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Snow Cover as an Indicator of Dust Pollution in the Area of Exploitation of Rock Materials in the Świętokrzyskie Mountains

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Abstract: Snow cover in environmental monitoring is a valuable resource for information on sources of air pollutants and the level of air pollution. Research in areas of intense industrial pressure without systematic air quality control is of particular importance in this aspect. This is the case in the vicinity of Łagów (an urban–rural municipality) in the eastern part of the Świętokrzyskie Mountains (southern Poland), where rock mining fields have been created over a large area. Limestone, marly limestone and dolomite are mined in this area. The carbonate dust accumulated during the two-week deposition significantly altered the physicochemical and chemical properties of the snow cover. An inductively coupled plasma-mass spectrometer-time-of-flight (ICP-MS-TOF), Dionex 3000 ion chromatograph and Hach HQ2200 water quality meter were used for chemical analyses. The pH, electric conductivity (EC), major ions and selected heavy metals (HM) were determined in water samples obtained after snow melt in two measurement campaigns. The comparative analysis performed showed an increase in pH, EC, Cl, Ca, NO_3, SO_4 and heavy metals in samples from the two-week old cover (second series) compared to fresh snow (first series). The conducted research indicates a potential hazard for the inhabitants of Łagów due to respirable dusts released into the atmosphere during extraction, processing and transport of rock materials.

Keywords: heavy metals; mineral industry; air pollution; indication

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1. Introduction

Mining activity within open-pit mining causes various changes in the natural environment. In addition to altering hydrological, morphological, edaphic and landscape conditions, the extraction and processing of rock materials has a degrading effect on air quality [1–8]. Respirable dusts are particularly hazardous to health [9–11]. Rock mining in Poland has been concentrated within two voivodships [12]. Dolnośląskie (41.7% of the national production) and Świętokrzyskie (33.3%) are characterized by a significant concentration of mining centers. The industrial resources of this district are about 2.5 million tons, of which about 2142 tonnes per year are extracted [12]. Exploitation and fragmentation of rock blocks causes uncontrolled emissions of dust into the atmosphere, which is particularly burdensome for the residents of the town and commune of Łagów. No automatic air quality station is located within the mining area, so a snow cover study can provide valuable information on the extent and variability of the mining industry's environmental impact on the area [13–17].

The purpose of this study was to demonstrate the usefulness of snow cover indicators in identifying anthropogenic impacts on the human habitation zone. Earlier studies of snow cover around the world have shown great effectiveness in identifying sources and levels of air pollution [18]. Researchers have proved the influence of urbanized spaces on the content of individual ions in snow [19–21]. Heavy metals present in the snow cover as a result of transport in the atmosphere over long distances are particularly dangerous in this respect [22,23]. They can freely get into soils and surface waters. Contained metals in fine dust can be dangerous to humans [24,25].

The research carried out by Jóźwiak [26] with the use of an automatic Airpointer type measuring station and dust precipitation collectors confirmed the negative impact of the nearby mines on the air quality in Łagów. The dust precipitation significantly exceeded the value of 200 g m^{-2} per month, which is the annual precipitation standard [27]; additionally, the permissible standards for $PM_{2.5}$ and PM_{10} were exceeded [28].

Kozłowski [29] and Szwed et al. [30] have shown that calcium and magnesium are the main components of dust deposited from the atmosphere around areas of extraction and processing of mineral resources. Cement dust as well as soot and fine slag particles during the winter heating season are also carriers of toxic metals. We deal with such sources of air pollution in the urbanized and industrialized zone near Łagów.

