



The Impact of Air Pollution on Rainwater Quality

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1. Introduction

Concentration of pollutants in the atmosphere varies in a wide range of values depending on the distribution of pollution source, chimneys' height, emissions, topographical conditions, and in particular the very changeable weather conditions (Leitmanová et al. 2007). Minimizing emission production is also related to issues of diagnosis and monitoring of emission and pollution load, especially densely populated economic and industrial sites. Significant air pollutants are heating plants and thermal power plants, waste incinerators, chemical industry, transportation, surface mining and nuclear energy. Emissions from these sources affect agricultural production cumulating at soil surface and decrease soil characteristics. This leads to soil acidification, alkalization of soils and metallization, it also causes reduction of yields and descent performance of animals.

Automatized monitoring systems associated with regional and international (global) networks, with the emphasis of monitoring human aspects, sufficiently cover this sector, in particular the agricultural and forest land. Frequently used quantitative methods for the registration of short-term extremes are quite hardware demanding and require energy facilities. Summation methods are inaccurate and certainly have not detected extreme situations that distort the system limit concentrations and critical loads ecosystems (Szomorová et al. 2013).

2. Material and methods

2.1. Materials and methodology are based on the following steps:

- The area Oslany was selected as a subject to research due to its close distance to thermal power plant being a source of pollution, Nitra as average-sized city in western Slovakia, with various industrial activities and vehicular traffic and Kežmarok town with relatively clean air and an average load of particulate pollutants substances where the Automatic monitoring station (AMS) data were collected and the collection containers for precipitation were placed,
- Research was realized from October, 1st, 2012 to the present time in the monthly sampling interval,
- The analyzes of rainfall were done using HI 991300, colorimeter DR / 890, the conductivity meter 14d HQ and DR 6000 spectrophotometer and the monitored parameters such as temperature, pH, conductivity, TDS (soluble), the amount of the compounds $\text{PO}_4^{-3}\text{-P}$ ($\text{mg}\cdot\text{l}^{-1}$), $\text{NO}_3^{-}\text{-N}$ ($\text{mg}\cdot\text{l}^{-1}$) and SO_4^{-2} ($\text{mg}\cdot\text{l}^{-1}$).

2.2. Characteristics of the monitored areas

We selected three locations for our experiment: The first monitored area was Oslany representing a load area, situated near the Slovak power plant Nováky. Nováky is one of the key industrial and energy centers. In the Nováky neighborhood has been mined lignite which is burned in the local power plant, whose chimney is one of the highest (300 m, diameter 13.8 meters at the inlet, outlet 8 m) in Slovakia. The second point source pollution in this power plant is 150 m high chimney with Ø 6.28 m input and Ø 9.64 m in the output. The third researched area is medium-sized regional town (87,533 inhabitants) Nitra representing urbanized area. The last area of research is Kežmarok located near High Tatra representing the lowest air pollution area.

2.3. Analysis of rainwater samples

Glass container with a capacity of 5 liters stored in metal containers were used to catch rainwater (Fig. 1). Rainwater collection was performed by quantitative pouring from the receiver to a clean, labeled and hermetically sealable container transport. Transport of rainwater samples was carried out as soon as possible, usually within 60 minutes. In most cases, analyzes were performed immediately after transportation of sam-

ples, only in rare cases, the samples were stored in the chemical laboratory in a cool (5°C), dark place. Analyses of the rainwater were conducted at the same temperature 22-25°C through all devices listed below.



Fig. 1. Container for collecting rainfall – area AMS Oslany (Author)

Rys. 1. Chwytnacz opadów atmosferycznych z powierzchni AMS Oslany

2.4. Analysis of rainfall using device HI 99300

The HI 99300 (HANNA INSTRUMENTS, Woonsocket, Rhode Island, USA, 2012) measures pH, conductivity, TDS (Total Dissolved Solids) and temperature. Prior to the immersion of the probe to the measuring sample we rinse the probe in sufficient amount of distilled water. The measured pH, conductivity and dissolved substances were subtracted by immersion probe in the sample and by selecting the desired parameter using the set hold.

2.5. Analysis by DR Colorimeter / 890

Colorimeter DR / 890 (Hach Lange 2009) is mainly used for rapid field measurements of water parameters using conventional packed HACH reagents. In our experiment, it was PO_4 ($\text{mg}\cdot\text{l}^{-1}$) and $\text{NO}_3\text{-N}$ ($\text{mg}\cdot\text{l}^{-1}$) pour into a cuvette reagent appropriate for a given parameter. The device subtracts the appropriate time needed for the reaction between rainwater sample and reagent in the cuvette.

2.6. Portable conductivity meter HQ 14d

It is a waterproof device for measuring conductivity, temperature and dissolved substances. Range and accuracy of the device for conductivity is $0.01 \mu\text{S}\cdot\text{cm}^{-1}$ and $200 \text{ mS}\cdot\text{cm}^{-1} \pm 0.5\%$ of the measured value and the temperature of -10°C to $110^\circ\text{C} \pm 0.3^\circ\text{C}$ (Hach Lange 2006). The device provides automatic 1-point calibration of conductivity with 0.1-0.01 to 0.001 $\text{mol}\cdot\text{l}^{-1}$ KCl.

