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Hidden in snow: Selected aspects of chemical composition of an urban snow cover (Kielce, SE Poland)

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Abstract

Snow cover is a valuable source of information about air quality. It enables detection of dust and other air pollutants which have been accumulated throughout the period since the snow cover was formed. Research conducted in Kielce confirms multidirectional human pressure from local and regional emission sources. Combustion of fuels resulted in lower pH and increased EC, SO₄ and NO₃ concentrations in the southern and northern parts of the city. Elevated concentrations of Cl and Na indicate the effect of transportation and winter road maintenance. Apart from local emitters, air quality in Kielce is affected by the regional sources, including the nearby center of the lime and cement industries. Climate change is reflected in the number of days with snow and thickness of snow cover, declining since the 1990s.

1. INTRODUCTION

Since the end of the 20th century researchers have been investigating snow cover in the studies on air pollution [e.g. Forland, Gjessing 1975, Gregurek et al. 1998, Jones, Sochanska 1985, Suzuki 1991]. Physical properties, including pH and electrolytic conductivity, as well as chemical composition of snow, have been studied [e.g. Allan, Jonasson 1978, Barrie, Vet 1984, Landsberger, Jervis 1985]. Numerous articles confirmed significant changes of snow cover properties in urban and industrial areas [including Douglas, Sturm 2004, Kushulina et al. 2014, Opekunova et al. 2021]. Recently, due to dynamic increase in fuel and energy prices [Inacio et al. 2023, Ślusarczyk et al. 2023, Wielgosiński et al. 2017, Wood et al. 2022], there is the risk of deteriorating air quality in inhabited zones – cities, suburbs and villages. Combustion of low-quality fuels in uncontrolled conditions (households) is the source of harmful gases (carbon monoxide and dioxide, sulphur dioxide, nitrogen oxides) and dust, containing polycyclic aromatic hydrocarbons and derivatives, dioxin-like compounds and heavy metals [Grochowalski, Koniecznyński 2008, Rybiński et al. 2021, Szwed et al. 2023, Szwed et al. 2022]. It has been proven that exposure to polluted air induces various diseases and shortens lifespan [Pope, Dockery 2006].

Numerous reports [EMEP 2022; EEA 2022] indicate critical exceeding of air quality standards in winter in central European countries, including Poland. The state monitoring network [www.gov.pl/web/gios] is supplemented with the

analysis of physico-chemical properties of snow in winter (Integrated Monitoring of the Natural Environment). Polish research on snow cover has a long history in the areas with low anthropogenic pressure, such as Spitsbergen [Nawrot et al. 2016], Obruchev Glacier in the Polar Urals [Stachnik, Uzarowicz 2011] and King George Island [Zwoliński 2007]. The studies on snow as an indicator of air pollution are applied to the areas under influence of local and regional emitters [Polkowska et al. 2010, Kozłowski et al. 2012]. The results point to changes in the natural character of snow cover, such as increased load of suspended matter, concentration of hydrocarbons, heavy metals, nutrients, as well as changes in pH and electrolytic conductivity [Jarzyna et al. 2017, Kasina 2008, Kozłowski et al. 2017, Ociepa et al. 2015, Siudek et al. 2015, Szwed, Kozłowski 2021, Szwed, Kozłowski 2022]. Pollutants migrate from atmosphere to snow cover with snowfall and with dust settling on its surface. Chemical composition of precipitation is shaped by the pollution of water droplets and ice crystals within the cloud and through removal of pollutants from the air under the cloud during snowfall. The composition of the cloud may result from the impact of distant emitters, while the amount of pollutants removed from the lower air column and sedimentation of dust on snow cover depends on the local sources [Jylha 2000, Parungo et al. 1987]. The research presented in this paper was conducted in winter 2022/2023 during the longest period of snow cover in Kielce. The aim of the study was to demonstrate usefulness of snow cover as an indicator of anthropogenic impact on

