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Chemical characterization of bulk depositions in two cities of Upper Silesia (Zabrze, Bytom), Poland. Case study

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Abstract: The chemical composition of bulk deposition is an important aspect of assessing ambient air pollution. It contributes significantly to the removal of pollutants from the atmosphere and their transfer to other ecosystems. Thus, it is a reliable determinant of environmental chemistry. Therefore, bulk deposition can be considered useful for tracking the migration path of substances from different sources.

The aim of the study carried out at five measurement points in Zabrze and Bytom was to assess the content of selected physico-chemical parameters in bulk deposition. Samples were collected continuously from November 2019 to November 2020. In the collected samples the following were determined: COD, pH, conductivity, dissolved organic carbon, inorganic carbon and total carbon; inorganic anions (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, Br^-, PO_4^{3-}) and cations (Li^+, Mg^{2+}, Ca^{2+}, Na^+, K^+, NH_4^+), metals and metalloids (Mn, Ni, Co, Cu, Zn, As, Cd, Pb, Cr, and Fe), and carboxylic acids (formic, acetic, oxalic). The obtained test results were statistically processed using Excel, and the normality of data distribution was verified by Shapiro-Wilk test. The results show that pollutants transported in the atmosphere and introduced with precipitation in the Zabrze and Bytom areas are a significant source of area pollution of the region.

Introduction

The high standard of living in highly industrialized countries results in a continuous increase in the demand for ever more goods and energy. It seems that the future belongs to alternative, renewable energy sources. The European Union has made a commitment to achieve so-called climate neutrality by 2050. In 2019, a statement on the European Green New Deal was published. This new EU growth strategy aims to transform the Union into a climate-neutral, fair and prosperous society with a modern, and competitive economy (EASAC 2020). Concern for the environmental quality and the resulting quality of our health has been the subject of numerous scientific studies as well as economic and environmental decisions for many years. Much has been done in this regard, but the introduction of new technologies and rapid civilization development systematically changes its condition. In addition, globalization, climate change, overconsumption, and emergencies such as the SARS-CoV-2 pandemic also contribute to adverse environmental changes (Saadat et al. 2020).

The costs of routine monitoring are high, and its scope and the results obtained do not always fully reflect the real threats to the environment and our health. The subjects of environmental studies are mainly substances and elements known for a long time, the lists of which are included in the appropriate regulations on water, sewage, air or soils. Changes in civilization and technological development, introduction of new substances and materials into circulation, as well as advances in analytical chemistry cause that the current scope of research is not sufficient and should be extended to include new analytes (Kurwadkar et al. 2020). The assessment of the environmental condition is carried out by means of various tools. One of them is study of the so-called bulk deposition. It includes, among others, physical and chemical studies of all forms of precipitation including: rain, snow, hail and fog and is the main way of removing organic carbon compounds from the atmosphere. The forms of precipitation vary in their efficiency of capturing solutes from the atmosphere. The chemical composition of precipitation reflects the air pollution level. The concentrations of chemicals present in precipitation are mainly influenced by geographical location, weather, climate, industrialization level and human activities (Liu et al. 2019). Precipitation is the most effective purifier of the atmosphere. Many substances that constitute air pollutants are present in rainwater, thus contributing to changes in its chemical composition and reaction. Examples of studies on bulk deposition have been described in the literature (D'Alessandro et al. 2013, Siudek et al. 2015, Tositti et al. 2018, Azimi et al. 2003, Wetherbee et al. 2019, Huston et al. 2009, Sanjeeva and Puttaswamaiah 2018, Polkowska et al. 2005, Pęczkowski et al. 2020, Kosior et al. 2018).

The Upper Silesia region is the most transformed by man area in Poland, where energy production is still based on combustion of solid fuels, mainly coal. The monitoring of precipitation chemistry conducted there since 1998 by the Institute of Meteorology and Water Management – National Research Institute includes the basic components of precipitation water, and the analysis of acid rain is based on the content of acid sulfur and nitrogen compounds present in precipitation (IMGW-PIB 2018, Czaplicka et al. 2014). The main sources of pollution in these areas include low emissions from outdated local boilers, households, emissions from means of transport associated with the rapid increase in the number of cars and still underdeveloped road infrastructure (Nowak et al. 2014).

Recognition of the quality and size of pollutants carried with precipitation should be monitored regularly, which allows to track the processes of progressive changes in the environment, as well as to assess the effects and effectiveness of remedial programs. The aim of this study was to analyze the chemical composition of bulk deposition in terms of inorganic anions (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, Br^-, PO_4^{3-}) and cations (Li^+, Mg^{2+}, Ca^{2+}, Na^+, K^+, NH_4^+), carboxylic acids (formic, acetic, oxalic), metals and metalloids (Mn, Ni, Co, Cu, Zn, As, Cd, Pb, Cr and Fe), as well as COD, pH, conductivity, dissolved organic carbon, inorganic carbon, and total carbon.

Materials and methods

Study area and sampling

The samples were collected continuously from November 2019 to November 2020, at 5 measurement points located in Zabrze and Bytom. These were: Zabrze-Kotarbiński Housing Estate (roof of the Institute of Environmental Engineering, Polish Academy of Sciences building; 50°18’53.4”N 18°46’19.7”E); Zabrze-Pawłów (property at Gen. W. Sikorskiego Street; 50°16’50.5”N 18°48’15.7”E); Zabrze-Centrum Północ (Fire Station area, intersection of Stalmacha Street and Bytomska Street; 50°18’33.6”N 18°47’20.0”E), Bytom-Miechowice (Nowa Street; 50°22’12.3”N 18°51’17.7”E), and Bytom--Szombierki (Family allotment gardens “Perła”, Zabrzańska Street; 50°20’09.5”N 18°52’58.2”E). Bulk deposition samples were collected by continuously open containers (20 L polyethylene bucket). Once a sampler was set up, it remained at the sampling location for a period as shown in Table 1. The containers were cleaned with ultrapure water after sampling. The sampling schedule is summarized in Table 1.

Analytical scope and methods

The following parameters were determined in the samples collected: pH, electrolytic conductivity, chemical oxygen demand (COD), dissolved organic carbon (DOC), total dissolved carbon (TDC), total dissolved inorganic carbon (DIC), selected ions (anions and cations), selected metals and metalloids. The pH was determined by potentiometric method according to PN-EN ISO 10523:2012 standard. The conductivity was measured by conductometric method according to PN-EN 27888:1999 standard. The COD was determined by spectrophotometric method according to PN-ISO 15705:2005 standard. Dissolved organic, total and inorganic carbon was determined by infrared spectroscopy using Shimadzu TOC-5000A total organic carbon analyzer according to PN-EN 1484:1999 standard.

