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INSIGHTS INTO THE CHEMICAL CHARACTERISTICS OF MELTED SNOW FROM URBAN-INDUSTRIAL SITES: CASE STUDY OF STARACHOWICE (POLAND)

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Abstract. This study analyses the chemical composition of snow cover in Starachowice, an industrial city in south-eastern Poland, to assess the extent and sources of atmospheric pollution. The research confirms the accumulation, in snow, of particulate pollutants that act as carriers of heavy metals. The analysis confirmed increased pH of water from the melted snow samples (pH 6.99) and significantly increased concentrations of Fe (110.96 μg/dm^3), Al (85.02 μg/dm^3), Zn (43.68 μg/dm^3) and Mn (10.92 μg/dm^3) in relation to the properties of snow precipitation observed in the Świętokrzyski National Park. The spatial variability of the analysed metals was demonstrated. The lowest values were found in the central part of the study area, in the immediate vicinity of a metal production plant, while the highest values were recorded near the metal processing plant in the southern part of the study area. The presence of particles of various shapes and chemical composition was confirmed using Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS) analyses of the glass filter used for filtering meltwater. The image showed the presence of larger sharp-edged particles and smaller spherical particles (spherules) with a significant share of Al, Mg and Fe. The study highlights the role of industrial activity in atmospheric contamination and emphasises the need for stringent air quality monitoring and control.

Key words: air pollution, SEM/EDS, ICP-MS/TOF, snow cover

Introduction

Air quality is poor in many regions of Poland, particularly in the heating season, and this directly impacts human health (Ratajczak *et al.* 2021; Adamkiewicz *et al.* 2022). This situation results from local sources of emissions, but also from the long-distance transport of pollutants (Nazar, Niedoszytko 2022). In an urban residential zone, low emissions and functioning industrial plants may create an additional load (Majewski *et al.* 2023; Gałka 2024). The combustion of fossil fuels, including coal, constitutes a potential threat of smog in the city. Metallurgical industry plants pose a serious threat to health, especially if particulate matter emitted during the technological process is inhaled (Lan *et al.* 2024; Machado *et al.* 2024). In urban areas covered by this type of activity, there is a potential risk of excessive pollution levels. Therefore, the use of an effective atmospheric air quality monitoring and control system should be a priority action with regard to protecting human health and the well-being of the natural environment. In this regard, analyses of the chemical composition of snow enrich the information about the state of atmospheric air quality in a given area. Pollutants deposited in the snow cover can be analysed to determine their source of origin and to predict potential health and environmental consequences, while constituting a relatively cheap and effective source of data for examining the atmosphere (Kampa, Castanas 2008; Francová *et al.* 2017). Urban-industrial zones, such as Starachowice, experience compounded effects from industrial facilities and

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residential heating. Heavy metals emitted from industrial processes pose significant risks to human health and the environment (Jadaa, Mohammed 2023; Edo *et al.* 2024). Snow cover serves as a useful medium for evaluating atmospheric deposition of pollutants, offering insights into their sources and potential impact. The objectives of the research carried out are (1) to determine the amount of atmospheric pollution deposition in the city of Starachowice, (2) to determine the source of their origin, and (3) to determine the spatial variability of selected metal concentration levels. For this purpose, a chemical analysis of melted snow was performed against the background of meteorological conditions. The studies used the chemical analysis of snow cover during the December retention of snow cover in the winter of 2023/24.

Materials and methods

Research area

The research area is located in the city of Starachowice (21°04′E, 51°04′N), in Świętokrzyskie Voivodeship in south-eastern Poland. The city has 43,883 inhabitants, according to data for the year 2023 (GUS 2024) (Fig. 1). According to the physical geographical division of the country, the city of Starachowice is in the Kielecka Upland macroregion and in two mesoregions, whose boundaries are demarcated by the Kamienna River flowing through the city and constituting the hydrographic axis (Solon *et al.* 2018). The highest point in the area is about 270 m a.s.l., and the lowest point is located at about 213 m a.s.l., with height differences of up to 50 m. The city is surrounded by the Iłżeckie Forests complex to the north and the Sieradowickie Forests complex to the south and west. Forest occupies 21.8% of the total area of the city. In the city, there are also three retention and recreational reservoirs – – "Pasternik", "Lubianka" and "Piachy" – fed by the Kamienna River and its tributaries. The total area of the city is 31.85 km^2, of which 40% is occupied by buildings and urbanised areas, 28% by agricultural land, 24.5% by forest land, 3.8% by land under water, and 3.7% by wasteland and others (Fig. 1).

Starachowice is a historical centre of ferrous metallurgy in Poland whose traditions date back to the Iron Age. Currently, the city hosts several larger industrial plants in the "Starachowice" Special Economic Zone, which was established in 1997 and covers an area of 168 ha. In the centre of the city is the Odlewnie Polskie S.A. industrial plant, which is a source of emissions of pollutants into the atmosphere. Plants, warehouses and wholesale stores of metal products are also located in the south of the city.

Research methods

In order to assess the human impact caused by the activity of metal industry plants, snow samples were collected on the day of the longest snow cover presence and immediately preceding the thaw, i.e. December 7, 2023. For sampling, a glass cylinder with a diameter of 50 mm was used. Each time, four samples were taken from each location (averaged sample). The whole profile of the snow cover layer was placed in a plastic receptacle with a capacity of 3 dm^3. The samples transported to the laboratory were melted in a thermostatic cabinet at a set temperature of +4°C.

The pH value and specific electrical conductivity (EC) were measured in meltwater using a multi-parameter HACH HQ2200 device (Loveland, USA) equipped with the PHC101 and CDC401 electrodes. Test results were controlled using Hamilton standard solutions (Bonaduz, Switzerland) with pH values 4.01 (Ref. No: 238917), 7.00 (Ref. No: 238218) and 9.21 (Ref. No: 238919) and certified reference material 15 µS/cm, CPAChem (Ref. No: CS15MOS.L5) 30% n-propanol (Stara Zagora, Bulgaria) and calibration standard 1,000 µS/cm, YSI 3167 (Yellow Springs, USA) potassium chloride 0.053% (Ref. No: CAS 7447407).