2. Materials and Methods

2.1. Field Measurements

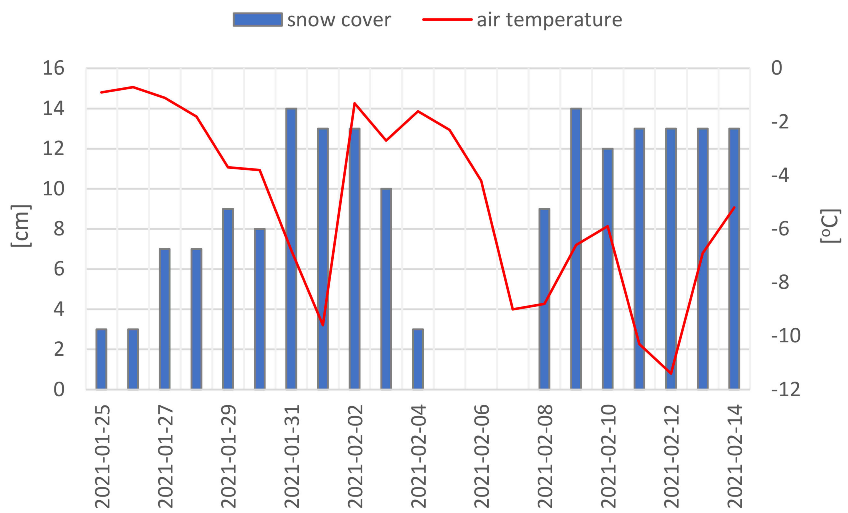
The research area was located within the mesoregion of the Świętokrzyskie Mountains [31,32] and the southeastern part of the microregion, including the Kielecko–Łagowski Vale [33]. Apart from the commonly known in this region center of the White Basin (Białe Zagłębie) in the Świętokrzyskie voivodeship [34–39], an example of the negative impact of rock mines is the mining area in the vicinity of Łagów (an urban–rural municipality with 6880 inhabitants and a population density of 61 inhabitants per 1 km^2 [33]). In the area of approx. 600 ha, 6 operators are located (Łagów II, Łagów III, Łagów IV, Łagów V, Łagów–Nowy Staw, Łagów–Zagościniec), in which dolomites, limestone and limestone marl are mined [40,41]. It is formed by an extensive synclinorium built of Middle and Upper Devonian marls and limestones and Lower Carboniferous sandstones and shales. Local environmental conditions allowed for the development of limestone soils around Łagów, which created good conditions for land cultivation [40]. The surrounding mountain ranges forming anticlinoria made of Cambrian sandstones are covered by mixed forests with pine, spruce, fir and beech.

Thirteen measurement points covering an area of approximately 600 ha were located in the study area (Figure 1), where snow samples were collected twice. Reference snow samples, devoid of influence of the carbonate raw materials from the mining industry, were taken in the Suchedniowsko–Oblęgorski Landscape Park, located about 50 km northwest of Łagów.

Figure 1. Study area with sample points number (developed on the basis of OpenStreetMap 2021).

The snow survey in the vicinity of Łagów was conducted during the longest period of snow cover in winter 2020/2021, i.e., from 25 January to 14 February 2021. The first measurement series took place on 31 January, i.e., at the time of the thickest snow cover in the area with maximum height of 14 cm (data from the Institute of Meteorology and Water Management in Kielce–Suków, located ca. 30 km on the west of Łagów). The study was repeated on 14 February, i.e., after a two-week period of snow accumulation without thaw (Figure 2a). The average air temperature in the period from 25 January to 14 February was −5 °C. The minimum daily temperature was measured on 1 February and was −19 °C, while the maximum was 0.1 °C on 25 January. The average height of snow cover was 8.4 cm. The analysis of anemometric conditions indicates that during the analyzed period, air masses flowed from the northern (36%), western (28%), eastern (20%) and southern (16%) sectors (Figure 2b). The longest snowfall was on 11 February (24 h), with the western wind direction creating a 13 cm snow cover.

