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# CHEMICAL PROPERTIES OF SNOW COVER AS AN IMPACT INDICATOR FOR LOCAL AIR POLLUTION SOURCES

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***Abstract***

In this article, selected physical and chemical properties of water originating from melted snow collected in the area of the city of Ostrowiec Świętokrzyski (Poland) in January 2017 were determined. The analysed samples of snow were collected at 18 measurement sites located along the axis of cardinal directions of the world and with a central point in the urban area of Ostrowiec Świętokrzyski in January 2017. Chemical composition was determined using the Dionex ICS 3000 Ion Chromatograph at the Environmental Research Laboratory of the Chair of Environmental Protection and Modelling at the Jan Kochanowski University in Kielce. The obtained results indicated a substantial contribution of pollutants produced by a local steelworks in the chemical composition of melted snow.

**Keywords:** precipitation chemistry, anthropopressure, snow cover

## INTRODUCTION

The use of snow cover as an indicator for the magnitude of deposition of atmospheric air pollutants has already had several decades of tradition in Poland and Europe (Engelhard et al. 2007, Kozłowski et al. 2012, Siudek et al. 2015, Stachnik et al. 2010,). The snow cover proves itself as an efficient collector of airborne pollutants which allows for quick and efficient estimation of airborne pollution concentrations over the entire period of lingering snow cover occurrence. Snowpack is a good indicator of air pollutants, especially nitrate, sulphate and trace metals. It is a known fact that accumulation of chemical substances in a snow cover have an impact on local environment and people health.

The aim of this article was to determine the spatial pattern of impact range of air pollution emittors located in Ostrowiec Świętokrzyski based on the analysis of physical and chemical and chemical properties of the snow cover occurring in the study area. Many publications emphasise that atmospheric cycling of chemical substances depends on weather conditions, orography and particle size distribution (*e.g.* Dossi et al. 2007, Siudek et al. 2011). The knowledge of the chemical composition of snow cover and meteorological conditions is a fundamental issue to know the impact of local anthropogenic sources. Some observations are able to explain the relationships between most air pollutants dynamics in snowpack and pH range, and proximity to major anthropogenic sources.

## STUDY AREA AND METHODS

The field studies were conducted on 31st January 2017 within a radius of 7-9 km around the steelworks CELSA "Huta Ostrowiec" Sp. z o.o. which, along with a heat and power plant in Ostrowiec Świętokrzyski, are the largest air pollution emittors in the county of Ostrowiec Świętokrzyski (Świętokrzyskie Province). The study area is located in the Kamienna river valley, on the border of two subregions of the Kielecka Upland: Iłżeckie Foothill and Opatowska Upland (fig. 1).

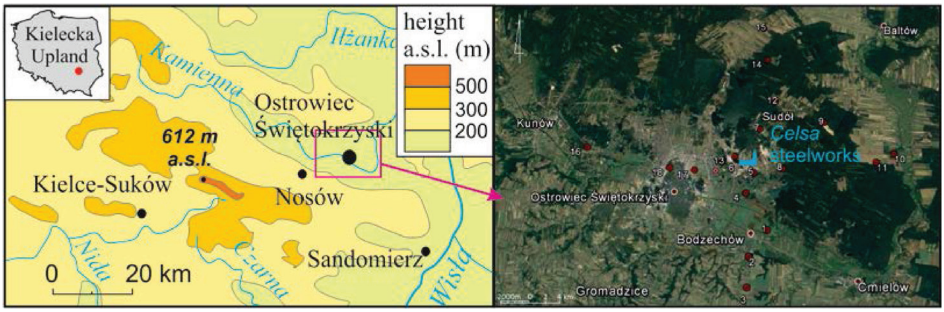



**Figure 1**. Study area and location of snow sampling sites – red circles (right panel – Google Earth 2016, changed).

To the south of Ostrowiec Świętokrzyski, in the loess Opatowska Upland where agricultural lands are dominant forms of land development which do not pose any major obstacles to air pollution propagation. To the east and north of Ostrowiec Świętokrzyski and the steelworks CELSA "Huta Ostrowiec" Sp. z o.o., at the Iłżeckie Foothill there are extensive forest complexes which may partially capture pollutants emitted into the air.

The collected snow samples were taken to the Environmental Research Laboratory of the Chair of Environmental Protection and Modelling at the Jan Kochanowski University in Kielce, where the water originating from the melted snow was analysed with regard to its physical and chemical properties and chemical composition. After a 24-hour heating period in a thermostatic cabinet with a set temperature of +4.8°C, such physical and chemical properties as: pH and specific electrolytic conductivity, as well as chemical composition were analysed. In order to analyse the chemical composition, the Dionex ICS 3000 Ion Chromatograph (Ca, Mg, Na, K, $NH_4$, Cl, $SO_4$, $NO_3$) equipped with the IonPac CS16 3x250 mm analytical column (cations) and IonPac AS18 2x250 mm (anions) was used. The detection level for each parameter was: 0.4 $mg \cdot dm^{-3}$ for $Ca^{2+}$; 0.2 $mg \cdot dm^{-3}$ for $Mg^{2+}$, $Na^{+}$, $NH_4^{+}$; and 0.1 $mg \cdot dm^{-3}$ for other ions. For the quality control of results being obtained, the KEIJM-02 certified reference material produced by *Environment Canada* was used. For measuring pH and conductivity, the Hach HQ 40d multi-parameter water quality meter with electrode, calibrated according to the Hamilton's parameters of pH 4.01, 7.00 and 9.01 as well as 15$\mu S \cdot cm^{-1}$, was used. The values of conductivity were converted from $\mu S \cdot cm^{-1}$ into $mS \cdot m^{-1}$.