After being taken in the field, the samples were transported in sterile PTFE receptacles with a capacity of 1,000 ml to the Laboratory of Environmental Research of the Institute of Geography and Environmental Sciences of the Jan Kochanowski University in Kielce. The chemical composition (Pb, Cd, Cr, Co, Cu, Mn, Ni, Zn, Al, Fe) was determined using an ICP-MS/TOF OptiMass 9500 mass spectrometer (GBC, Melbourne, Australia). The test results were verified based on certified reference materials CLMS-2AN (Spex Claritas PPT® Grade ICP-MS Multi-Element Solution 2A without Mercury, 10 µg/mL (10 ppm) in 5% HNO_3, 125 mL, NJ, USA). For the analysis of snow pollutants, the GF/D Whatman quartz ø25 mm filters were used, after filtration of ~100 ml of meltwater from the snow sample. From each filter, a ø1-cm section for analysis was cut out and stuck to ø12.5-mm aluminium tables using carbon discs. The tables with the samples were placed in the Leica EM SC050 and then sputtered

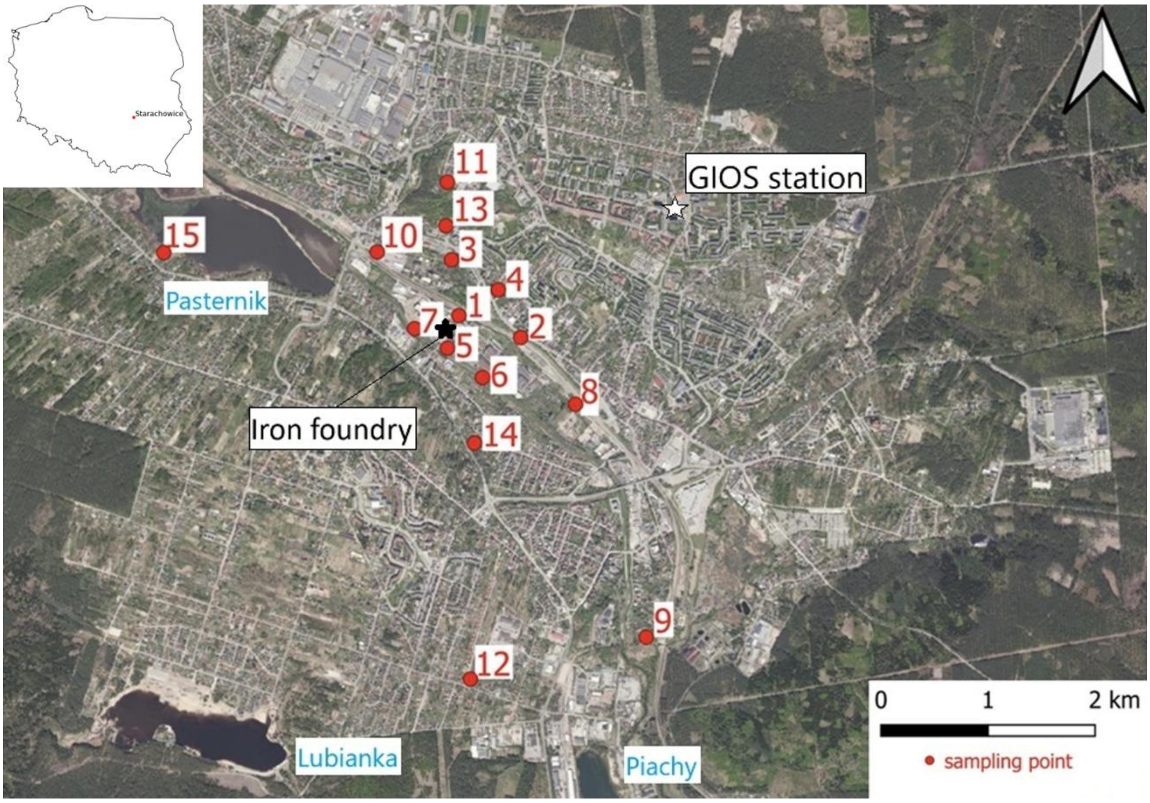


Fig. 1. Location of the area iron foundry (marked with a black star), measurement station of the Chief Inspectorate of Environmental Protection (marked with white star) and the Pasternik, Lubianka and Piachy recreational reservoirs in Starachowice (based on GEOPORTAL2 GEOBID)

with 24 carat gold in an argon atmosphere with layer thickness control (10 nm of Au) with a quartz crystal microbalance. Once the sputtering was completed, the samples were placed in an FEI Quanta 250 scanning electron microscope (SEM) and then subjected to EDS (Energy Dispersive Spectroscopy) chemical analysis using the EDAX Genesis X-ray wavelength spectrometer.

The air quality assessment was made based on measurement data from the automatic measuring station of the Chief Inspectorate of Environmental Protection (GIOS 2024) in Starachowice (Φ51.050611, λ 21.084175). Meteorological data regarding the conditions of snow cover formation are derived from the precipitation station of the Institute of Meteorology and Water Management (IMGW–PIB) in Starachowice. The direction of influx of air masses into the study area during snow cover formation was investigated using the American NOAA (Hysplit model 2024) (Air Resources Laboratory, NOAA's Office of Atmospheric Research, National Oceanic and Atmospheric Administration). An additional (control) snow sample was taken in the Świętokrzyski National Park. Statistical processing of the data was performed using TIBCO Statistica version 13.3. The spatial analysis of the concentrations of the analysed physicochemical and chemical properties was conducted using Surfer software version 26 (Golden Software, USA).

Results

Meteorological background

From 1 to 17 November 2023, Poland was under the influence of western circulation. There was warm polar and marine air, periodically tropical, resulting in temperatures above 10°C being recorded during this period. It was only towards the end of this period that there was a clear cooling, and snowfall appeared. At the end of November, many regions of Poland experienced winter weather phenomena, such as snowfall, ground frost and continuous sub-zero temperatures. At the beginning of December 2023, Poland was under the influence of lows from over southern and central Europe. Cloudiness was high and snowfall was observed, which had moderate and strong intensity at times. During this period, there was the lowest minimum temperature of

December recorded at synoptic stations, at -16.7°C. From December 16, 2023, a high pressure from western and central Europe extended over Poland, and fairly warm polar air arrived. The snow cover was present virtually throughout the country until December 9, then gradually faded, lasting the longest in eastern Poland. Towards the end of the month, temporary snow cover appeared in some parts of the country. In the first days of January, Poland was in the range of low-pressure systems moving from west to east. Cloudiness was high, rain and sleet occurred, and snowfall was reported in the north-east and mountainous areas. From 6 to 10 January, Poland was affected by high pressure from northern Europe, bringing Arctic air. Between 11 and 15 January, Poland was influenced by a low-pressure system centered over northern Europe. As a result, cold Arctic air masses were advected from the north. Occasionally, following the passage of warm fronts, these were temporarily replaced by milder polar maritime air. From 16 to 21 January, southern Poland came under the influence of a high-pressure system, while northern Poland remained affected by low-pressure systems moving in from Scandinavia. During this period, cold Arctic air was initially dominant, but was later replaced by warmer polar maritime air. After 21 January 2023, deep low-pressure systems developed over northern Europe, bringing continued advection of polar maritime air into Poland. Following 27 January, high-pressure systems over southern Europe became dominant. This shift in circulation led to the arrival of warm polar maritime air. Towards the end of the month, however, slightly cooler air masses moved in again.