Before metals and metalloids analysis, the samples were filtered through 0.22 µm PES syringe filters and acidified with concentrated ultrapure HNO_3 to a pH <2. The concentrations of Mn, Ni, Cu, Zn, As, Cd, Pb were determined by using a PerkinElmer inductively coupled plasma mass spectrometer ICP-MS (Elan 6100 DRC-e, Shelton, USA), according to own procedure (PB18, edition 4, 10.02.2016). The operating conditions were: radio frequency power 1125 W; plasma gas flow 15 L/min; auxiliary gas flow 0.9 L/min; lens voltage 6.5 V. Nebulizer gas flow was optimized as needed for highest signal in the range of 0.78–0.82 L/min. The concentration of Fe was measured by ICP-OES inductively coupled optical emission spectrometry (Avio 200, Perkin Elmer), according to

Table 1. Sampling schedule for bulk deposition

Period	From (date)	To (date)	Total number of sampling days in the measurement period	Total bulk deposition volume for each sampling period and each zone, mL				
				Zabrze – Kotarbiński Housing Estate	Zabrze – Pawłów	Zabrze – Centrum Północ	Bytom – Miechowice	Bytom – Szombierki
I	1.11.2019	18.11.2019	17	548	546	525	758	744
II	18.11.2019	17.12.2019	29	82	66	90	334	302
III	17.12.2019	13.01.2020	27	1325	970	1310	1640	2950
IV	13.01.2020	10.02.2020	28	1090	754	1015	1410	1240
V	10.02.2020	9.03.2020	28	1120	880	1065	1660	1580
VI	9.03.2020	8.05.2020	59	630	171	402	56	633
VII	8.05.2020	4.06.2020	27	720	800	640	1019	1540
VIII	4.06.2020	1.07.2020	27	3360	3450	2980	3990	5470
IX	1.07.2020	5.08.2020	35	1155	1290	910	1200	3490
X	5.08.2020	9.09.2020	35	1850	2030	1890	2320	3370
XI	9.09.2020	7.10.2020	28	1470	1450	890	880	1560
XII	7.10.2020	5.11.2020	29	2770	2180	2520	1890	3160
∑			369	16120	14587	14237	17157	26039

PN-EN ISO 11885:2009 standard. The instrumental parameters were: plasma gas flow – 10 L/min; auxiliary gas flow – 0.2 L/min; nebulizer gas flow – 0.6 L/min; radio frequency power – 1400W; pump flow – 1.0 mL/min.

Before ions analysis, the samples were filtered through a 0.22 µm PVDF syringe filter. Determination of cations was performed by ion chromatography, according to PN-EN ISO 14911:2002 standard, using Thermo Scientific Dionex ICS-1100 ion chromatograph equipped with a conductivity detector. For determination of cations, 25 µL of sample volume was introduced onto a Dionex IonPac CS16 separation column and eluted with 1.5 mL/min of 30 mM MSA at 40°C. Anions were determined by ion chromatography, according to PN-EN ISO 10304-1:2009 standard, using Thermo Scientific Dionex ICS-1100 ion chromatograph equipped with a conductivity detector. For quantification of anions, 100 µL of sample volume was added on a Dionex IonPac AS22 and eluted isocratically with 1.2 mL/min of 4.5 mM Na_2CO_3 + 1.4 mM $NaHCO_3$ at 30°C. Detection of cat- and anions was carried out by a conductivity cell. Determination of carboxylic acids content was performed according to the developed own methodology (Pecyna-Utylska et al. 2021) using Thermo Scientific Dionex ICS-1100 ion chromatograph with conductometric detection and isocratic elution.

Data Analysis

Experimental data were processed in Excel (Microsoft, USA). The difference in metal and metalloid deposition between sampling points was assessed using an independent t-test (one-tailed, $\alpha = 0.01$). The normality of data distribution was checked by Shapiro-Wilk test (the null hypothesis was that the collected data are normally distributed and significance level was 5%). Correlation analysis was performed by calculating the Spearman correlation coefficient.

Results

Chemical characterization of bulk depositions

The periods of precipitation sampling (bulk deposition) were not uniform, which was mainly due to the different intensity of precipitation. Based on the obtained data in Figure 1 (total precipitation volume in each sampling period), it can be concluded that the periods with the lowest precipitation volume were period II (18.11.2019–17.12.2019, <350 mL) and VI (09.03.2020–08.05.2020, <700 mL). The highest total precipitation occurred in period VII (04.06–01.07.2020 > 5.4 L in Bytom-Szombierki) and periods III, IX, X and XII. In the vast majority of cases the measurement point Bytom-Szombierki dominated. Several times larger precipitation volumes as compared with other points in the same measurement period were recorded there.

In Poland, the pH of precipitation is determined according to 6 classes, from class I (pH > 6.5, elevated pH) to class VI (pH < 4.1, strongly decreased pH). The pH of the investigated precipitation samples ranged from 4.84 at the measurement point Zabrze-Kotarbiński Housing Estate (measurement period III – 17.12.2019–13.01.2020) to 7.93 at the measurement point Bytom-Miechowice (measurement period VI, 09.03.2020–8.05.2020) (Figure 2). Much greater differences than in the case of pH were found for the measured conductivity values at different measurement points and sampling period. In measurement periods such as I, III–V, VIII and X they are low (< 80 µS/cm) in all measurement points. The large differences are mainly related to measurements in period II (18.11.2019–17.12.2019, conductivity value: 73.4–389 µS/cm), VI (09.03.2020–08.05.2020, conductivity value: 72.1–897 µS/cm) and XI (09.09.2020–07.10.2020, conductivity value: 30.7–494 µS/cm). Comparison of individual measurement points in a given measurement period shows the highest differences in conductivity for measurement point no. 4 (Bytom-Miechowice) (Figure 3).

Values of bulk deposition for individual determinations in five measurement points are presented in Figs. 4–9.