In order to assess the meteorological conditions of snow cover formation and snowmelt in the Kielecka Upland, including the area of Ostrowiec Świętokrzyski, the daily data for air temperature, amount and type of precipitation, and snow cover depth was collected from the following meteorological stations of the Institute of Meteorology and Water Management – National Research Institute (IMGW-PIB): Kielce-Suków, Sandomierz and Nosów (precipitation station). Hourly data for wind direction and speed retrieved from the Spanish OGIMET website (https://www.ogimet.com/) and the IMGW-BIP website (https://dane.imgw.pl/) were used as well. The data collected from the IMGW-BIP had been previously processed.

Basic statistics were calculated, such as: arithmetic mean, median, lower quartile, upper quartile, minimum and maximum values, coefficient of variation, as well as coefficient of skewness and kurtosis. The values of Pearson linear correlation coefficient among all determined characteristics of physical and chemical properties and chemical composition were then calculated. Prior to the correlation analysis, a series of variables had been tested for normal distribution which is one of the conditions for proper use of the parametric Pearson correlation coefficient. The Shapiro–Wilk test was used as the normality test. If the test sample did not meet the criterion for normality, the data was transformed in order to normalise them using the *Tukey's Ladder of Powers* procedure. The table only shows those coefficient values being statistically significant at the level of 0.05.

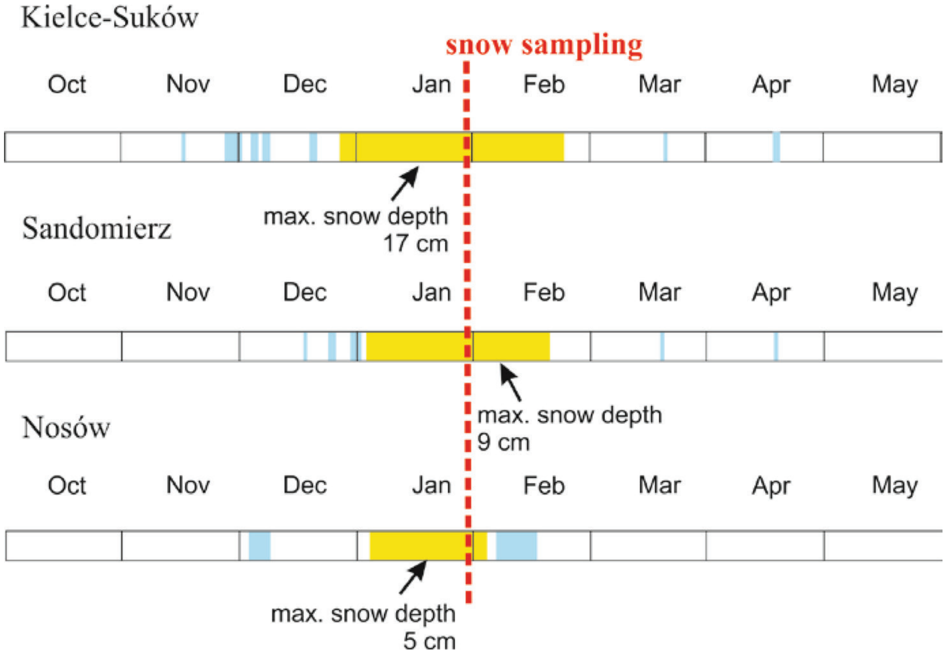
The study also present W-E and N-S cross-section profiles for pH, specific electrolytic conductivity and selected ionic concentrations.

## RESULTS

### *Weather conditions for the winter season 2016/2017*

During the winter season 2016/2017, both the period of lingering snow cover occurrence with a thickness of ≥1 cm and its maximum thickness showed significant spatial diversity in the Świętokrzyskie Province.

At the IMGW-PIB weather station – Kielce-Suków located 50 km west-southwest of the study area, the snow cover had been firstly recorded on 16$^{th}$ November 2016, and for the last time – on 19$^{th}$ April 2017. Thus, the potential period of snow cover occurrence lingering amounted up to 156 days. At the same time, however, the number of days with snow cover (with a thickness ≥1 cm) was only 66 (fig. 2). The maximum thickness of snow cover observed on 16$^{th}$ January 2017 was 17 cm. The values were similar to those mean ones reported for the periods of 2000/2001-2016/2017 (mean number of days with snow cover – 60; maximum thickness of snow cover – 22 cm).




Sources: https://www.ogimet.com and https://dane.imgw.pl)

**Figure 2.** Snow cover occurrence (snow depth ≥1 cm) and maximum snow depth in the Kielecka Upland during the 2016/2017 winter season (own study)

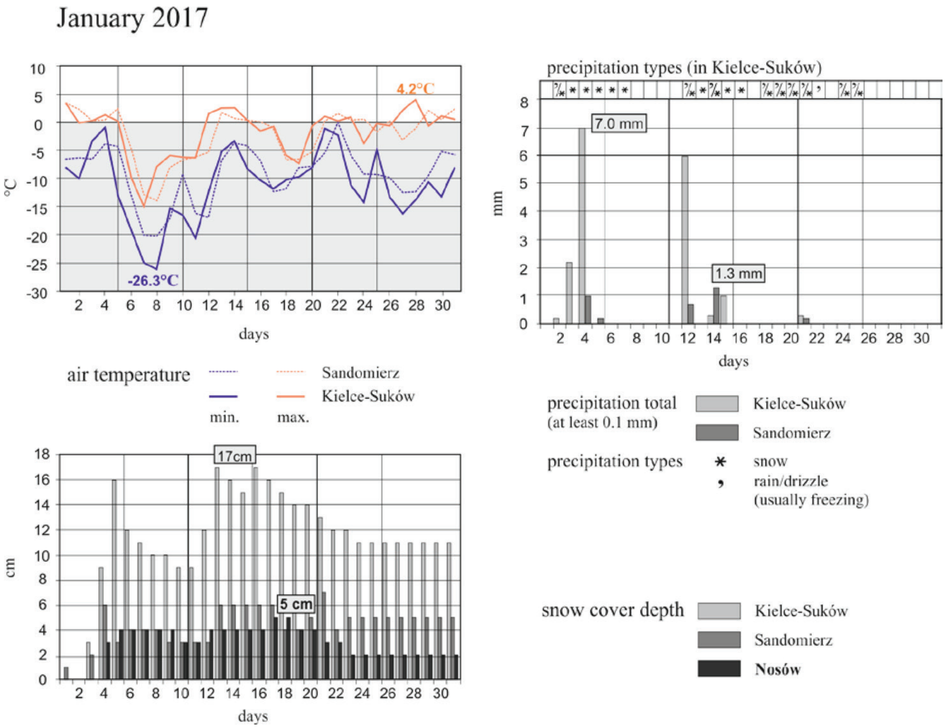
In the eastern part of the Świętokrzyskie Province, the winter of 2016/2017 was much less snowy than in its western and central parts. At the IMGW-PIB meteorological station in Sandomierz located 35 km southeast of the study area, the snow cover had been firstly recorded on 17th December 2016, and for the last time – on 16th April 2017. The number of days with snow cover was lower than in Kielce – 56 days, likewise its maximum thickness – 9 cm in the days 6th-8th February 2017 (fig. 2). The number of days with snow cover was significantly lower than in the 2000/2001-2016/2017 periods (64 days, on average). The maximum thickness of snow cover was also lower than the mean one (21 cm, on average).