In the selected three-month period, the inflows of air mass from the east were accompanied by drops in temperatures and an increase in snow cover. (IMGW 2024). The first snowfall in the 2023/24 winter season was recorded in Starachowice on 25 November and as a 2-cm layer that remained for two days (Fig. 2). The snowfall was accompanied by an influx of air masses from the north (Fig. 3a). Snow fell again on 29 November, and the dense snow cover remained until 11 December (13 days) (Fig. 3b). The average thickness of the cover was 11.4 cm (average air temperature -5.9°C), and the maximum thickness of the layer (20 cm) was recorded on 3 and 4 December 2023, following a 15 cm increase in freshly fallen snow (3 December 2023) (Fig. 3c). Moisture-rich air masses came from the western sector. On the day of sampling, the wind changed direction from south-easterly. In the following days it brought warmer masses from the south, which contributed to the snow cover disappearing (Fig. 3d).

A short snow episode (two days) took place on 23–24 December. The last one in the season took place in January 2024. The snow cover increase was accompanied by an influx of air masses from the east with continental features associated with the Eastern European high. Such circulation lasted from 7 to 9 January (average air temperature -6.9°C). The average thickness of the cover was 10.3 cm, and the largest increase (15 cm) was recorded on 14 January 2024. At the end of this period, the wind direction changed to westerly, significantly limiting the conditions for the snow to remain. As the wind turned southerly, the snow disappeared completely.

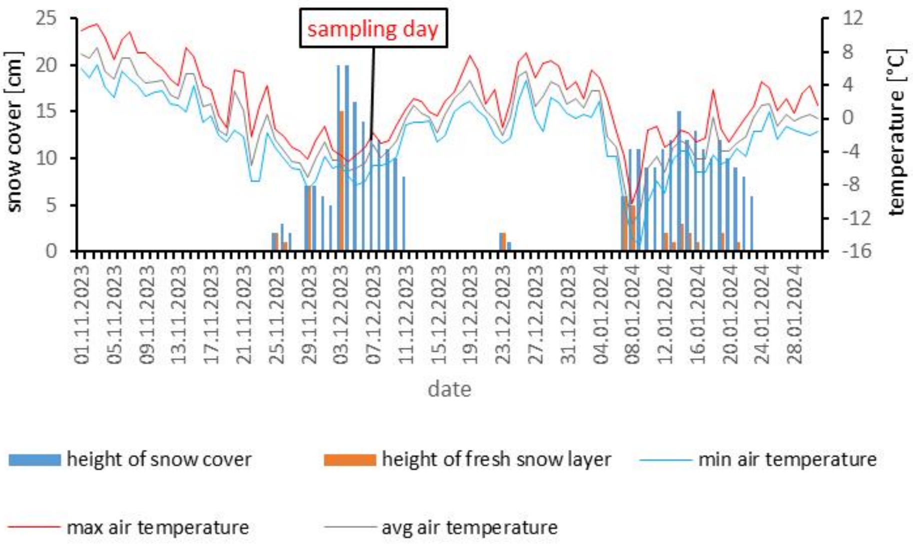


Fig. 2. Snow cover thickness and increase in November 2023 to January 2024 (IMGW Starachowice)

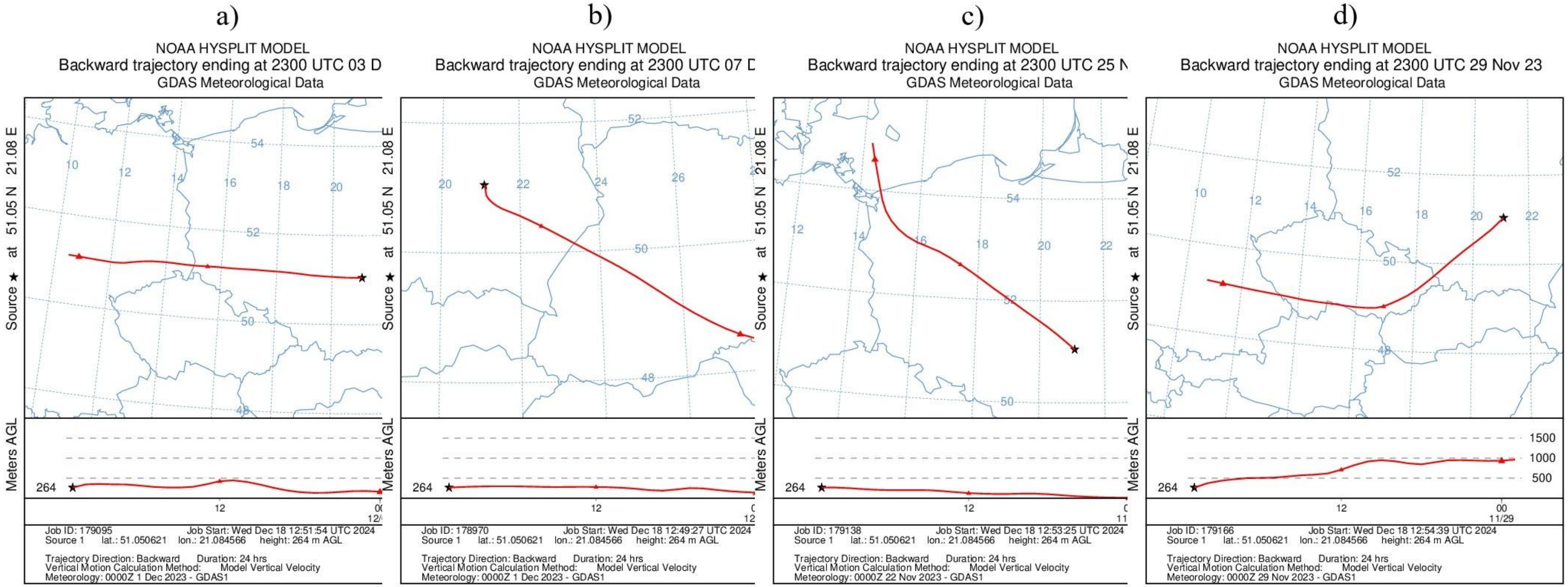


Fig. 3. Backward trajectories of air masses (NOAA Hysplit 2024)

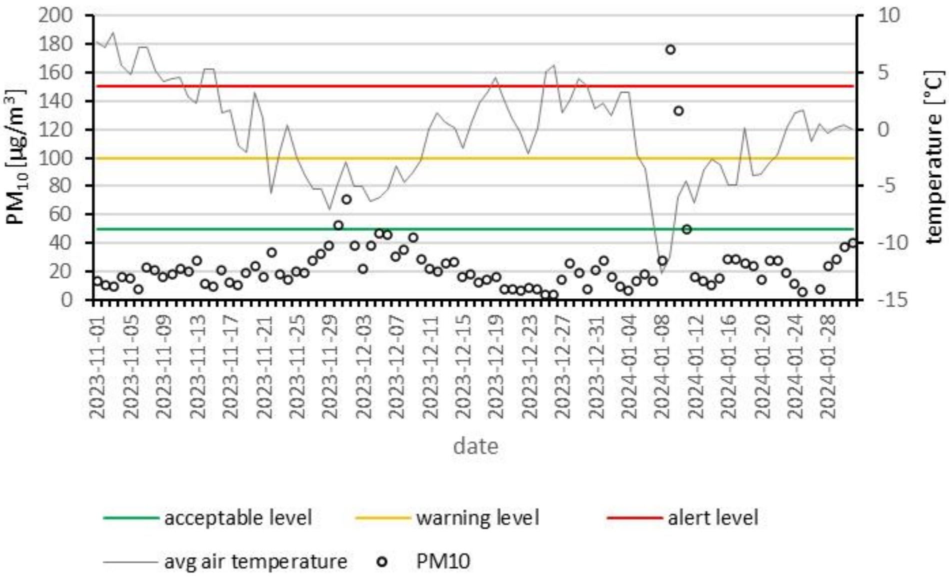


Fig. 4. Concentration of PM_{10}, November 2023 to January 2024 (based on GIOS in Starachowice)