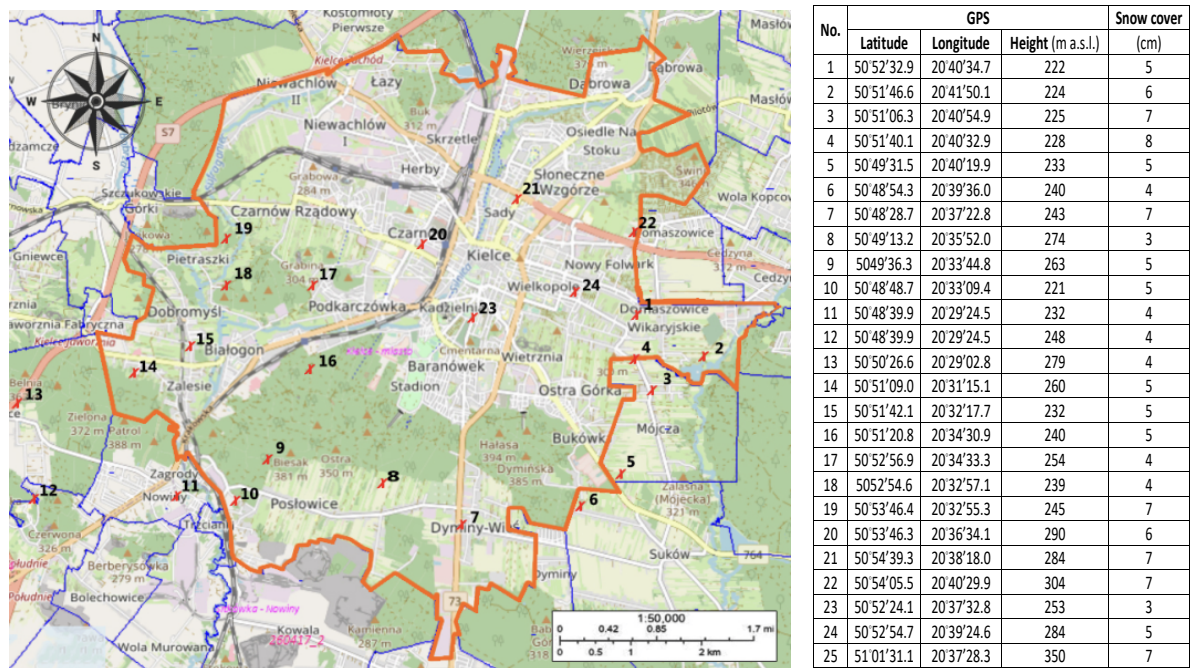


Figure 1. Research area (geoportal.powiat.kielce.pl; changed)

air quality in developed areas and to point to some aspects of climate change, as well as the effects of dramatic increases in fuel and energy prices. We assumed that air quality in the study area is affected by local, regional and distant emitters and that chemical composition of snow will reflect this impact. We hypothesised that wind direction and topographic conditions will be among the factors affecting deposition of pollutants. We also expected that snow cover thickness and the number of days with snow have decreased over the last decades.

2. MATERIALS AND METHODS

2.1. Study area

Kielce is a city located in south-eastern Poland, in the Świętokrzyskie Mountains. It is the capital city of Świętokrzyskie Province and a regional economic, scientific, and cultural centre, which hosts trade fairs and exhibitions. The city covers an area of 109.5 km² and has around 200,000 inhabitants. Samples of snow cover were collected from 24 points (Fig. 1), and an additional reference sample was collected from the Suchedniów-Oblęgorek Landscape Park, located 20 km north from Kielce.

2.2. Data Collection and Analysis

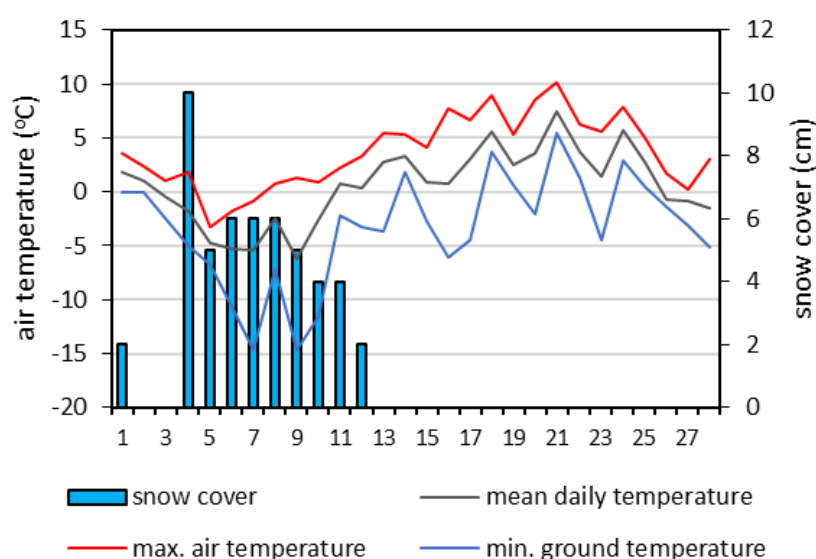
Samples of snow cover were collected on 10.02.2023 with the use of a 1 m long plastic tube (diameter: 100 mm), in order to obtain vertical sections of the entire cover at

sampling points. Snow cores were closed in 2 litre PTFE containers and transported to the Environmental Research Laboratory of the Jan Kochanowski University of Kielce. In melted samples pH and electrolytic conductivity (EC) were determined using a Hach HQ2200 multi-parameter water quality sensor with Intellical electrodes, calibrated with Hamilton standards (Reno, NV, USA, pH 4.01, 7.00, 9.21, EC 15 mS cm⁻¹). The content of selected ions (Ca²⁺, Cl⁻, Mg²⁺, Na⁺, K⁺, SO₄²⁻, NO₃⁻, NH₄⁺) was analysed using a DIONEX ICS 3000 ion chromatograph (Sunnyvale, CA, USA) equipped with an IonPac CS16 3 × 250 mm analytical column (cations) and IonPac AS18 2 × 250 mm (anions). Detection level for individual parameters was: 0.4 mg · dm⁻³ for Ca²⁺, and 0.1 mg · dm⁻³ for other ions. In order to control the quality of obtained results, certified reference material KEJIM-15 (Environment Canada) was used (Table 1). The results were visualised on maps with Surfer vs. 16 software (Golden Software, LLC, Golden, CO, USA) and statistics were generated in Statistica vs. 13 (Tibco Software Inc., Palo Alto, CA, USA). Meteorological data were obtained from the Institute of Meteorology and Water Management (IMGW), station Kielce-Suków. NOAA Hysplit model (Air Resources Laboratory, NOAA's Office of Atmospheric Research, National Oceanic and Atmospheric Administration) was used to visualise air mass trajectories. Concentrations of PM 2.5 and PM10 were obtained from the Chief Inspectorate for Environmental Protection (GIOŚ). Spatial analyses and visualisations were used in delimiting the increased impact of local emitters of pollutants deposited in snow.

