent Technologies 200 Series AA 240 FS AA with flame atomization. Standard solutions of metals have been prepared by appropriate dilution of 1000 μg/mL stock standard solution J. T. Baker (Baker Instra-Analyzed, Atomic Spectral Standard). N_2O was used as an oxidizer only to determine Al amount, whereas the acetylene/air flame was used to determine the other metals. All measurements were performed in triplicate. The detection limits for the metals being examined were: Al – 6.1 mg/kg; Co – 2.6 mg/kg; Cr – 2.7 mg/kg; Cu – 1.2 mg/kg; Fe – 3.8 mg/kg; Mn – 1.6 mg/kg; Ni – 2.8 mg/kg; Pb – 3.0 mg/kg; and Zn – 1.0 mg/kg.

Next, Mössbauer studies have been carried out using a ^{57}Fe transmission spectrometer operating in vertical geometry with a ^{57}Co(Rh) source of gamma radiation. Measurements were performed at room temperature with a vibrator operating in constant acceleration mode. Mössbauer spectra were fitted using non-commercial PolMöss package based on MS Excel and Solver module. This software enables fitting both discrete components and Gaussian distributions of hyperfine parameters. PolMöss package utilizes various optimizing methods (gradient, multistart-gradient and evolutionary algorithms) and is dedicated to multi-core processors offering parallel calculations.

In addition to this, magnetic susceptibility measurements were performed at room temperature by means of a simple differential AC magnetometer. This system consists of a magnetizing coil (supplied with 50 Hz current) and two identical signal coils coupled in push-pull configuration. After balancing of magnetometer, the sample has been placed inside one of the signal coils. The differential signal has been detected and processed with lock-in amplifier.

Table 1. Concentration of metals and organic carbon in the samples of road dust

Metal	Content (mg·kg⁻¹)	
	P-1 $X_{avr.} \pm SD$	P-2 $X_{avr.} \pm SD$
Al	10 030 ± 340	20 080 ± 370
Co	6.36 ± 0.06	8.8 ± 0.4
Cr	56.6 ± 2.5	99.6 ± 1.5
Cu	102.6 ± 0.6	137.9 ± 2.6
Fe	14 460 ± 270	20 320 ± 610
Mn	442.5 ± 6.1	559 ± 15
Ni	25.5 ± 0.8	32.6 ± 0.7
Pb	48.1 ± 7.0	57.3 ± 1.7
Zn	2 803 ± 66	3 114 ± 41
C_{org} (%)	8.76 ± 0.08	12.06 ± 0.06

Results and discussion

The concentration values of the detected metals are listed in Table 1. The lower content of metals in the bottom sample P-1 (particularly Al, Cr, Cu, Mn, Fe, Ni and Pb) than in the upper sample P-2 results presumably from the higher concentrations of the metals in particles of a weaker tendency for sedimentation. A similar trend is observed for organic carbon C_{org} concentration, which is a measure of the organic substances contribution in the investigated road dusts. Dominating metals in the road dusts are: Fe, Al and Zn – which seems to be very natural taking into account an intensive process of wear of vehicles engines as well as corrosion of vehicles bodies and of the road infrastructure. High concentration of iron reflects its anthropogenic origin, derived from vehicle traffic (local soil contains only (4.4 ± 0.2) g·kg⁻¹ of iron).

Mössbauer spectra collected at room temperature enabled identification of the iron-containing phases in the dust and determination of their relative contributions. The spectra are presented in Figs. 1 and 2 for the samples P-1 and P-2, respectively. The hyperfine parameters of fitted components are listed in Table 2.
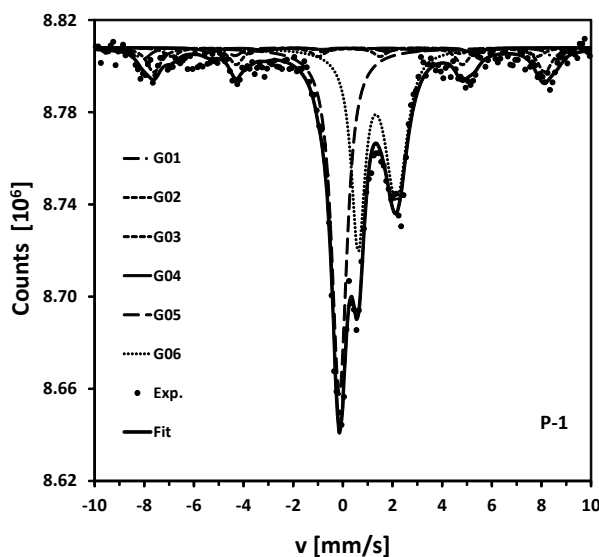

Fig. 1. Transmission Mössbauer spectra with specified components for road dust sample P-1 at room temperature.