The average daily concentration of PM_{10} in December 2023 was 22.8 µg/m^3. The acceptable level for the average daily concentration (50 µg/m^3) was exceeded once (on 1 December – – 70.7 µg/m^3). The average daily information level (100 µg/m^3) and the alert level (150 µg/m^3) were not exceeded, although such situations occurred in the following month. The temperature falls were accompanied by an increased concentration of PM_{10} (Fig. 4).

Physicochemical analysis

The results of the tests of physico-chemical and chemical properties are presented in Table 1. Based on the tests carried out, the weighted average pH value of melted snow was found to be 6.88 (with a variable within the range from pH 6.71 to pH 7.23). All samples were within the first range – increased pH value of the European classification of precipitation according to Jansen *et al.* (1988). Specific electrical conductivity varied within the range from 14.16 µS/cm to 50.70 µS/cm with an average of 23.73 µS/cm. The average concentrations of the elements selected for the analysis formed the following decreasing sequence Fe>Al>Zn>Mn>Pb>Co>Cu>Cd>Cr>Ni). The highest concentrations (e.g., lead, chromium, iron and aluminium) were recorded at points 9 and 12, located ~3 km south-east of the foundry. Similarly, the highest concentrations of zinc (70.35 µg/dm^3) were found 1.5 km from the plant (point no. 8).

The cluster analysis conducted (Ward's method, Manhattan distance) revealed the existence of several areas differing in recorded concentration levels (Fig. 5). In the central part of the study area, in the immediate vicinity of the metal production plant, the lowest metal concentrations in melted snow samples were recorded. These were points 1, 4, 6, 7 and 14 – subgroup A, where the average concentration was below 13 µg/dm^3. In contrast, subgroup B included points where the average concentration was nearly twice as high (with an average exceeding 22 µg/dm^3; points 2, 3, 5, 8–13 and 15). These points were located at more than 1 km from the metal production plant. The highest average concentrations were recorded at points 11 and 9. In the case of point 9, the direct proximity to the metal processing plant, a significant source of metal emissions into the environment, played a crucial role. The highest concentrations were observed here and were more than ten times higher than subgroup A and 5 times higher than subgroup B. The observed differences indicate that, in the central part of the study area, the presence of a chimney and the energy of flue gas ejection cause pollutants to be transported over a certain distance (beyond 1 km). In the case of the metal processing plant (around point 9), diffuse emissions from production halls lead to contamination of the immediate surroundings (Fig. 6).

Table 1

Chemical composition of snow cover in Starachowice

Sample No.	H	pH	EC	Pb	Cd	Cr	Co	Cu	Mn	Ni	Zn	Al	Fe
	[cm]	[-]	[μS/cm]	[μg/dm^3]									
reference sample (ŚNP)	19.0	6.63	15.85	4.80	3.90	3.75	4.74	2.43	11.08	0.00	24.69	17.69	12.65
1	15.0	6.90	14.16	4.84	6.84	4.10	4.87	4.96	9.60	0.00	57.13	17.61	50.55
2	14.5	7.16	18.77	5.06	3.98	3.98	4.80	4.61	10.02	1.41	32.59	40.64	80.46
3	15.5	6.90	16.07	4.96	5.28	3.74	4.89	4.96	9.89	0.00	70.31	15.14	100.24
4	14.0	7.23	21.98	4.88	3.56	3.16	4.92	4.92	8.53	0.00	48.75	19.60	27.19
5	13.0	7.18	33.20	5.11	4.65	4.02	4.89	5.55	10.69	0.00	40.16	64.55	142.30
6	15.5	6.72	14.36	4.76	3.70	3.45	4.83	5.03	8.69	0.00	30.24	7.80	45.30
7	17.5	6.71	14.50	4.80	4.33	4.44	4.84	4.15	7.99	0.44	40.85	14.74	46.61
8	14.0	6.84	26.80	5.01	4.44	3.65	4.80	6.36	9.50	1.05	70.35	31.07	123.36
9	16.0	7.06	27.40	5.18	4.51	4.58	4.83	4.90	8.78	0.00	34.72	832.80	394.22
10	16.0	7.17	41.40	4.78	3.53	3.74	4.82	3.11	7.07	0.00	32.37	36.73	110.73
11	12.5	6.87	20.42	4.91	3.50	4.17	4.77	4.20	5.55	2.10	29.25	90.05	207.49
12	21.0	7.02	15.79	5.28	3.63	4.54	4.73	5.66	14.46	0.30	56.61	27.73	119.19
13	13.5	6.84	16.94	5.06	3.79	3.92	4.84	3.92	9.90	0.00	44.09	11.71	91.30
14	16.0	7.19	23.40	4.85	3.14	3.22	4.86	3.25	8.85	0.00	33.69	23.50	12.18
15	11.0	7.12	50.70	5.08	4.17	3.94	4.77	5.61	34.30	0.00	34.17	41.67	113.23
min	11.0	6.71	14.16	4.76	3.14	3.16	4.73	2.43	5.55	0.00	24.69	7.80	12.18
max	21.0	7.23	50.70	5.28	6.84	4.58	4.92	6.36	34.30	2.10	70.35	832.80	394.22
mean	15.0	6.88	23.04	4.97	4.20	3.91	4.83	4.73	10.72	0.37	43.56	77.01	107.84
standard deviation	-	0.17	10.40	0.15	0.88	0.42	0.05	0.87	6.52	0.63	13.48	200.96	89.84
coefficient of variation	-	0.02	0.44	3.04	21.06	10.70	1.02	18.30	59.70	177.65	30.85	236.36	80.97