Table 1. Comparison of measured and certified concentrations in KEJIM-15

Ion	KEJIM-15		DIONEX ICS 3000		Dev.**
	Concentration	±Uncertainty	Average	±SD*	
	[mg/l]				[%]
Ca	0,488	0,046	0,47	0,02	-4,30
Mg	0,294	0,024	0,31	0,01	4,20
K	0,252	0,026	0,25	0,02	-2,78
Na	2,66	0,23	2,63	0,10	-1,13
Cl	3,79	0,18	3,64	0,10	-3,96
SO4	1,13	0,08	1,11	0,09	-1,77

* - standard deviation, ** - relative difference between the measured and certified concentration $100\% \cdot (c_m - c_c) / c_c$

**Figure 2.** Meteorological conditions in Kielce in February 2023 (based on data from IMGW, station Kielce-Suków)

3. RESULTS

3.1. Characteristics of selected climate elements in Poland in February 2023

The mean monthly air temperature in Poland in February 2023 amounted to 1.5°C (0.6°C in Kielce); the value was 1.6°C higher than the average from 1991–2020. The average precipitation sum for Poland in this month was 40.3 mm (50.7 mm in Kielce) – 8.7 mm higher than the 1991–2020 average. According to the classification proposed by Kaczorowska (1962), February 2023 was exceptionally wet (128% of the average). The day the samples were collected (10 February) the wind in the area of Kielce was moderate, SW and W. Snow cover was determined by meteorological conditions prevailing from 4 to 12 February (Fig. 2). The thickest cover occurred at the beginning of its formation (10 cm on 04.02.2023 and 4 cm on the day of sample collection); afterwards thawing began (0 cm on 13.02.2023).

In the first ten days of February, during the accumulation of snow cover (lowest temperature and snowfall), the prevailing source of air masses in Kielce was the eastern one (Fig. 3). At the end of this period (9 and 10 February) wind direction changed and air masses flowed from the south and south-west, which induced an increase in air temperature, and as a result, thawing of the snow cover (Figs. 2–3).

3.2. Characteristics of snow cover in Kielce (1996–2022)

During the analysed period (1996–2022) the longest time with snow cover was noted in 2005: 76 days (Fig. 4). The lowest number of days with snow was recorded in 2014: 26 days. The average from these years was 49 days. During the last decade this value was exceeded only in three years (2013, 2016, 2019) and the average for the last ten years decreased to 42 days. Significant decline in the number of

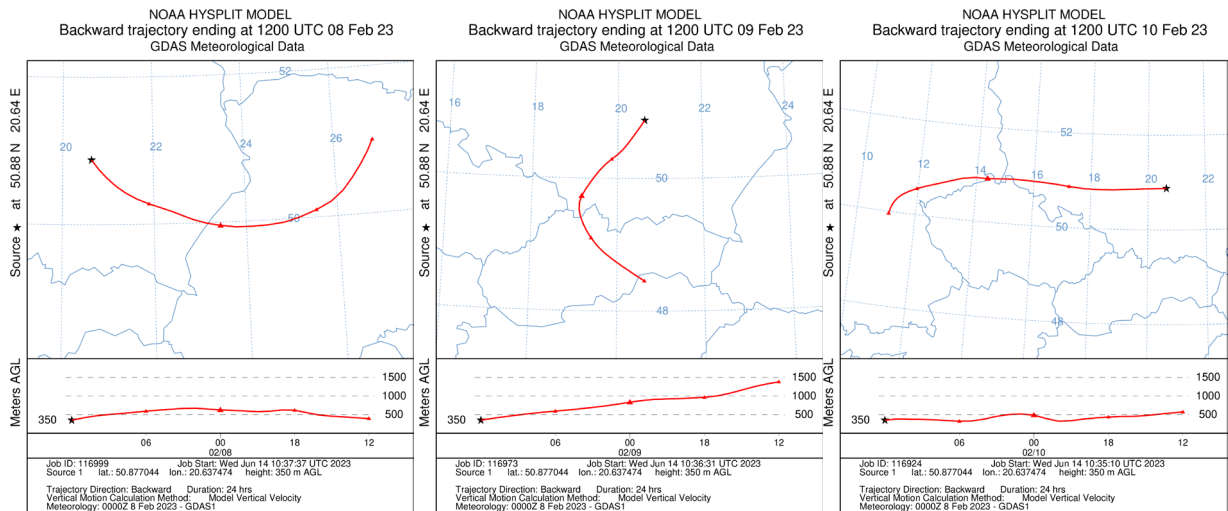


Figure 3. Direction of air mass flows on 8–10 February 2023 (NOAA Hysplit)