Table. 2. Mössbauer spectra parameters for road dust samples P-1 and P-2 at room temperature (P – percentage contribution of the component, IS_0 – mean value of the isomer shift, QS_0 – mean value of quadrupole splitting, B_0 – mean value of hyperfine magnetic field, DB – standard deviation of hyperfine field distribution)

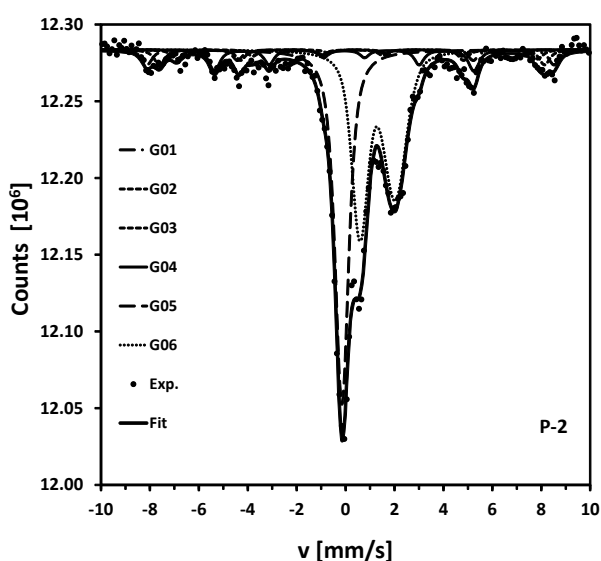| Sample	Component	P (%)	IS_0 (mm/s)	QS_0 (mm/s)	B_0 (T)	DB (T)
P-1	G01	4.9	0.48	–0.2	51.8	0.5
	G02	10.4	0.37	0	49.0	0.5
	G03	3.8	0.58	0	45.9	0.5
	G04	2.1	0.05	0	33.0	0.5
	G05	38.5	–0.03	0	0.0	0.5
	G06	40.3	1.49	1.54	0.0	0.5
P-2	G01	5.2	0.41	–0.2	51.8	0.5
	G02	5.1	0.37	0	49.0	0.5
	G03	3.2	0.58	0	45.9	0.5
	G04	7.3	0.05	0	33.0	0.5
	G05	36.4	–0.04	0	0.0	0.5
	G06	42.8	1.42	1.44	0.0	0.5

Fig. 2. Transmission Mössbauer spectra with specified components for road dust sample P-2 at room temperature.

In both samples the iron oxides (no more than 20% in total) were found: hematite (component G01) and magnetite (components G02 and G03). There are also traces of α-Fe phase in ferromagnetic state represented by Zeeman sextet characterized by magnetic hyperfine field of 33 T (component G04) and almost zero isomer shift (relatively to reference iron foil). Another significant component (over 35%) takes the form of a singlet (G05). It could be assigned to pure iron in paramagnetic state which is a proof for the nanometric size of some dust particles. The dominating component (over 40%) takes the form of a broad, asymmetric doublet (G06). Its quadrupole splitting (ca. 1.4 mm/s) and isomer shift (ca. 1.4 mm/s) is much higher than expected for wustite iron oxide [15], however it could correspond to iron carbonates (siderite or ankerite) [3]. Contrary to the case of atmospheric aerosols [7, 8], the investigated road dusts do not contain iron sulfides and sulfates. Both hyperfine parameters and relative contributions of individual phases are very similar for samples P-1 and P-2. It means that the iron-rich phases content is independent of the height on which the road dusts have been collected. However, absolute concentration of iron in the samples differs – what is clearly seen from chemical analysis and qualitatively from the Mössbauer effect intensity. In both samples the ratio of line amplitudes in Zeeman sextets points to the random orientation of spins – which is natural for powdered samples.

Complementary measurements of low-field (< 1 mT) AC magnetic susceptibility indicate that magnetism of the sample P-2 is about 10^4 times weaker than that of an α-Fe reference sample of the same mass. Since the iron content in the sample is about 2%, it means that from the macroscopic point of view only about 0.5% of iron is in the ferromagnetic state. From Mössbauer spectrometry, this fraction is about 7% (G04 component). This discrepancy is a natural consequence of the fact that Mössbauer effect is characterized by a short life span of the ^{57}Fe nucleus excited state – in this case shorter than the spin relaxation time of iron particles. The ratio of magnetic susceptibility of sample P-2 and P-1 is consistent with the ratio of magnetic atom concentrations (Fe, Co, Ni) in the samples (within experimental uncertainty). Thus, susceptibility measurements could be applied in practice as a simple and very fast test for the first step determination of magnetic metals content in dusts.

Conclusions

Road dusts collected from the acoustic barriers of E-77 dual carriageway abound in Fe, Al and Zn metals which points to the road traffic origin of these elements. The particle of the mentioned metals are not considered to be highly toxic, however they irritate the skin and respiratory system. In addition, the occurrence of these elements is also accompanied by carcinogenic heavy metals such as Pb, Cr and Ni. Moreover, the chemical compounds of Fe, Al and Zn metals are usually more serious pollutants than pure elements. Mössbauer spectrometry have pointed to the dominance of paramagnetic fine iron particles and iron carbonates in the dusts. Magnetic susceptibility seems to be very simple and quick test for polluting metals presence in road dusts.

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