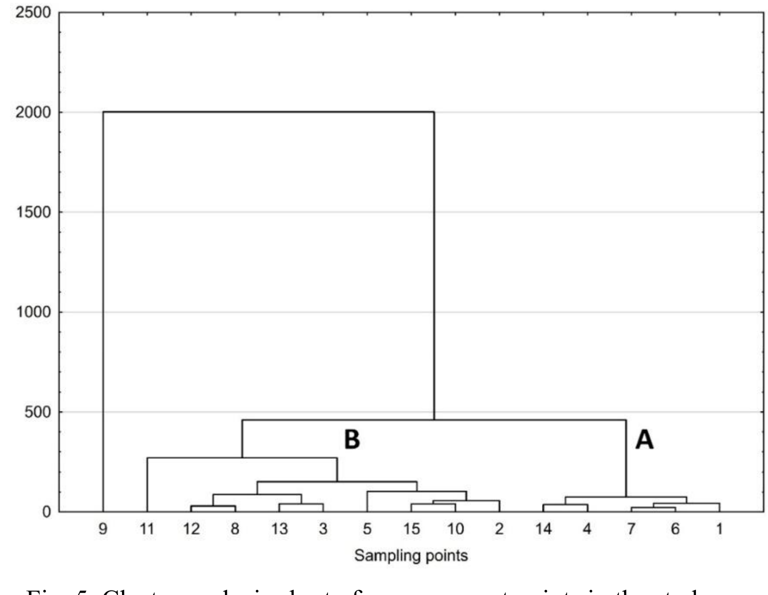


Fig. 5. Cluster analysis chart of measurement points in the study area

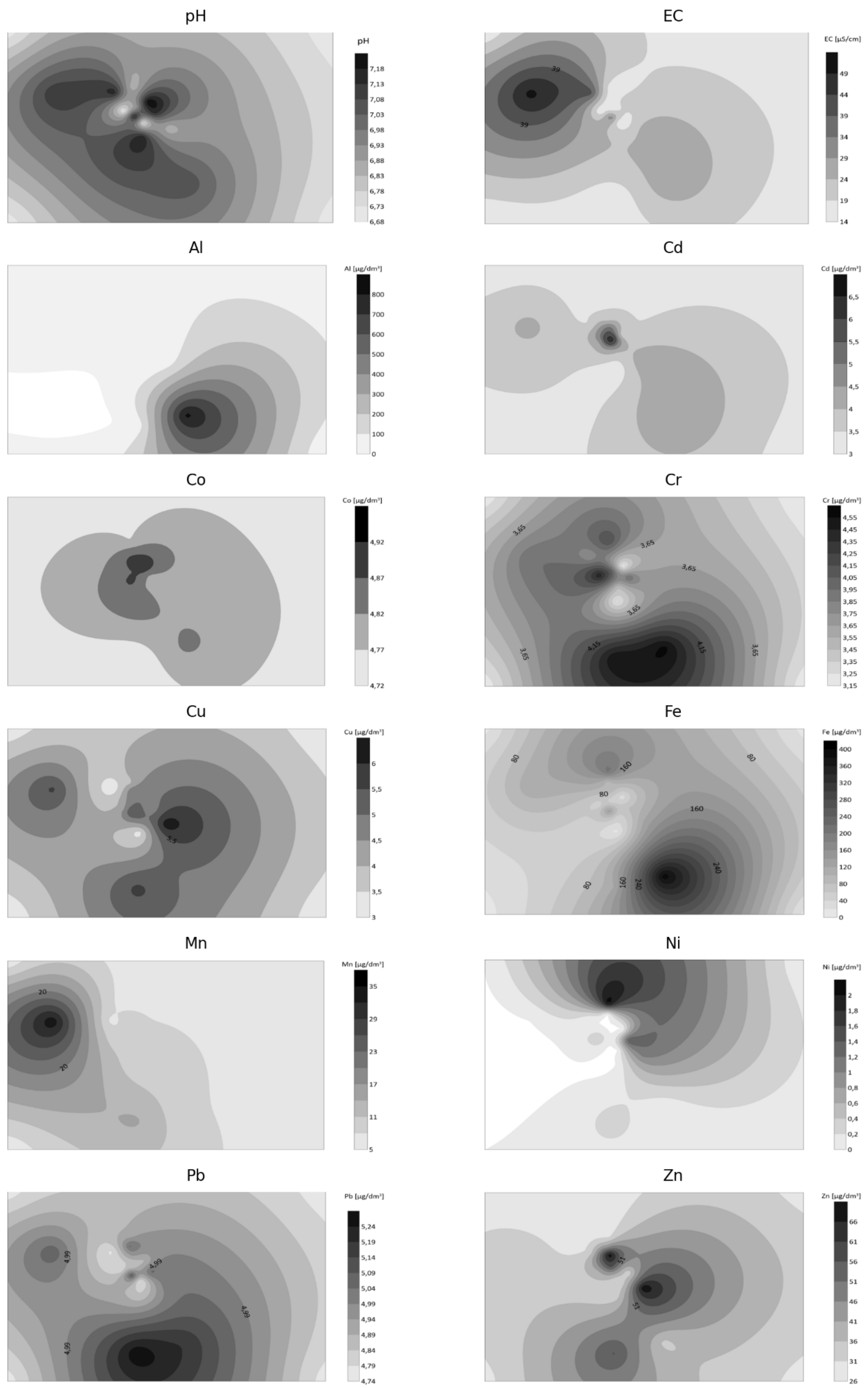


Fig. 6. Concentration maps of the analysed physicochemical and chemical properties

Comparing the results, it can be stated that the lowest concentrations of Pb, Co, Cu, Zn, Ni, and Fe were observed in the sample from the Świętokrzyski National Park – reference sample (Tab. 1). Nickel concentrations were low in all samples and exceeded 2 µg/dm³ in only one case within the Starachowice area (point no. 11). On the other hand, cobalt concentrations were consistent across all samples (coefficient of variation 1.02). Studies conducted in the protected area unfortunately revealed that it cannot serve as a representative site for urbanised areas. The elevation of this area by ~400 m above the surrounding terrain results in the deposition of pollutants from distant urban-industrial centres, including the Upper Silesian Industrial District, leading to increased concentrations of recorded metals (Kozłowski 2013). The PCA (Principal Component Analysis) analysis showed the presence of four components (PC1–PC4) together explaining 77.14% of the total variability. This means that they largely cover the key differences in the data (Fig. 7).