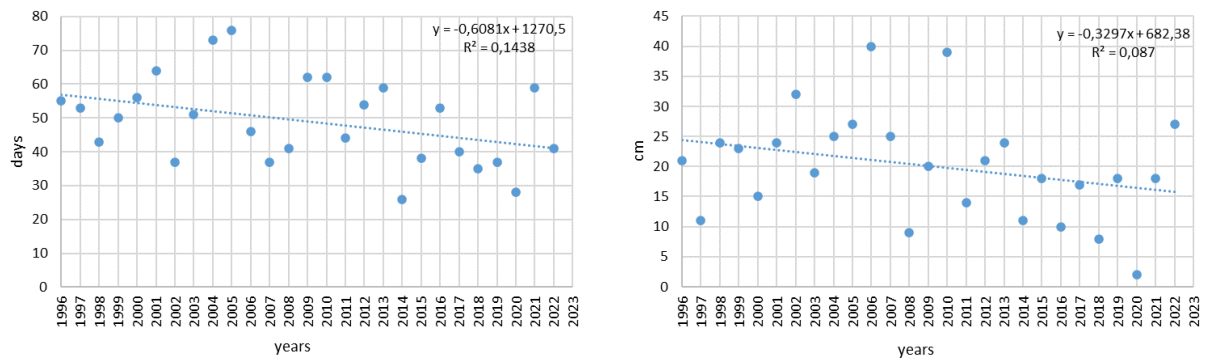


Figure 4. Number of days with snowfall and maximum snow cover thickness in 1996–2022 (data from IMGW, station Kielce-Suków)

days with snowfall and the maximum thickness of snow cover is visible (Fig. 4). The average thickness of snow cover in 1996–2022 amounted to 20 cm, while in the last decade it was 15 cm, never exceeding 30 cm.

3.3. Physico-chemical analysis of snow cover

The average EC value of the analysed samples amounted to $27.3 \mu\text{S cm}^{-1}$ (slightly elevated, according to Jansen et al. 1988), with a maximum of $63.6 \mu\text{S cm}^{-1}$ (sample No. 12): Fig. 5–7. The value of pH was from 4.34 (significantly low) to 6.85 (highly elevated), with the mean value of 5.15 (normal, according to Jansen et al. 1988).

The highest concentrations of the analysed ions were those of chloride: over 12 mg dm^{-3} (point No. 22, in NE part of the city; Fig. 8), with the average of 4 mg dm^{-3} . The second one was sodium, with the mean value of 2.4 mg dm^{-3} . Both ions reached the highest concentrations in the sample from point No. 22. The third one, with maximum concentrations below 5 mg dm^{-3} , was calcium (max. 4.6 mg dm^{-3} in sample from point No. 8 in the southern part of the city).

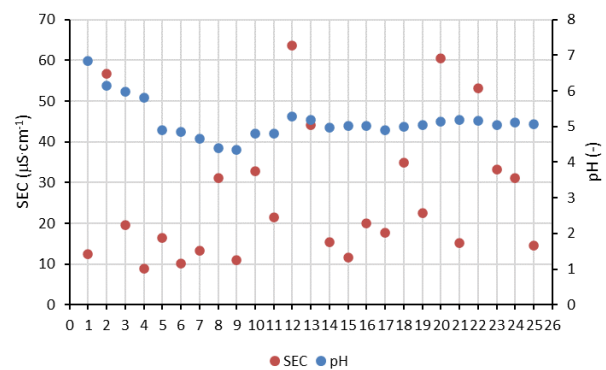
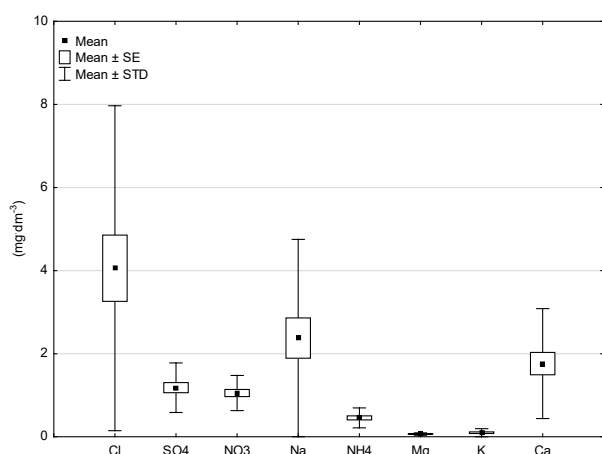


Figure 5. Physico-chemical properties of snow samples in Kielce in 2023

Principal component analysis (PCA; Fig. 9, Table 3) shows three components, explaining 78.5% of the variability. The first component (PC1), connected with winter road maintenance and fuel combustion in households,