In the case of COD and total carbon, the highest annual depositions concern the point Bytom-Miechowice (132 and 40.5 $g/m^2/year$) (Fig. 4 and 5), followed by Zabrze-Centrum Północ (70.9 and 20.6 $g/m^2/year$), Zabrze-Pawłów (14.6 and 3.92 $g/m^2/year$), Bytom-Szombierki (14.3 and 2.81 $g/m^2/year$) and Zabrze-Kotarbiński Housing Estate (7.41 and 1.63 $g/m^2/year$.

Taking into account the bulk deposition of designated inorganic cations, it ranged from 1.82 $g/m^2/year$ (Zabrze-

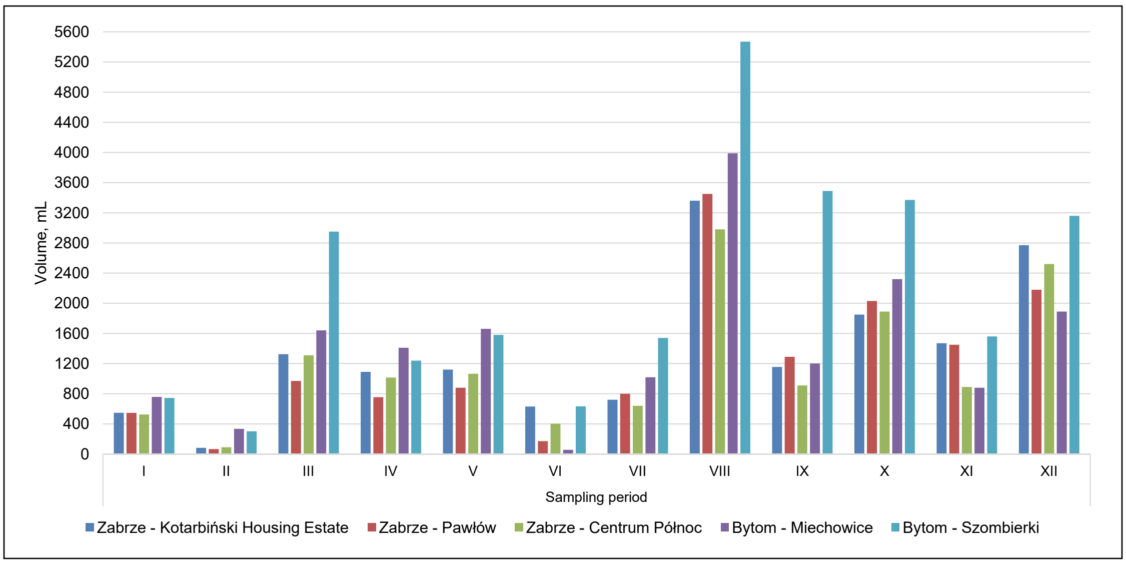

Fig. 1. Total bulk deposition volume for each sampling period

-Kotarbiński Housing Estate) up to 10.2 g/m^2/year (Zabrze--Centrum Północ). The dominant cations depending on the measurement point are ammonium ions, sodium and calcium.

In the case of inorganic anions, the highest value of bulk deposition was 11.7 g/m^2/year at the point Bytom--Miechowice. At the remaining sampling points it was about two times lower, with the lowest value of 3.18 g/m^2/year in Zabrze-Kotarbiński Housing Estate. The dominant anions at all measurement points are sulfate(VI), followed by chloride and nitrate(V).

Bulk deposition of the determined carboxylic acids was at the level of detection limits, and the highest was at the