The IMGW-PIB precipitation station in Nosów is located in close proximity to the study area (10 km west-southwest of Ostrowiec Świętokrzyski). The number of days with snow cover in the season 2016/2017 amounted only to 46 days there; the snow cover (with a thickness ≥1 cm) had been firstly recorded on 3rd December 2016, and for the last time – on 15th April 2017 (fig. 2). The thickness of snow cover did not exceed 5 cm (17th-18th January 2017).

Regardless of the differences reported in all 3 meteorological stations, the period during which the snow cover was the most persistent lasted from January to early February 2017. The snow samples were collected on 31st January 2017. On that day, the snow cover in the study area had already existed over 4 weeks; thus, during that time, it was a collector for pollutants provided by both precipitation and solid particles deposited on its upper layer.

The mean temperature for January 2017 at the IMGW-PIB meteorological station in Kielce-Suków was – 6.1°C and in Sandomierz – – 5.2°C. In general, the mean air temperature in January 2017 was by 2.0-4.0°C lower than that reported for the Kielecka Upland in the period of 1971-2000 (Climate Monitoring Bulletin of Poland – January 2017, 2017). The mean daily maximum air temperature in Kielce and Sandomierz was as follows: – 1.6°C and – 1.7°C; and the mean daily minimum air temperature: – 11.2°C and – 8.8°C. All the days in the analysed month, both in Suków and in Sandomierz, were days with frost ($t_{min.}$<0.0°C). At the same time, only 16 days in Suków and 14 days in Sandomierz were cold ($t_{maks.}$< 0.0°C). Over the course of months, the largest decrease in air temperature (up to – 26.3°C in Suków and – 20.2°C in Sandomierz on 7th January) was recorded in the second half of the first decade of January 2017 (fig. 3). The highest air temperature – 4.2°C was recorded at the end of the analysed month, i.e. on 28th January 2017.

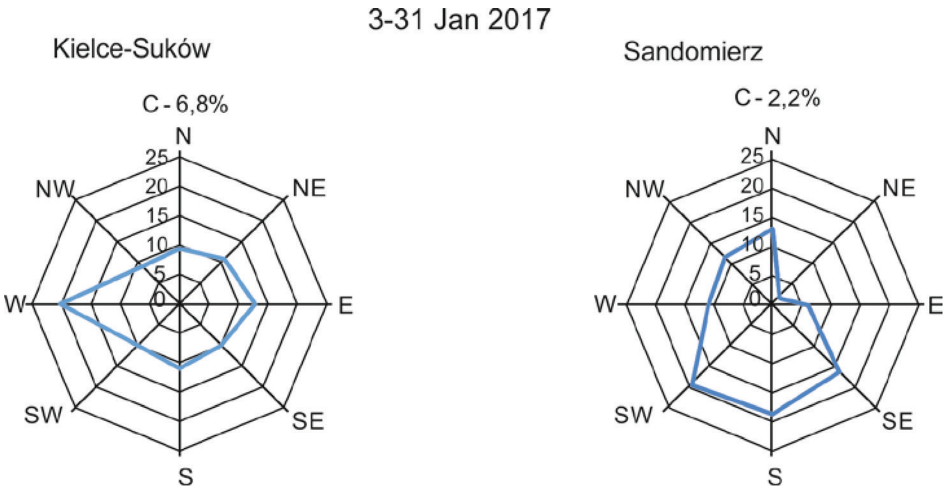
In the periods of 2nd-7th and 12th-25th (with breaks) January 2017, there was precipitation of snow and/or freezing drizzle (rarely frezzing rain) in the Kielecka Upland. Usually, they were bringing very low daily sums of precipitation whose amount was often below 0.1 mm (trace of precipitation). Slightly higher precipitation (the highest one on 3rd January – 7.0 mm) was reported for the central part of the Kielecka Upland compared to its eastern areas (fig. 3). There, the snow cover was thicker as well. The occurrence of precipitation was associated with the appearance of snow cover in the middle of the first decade of January and the increase of its thickness at the beginning of the second decade of January 2017. The least visible increase in the snow cover thickness was reported for the IMGW-PIB precipitation station in Nosów (fig. 2). Sub-zero daily minimum air temperature throughout the entire month made the snow cover thickness stable even during non-precipitation periods.