Table 2. Physico-chemical properties of water from melted snow

No.	Cl	SO ₄	NO ₃	Na	NH ₄	Mg	K	Ca	pH	EC	Snow cover
	mg dm ⁻³								-	μS cm ⁻¹	cm
1	1.37	0.63	0.95	0.86	0.37	0.05	0.12	0.39	6.85	12.35	5
2	11.22	1.69	0.08	6.70	0.57	0.06	0.05	2.22	6.15	56.6	6
3	0.92	0.67	1.12	0.55	0.47	0.05	0.09	1.57	5.98	19.47	7
4	0.81	0.78	1.30	0.17	0.16	0.03	0.02	0.12	5.81	8.97	8
5	1.93	0.67	0.86	1.13	0.29	0.08	0.00	1.29	4.91	16.46	5
6	1.30	0.56	0.95	0.80	0.41	0.05	0.06	0.61	4.84	10.2	4
7	1.84	0.77	0.74	1.16	0.40	0.08	0.10	0.64	4.67	13.28	7
8	1.16	0.85	0.86	0.68	0.32	0.06	0.12	4.58	4.39	31.2	3
9	0.65	0.59	0.64	0.48	0.27	0.04	0.05	1.10	4.34	11	5
10	1.69	0.90	0.74	0.98	0.28	0.04	0.09	4.54	4.81	32.7	5
11	1.50	1.26	0.67	0.70	0.21	0.02	0.18	2.52	4.81	21.54	4
12	11.38	1.20	1.05	6.70	0.44	0.05	0.03	4.56	5.27	63.6	4
13	8.40	1.10	0.81	4.97	0.44	0.07	0.09	2.49	5.18	44.2	4
14	2.16	1.03	0.70	1.17	0.38	0.10	0.04	0.75	4.97	15.35	5
15	1.18	0.77	0.73	0.74	0.33	0.03	0.09	0.76	5.02	11.57	5
16	3.83	1.05	1.03	1.73	0.48	0.05	0.08	0.90	5.02	19.92	5
17	1.37	0.97	0.90	0.73	0.00	0.08	0.00	0.84	4.89	17.78	4
18	4.69	2.21	1.71	2.74	0.90	0.09	0.23	2.60	4.99	34.9	4
19	3.64	1.23	1.57	2.26	0.48	0.09	0.41	1.47	5.03	22.5	7
20	11.42	2.89	1.77	6.99	0.71	0.11	0.28	3.08	5.14	60.4	6
21	2.19	1.00	1.50	1.36	0.63	0.08	0.01	0.70	5.19	15.24	7
22	12.49	1.85	1.29	7.66	0.59	0.11	0.01	1.41	5.17	53.2	7
23	4.74	2.18	1.66	2.61	1.13	0.13	0.15	1.77	5.05	33.2	3
24	5.55	1.55	1.66	3.16	0.68	0.06	0.06	1.38	5.12	31.1	5
MIN	0.65	0.56	0.08	0.17	0.00	0.02	0.00	0.12	4.34	8.97	3
MAX	12.49	2.89	1.77	7.66	1.13	0.13	0.41	4.58	6.85	63.60	8
MEAN	4.06	1.18	1.05	2.38	0.46	0.07	0.10	1.76	5.15	27.36	5,2
STD	3.91	0.60	0.42	2.37	0.24	0.03	0.10	1.32	0.55	16.95	1,38
Reference sample	1.32	1.04	1.63	0.82	0.54	0.07	5.63	1.07	5.07	14.62	7

**Figure 6.** Chemical composition of snow cover (selected ions)

generated 46.7% of the total variability. The second component (PC2), shaping 18.8% of the variability, can be linked with urban traffic. The third component (PC3), explaining 13.0%, is connected with the inflow of air masses with elevated concentration of Ca from the regional centre of the lime and cement industry (*Białe Zagłębie* – ‘White Basin’) located SW from Kielce.

4. DISCUSSION

Changes in the Earth’s climate, apart from the increase in global air temperature, affect the snow cover [Pant et al. 2023]. Its thickness, as well as the number of days with snow, is declining in many regions of Europe [Olefs et al. 2020, Gentilucci et al. 2023, Stucchi et al. 2023, Szwed et al. 2017, Szyga-Pluta 2021]. Analysis of the data from IMGW,

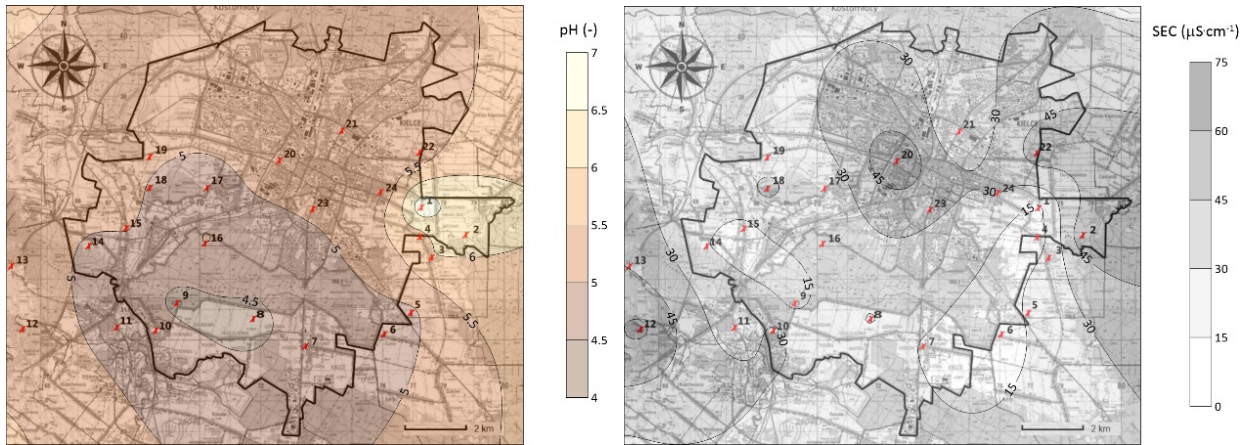


Figure 7. Spatial distribution of physico-chemical properties of snow from Kielce