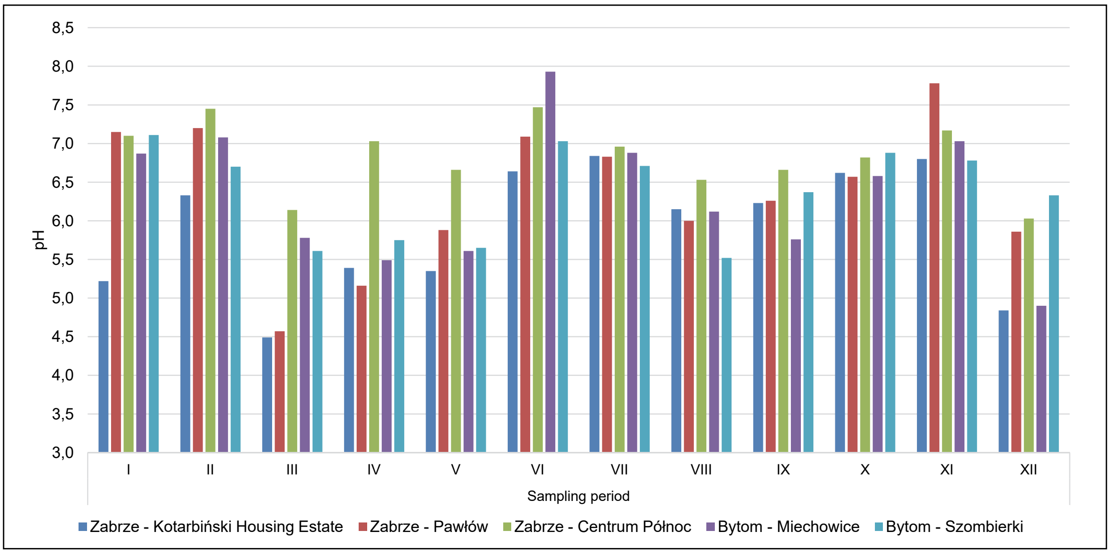

Fig. 2. pH of bulk deposition for each sampling period

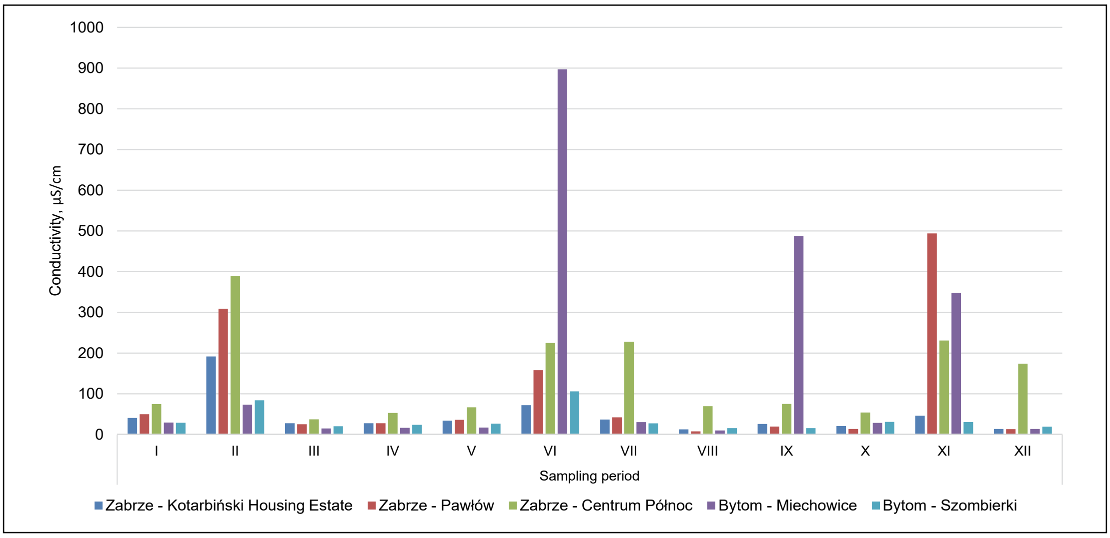

Fig. 3. Conductivity of bulk deposition for each sampling period

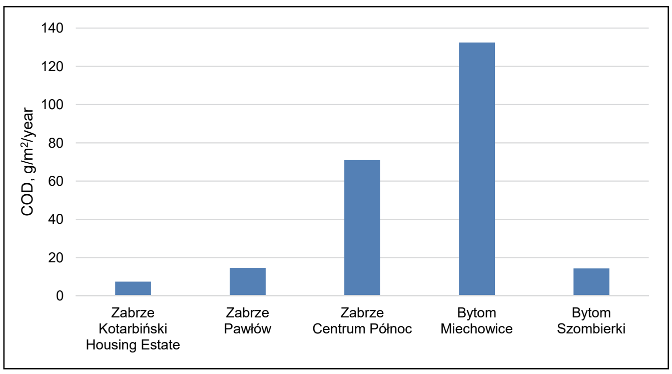

Fig. 4. Total COD deposition throughout the study period (annual deposition)

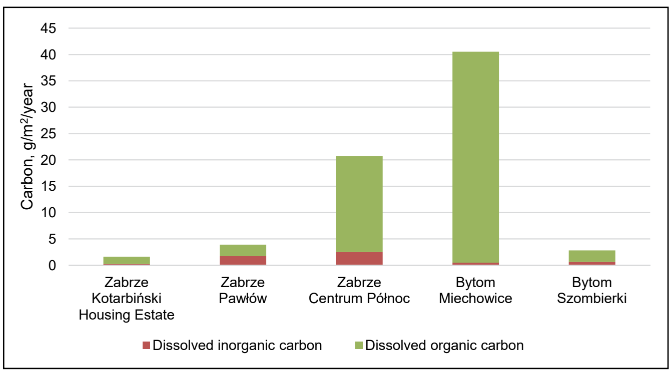

Fig. 5. Total carbon deposition over the entire study period (annual deposition)

sampling point Zabrze-Centrum Północ and amounted to 1048 mg/m^2/year.

In the case of metals and metalloids (Mn, Co, Ni, Cu, Zn, As, Cd, Pb, Cr, Fe) (Fig. 9) the differences are not so significant and range from 31.5 mg/m^2/year at the sampling point Zabrze-Pawłów to 196 mg/m^2/year at the point Zabrze-Centrum Północ, which is mainly due to intensive traffic in that point. The results of independent t-test showed no significant statistical difference in metal and metalloid deposition between sampling points (Table 2).

Minimum and maximum deposition of carbon, individual cations, anions and selected metals/metalloids for each sampling point has been summarized in Table 3.

The values of substances introduced during the year with precipitation at the point Zabrze-Kotarbiński Housing Estate decrease according to the series: SO_4^{2-} > NO_3^- > Ca^{2+} > Cl^- > NH_4^+ > Mg^{2+} > K^+ > Na^+ > PO_4^{3-} > NO_2^- > $HCOO^-$ > CH_3COO^- > F^- > Zn > Fe > Mn > Li+ > Pb > Cu > $C_2O_4^{2-}$ > Ni > Cd > As > Br^-. The values of substances introduced during the year with precipitation at the point Zabrze-Pawłów decrease according to the series: SO_4^{2-} > Ca^{2+} > Cl^- > Mg^{2+} > NO3$^-$ > K^+ > Na^+ > NH_4^+ > PO_4^{3-} > NO_2^- > F^- > Zn > $HCOO^-$ > Fe > CH_3COO^- > Mn > Li+ > Pb > Cu > $C_2O_4^{2-}$ > Br^- > Ni > As > Cd. The values of substances introduced during the year with precipitation at the point Zabrze-Centrum Północ decrease according to the series: K^+ > Ca^{2+} > SO_4^{2-} > Cl^- > Mg^{2+} > CH_3COO^- > PO_4^{3-} > Na^+ > NO_3^- > NH_4^+ > F^- > $HCOO^-$ > Fe > NO_2^- > $C_2O_4^{2-}$ > Zn > Mn > Pb > Cu > Li^+ > As > Ni > Cd > Br^-. The values of substances introduced during the year with precipitation at the point Bytom-Miechowice decrease according to the series: SO_4^{2-} > Na^+ > Cl^-> Ca^{2+} > K^+ > NO^{3-} > Mg^{2+} > NO_2^- > NH_4^+ > PO_4^{3-} > CH_3COO^- > $HCOO^-$ > $C_2O_4^{2-}$ > F^- > Zn > Fe > Mn > Pb

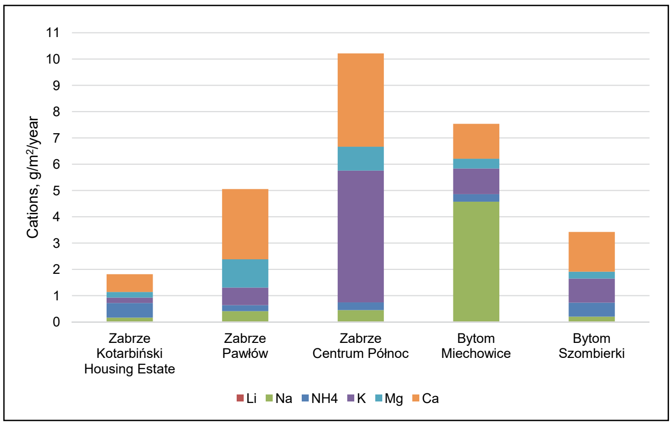

Fig. 6. Total cations deposition over the entire study period (annual deposition)