Sources: https://www.ogimet.com and https://dane.imgw.pl)

**Figure 3**. Weather pattern in the Kielecka Upland in January 2017

During the period of snow cover occurrence, preceding the collection of snow samples (3rd-31st January 2017), the analysed meteorological stations were characterised with predominance of winds from the west (Kielce-Suków – 20.2%) and south-west (Sandomierz – 19.4%) – fig. 4. Calms (C) constituted 6.8% and 2.2% of observations, respectively. The mean wind speed was 2.3 $m \cdot s^{-1}$ at the Kielce-Suków meteorological station and 3.1 $m \cdot s^{-1}$ in Sandomierz. At the Kielce-Suków meteorological station, the highest speed ($\geq$3.0 $m \cdot s^{-1}$, on average) was recorded for winds blowing from the western sector – SW-NW. In Sandomierz, similar speed was reported for winds blowing from a broader sector – from S, through W and to N.




Sources: https://www.ogimet.com and https://dane.imgw.pl)

**Figure 4**. Frequency of wind directions in the meteorological stations located in close proximity to the study area during the snowy period of $3^{rd}$-$31^{st}$ January 2017 (before collecting the snow samples)

On the day of collecting snow samples ($31^{st}$ January 2017), there were numerous gaps in the snow cover in the study area. At the IMGW-PIB precipitation station in Nosów, there were 2 cm of snow on that day. The thickest snow cover (up to 6 cm) was found northeast of Ostrowiec Świętokrzyski. The snow water equivalent reached 17 mm and the measured snow density was in the range of 0.24-0.33 $g \cdot cm^{-3}$.

## PHYSICAL AND CHEMICAL PROPERTIES AND CHEMICAL COMPOSITION OF SNOW COVER

The mean pH value of the analysed snow samples was 7.38 (with variation in the range from 6.31 to 10.18) – tab. 1. All the snow samples had slightly elevated and significantly elevated pH values according to the classification by Jansen et al. (1988); those which were significantly elevated (pH > 6.5) constituted almost 80% of the snow samples.

Specific electrolytic conductivity (SEC) of the samples was ranging from 2.56 to 10.67 $mS \cdot m^{-1}$, with an average of 4.15 $mS \cdot m^{-1}$ (tab. 1). Its values were varying from slightly elevated to very much elevated according to the classification by Jansen et al. (1988). Among the ions found in the snow samples, the highest concentrations were found for: calcium cation $Ca^{2+}$ (mean concentration: 4.00

mg$\cdot$dm$^{-3}$) and sulphate anion $SO_4^{2}$ – (mean concentration: 3.63 mg$\cdot$dm$^{-3}$). Much lower concentrations in the snow samples were recorded for: nitrate anion $NO_3$ – (2.61 mg$\cdot$dm$^{-3}$, on average) and chloride anion Cl – (2.00 mg$\cdot$dm$^{-3}$, on average), as well as ammonium cation $NH_4^+$ (1.30 mg$\cdot$dm$^{-3}$, on average) and sodium cation $Na^+$ (1.04 mg$\cdot$dm$^{-3}$, on average). Potassium cation $K^+$, magnesium cation $Mg^{2+}$ and fluoride anion F – had the lowest concentrations in the snow cover near Ostrowiec Świętokrzyski (tab. 1).

**Table 1**. Basic statistics of physical and chemical properties and concentrations of principal ions in the snow cover in the study area

| Characteristic | | Mean | Minimum | Maximum | Coefficient of variability (%) | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|
| pH | | 7.38 | 6.31 | 10.18 | 17 | 1.18 | -0.14 |
| SEC (mS$\cdot$m$^{-1}$) | | 4.15 | 2.56 | 10.67 | 55 | 2.12 | 4.69 |
| $Ca^{2+}$ | (mg$\cdot$dm$^{-3}$) | 4.00 | 0.90 | 12.61 | 79 | 1.54 | 1.92 |
| $Mg^{2+}$ | | 0.35 | 0.16 | 0.92 | 57 | 1.90 | 3.45 |
| $NH_4^+$ | | 1.30 | 0.77 | 1.90 | 22 | 0.06 | -0.17 |
| $Na^+$ | | 1.04 | 0.72 | 1.83 | 35 | 1.20 | 0.31 |
| $K^+$ | | 0.37 | 0.14 | 1.34 | 75 | 2.78 | 8.77 |
| $SO_4^{2-}$ | | 3.63 | 2.01 | 7.41 | 37 | 1.37 | 2.38 |
| $NO_3^-$ | | 2.61 | 2.01 | 4.26 | 21 | 1.83 | 4.37 |
| $Cl^-$ | | 2.00 | 1.43 | 3.38 | 28 | 1.31 | 1.36 |
| $F^-$ | | 0.15 | 0.03 | 0.37 | 60 | 1.01 | 0.96 |

The coefficient of variation of the snow cover physical and chemical properties and the concentration of the analysed ions was ranging from 17% to 79%. The latter value refers to calcium cation whose concentrations were changing over 14 times and ranging from 0.90 to 12.61 mg$\cdot$dm$^{-3}$. Specific electrolytic conductivity (SEC) and concentrations of such ions as $K^+$, F – and $Mg^{2+}$ were characterised with large dispersion of values (tab. 1).

Except for ammonium ion $NH_4^+$ whose concentrations had almost a symmetric distribution, the other analysed characteristics of the physical and chemical properties and chemical composition of the snow cover were characterised with a right-skewed distribution, as evidenced by the visibly positive values of coefficient of skewness (tab. 1). The most skewed distribution was found for the concentrations of potassium cation $K^+$ and specific electrolytic conductivity (SEC). In both cases, it could be observed that the maximum measured value of the analysed properties was several times greater than the mean value. The samples characterised with the highest values of SEC and $K^+$ concentrations were collected near the steelworks in Ostrowiec Świętokrzyski.

Except for the pH and concentrations of ammonium ion $NH_4^+$, a distribution of the analysed characteristics was leptokurtic (positive values of kurtosis), i.e. their values were more concentrated around the mean than in the case of normal distribution. This concerned especially the concentrations of $K^+$, NO3 – and $Mg^{2+}$, as well as the values of SEC (tab. 1).