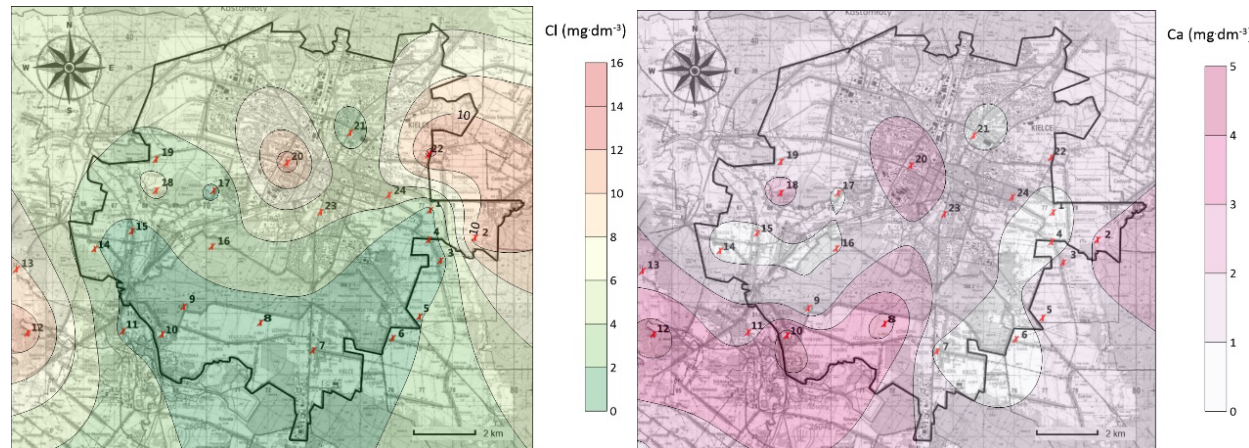


Figure 8. Spatial distribution of Cl and Ca concentrations in snow from Kielce

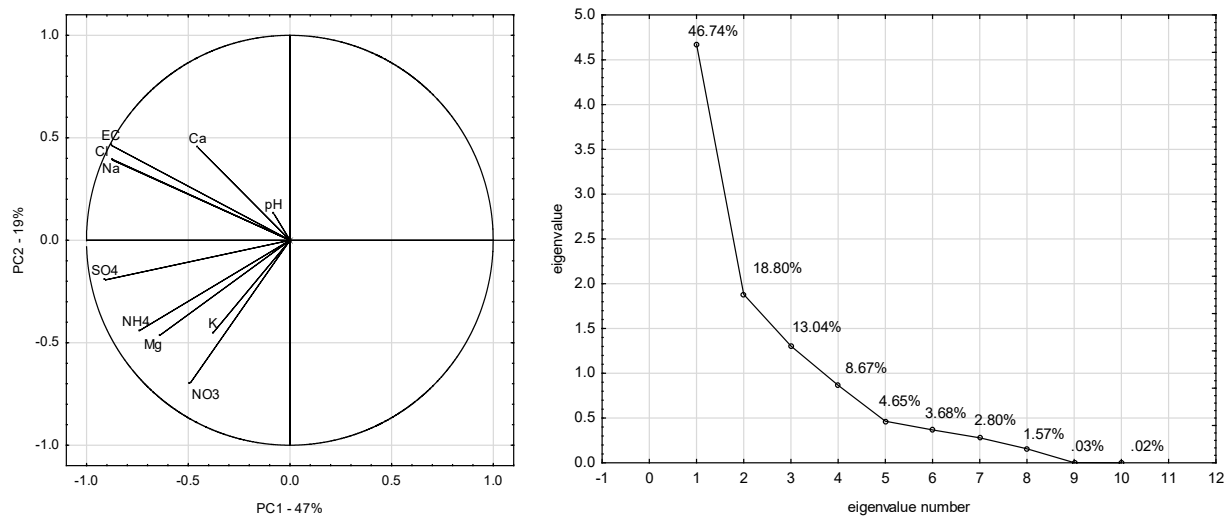


Figure 9. Graphic image of relationships among PC1 and PC2 with a scree plot

Table 3. Principal component analysis (PCA) analysis of studied physico-chemical parameters

Variable	PC 1	PC 2	PC 3
Cl	-0.9*	0.4	-0.2
SO ₄	-0.9*	-0.2	0.0
NO ₃	-0.5	-0.7*	0.0
Na	-0.9*	0.4	-0.2
NH ₄	-0.7	-0.4	-0.1
Mg	-0.6	-0.5	-0.1
K	-0.4	-0.5	0.4
Ca	-0.5	0.5	0.7
pH	-0.1	0.1	-0.8*
EC	-0.9*	0.5	0.1
% of variance	46.7%	18.8%	13.0%
% in total	46.7%	65.5%	78.5%