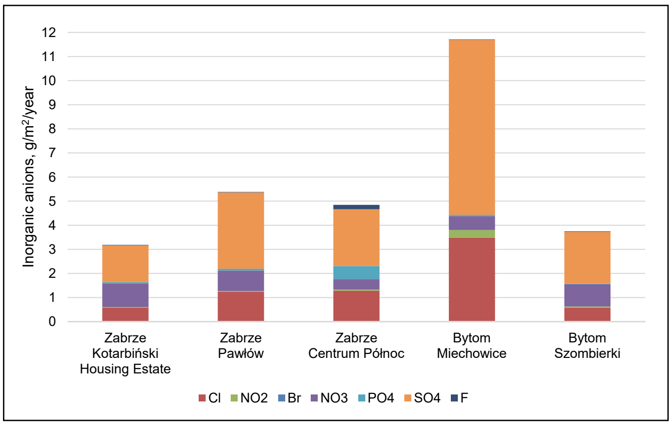

Fig. 7. Total deposition of inorganic anions during the whole measurement period (annual deposition)

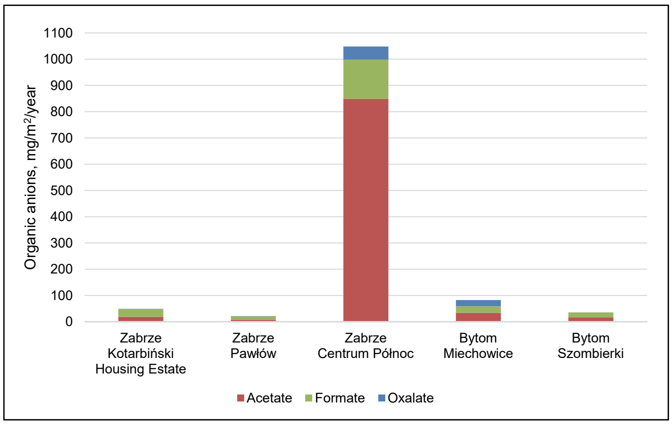

Fig. 8. Total organic anions deposition over the entire study period (annual deposition)

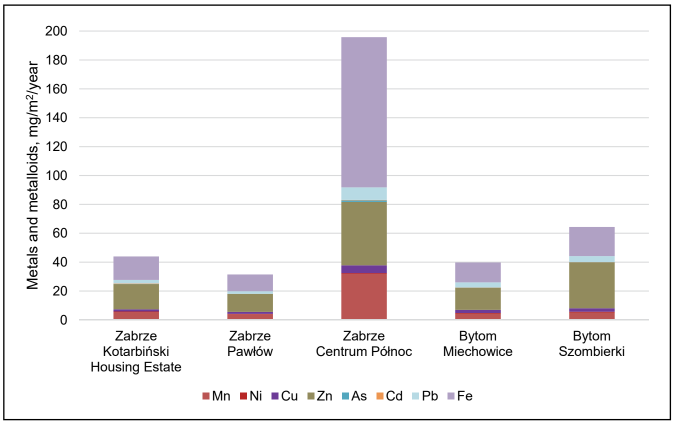

Fig. 9. Total deposition of metals and metalloids throughout the study period (annual deposition)

Table 2. The results of independent t-test

	Zabrze – Kotarbiński Housing Estate	Zabrze – Pawłów	Zabrze – Centrum Północ	Bytom – Miechowice
Zabrze – Pawłów	t = 0.498, p = 0.313			
Zabrze – Centrum Północ	t = -1.46, p = 0.083	t = -1.60, p = 0.066		
Bytom – Miechowice	t = 0.156, p = 0.439	t = -0.369, p = 0.359	t = 1.51, p = 0.076	
Bytom – Szombierki	t = -0.527, p = 0.303	t = -0.912, p = 0.188	t = 1.23, p = 0.120	t = -0.662, p = 0.259

Table 3. Minimum and maximum deposition of carbon, individual cations, anions and selected metals/metalloids for each sampling point