Only in the case of ionic concentrations of $NH_4^+$ and $F^-$, the requirement of normal distribution was met, which is required when using parametric statistical methods, such as the Pearson correlation coefficient. The other variables were thus transformed using the *Tukey's Ladder of Powers* procedure. Most of the observed correlations, statistically significant at the 0.05 level, were positive (tab. 2).

**Table 2.** Pearson linear correlation coefficient among the mean values of physical and chemical properties (only statistically significant at the level of $p<0.05$)

| Characteristics | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | pH | | | | | | | | | | |
| SEC | 0.90 | SEC | | | | | | | | | |
| $Ca^{2+}$ | 0.77 | 0.61 | $Ca^{2+}$ | | | | | | | | |
| $Mg^{2+}$ | 0.84 | 0.80 | 0.85 | $Mg^{2+}$ | | | | | | | |
| $NH_4^+$ | | | -0.47 | -0.49 | $NH_4^+$ | | | | | | |
| $Na^+$ | | | | | | $Na^+$ | | | | | |
| $K^+$ | | | | | | | $K^+$ | | | | |
| $SO_4^{2-}$ | 0.69 | 0.76 | | | | | | $SO_4^{2-}$ | | | |
| $NO_3^-$ | | | | | 0.69 | | | 0.59 | $NO_3^-$ | | |
| $Cl^-$ | | | | | | 0.93 | | | | $Cl^-$ | |
| $F^-$ | | 0.58 | 0.62 | 0.67 | | | | | | | $F^-$ |

The strongest correlation ($r \geq 0.9$) was found among the pH and specific electrolytic conductivity (SEC) as well as among the concentrations of sodium ion $Na^+$ and chloride ion $Cl^-$. Moreover, the pH values were positively correlating with the concentrations of ions: $Mg^{2+}$, $Ca^{2+}$ and $SO_4^{2-}$, and the specific electrolytic conductivity (SEC) was additionally correlated with the ionic concentrations of $F^-$. The ionic concentrations of $Mg^{2+}$, $Ca^{2+}$ and $F^-$, as well as $SO_4^{2}$ – and $NO_3$ – were positively correlated as well. In the case of ammonium ion $NH_4^+$, in turn, its concentrations were correlating with the concentrations of nitrate ion $NO_3$ – and at the same time, but negatively (moderate correlations), with the concentrations of cations: $Mg^{2+}$ and $Ca^{2+}$ (tab. 2).

The pH and specific electrolytic conductivity (SEC) as well as concentrations of selected cations and anions were analysed in the two cross-section profiles, i.e. the parallel (W-E) and the meridional (N-S) ones intersecting at the central point constituted by the steelworks CELSA "Huta Ostrowiec" Sp. z o.o.

In the case of pH and specific electrolytic conductivity (SEC), the increase in their values was clearly visible in the immediate vicinity of the steelworks (fig. 5). In the W-E cross-section profile, the highest pH and SEC values were reported for the snow sample collected in about 1.3 km east of the steelworks.

In the N-S cross-section profile, the highest pH and SEC values were reported for the snow sample collected near the southern boundary of the steelworks, about 1.0 km from its main emittors.

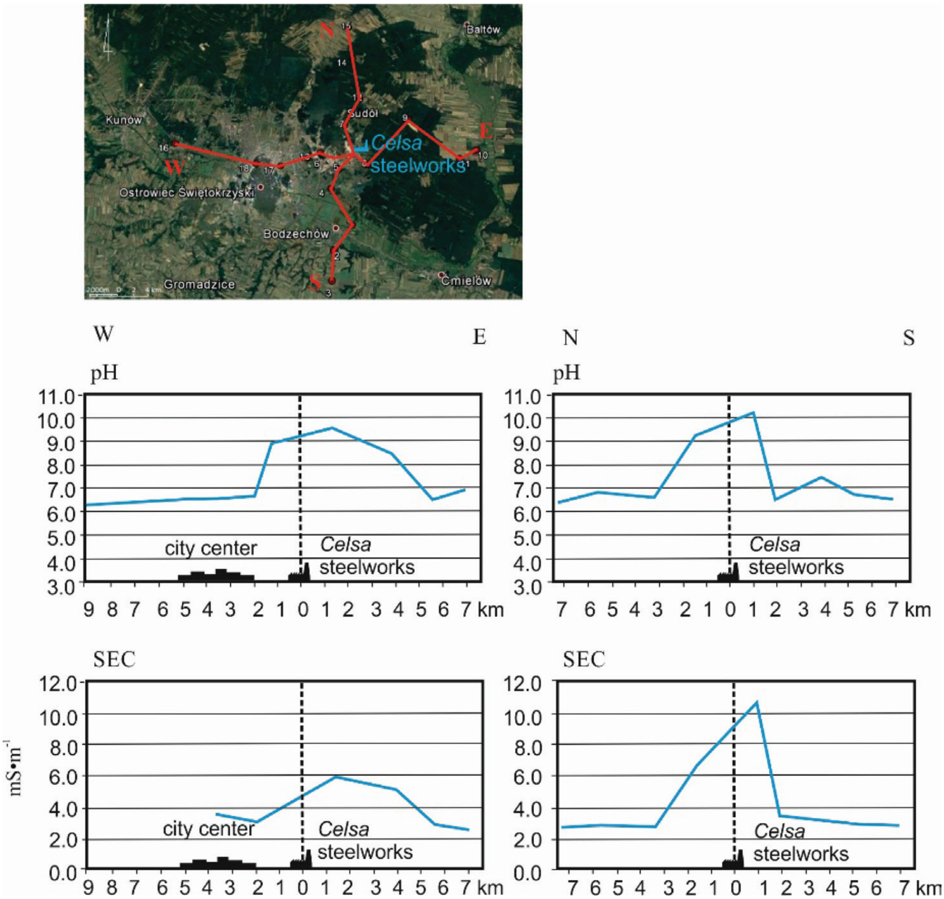



**Figure 5.** W-E and N-S cross-section profiles of pH and specific electrolytic conductivity (SEC, $ms{\cdot}m^{-1}$) recorded for the snow samples collected near Ostrowiec Świętokrzyski and the CELSA steelworks.