*PC1 ≤ -0.9; PC2 ≤ -0.7; PC3 ≤ -0.8

station Kielce-Suków (Fig. 4) shows a declining trend for both parameters in 1996–2022; it does not, however, reach statistical significance. Statistically significant negative trends were noted in Poland for a longer period of 1950–2018 [Falarz, Bednorz 2021]. The results of research conducted in both inhabited and natural areas (polar zones) indicate changes in snow cover properties. Human pressure on air quality effects an increase in the amount of anthropogenic substances (suspended matter, hydrocarbons, metals) in precipitation [Douglas, Sturm 2004, Fonseca-Salazar et al. 2023, Kashulina et al. 2014, Opekunova et al. 2021]. Air quality is directly correlated with the properties of precipitation in a given area. EC, pH and chemical composition are affected by air pollution from natural and anthropogenic sources. In the case of Kielce, specific topography is decisive in the flow of air masses [Ciupa et al. 2011]. The city is located in an area surrounded by hills reaching over 400 m AMSL, with the Silnica River valley in the central part. Air quality in Kielce is affected by local emitters, including households and road transport, as well as neighboring pollution sources. Among the latter the 'White Basin' is a major source of dust from the lime and cement industry [Szwed et al. 2022]. The average chemical composition of snow samples shows the following concentration of the analysed ions (in descending order): Cl⁻ > Na⁺ > Ca²⁺ > SO₄²⁻ > NO₃⁻ > NH₄⁺ > K⁺ > Mg²⁺. The highest concentrations of chlorides (12.5 mg·dm⁻³) and sodium (7.7 mg·dm⁻³) were noted near the junction of two state roads No. S74 and S73 (point No. 22). Elevated concentrations of calcium in the southern part of the city (4.6 mg·dm⁻³ in point No. 8 and 4.5 mg·dm⁻³ in point No. 10) are connected with the inflow of air masses polluted with lime-cement dust from the 'White Basin' (Fig. 3, Table 1). In the southern part of Kielce, where housing estates are located, acidifying impact of sulfates and nitrates is noted (emission from households).

The results from 2023 are similar to the values reported in Kielce in 2016 [Kozłowski et al. 2016]. Both the average and the maximum concentrations of the analysed ions and the values of pH and EC were lower than the results obtained in the 'White Basin' [Kozłowski et al. 2012, Kozłowski et al. 2016, Szwed et al. 2022], in urbanised areas under strong pressure from industry in Kraków, in the Upper Silesian Industrial Region [Siudek et al. 2015] and in other cities, where snow cover was analysed (Table 4). The values of physico-chemical parameters (pH and EC) were more diversified in the snow cover studied in 2008–2012 in the Sudetes by Cichała-Kamrowska (2012). The values of pH ranged from 3.56 to 7.50, while EC from 2.16 to 75.60 μS·cm⁻¹. Concentrations of analysed ions (SO₄²⁻ i NO₃⁻) in the Iżera Mountains and Giant Mountains were significantly higher than in Kielce (12.04 and 4.47 mg·dm⁻³ respectively). Only the concentration of Ca (maximum value: 3.17 mg·dm⁻³) in Orle, Iżera Mountains, was lower than in Kielce (Ca²⁺_{max} 4.58 mg·dm⁻³).