(**a**)



(**b**)

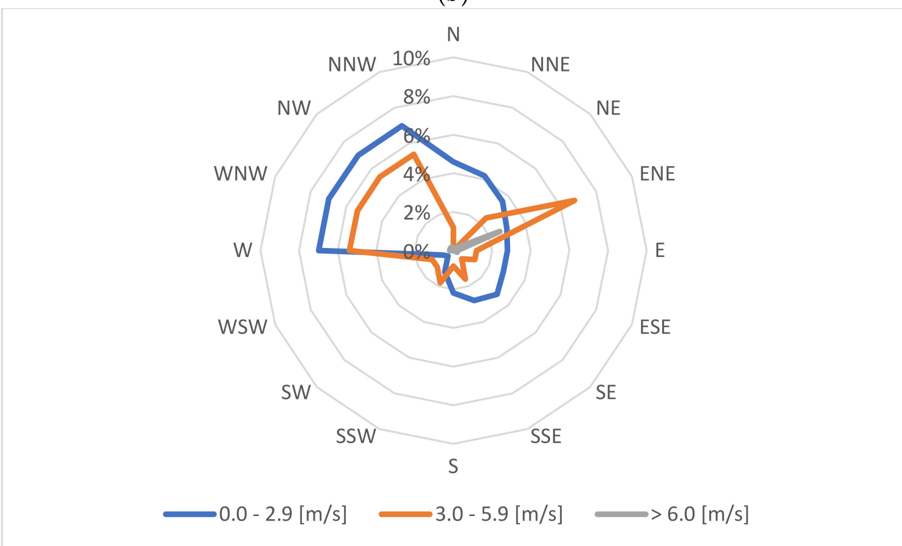


Figure 2. Meteorological conditions: (**a**) air temperature and snow cover depth, (**b**) wind speed and direction during the snow cover research (data from the Institute of Meteorology and Water Management in Kielce–Suków).

Snow sampling was carried out using a 1 m long plastic pipe with a diameter of 100 mm. Each collected sample was a cross-section through the entire thickness of snow cover in a given location. The Suchedniowsko–Oblęgorski Landscape Park, located approximately 50 km northwest of the study area, was adopted as the reference area. Maps of reach of selected elements were plotted using Surfer vs. 16 software. The results of the study were statistically processed using Statistica vs. 13.3. Principal component analysis of variables (PCA) was used for this purpose.

2.2. Laboratory Analysis

The collected cores were entirely transferred to 2 dm^{-3} vessels and transported to the Environmental Research Laboratory of the Jan Kochanowski University in Kielce. In the melted snow samples, after filtration through a Whatman GF/D glass filter (Maidstone, UK, poor size 2.7 μm), pH and electrolytic conductivity (EC) were determined using a Hach HQ2200 multi-parameter water quality sensor (Loveland, CO, USA), the content of Ca^{2+}, Cl^-, SO_4^{2-} and NO_3^- ions using a DIONEX ICS 3000 ion chromatograph (Sunnyvale, CA, USA) and selected metals (Al, Cd, Co, Cr, Cu, Ni, Sr, Pb, Zn) using an ICP-MS-TOF OptiMass 9500 mass spectrometer (GBC Scientific Equipment, Perai, Malaysia). The results obtained were controlled using ERM reference material CA713 (London, UK), wastewater (Table 1). The pH and electrolytic conductivity (EC) were measured using a Hach HQ2200 with an Intellical electrode calibrated with Hamilton buffer solutions (Reno, NV, USA, pH 4.01, 7.00, 9.21, EC—15 mS cm^{-1}).

Table 1. The concentration of elements in the certified ERM-CA713 reference material.

Metals	ERM CA713		ICP-MS-TOF		Difference * %
	Content (μg L^{-1})	**Uncertainty (μg L^{-1})**	**Content (μg L^{-1})**	**Standard Deviation**	
Cr	20.9	0.2	19.7	±2.0	−5.0
Cu	101.0	1.3	99.4	±1.9	−1.0
Ni	50.3	1.4	53.0	±4.3	5.0
Pb	49.7	1.7	51.8	±3.7	4.0

* Relative difference between measured and certified concentration 100%·(cz − cc)/cc.