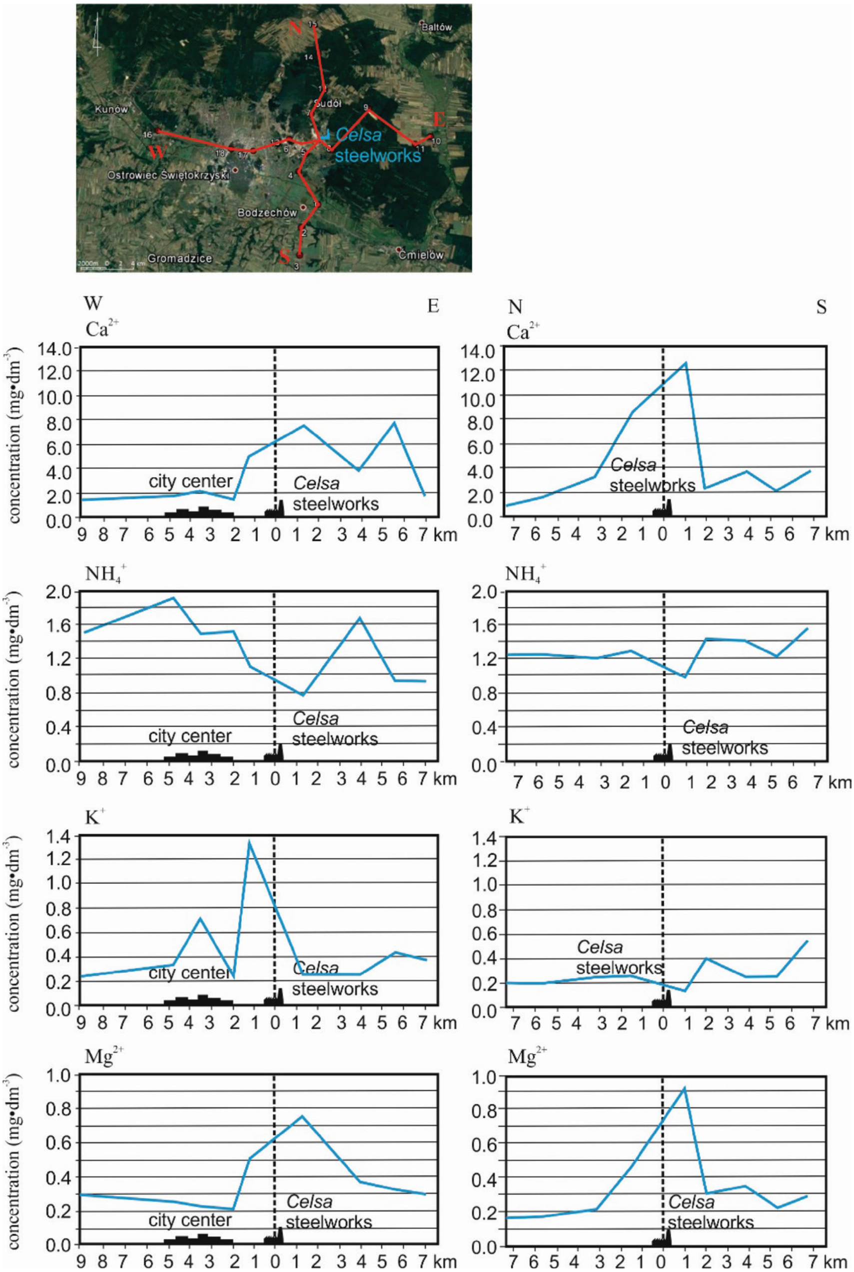



**Figure 6**. W-E and N-S cross-section profiles of principal cation concentrations (mg·m[-1]) recorded for the snow samples collected near Ostrowiec Świętokrzyski and the CELSA steelworks.