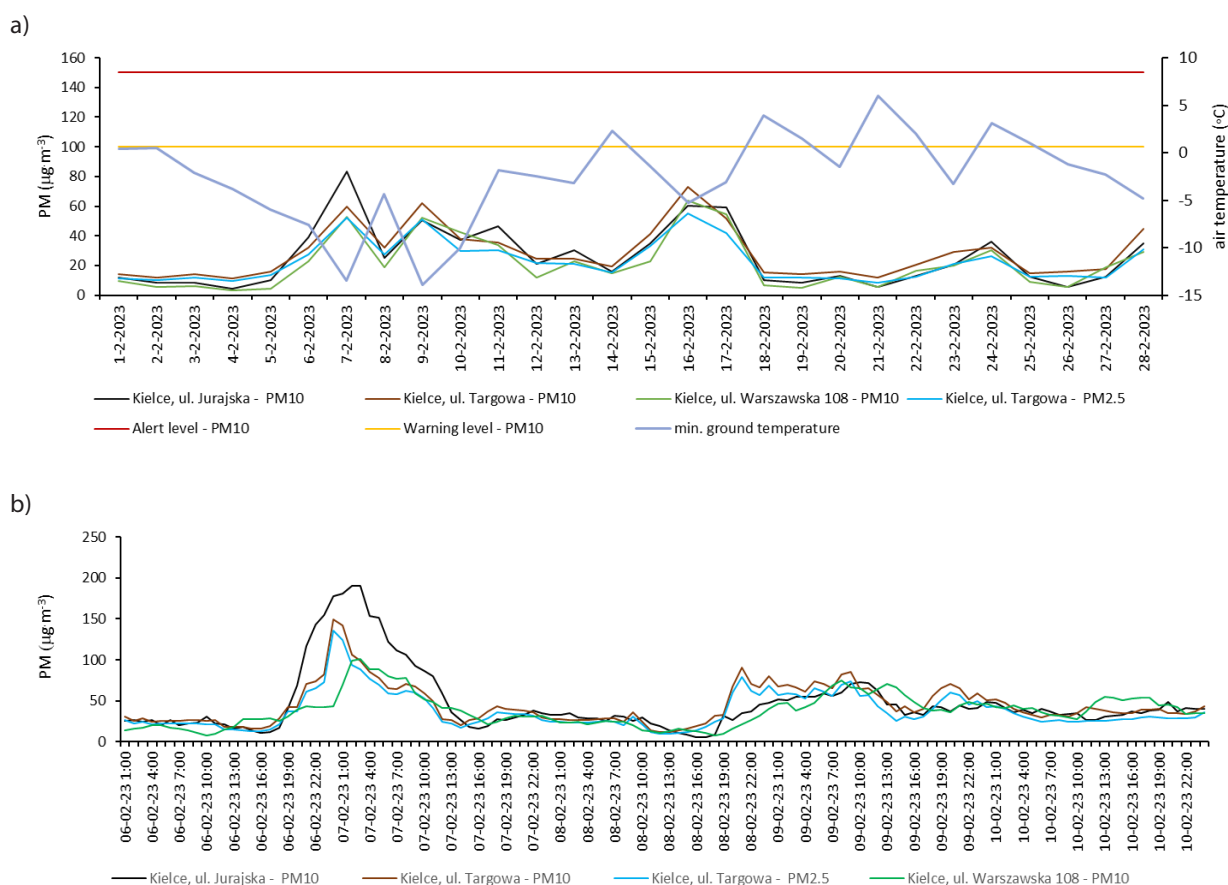
Spatial distribution of the analysed parameters indicates the effect of terrain on deposition of pollutants. A city centre located in a river valley, with insufficient ventilation, pressure from industry and – in adverse meteorological conditions – heating households, can lead to high local levels of pollutants, which are damaging to human health. The analysis of PM_{2.5} and PM₁₀ concentrations in Kielce in the studied period shows that the air quality standards were not exceeded: see Fig. 10a [Regulation of the Minister of Climate and Environment, J. Laws 2021, 845]. However, high concentrations, reaching over 150 μg·m⁻³, were noted in the nights with the lowest temperature, e.g., on 6 and 7 February (Fig. 10b).

5. CONCLUSIONS

Our research confirmed that the snow cover can be applied as a useful and relatively inexpensive source of information about air quality. As was expected, meteorological conditions affected the occurrence of winter smog, with elevated concentration of pollutants in the air. Episodes of sudden air temperature drops were accompanied by increased concentrations of fine particles from household heating. Wind direction and speed also modify air quality, either by dispersing pollutants or by bringing polluted air masses from suburban areas and regional industrial emitters. Intensive development of urban areas leads to elevated emissions from housing estates. The analysis of EC, concentrations of chlorides, sulfates and sodium, indicated the districts which are particularly vulnerable to air pollution in the southern part of Kielce, where fossil fuels are used for heating houses and for transportation. Increased concentration of calcium in this area stems from the impact of the lime and cement industry in the 'White Basin'. As we assumed, declining trends in snow cover thickness and number of days with snow were detected for Kielce in 1996–2022. Therefore, long-term studies of air quality based on this indicator, in dynamic environmental and economic conditions, are difficult. As the presented

Table 4. Selected physico-chemical properties of snow in different regions

Parameter	Unit	Cement and lime industry			Metallurgical industry	Remote pollution	Urban area			
		White Basin, Poland (Kozłowski et al. 2012, Kozłowski, Szwed 2016)	Kunda, Estonia (Kaasik et al. 2000)	Łagów, Poland (Szwed, Kozłowski 2021)	Ostrowiec Św., Poland (Jarzyna et al. 2017)	Świętokrzyski National Park, Poland (Kozłowski, Szwed 2016)	Kielce, Poland 2016/2023 (Kozłowski et al. 2017)	Poznań, Poland (Siudek et al. 2015)	Primorsky Krai, Russia (Kondrat'ev et al. 2015)	Svirsk, Russia (Grebenshchikova et al. 2017)
pH	(-)	6.39		8.05	7.38	5.23	5.59/5.15	4.8	5.05	6.63
EC	(mS m ⁻¹)	3.28		5.91	4.15	2.61	2.78/2.74	2.07	4.2	
Ca ²⁺	(mg L ⁻¹)	4.4	18.8	10	4		2.5/1.8		2.5	8.7
Mg ²⁺	(mg L ⁻¹)	0.2			0.4		0.2/0.1		0.4	1.4
SO ₄ ²⁻	(mg L ⁻¹)	3.2	18.8	1.7	3.6		1.8/1.2		4.9	14.9
NO ₃ ⁻	(mg L ⁻¹)		2.3	2	2.6		3.1/1.1		3.4	1.2

**Figure 10.** Pollution with PM10 and PM2.5 in Kielce – mean daily concentration (a) and hourly data (b). (Based on data from GIOŚ)

research did not give the answer about an eventual increase in air pollution from households, caused by the current geopolitical situation, we plan further studies on polycyclic aromatic hydrocarbons with the use of passive air samplers in the next heating season.

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