Parameter	Unit	Sampling point									
		Zabrze – Kotarbiński Housing Estate		Zabrze – Pawłów		Zabrze – Centrum Północ		Bytom – Miechowice		Bytom – Szombierki	
		Min (period)	Max (period)	Min (period)	Max (period)	Min (period)	Max (period)	Min (period)	Max (period)	Min (period)	Max (period)
COD	mg/m^2	173 (I)	1800 (VII)	163 (II)	3495 (IX)	334 (II)	34406 (XII)	165 (VI)	99123 (IX)	235 (I)	4213 (VII)
TC	mg/m^2	31.2 (IV)	348 (XI)	< LOD (XII)	1625 (XI)	92.1 (IV)	12132 (XII)	32.2 (IV)	29674 (IX)	47 (IV)	560 (X)
Li^+	mg/m^2	< LOD (VI, X)	0.874 (XII)	< LOD (VI, X)	0.688 (XII)	< LOD (VI, X)	0.928 (XII)	< LOD (VI, X)	0.630 (VIII)	< LOD (VI, X, XII)	0.863 (VIII)
Na^+	mg/m^2	< LOD (VIII)	43.3 (XI)	< LOD (VIII)	293 (XI)	6.62 (I)	76.5 (V)	7.95 (XII)	3116 (IX)	< LOD (VIII)	32.6 (II)
NH_4^+	mg/m^2	10.1 (II)	131 (XI)	< LOD (VIII, XI)	53 (VII)	< LOD (VII, XII)	107 (VIII)	< LOD (VII, XI)	93.4 (IX)	5.35 (II)	107 (VIII)
K^+	mg/m^2	1.77 (II)	85.5 (XI)	10.7 (II)	174 (I)	7.93 (IV)	2002 (XII)	4.72 (II)	324 (X)	4.04 (IV)	323 (X)
Mg^{2+}	mg/m^2	5.65 (III)	29.8 (XI)	1.15 (III)	961 (XI)	9.79 (III)	293 (XII)	4.23 (I)	109 (IX)	3.26 (III)	62 (X)
Ca^{2+}	mg/m^2	11.7 (III)	112 (VI)	12.1 (III)	2094 (XI)	77.5 (III)	1087 (XII)	18.3 (III)	492 (IX)	39.5 (II)	246 (VI)
F^-	mg/m^2	0.812 (XI)	3.80 (V)	0.746 (XII)	3.81 (XI)	1.31 (I)	141 (XII)	0.538 (I)	3.28 (IX)	0.651 (II)	3.12 (V)
Cl^-	mg/m^2	25.5 (I)	96.3 (XI)	18.9 (VI)	893 (XI)	46.5 (I)	279 (XII)	22.5 (XII)	1531 (IX)	24 (VII)	75.6 (III)
NO_2^-	mg/m^2	< LOD (I)	6.38 (XI)	< LOD (VIII, IX)	7.96 (VI)	< LOD (XII)	10.4 (V)	< LOD (VII)	244 (IX)	< LOD (XI)	8.20 (VIII)
Br^-	mg/m^2	< LOD (I, III–XI)	0.058 (II, XII)	< LOD (I, III–X, XII)	0.687 (XI)	< LOD (I, III–XII)	0.078 (II)	< LOD (I–V, VII–XII)	0.134 (VI)	< LOD (I–XII)	–
NO_3^-	mg/m^2	25.4 (II)	139 (VIII)	< LOD (VIII)	427 (XI)	< LOD (VII, X, XII)	92.2 (V)	< LOD (X)	122 (VIII)	13.3 (XI)	174 (VIII)
PO_4^{3-}	mg/m^2	< LOD (I, III, IV, VIII–X, XII)	38.2 (XI)	< LOD (V, VIII, X)	30.4 (VI)	< LOD (II–V, X)	216 (VIII)	< LOD (III–V, VII, VIII, XII)	19.9 (VI)	< LOD (I–V, VII–IX)	9.04 (X)
SO_4^{2-}	mg/m^2	69.9 (VII)	211 (V)	54.6 (IX)	2117 (XI)	107 (I)	363 (XI)	59.0 (I)	5556 (IX)	72.6 (I)	306 (III)
Acetate	mg/m^2	< LOD (VII, IX, X, XII)	5.39 (VII)	< LOD (I, VII–XII)	2.80 (V)	< LOD (I, VII, IX–XI)	822 (XII)	< LOD (I, III, V, X–XII)	14.7 (IX)	< LOD (I, III, V, IX–XII)	6.19 (VIII)
Formate	mg/m^2	< LOD (XI)	6.48 (IV)	< LOD (VIII, XI)	2.37 (III)	< LOD (VII, X)	137 (XII)	< LOD (I, X)	5.90 (IV)	< LOD (IX, X, XII)	4.26 (III)
Oxalate	mg/m^2	< LOD (I, III–XII)	1.26 (II)	< LOD (I, III–XII)	1.31 (II)	< LOD (I, III–XI)	49.8 (XII)	< LOD (I, III–V, VII–X, XII)	22.4 (XI)	< LOD (I, III–XII)	0.501 (II)
Mn	$\mu g/m^2$	94.4 (X)	2084 (II)	49.7 (II)	1003 (XI)	589 (II)	10806 (XII)	91.2 (VI)	838 (V)	141 (IX)	722 (XII)
Ni	$\mu g/m^2$	11.2 (IX)	279 (II)	11.6 (II)	95 (XI)	21.5 (II)	100 (XII)	12.9 (VII)	70.1 (IX)	21.5 (II)	92.3 (III)
Cu	$\mu g/m^2$	61.3 (X)	255 (XI)	36.5 (II)	255 (XI)	174 (II)	1081 (VII)	77.2 (VI)	363 (IX)	65.4 (I)	444 (IX)
Zn	$\mu g/m^2$	1002 (VII)	2554 (VIII)	559 (II)	2926 (XI)	1639 (XI)	8822 (VII)	139 (VI)	2207 (IX)	1338 (XII)	6401 (X)
As	$\mu g/m^2$	< LOD (VII–X, XII)	69.8 (V)	< LOD (VIII, X, XII)	26.7 (XI)	49.5 (II)	222 (VII)	< LOD (V, VII, VIII, X, XII)	27.1 (IX)	< LOD (VII–X, XII)	33.6 (VI)
Cd	$\mu g/m^2$	< LOD (IX, XI)	159 (V)	< LOD (IV, V, VIII, X–XII)	24.1 (III)	8.93 (III)	48.5 (I)	< LOD (IV)	43.0 (VIII)	< LOD (V, IX, X, XII)	47.5 (VIII)
Pb	$\mu g/m^2$	41.4 (X)	772 (V)	21.2 (II)	215 (I)	181 (XI)	1600 (V)	47.6 (VI)	578 (IX)	118 (IX)	659 (IV)
Fe	$\mu g/m^2$	< LOD (XII)	3536 (V)	< LOD (VIII)	2546 (V)	< LOD (VIII, XII)	42427 (VII)	< LOD (VIII, XII)	3174 (X)	< LOD (VIII, IX, XII)	4035 (III)

> Li^+ > Cu > Ni > Cd > Br^- > As. The values of the substances introduced during the year with precipitation in the point Bytom-Szombierki decrease according to the series: SO_4^{2-} > Ca^{2+} > NO_3^- > K^+ > Cl^- > NH_4^+ > Mg^{2+} > Na^+ > NO_2^- > Zn > PO_4^{3-} > F^- > Fe > $HCOO^-$ > CH_3COO^- > Mn > Pb > Li^+ > Cu > $C_2O_4^{2-}$ > Ni > As > Cd > Br^-.

Inter-Elemental Relationships

According to the results of the Shapiro-Wilk test, most of the data did not have a normal distribution (more than 50% of the data). The results are shown in Table 4.

Data with normal distribution are marked in bold. The Spearman's rank correlation coefficient was used to determine the strength of the relationship between the two variables because over 50% of the data did not have a normal distribution and the sample sizes were relatively small. The strength of the correlation was assessed by using the following guide for the value of R_s: 0.00 to 0.19 – a very weak correlation; 0.20 to 0.39 – a weak correlation; 0.40 to 0.69 – a moderate correlation; 0.70 to 0.89 – a strong correlation; 0.90 to 1.00 – a very strong correlation (Fowler et al. 2013). The results have been summarized in Tables 5–6. The Spearman's rhos ≥ 0.70 (a strong and very strong correlation) were marked in bold.