3. Results

The chemical composition of the analyzed samples revealed the presence of ions whose content was arranged in the following descending order: $Ca^{2+} > Cl^- > NO_3^- > SO_4^{2-}$. Concentrations of all analyzed ions in samples collected in the study area were higher compared to reference samples. The highest multiplicity calculated as the ratio of the mean value to the concentration in the reference sample was found for Al (11.2), Cl (9.3), Sr (8.8) and Ca (7.1). The different sampling locations were accompanied by significant variations in concentration (Table 2, Figure 3). The highest variability was observed for Al (coefficient of variation 154.2), Zn (130.1) and Cl^- ions (105). The source of Cl was probably sodium chloride used for winter road maintenance, as indicated by elevated concentrations in samples from melted snow from the town of Łagow (point 12) and the national route DK 74 (point 10). Elevated Sr, Al, Ca, electrolytic conductivity and pH values of samples collected from the central part of the study area strongly suggested the influence of nearby carbonate rock mining operations fragmenting them on the spot. The geochemical analysis of the Polish Geological Institute (PIG) showed that the composition of the core collected from the nearby field was pH 7.40, Mn 216 mg kg^{-1}, Zn 30 mg kg^{-1}, Pb 8 mg kg^{-1}, Ni 6 mg kg^{-1}, Cu 4 mg kg^{-1} and Cr 3 mg kg^{-1} [29]. Increased vehicle traffic was marked by elevated NO_3^- concentrations in snow collected from the vicinity of the intersection of the Winna and Łagów V mines haulage roads (point 6) as well as DK 74 (point 10) and Łagów market square (point 12).

Table 2. Physico-chemical and chemical properties of the snow samples taken (N-13).

Variable	Series	Unit	Average	Minimum	Maximum	Standard Deviation	Coefficient of Variation	Reference Sample	Multiplication Factor
Ca	I	(mg L^{-1})	2.57	0.1	4.8	1.3	50.6	0.361	7.1
	II		9.97	4.2	21	4.5	44.6	4.341	2.3
Cl	I		4.47	0.1	17.5	4.7	105.3	0.476	9.3
	II		3.50	0.9	12.1	3.1	88.4	0.935	3.8
SO_4	I		0.69	0	1.1	0.4	55	0.939	0.7
	II		1.65	0.9	3.6	0.7	42.3	0.798	2.1
NO_3	I		1.37	0.1	2	0.6	45.3	1.769	0.8
	II		1.96	0.7	3.3	0.9	47.2	1.772	1.1
pH	I	(-)	7.71	6.3	8.4	0.7	8.5	6.76	1.1
	II		8.05	7.1	8.7	0.5	5.8	7.47	1.1
EC	I	(mS cm^{-1})	44.77	20.7	115.3	26.3	58.8	8.91	5
	II		59.10	27.9	90.2	16.5	27	12.67	4.7
Al	I	(μg L^{-1})	22.231	1.6	84.7	24.7	111.3	2.781	8
	II		60.082	1.9	353.7	92.7	154.2	5.346	11.2
Co	I		0.011	<0.039 *	0.1	0.0	360.6	<0.039 *	0.3
	II		0.006	<0.039 *	0.1	0.0	300.2	<0.039 *	0.2
Cr	I		0.612	<0.116 *	2.5	0.9	149.4	<0.116 *	5.3
	II		0.046	<0.116 *	0.6	0.2	360.6	<0.116 *	0.4
Cu	I		0.336	<0.120 *	0.8	0.3	100.1	<0.120 *	2.8
	II		0.045	<0.120 *	0.6	0.2	360.6	<0.120 *	0.4
Ni	I		0.191	<0.018 *	0.9	0.3	156.9	<0.018 *	10.6
	II		0.096	<0.018 *	1.2	0.3	360.6	<0.018 *	5.3
Sr	I		13.164	5.3	39.6	10.7	81.2	1.491	8.8
	II		13.431	7.7	22.3	4.6	34.4	5.114	2.6
Pb	I		0.009	<0.096 *	0.1	0.0	360.6	<0.096 *	0.1
	II		0.014	<0.096 *	0.2	0.1	360.6	<0.096 *	0.1
Zn	I		8.417	<0.139 *	20.5	6.0	71.2	11.367	0.7
	II		3.314	<0.139 *	15.0	4.3	130.1	10.403	0.3

* Under detection limit. N—number of samples.