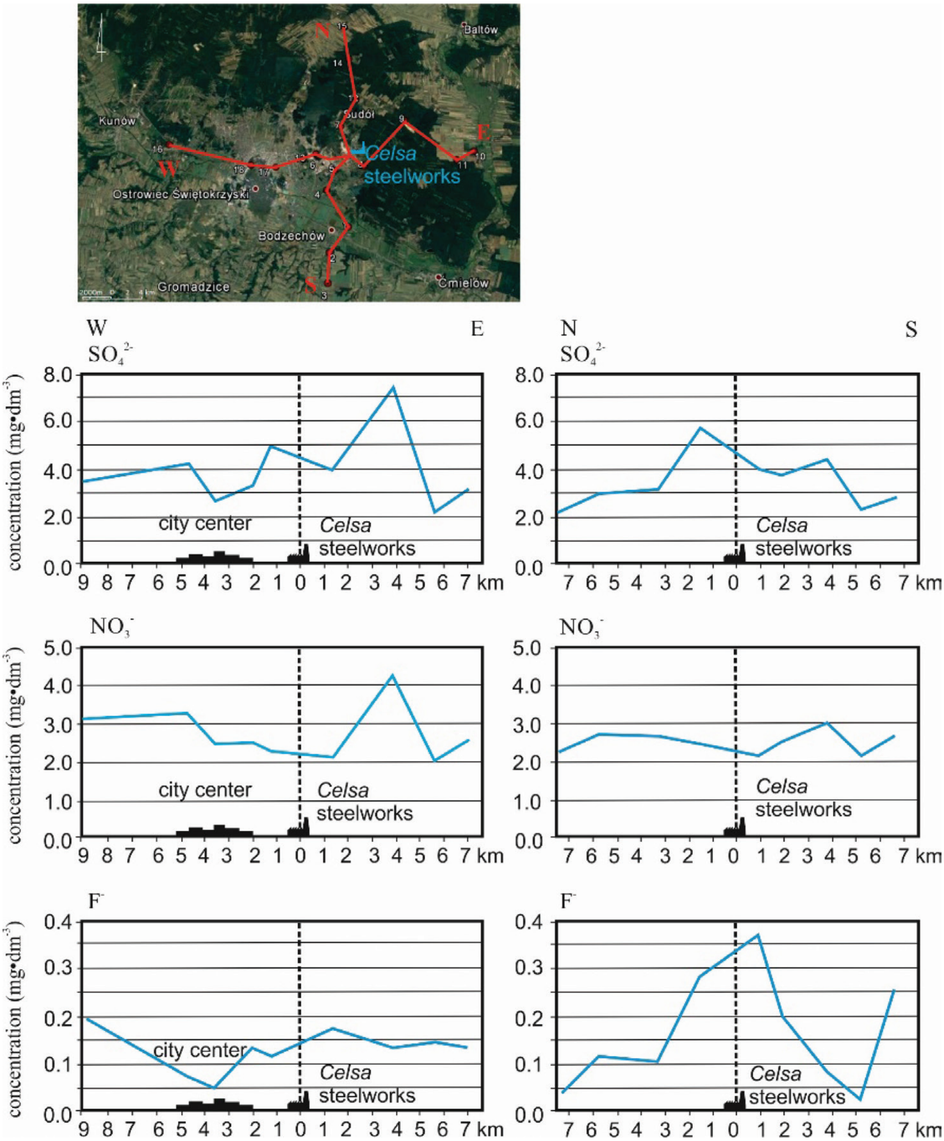



**Figure 7**. W-E and N-S cross-section profiles of principal anion concentrations (mg·m$^{-1}$) recorded for the snow samples collected near Ostrowiec Świętokrzyski and the CELSA steelworks.

The clear impact of the steelworks CELSA "Huta Ostrowiec" Sp. z o.o. on surrounding areas is indicated by the spatial distribution of concentrations of calcium cation $Ca^{2+}$ and magnesium cation $Mg^{2+}$ (fig. 6). In this case, the highest concentrations of the analysed cations were also found in the snow samples collected in the immediate vicinity of the steelworks, as well as in the areas lying east and south of its emittors. High concentrations of calcium ion $Ca^{2+}$ were also found further east of the steelworks, in the snow sample collected in the fields located in the western part of the village of Ruda Kościelna.

Considering the location of snow samples with the highest values of pH, SEC as well as $Ca^{2+}$ and $Mg^{2+}$ concentrations, a dominant wind direction has to be taken into account. As mentioned in the previous subsection, during the period of snow cover occurrence, preceding the collection of snow samples, the dominant winds had been those blowing from the western sector.

The spatial distribution patterns for the ionic concentrations of $NH_4^+$ and $K^+$ in the collected snow samples do not seem to be related to the emission of pollutants by the steelworks CELSA "Huta Ostrowiec" Sp. z o.o. In the W-E cross-section profile, the highest ionic concentrations of $NH_4^+$ and $K^+$ were noted west of the steelworks, which could indicate their emission by the sources found in Ostrowiec Świętokrzyski city (fig. 6). In the meridian profile, there was poorly expressed increase in the concentrations of these ions in the snow cover in the southern part of the study area – in the agricultural Opatowska Upland, compared to the northern part of the study area.

In the case of analysed anions, the relationship among their concentrations and the steelworks CELSA "Huta Ostrowiec" Sp. z o.o. may be indicated by the spatial distribution of concentrations F – (fig. 7), for which the highest values were found near the southern border of the steelworks.

With regard to the concentrations of sulphate ion $SO4_2$ – and nitrate ion $NO_3^-$, the spatial distribution pattern for their variability was more difficult to interpret. In the W-E cross-section profile, their highest concentrations were reported for the snow sample collected in about 3.5 km east of the steelworks, in a large forest glade near the Krzemionki Opatowskie inanimate nature reserve. High concentrations of these ions were also recorded in the snow sample colleted in the very centre of Ostrowiec Świętokrzyski.

## DISCUSSION OF RESULTS

Among the physical and chemical parameters and ions whose concentrations were analysed, there were those whose spatial distribution seemed to be primarily associated with the emission of air pollutants by the steelworks CELSA "Huta Ostrowiec" Sp. z o.o., as well as those which were less associated with it.

The highest values of pH, specific electrolytic conductivity as well as ionic concentrations of $Ca^{2+}$, $Mg^{2+}$ and F – were found at the sampling sites located in the closest proximity to the steelworks. The above-mentioned components of snow cover chemistry were closely and positively correlated with themselves.

Steel dust is an important source of CaO and MgO (Sitko, 2014). Steel production uses limestone and dolomite, among others (Burchart-Korol, 2010). According to Sorek and Ostrowska-Popielska (2012), the process of steel smelting in electric arc furnaces, which are used in the CELSA steelworks, is an important source of emission of particulate and gaseous pollutants, including metal oxides. Steel production process in this type of furnaces along with downstream processing may also be an important source of emissions of dioxins and furans (PCDD – polychlorinated dibenzo-p-dioxin, PCDF – polychlorinated dibenzo-p-furan, PCB – polychlorinated biphenyls), as well as aromatic hydrocarbons (Chen et al., 2011). As noted by Jarzębski and Kapała (1975), the amount of emitted dust from electric furnaces ranges from 1 to 17 $mg \cdot kg^{-1}$ of steel, including, among others, calcium oxides in the amount from 4 to 20%. Mróz (2006), when analysing the chemical composition of steel dust, finds that 7% (mass fraction) was MgO and 6% – CaO.