The correlations between selected ions in bulk deposition for each sampling point have been examined. At Zabrze-K-otarbiński Housing Estate sampling site, a strong or very strong correlation appears for the ion pairs: Na^+–Cl^- (positive), NH_4–SO_4^{2-} (positive), K^+–Mg^{2+} (positive), Mg^{2+}–Ca^{2+} (positive). At Zabrze-Pawłów sampling site, a strong or very strong correlation appears for the only one ion pair: Na^+–Cl^- (positive). At Zabrze-Centrum Północ sampling site, a strong or very strong correlation appears for the ion pairs: Na^+–Cl^- (positive), Na^+–NO_3^- (positive), K^+–Mg^{2+} (positive), K^+–NO_3^- (negative), Mg^{2+}–Ca^{2+} (positive), Cl^-–SO_4^{2-} (positive). At Bytom-Miechowice sampling site, a strong or very strong correlation appears for the ion pairs: Na^+–Mg^{2+} (positive), Na^+–Cl^- (positive), NH_4^+–NO_3^- (positive), K^+–NO_3^- (negative), Mg^{2+}–Ca^{2+} (positive), Mg^{2+}–Cl^- (positive), Mg^{2+}–SO_4^{2-} (positive), Ca^{2+}–Cl^- (positive), Ca^{2+}–SO_4^{2-} (positive). At Bytom-Szombierki sampling site, a strong or very strong correlation appears for the ion pairs: NH_4^+–NO_3^- (positive), Mg^{2+}–Ca^{2+} (positive), NO_3^-–SO_4^{2-} (positive). The strong and very strong correlation between the selected ions indicates that these ions are mainly from the same source and their temporal variation is similar.

Correlations between selected metals/metalloids in bulk deposition for each sampling point were also investigated. At Zabrze-Kotarbiński Housing Estate sampling site, a strong or very strong positive correlation appears for the metal/metalloid pairs: Ni–Cu, Ni–Pb, and Cu–As. At Zabrze-Pawłów sampling site, a strong or very strong positive correlation appears for the metal/metalloid pairs: Mn–Ni and Ni–Cu. At Zabrze-Centrum Północ sampling site, a strong or very strong positive correlation appears for the ion pairs: Mn–Ni, Ni–Cu, Ni–Zn, Ni–As, Cu–Zn, Cu–As, Zn–As, Zn–Cd, Zn–Pb, As–Cd, As–Pb. A strong or very strong positive correlation was not observed between metals/metalloids at Bytom-Miechowice sampling site. At Bytom-Szombierki sampling site, a strong positive correlation appears for the only one metal pair: Mn-Pb. A strong or very strong positive correlation between metals/metalloids suggests that they come from similar sources.

Conclusions

Monitoring of precipitation chemistry and assessment of pollution deposition to the ground is currently the most complete source of knowledge on the condition of

Table 4. Shapiro-Wilk test results ($W_{critical}$ = 0.861)

Parameter	Zabrze – Kotarbiński Housing Estate		Zabrze – Pawłów		Zabrze – Centrum Północ		Bytom – Miechowice		Bytom – Szombierki	
	$W_{calculated}$	p	$W_{calculated}$	p	$W_{calculated}$	p	$W_{calculated}$	p	$W_{calculated}$	p
Na^+	0.848	< 0.05	0.358	< 0.05	**0.934**	**0.425**	0.449	< 0.05	**0.935**	**0.440**
NH_4^+	0.780	< 0.05	**0.915**	**0.251**	0.768	< 0.05	0.803	< 0.05	**0.882**	**0.092**
K^+	0.631	< 0.05	0.780	< 0.05	0.735	< 0.05	0.774	< 0.05	0.723	< 0.05
Mg^{2+}	**0.938**	**0.470**	0.313	< 0.05	0.760	< 0.05	0.784	< 0.05	0.820	< 0.05
Ca^{2+}	**0.956**	**0.727**	0.327	< 0.05	0.713	< 0.05	0.615	< 0.05	**0.922**	**0.307**
Cl^-	**0.878**	**0.082**	0.325	< 0.05	0.825	< 0.05	0.485	< 0.05	**0.970**	**0.909**
NO_3^-	**0.965**	**0.857**	0.499	< 0.05	0.858	< 0.05	**0.938**	**0.470**	**0.937**	**0.458**
SO_4^{2-}	**0.963**	**0.826**	0.337	< 0.05	**0.928**	**0.359**	0.349	< 0.05	**0.952**	**0.667**
Mn	0.491	< 0.05	0.807	< 0.05	0.663	< 0.05	0.805	< 0.05	**0.928**	**0.356**
Ni	0.493	< 0.05	0.570	< 0.05	0.858	< 0.05	**0.878**	**0.083**	0.726	< 0.05
Cu	**0.881**	**0.091**	**0.918**	**0.266**	0.854	< 0.05	**0.925**	**0.334**	**0.902**	**0.170**
Zn	0.806	< 0.05	0.682	< 0.05	0.817	< 0.05	**0.985**	**0.997**	0.800	< 0.05
As	0.781	< 0.05	**0.885**	**0.101**	0.849	< 0.05	0.851	< 0.05	0.838	< 0.05
Cd	0.546	< 0.05	0.723	< 0.05	**0.890**	**0.117**	**0.938**	**0.472**	0.843	< 0.05
Pb	0.669	< 0.05	**0.913**	**0.231**	**0.907**	**0.196**	**0.969**	**0.904**	**0.913**	**0.237**
Fe	**0.927**	**0.352**	**0.930**	**0.376**	0.677	< 0.05	**0.930**	**0.378**	**0.880**	**0.088**

Table 5. Spearman's rhos for major ions in bulk deposition collected at sites in Zabrze and Bytom