The decreasing sequence of mean metal concentrations in snow was arranged as follows: Al > Sr > Zn > Mn > Cr > Cu > Ni > Co > Pb. In both series, the highest mean concentrations were recorded for Al (60.1 μg L^{-1}), Sr (13.4 μg L^{-1}) and Zn (8.4 μg L^{-1}). Average concentrations of other metals did not exceed 1 μg L^{-1}.

In order to reduce the number of variables and simplify the description of the research results, a component analysis of the variables was conducted. After standardizing the data and checking for the presence of over-correlated data (correlation matrix), the number of PC1–PC3 components was determined (Table 3).

The sum of the three components represents 75% of the variable components analyzed within the study area. They are related to the location of the mining industry and the preparation of aggregates and their transportation. The first component (PC1) generated 33% of the total variability with high weights for Ca and Sr (≤ -0.7), which explains the strong association with the geogenic source of contamination of the samples. Successively, PC2 shapes 24% of the total variability (highest weights for Cl and pH), which should be associated with the use of road salt to maintain vehicle traffic. PC3 of 18% (with the highest weight for NO_3) is responsible for fuel combustion (Figure 4).

(**a**) (**b**)

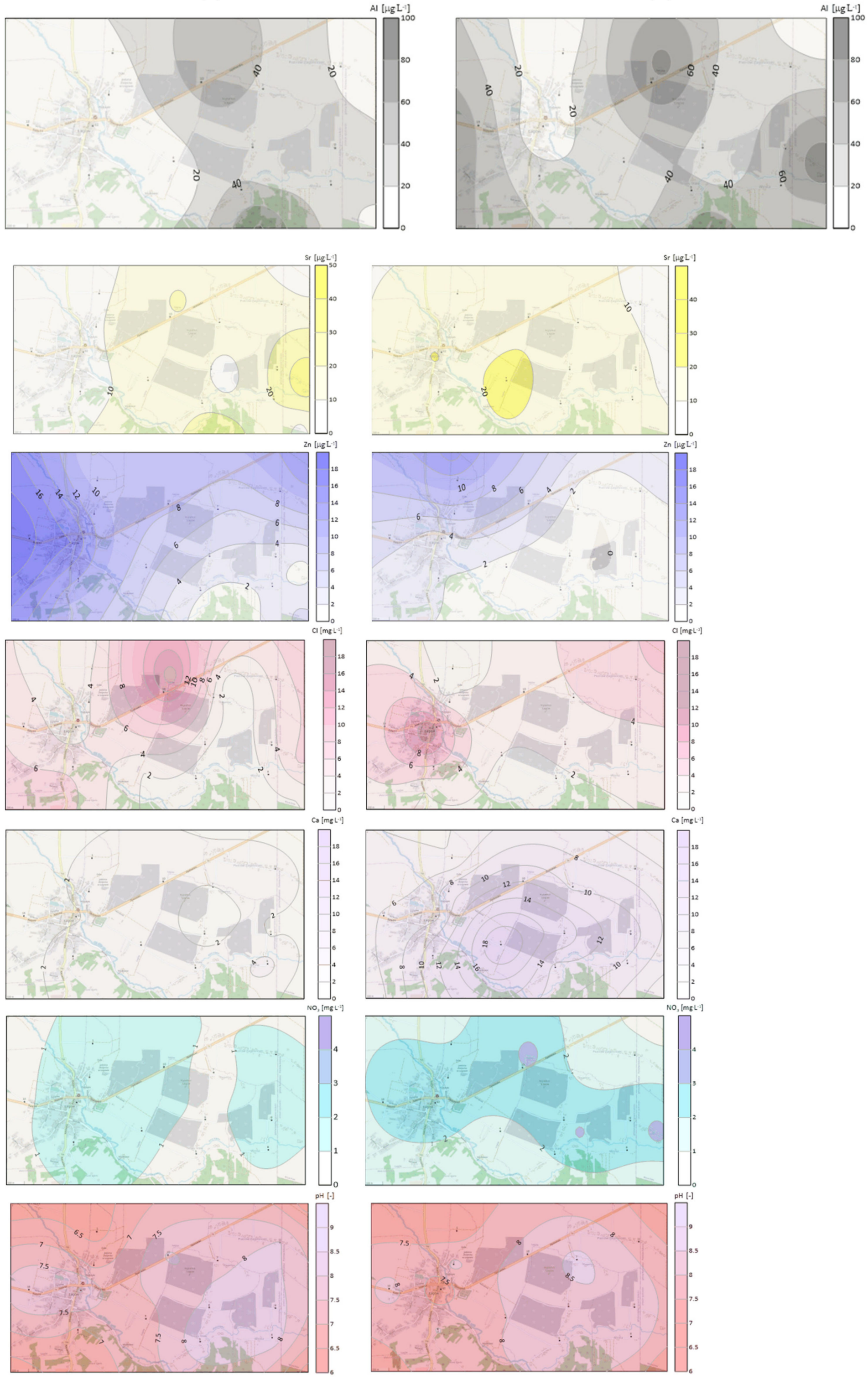


Figure 3. Spatial distribution of selected analytes in the snow cover in the study area: (**a**) first series, left column; (**b**) second series, right column.

Table 3. PCA analysis of the studied physico-chemical parameters (N-13).

Variable	Component		
	PC1	PC2	PC3
Ca	−0.821	0.198	0.252
Cl	−0.067	−0.683	0.130
SO_4	−0.587	−0.246	−0.600
NO_3	−0.486	−0.265	−0.802
pH	−0.340	0.873	−0.005
EC	−0.700	−0.243	0.481
Al	−0.321	0.580	−0.422
Sr	−0.707	−0.534	0.117
Zn	0.706	−0.312	−0.346
% of variance	33	24	18
% in total	33	57	75

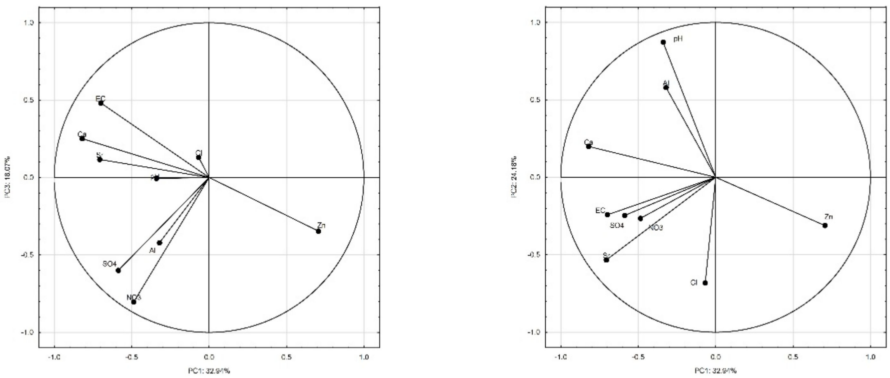


Figure 4. Graphic image of relationships among PC1, PC2 and PC3 components.