The first component PC1 explains 26.74% of the total variability, with dominant elements being Pb (-0.81), Fe (-0.83) and Cr (-0.73). PC2 accounts for 19.64% with Zn (0.75) and Cd (0.69). PC3 (16.91%) with Cu (0.51), Mn (0.66) and Ni (-0.59). PC4 (13.85%) is dominated by elements such as Co (-0.68) and Al (-0.64). Long vectors (Pb and Fe) pointing in the same direction indicate that these elements have a strong correlation and are related to the main source of variability in the data (PC1), similarly to Zn and Cd (PC2).

a)

Variables	PC1	PC2	PC3	PC4
pH	-0.13	-0.66	0.37	-0.25
EC	-0.35	-0.66	0.45	0.01
Pb	-0.81	0.09	0.22	0.07
Cd	-0.05	0.69	0.33	-0.31
Cr	-0.73	0.33	-0.30	-0.01
Co	0.59	0.11	0.26	-0.68
Cu	-0.45	0.49	0.51	0.25
Mn	-0.41	-0.26	0.66	0.37
Ni	-0.18	0.08	-0.59	0.52
Zn	0.07	0.75	0.44	0.05
Al	-0.66	-0.05	-0.24	-0.64
Fe	-0.83	0.00	-0.28	-0.39

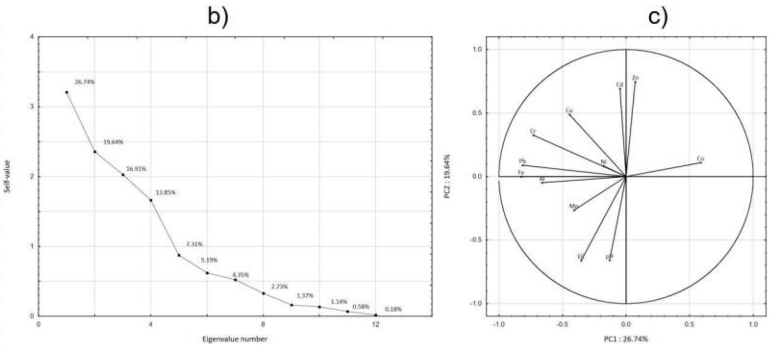
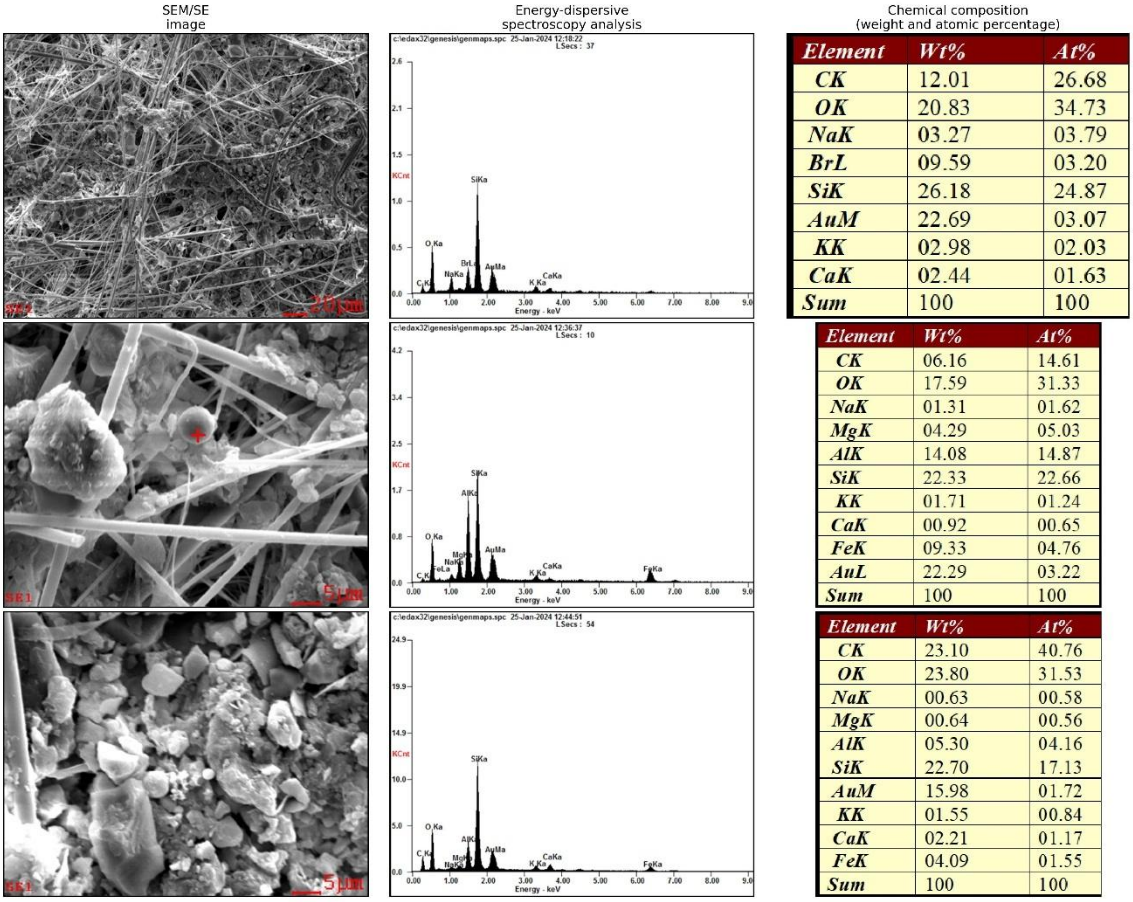


Fig. 7. PCA analysis
a – loadings,
b – scree plot,
c – biplot.

SEM/EDS analysis

The obtained SEM image confirms the significant diversity of deposited particles (in terms of size and shape) on the surface of the analysed filter. The presence of glass fibres from the filter complicates the interpretation of the results, but the achieved magnifications allowed for the visualisation of characteristic contaminants in the snow cover in the Starachowice area. The EDS analysis of the identified particles revealed a similarly high elemental diversity. The largest share in the chemical composition was that of C, O, Si and Au. However, a diversified percentage was found in the case of C, evidencing a variable amount of soot on the samples. A significant percentage was observed for Al (5.3%) and Fe (4.1%), lower for Ca (2.2%) and K (1.6%), while Na and Mg did not exceed 1%. The ×2,500 magnification of the analysed sample allowed to image significantly diversified shapes and sizes of particles characteristic of high-temperature transformations of fossil fuels with Si, Al and Fe in their composition (Fig. 8) – marked by point EDS analysis (red cross in the image).

The plotted concentration maps (Fig. 9) show a diverse chemical composition of individual particles. The largest ones, exceeding 20 µm, are composed of Si, Al and C. Significantly smaller and more dispersed are the particles containing Mg and Fe.