In the W-E cross-section profile, the highest values of pH, specific electrolytic conductivity (SEC) as well as ionic concentrations of $Ca^{2+}$, $Mg^{2+}$ and F – were reported for the site located about 1.5 km east of the steelworks, so in the direction in which the wind was blowing the most. In the N-S cross-section profile, their highest values were found about 1 km south of the main steelworks emittors. Considering the most dominant wind direction at the IMGW-PIB meteorological station in Sandomierz (SW), it could be expected that the higher values of the analysed characteristics would be found north of the steelworks. However, the site with the highest values of pH, SEC and ionic concentrations of $Ca^{2+}$, $Mg^{2+}$ and $F^-$ was located more closely to the steelworks centre.

The ionic concentrations of $SO_4^{2-}$ and $NO_3^-$ were more weakly related to the air pollution emittors belonging to the steelworks CELSA "Huta Ostrowiec" Sp. z o.o. Their highest values were reported for the site located about 4 km east of the steelworks. Probably, this could be due to greater mobility of sulphur and nitrogen oxides, i.e. the main source of ions $SO_4^{2-}$ and $NO_3^-$, than dust pollution being the source of ions $Ca^{2+}$ and $Mg^{2+}$. It could also be seen that $Ca^{2+}$ was the most important ion in close proximity to the steelworks (within a radius of 2-3 km); however, the further from it, the most common among the analysed ions were sulphate ion $SO_4^{2-}$ and nitrate ion $NO_3^-$. According to Siudek et al. (2011) during heating period, anthropogenic emission of potentially toxic substances from coal combustion is much higher than non-heating season, causing the pronounced increase in air pollution.

The highest concentrations of $K^+$ were found at the site near the steelworks (about 1.5 km from its centre), but on its western side, i.e. in the opposite direction than that the most dominant one. Perhaps, the increase in the concentrations of $K^+$ could be caused by the sources located in the area of the city. The ionic concentrations of $NH_4^+$, $Na^+$ and Cl– (the two latter ones are not presented in fig. 6) had the weakest relations with the air pollution emittors of the steelworks CELSA "Huta Ostrowiec" Sp. z o.o. The concentrations of $NH_4^+$ were quite closely and negatively correlated with the concentrations of $Ca^{2+}$ and $Mg^{2+}$. The highest values of $NH_4^+$concentrations were found in the very centre of Ostrowiec Świętokrzyski.

To some extent, also noteworthy is to mention about the effect of a barrier to air pollution dispersion, which is a forest complex located to the east and north of the steelworks. The values of the majority of analysed chemical and physical and chemical parameters were becoming lower east of it. One exception was constituted by relatively high concentrations of calcium ion $Ca^{2+}$, also at a distance of about 6 km east of the steelworks – already outside the forest complex. Probably, they could be related to a deposition of soil particles rich in calcium carbonate as a result of the intensification of wind erosion, which is typical for winter seasons. This is even more likely, because, as described earlier, there were gaps in snow cover during its sampling. Soil particles deposited on the snow surface could also affect the high pH values of snow samples collected in the study area – not lower than pH 6.31.

These values were, however, lower than those in the so-called *Białe Zagłębie* district (with the cement plant belonging to Dyckerhoff Polska located in the village of Nowiny, in the centre of that district), where similar studies were conducted in the winter season 2011/2012, among others (Kozłowski et al., 2012). In the *Białe Zagłębie* district, the ionic concentrations of $Ca^{2+}$ in the analysed snow samples were also higher. However, the concentrations of $Mg^{2+}$ and $SO_4^{2-}$ were slightly lower there.

The impact of the steelworks CELSA "Huta Ostrowiec" Sp. z o.o. and other sources of air pollution in the city of Ostrowiec Świętokrzyski on the surrounding areas, determined on the basis of the analysis of snow cover chemistry, proved to be greater than in the area east of the metallurgical complex ArcelorMittal Poland located in the district of Nowa Huta in Kraków during the winter season 2005/2006 (Stachnik et al., 2010). The pH values found in this area were significantly lower (pH 5.95, on average) than around the steelworks CELSA "Huta Ostrowiec" Sp. z o.o. East of Nowa Huta, the mean values of specific electrolytic conductivity as well as concentrations of all analysed ions, except for magnesium one, were also lower. However, it is important to underline that the coefficient of variation in the area adjacent to the iron-and steelworks ArcelorMittal Poland was much higher than in the study area, often exceeding 100%. Probably, this could be the effect of lower average wind speed. Before collecting the snow samples, the average wind speed in Kraków was 0.9 $m \cdot s^{-1}$, and in the Kielecka Upland – >2,0 $m \cdot s^{-1}$, on average. Significantly lower pH values were found during the winters of 2009 and 2010 in the snow cover on the island of Wolin, which is not subjected to such strong anthropopressure as the areas lying in close proximity to Ostrowiec Świętokrzyski. At the same time, however, a number of analysed snow samples showed elevated values of specific electrolytic conductivity, comparable to those found around Ostrowiec Świętokrzyski. This mainly concerned the snow samples collected in the vicinity of the sea shore, where there is the largest deposition of sea aerosols. Snow pH values found in the city of Częstochowa, especially in car parks and close to busy traffic arteries, were much lower than in the study area as well (Ociepa et al., 2015).

## CONCLUSIONS

Basing on the conducted studies, the following conclusions may be drawn:

- CELSA "Huta Ostrowiec" Sp. z o.o. constitutes an important emission source of calcium and magnesium ions
- as a result of emissions of gaseous and particulate pollutants, the values of pH, specific electrolytic conductivity as well as calcium and magnesium ions increase in the immediate vicinity of the steelworks
- values of pH and specific electrolytic conductivity are the most strongly correlated with calcium and magnesium ions
- snow cover appeared to be good indicator of pollution emitted by the metal processing industry.

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