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Zabrze – Kotarbiński Housing Estate								
Na^+	1.000							
NH_4^+	0.454	1.000						
K^+	0.140	0.413	1.000					
Mg^{2+}	0.196	0.399	**0.706**	1.000				
Ca^{2+}	0.413	0.252	0.650	**0.769**	1.000			
Cl^-	**0.713**	0.643	0.245	0.517	0.441	1.000		
NO_3^-	0.126	0.594	0.287	0.461	0.489	0.482	1.000	
SO_4^{2-}	0.385	**0.720**	0.294	0.580	0.427	0.622	0.629	1.000
Zabrze – Pawłów								
Na^+	1.000							
NH_4^+	0.059	1.000						
K^+	-0.203	-0.147	1.000					
Mg^{2+}	0.531	0.140	0.196	1.000				
Ca^{2+}	0.461	-0.256	0.203	0.580	1.000			
Cl^-	**0.811**	-0.249	-0.203	0.385	0.552	1.000		
NO_3^-	0.657	0.130	-0.014	0.545	0.175	0.489	1.000	
SO_4^{2-}	0.098	-0.308	-0.196	0.448	0.259	0.230	0.448	1.000
Zabrze – Centrum Północ								
Na^+	1.000							
NH_4^+	0.322	1.000						
K^+	-0.496	-0.413	1.000					
Mg^{2+}	-0.182	-0.382	**0.881**	1.000				
Ca^{2+}	0.231	-0.350	0.643	**0.853**	1.000			
Cl^-	**0.776**	0.168	0.000	0.273	0.552	1.000		
NO_3^-	**0.768**	0.677	**-0.725**	-0.451	-0.211	0.401	1.000	
SO_4^{2-}	0.622	0.242	0.259	0.496	0.678	**0.902**	0.289	1.000
Bytom – Miechowice								
Na^+	1.000							
NH_4^+	-0.259	1.000						
K^+	0.615	-0.417	1.000					
Mg^{2+}	**0.776**	-0.242	0.636	1.000				
Ca^{2+}	0.608	-0.130	0.559	**0.958**	1.000			
Cl^-	**0.895**	-0.165	0.671	**0.839**	**0.720**	1.000		
NO_3^-	-0.378	**0.788**	**-0.720**	-0.454	-0.350	-0.322	1.000	
SO_4^{2-}	0.657	0.049	0.441	**0.797**	**0.783**	0.664	-0.105	1.000
Bytom – Szombierki								
Na^+	1.000							
NH_4^+	-0.154	1.000						
K^+	-0.028	-0.678	1.000					
Mg^{2+}	0.266	-0.385	0.664	1.000				
Ca^{2+}	-0.126	-0.007	0.531	**0.741**	1.000			
Cl^-	0.357	0.259	-0.336	-0.049	0.063	1.000		
NO_3^-	-0.091	**0.846**	-0.594	-0.175	0.175	0.475	1.000	
SO_4^{2-}	-0.175	0.622	-0.189	0.105	0.545	0.524	**0.734**	1.000

Table 6. Spearman's rhos for selected metals and metalloids in bulk deposition collected at sites in Zabrze and Bytom

	Mn	Ni	Cu	Zn	As	Cd	Pb	Fe
Zabrze – Kotarbiński Housing Estate								
Mn	1.000							
Ni	0.084	1.000						
Cu	0.028	**0.783**	1.000					
Zn	0.329	0.343	0.245	1.000				
As	0.275	0.522	**0.761**	0.246	1.000			
Cd	0.305	0.378	0.140	0.476	0.120	1.000		
Pb	0.322	**0.741**	0.510	0.371	0.486	0.256	1.000	
Fe	0.361	0.291	0.357	-0.031	0.421	0.296	0.483	1.000
Zabrze – Pawłów								
Mn	1.000							
Ni	**0.727**	1.000						
Cu	0.510	**0.783**	1.000					
Zn	0.664	0.657	0.552	1.000				
As	0.380	0.225	0.253	0.113	1.000			
Cd	-0.034	-0.146	-0.101	-0.104	0.387	1.000		
Pb	0.042	-0.224	-0.315	-0.077	0.324	0.452	1.000	
Fe	-0.017	0.119	0.312	0.024	0.494	0.209	0.235	1.000
Zabrze – Centrum Północ								
Mn	1.000							
Ni	**0.720**	1.000						
Cu	0.657	**0.888**	1.000					
Zn	0.531	**0.706**	**0.748**	1.000				
As	0.629	**0.811**	**0.762**	**0.895**	1.000			
Cd	0.294	0.434	0.510	**0.706**	**0.762**	1.000		
Pb	0.245	0.629	0.552	**0.783**	**0.818**	0.629	1.000	
Fe	-0.021	0.284	0.319	0.392	0.311	0.042	0.473	1.000
Bytom – Miechowice								
Mn	1.000							
Ni	0.371	1.000						
Cu	0.406	0.434	1.000					
Zn	0.238	0.308	0.343	1.000				
As	-0.210	0.058	0.319	0.087	1.000			
Cd	0.538	0.161	0.098	0.189	-0.674	1.000		
Pb	0.531	0.552	0.573	0.608	0.246	0.119	1.000	
Fe	0.588	0.574	0.105	0.172	0.036	-0.004	0.469	1.000
Bytom – Szombierki								
Mn	1.000							
Ni	0.552	1.000						
Cu	0.329	0.364	1.000					
Zn	-0.385	-0.042	0.063	1.000				
As	0.246	0.217	0.109	-0.290	1.000			
Cd	0.032	-0.335	-0.370	0.103	0.155	1.000		
Pb	**0.713**	0.489	0.147	-0.098	0.522	0.196	1.000	
Fe	0.408	0.296	0.218	0.239	0.599	0.064	0.634	1.000

precipitation water quality and spatial distribution of wet pollutant deposition. The presented results of monitoring studies show that the pollutants transported in the atmosphere and introduced with wet precipitation in Zabrze and Bytom constitute a significant source of area pollution affecting the environment of this area. Among the analyzed substances, acidogenic sulphur and nitrogen compounds, biogenic compounds, carboxylic acids and metals have a particularly negative impact on the environmental condition. Precipitation with decreased pH ("acid rain") poses a significant threat to the environment causing negative changes in the structure and functioning of terrestrial and aquatic ecosystems as well as technical infrastructure. In turn, biogenic compounds affect the changes in trophic conditions of soils and waters. Heavy metals pose a threat to plant production and water catchments. Many examples of similar studies have been described in the scientific literature, taking into account both the analytical scope and characteristics of the study area. Examples include different countries and regions, such as France (suburbs of Paris) (Azimi et al. 2003), USA (Colorado) (Wetherbee et al. 2019), Australia (6 measurement points in Queensland) (Huston et al. 2009), or India (cities: New Delhi, Ahmedabad, Bengaluru, Hyderabad, and Chennai) (Sanjeeva and Puttaswamaiah 2018). Comparing these results with data from several measurement points in Poland (Polkowska et al. 2005), including areas of Upper Silesia (Pęczkowski et al. 2020, Kosior et al. 2018, IMGW-PIB 2018), has shown that for the vast majority of studied components is lower, and the total annual surface load of the area with the load of studied substances deposited from the atmosphere by wet precipitation was reduced by about 6%.

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