Element	Wt%	At%
CK	12.01	26.68
OK	20.83	34.73
NaK	03.27	03.79
BrL	09.59	03.20
SiK	26.18	24.87
AuM	22.69	03.07
KK	02.98	02.03
CaK	02.44	01.63
Sum	100	100

Element	Wt%	At%
CK	06.16	14.61
OK	17.59	31.33
NaK	01.31	01.62
MgK	04.29	05.03
AlK	14.08	14.87
SiK	22.33	22.66
KK	01.71	01.24
CaK	00.92	00.65
FeK	09.33	04.76
AuL	22.29	03.22
Sum	100	100

Element	Wt%	At%
CK	23.10	40.76
OK	23.80	31.53
NaK	00.63	00.58
MgK	00.64	00.56
AlK	05.30	04.16
SiK	22.70	17.13
AuM	15.98	01.72
KK	01.55	00.84
CaK	02.21	01.17
FeK	04.09	01.55
Sum	100	100

Fig. 8. SEM/EDS image of the quartz filter surface and EDS of the snow sample from Starachowice

Discussion

The authors acknowledge the short deposition period and the single series of studies; therefore, the conclusions drawn from this work are cautious and require further research. Given the significant reduction in the snow cover retention time, the conducted experiment in a city under substantial industrial pressure appears justified. Based on the analysis of meteorological data, it is evident that the sampling period was chosen to coincide with the most extensive and longest-lasting snow cover, without positive temperatures in the period preceding sampling. This is crucial because the actual deposition released from the snow cover is closely related to the number and depth of thaw episodes (Błaś *et al.* 2010). The physico-chemical and chemical properties noted in the melted snow samples differ significantly from the uncontaminated ones (Jansen *et al.* 1988; Nawrot *et al.* 2016; Degórska *et al*. 2022; Bogucka *et al.* 2023; Si, Li 2024). During the measurement month, there was no concentration of PM_{10} above the alert level, although such a situation occurred in the following month. The analysis of the physico-chemical properties of snow showed the influence of local pollutants (the pH value of all samples was increased). The increased concentrations of lead, cadmium and chromium present a high risk for the inhabitants of Starachowice. They indicate that industrial plants located in the city are having the highly negative impact on air quality. This impact and pollutant concentrations in snow samples were observed not only near the foundry but also near metal product plants in the southern part of the city. It should be remembered that fine dust can be transported due to distance and further reduce air quality. The backward trajectory determined by the Hysplit model highlighted that, in the analysed period, air from southern Ukraine was deposited over Starachowice. Particulate matter delivered to the atmosphere is also a carrier of zinc, copper and nickel, but reduces air quality to an insignificant extent. Similar anthropic impact from industry was identified around the steelworks in Ostrowiec Świętokrzyski (Kozłowski *et al*. 2018) (Tab. 2). The studies in the area of Lublin (Kujawska *et al.* 2024) showed similar concentrations of lead, zinc and iron in snow, significantly lower concentration of cadmium and

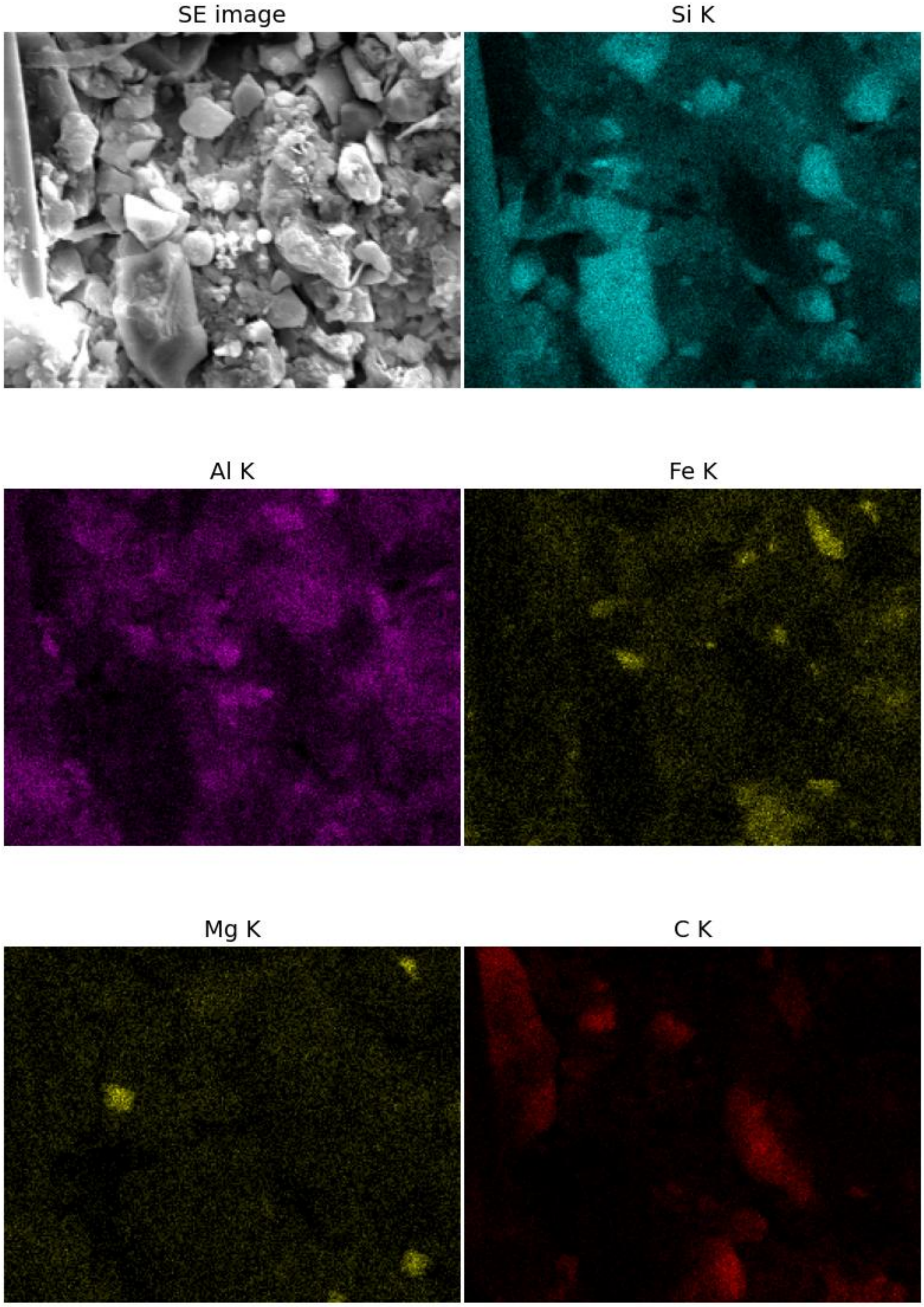


Fig. 9. Concentration maps of selected elements (SE image)

Table 2

Comparison of the results of snow cover as geoaccumulator studies, with locations

Locations	H	pH	EC	Pb	Cd	Cr	Co	Cu	Mn	Ni	Zn	Al	Fe	References
	[cm]	[-]	[µS/cm]	[µg/dm³]										
Świętokrzyski National Park	19	6.6	15.9	4.8	3.9	3.8	4.7	2.4	11.1	0	24.7	17.7	12.7	
Starachowice (Poland)	15	7.0	23.7	5.0	4.2	3.9	4.8	4.8	10.9	0.4	43.7	85	111	
Lublin (Poland)				4.2	0.4	0.3		9.4	17.7		42		77.4	(Kujawska *et al.* 2024)
Łagów (Poland)	13	8.1	59.1	0.01		0.1	0.01	0.1		0.1	3.3	60.1		(Szwed, Kozłowski 2022)
Ostrowiec Św. (Poland)	5	7.4	41.5	0.1	0.1	0.6	0.1	1.7	15.5	0.4	57.1	8.1	62.5	(Kozłowski *et al.* 2018)
Białystok (Poland)	30–40			8.7–91.1	0.1–1.3	187.5–353.2		18–522.2			419–1956.2			(Bełcik *et al.* 2024)
Tobolsk (Russia)	50	6.0	67.7											(Tigeev *et al.* 2021)
Korkino (Russia)	25–30	5.4–6.7		14		87	15	197	410		439	420	459	(Krupnova *et al.* 2021)
Vorkuta (Russia)		5.2			<0.2*	0.1*	0.1*	0.2*	1.2*	0.2*	0.5*	31*		(Vasilevich *et al.* 2019)