4. Discussion

Comparing the obtained results with other industrialized regions of Poland, an unfavorable influence of industrial impacts in the southeastern part of the Kielce–Łagów Vale on the physico-chemical properties of snow cover was found. Both mean and maximum concentrations of analyzed ions as well as pH and EC in the vicinity of Łagów were higher than those recorded in previous years within the Białe Zagłębie [37], Odra Cement Plant [13], Krakow and Upper Silesian Industrial District [14]. The obtained results for elemental composition are also several tens of times higher than those recorded in the monitored reference areas for the Spitsbergen [15] and Waldai Highlands [16] snow cover studies. Similar values of Ca^{2+} ion concentration, $NO_3{}^-$, $SO_4{}^{2-}$ as well as two-fold higher Cl^- concentrations and pH values higher by 1.5 units were found in the Moscow agglomeration [17] with respect to the Kielce–Łagowski Vale. Spatial variation of individual analytes indicates the influence of landforms in pollutant deposition. Mining fields located on hillsides are characterized by elevated concentrations of Al and Sr. In contrast, there was an increase in Zn within the river valley town. Its presence is most probably connected with the presence of ash from domestic coal-fired boiler houses. Its composition, apart from Al (9505.0 mg kg^{-1}), is dominated by Zn (274.9 mg kg^{-1}) [42].

Research on snow cover in Western Moscow [43] and Western Siberia [23] showed the possibility of deposition and transport of the finest particles of anthropogenic origin. Using electron microscopy, they identified, inter alia, carbon particles, slags and dust of anthropogenic origin [23].

The inflow of air from the northwest and northeast directions is typical of the cold winter in this part of Europe. Poor natural ventilation of the city located in the valley [44] combined with unfavorable meteorological conditions (wind speed and direction) [45,46], pressure from the mineral industry and the heating sector may result in the accumulation of pollutants in the air dangerous to human life and health.

5. Conclusions

Fine particles deposited on the snow cover modify the properties of snow and provide valuable information on air pollution. It is therefore an indicator collector of various sources of pollution, both local and remote (Table 4).

Table 4. Comparison of the chemical analysis of the snow cover in Poland and other locations.

Source of Air Pollution	Unit	Cement and Lime Industry		Metallurgical Industry	Remote Pollution	Urban Area			
		Białe Zagłebie, Poland [6,7]	Kunda, Estonia [47]	Ostrowiec Św., Poland [21]	Świętokrzyski National Park, Poland [7]	Kielce, Poland [20]	Poznań, Poland [48]	Primorsky Krai, Russia [49]	Svirsk, Russia [50]
pH	(-)	6.39		7.38	5.23	5.59	4.8	5.05	6.63
EC *	(mS m^{-1})	3.28		4.15	2.61	2.78	2.07	4.2	
Ca^{2+}	(mg L^{-1})	4.4	18.8	4		2.5		2.5	8.7
Mg^{2+}		0.2		0.4		0.2		0.4	1.4
$SO_4{}^{2-}$	(mg L^{-1})	3.2	18.8	3.6		1.8		4.9	14.9
$NO_3{}^{-}$			2.3	2.6		3.1		3.4	1.2
Zn		48.8		57.1	66	49.1	13.2	32	18
Pb			7.7	0.1	0.1	0.5	4.9	0.9	0.5
Cr				0.6	0.1	0.3	0.4		0.4
Cd				0.1			0.1	0.1	0.1
Ni				0.34	0.5	0.2	3.8	0.6	2.3

* EC—electric conductivity.

On the basis of analysis of the study results, a significant contribution of anthropogenic pollution (industrial, municipal and transport) in the formation of the chemical composition and physico-chemical properties of snow samples in the vicinity of Łagów was found. Apart from the elevated concentration of characteristic ions and selected metals, the deposition of alkaline dust is also evidenced by the elevated pH and specific electrolytic conductivity of the slush water (according to Jansen's classification [51] classified as significantly elevated for pH and very strongly elevated for EC). The negative course of deposition of pollutants from the atmosphere, apart from the distance from the emission source, is also strongly affected by the topography, which under certain meteorological conditions may lead to the exceeding of permissible air quality standards. Water capacity is an important parameter when analyzing the variability of the content of selected pollutants in the sampled snow samples. It has a significant impact on the size of the recorded concentrations.

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