* results in [mg/dm³]

chromium, and twice as high concentrations of copper and man ganese in meltwater. The studies of snow cover in the impact zone of plants processing rock (calcareous) raw materials showed the emissions of alkaline particulate matter and the much higher pH value of the cover in the vicinity of Kielce (Szwed, Kozłowski 2022). A significant transformation of the natural environment as a result of the exploitation and processing of hard coal in Siberia results in the emissions of harmful particulate matter into the neighbouring cities (Vasilevich *et al.* 2019; Krupnova *et al.* 2021). The concentrations of chromium, cobalt, manganese, copper and iron recorded in this region (Vorkuta, Korkino) significantly exceed those observed in Starachowice. The authors of the papers, indicating the possibility of transport over long distances, confirmed the occurrence of porous and spherical coal ash in the snow in Vorkuta (SEM/EDS analyses). These molecules, with spongy interiors, were composed of S, Na, K, Mg, Ca and Fe (Krupnova *et al.* 2021). They are formed during the combustion of coal and have been imaged earlier, among others, in the Czech Republic (Francová *et al.* 2017), in an industrial and mining coal centre concentrated around Ostrava, and now also in Starachowice. Mineral particles with a predominance of Si and Al were also numerously represented, mainly as a result of the weathering of rocks and minerals (Kabata-Pendias, Pendias 1999; Hartmann *et al.* 2013). The areas of carbonate rock extraction and processing were associated with particles with characteristic crystalline lumps with a predominance of Ca, identified on SEM micrographs in the Świętokrzyskie Mountains (Szwed *et al.* 2021).

Particulate matter present in the atmospheric air contributes to the degradation of forest complexes. For popular coniferous species, strong impregnation with particulate matter containing heavy metals prevents gas exchange and disturbs physiological processes (Maňkovská *et al.* 2004). The harmfulness of particulate matter inhaled into the human body is not limited to allergies, runny nose or aggravated cough (Kim, Radoias 2022), but has a negative impact on the psychomotor development of children (Compa *et al.* 2023), results in cardiovascular problems, lung tumours, atherosclerosis, impaired lung growth in children, and lower birth weight in newborns (Sonwani *et al.* 2021).

In the area of Starachowice, an increase in the pH value of precipitation and significant pollution with heavy metals were found. In the case of chromium and cadmium, the pollution can be described as extreme. The size and shape of the particles deposited on the surface of the analysed filter, along with their chemical composition, indicate the source of the contamination. The SEM/EDS analyses of the quartz filter surface confirm the presence of particles characteristic of anthropogenic pollutants in the air during the heating season (C, Si, K, Ca) in the urbanised area. Concentric particles of size not exceeding 5 µm in the analysed material are characteristic of the combustion of solid fuels in industrial plants (cement plants, combined heat and power plants, metalworks). Their presence may prove to be due to both local and remote emissions typical of a coal-based economy. The chemical composition, physical properties and density of the depicted (SEM/EDS) pollutants indicate a potential threat to human health. Exposure to poor air quality, also observed in other regions of Poland during the heating season, represents a very serious environmental issue. The particles identified in snow samples from Starachowice, considering their size and shape, remain in the atmosphere for a longer period and can be transported over considerable distances. It has been proven that particles with an aerodynamic diameter of less than 2.5 μm stay longest in the atmosphere and can be transported between continents (Prospero 1999). The integration of methods based on chemical composition analysis (ICM-MS/TOF) and SEM/EDS allows a determination of the level of pollution at a given place and time. Nevertheless, this synthesised approach could be further developed with the involvement of artificial intelligence (Szwed, Pasieka 2024). In practice, however, a significant amount of input material is needed to build a model using deep neural networks.

Conclusions

The study of snow cover in Starachowice during the winter of 2023/24 provided valuable insights into atmospheric pollution deposition and its potential sources. The results confirm that industrial activity, specifically from Odlewnie Polskie S.A., significantly contributes to the presence of heavy metals and other pollutants in the urban environment. The main findings of this research are as follows:

- Air Pollution Sources: The analysis of snow samples confirmed the presence of heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), cobalt (Co) and iron (Fe), with concentration levels indicating anthropogenic influences. The enrichment factor (EF) calculations highlight significant contributions from industrial emissions. Air quality remains under the impact of the dominant economic activity in a given area. The PC1–PC4 components explain the main variability of the data (PCA analysis). Elements with high loadings in these components (Pb, Fe, Zn, Cd) suggest that the analysis performed concerns mainly the variability related to heavy metals from the foundry plant and their influence on environmental variables (snow cover composition).
- Meteorological influence: The study demonstrated that air mass movements, particularly those from the east, contributed to lower temperatures and increased snow cover retention, which in turn allowed for greater accumulation of pollutants in snow. Changes in wind directions influenced the dispersion and deposition of contaminants.
- Physico-chemical properties: The pH values of the melted snow samples ranged from 6.71 to 7.23, suggesting a slightly alkaline nature, likely influenced by atmospheric deposition of industrial emissions. The electrical conductivity (EC) values varied significantly, reflecting the different levels of dissolved pollutants present in the snow cover.
- Comparison with background levels: The control sample collected from Świętokrzyski National Park showed significantly lower concentrations of pollutants compared to urban samples, reinforcing the impact of local industrial and urban sources on atmospheric pollution levels in Starachowice.
- Air Quality Monitoring and public health: The PM10 concentration data from the monitoring station revealed occasional exceedances of acceptable levels, particularly during temperature drops, indicating the impact of heating and industrial emissions on air quality. While critical alert levels were not reached in December, trends suggest that prolonged exposure to such pollution could pose health risks to residents.
- Implications for environmental policy: the study underscores the importance of continuous air quality monitoring and the necessity for stricter emission control measures. Snow analysis proves to be an effective method for assessing atmospheric pollution and should be incorporated into regular environmental monitoring strategies.
- Integrated chemical analysis (ICP-MS/TOF) with scanning microscopy can be an innovative method for identifying contaminants using machine learning.

In conclusion, the findings highlight the need for proactive measures to mitigate industrial pollution in urban areas. Further research, including year-round monitoring and broader spatial analysis, would provide deeper insights into pollution dynamics and support the development of effective environmental policies to improve air quality and public health in Starachowice and similar urban-industrial regions.

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