2.7. DR 6000 Spectrophotometer

Pipetted sample in the cuvette is inserted into the device. In the next step we pour or pipette (depends on methods used) the reagent into the cuvette, start the timer and thoroughly mix the sample. The time required for the reaction of the sample with the reagent as well as the type of reagents is specified for each compound separately. In our case it was 15 minutes for nitric nitrogen, 5 minutes for sulphato sulfur and 3 minutes for phosphate phosphorus. Subsequently we insert the cuvette into the sample cuvette adapter, we close the cover and run the analysis.

3. Results and discussion

3.1. Air quality

Anthropogenic air pollution gets mostly into the elements of rainwater in the under clouds layer. Precipitation is in this respect an important element of self-cleaning air. Observations have shown that immediately after the rain or even in the duration of the rain, the air contains significantly less polluting impurities than before the start (Braniš & Hůnová 2009).

Air quality measured AMS station Nitra and Oslany for the pollutants SO_2 and NO_x in the period from October 2012 to May 2014 is shown in Figure 2.

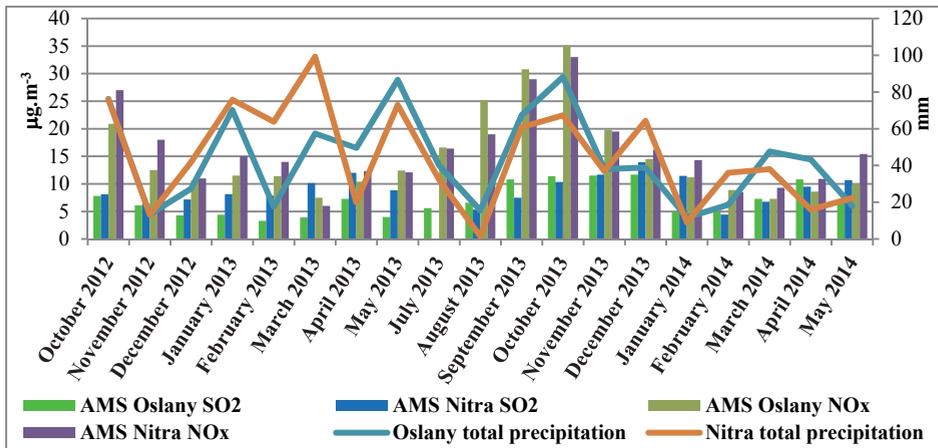


Fig. 2. The measured emissions of NO_x and SO₂ in the area of Nitra and Oslany and average rainfall

Rys. 2. Pomierzone emisje NO_x i SO₂ oraz średnia suma opadów atmosferycznych na terenie Nitry i Oslany

3.2. Analysis of samples of rainwater

The analyzes of rainwater were carried out using HI 99300, Colorimeter DR/890, the conductivity meter HQ 14d and DR 6000 spectrophotometer. With these instruments in the laboratory, we monitor parameters such as temperature, pH, conductivity, TDS (organic substances), the amounts of the compounds PO₄⁻³-P (mg·l⁻¹), NO₃⁻-N (mg·l⁻¹) and SO₄⁻²-S (mg·l⁻¹). The pH was set at 30 day intervals, which could affect the increased incidence of basic values. Random analyses (immediately after the end of rain), however, failed to prove this claim. It is necessary to mention the fact that the development of recent years in reducing concentrations of acidifying compounds (SO₂, NO_x, CO₂), has resulted in increasing the pH measured in precipitation. This argument is shared by the authors of the report to EMEP, Mitošinková, Závodský, Marečková and Pukančíková. The report summarizes the results measured by meteorological stations included in the European EMEP monitoring network, which shows the trend of the pH values increase with the decrease of sulfur compounds in the atmosphere (EMEP 2004). pH of rainwater can be modified by dissolution, and reactions of substances that cause air pollution or substances presence in the air. It is mainly NH₃, SO₂, and NO₂ (Ibanez et al. 2010). Network of about a hundred EMEP monitoring

stations distributed in 30 countries across Europe also recorded parameter pH, which ranges from 3 to 7.5 (Namiesnik 2010).

In captured rainwater pH reached an average value of 7.12 ± 0.614 (maximum 7.92, minimum 5.38) in the area of Oslany; Nitra 6.85 ± 0.760 (maximum 8.38, minimum 4.82) and location Kežmarok 6.61 ± 1.139 (maximum 7.91, minimum 4.45) (table 1). Figure 3 shows that most values measured in all the 3 locations exceeded “normal value – pH 5,6”, yellow line. Parameter pH was relatively stable, as it was in the basic values and showed no extreme measured values. The highest reached value of 8.38 was recorded in August 2013 in Nitra. The minimum pH of 4.45 was recorded in the area of Kežmarok in February 2013. Today's typical pH values of precipitation in Central Europe are in the range of values from 4.5 to 5.0 (Horák et al. 2011). Precipitation with a pH of 4.5 can e.g. contain high levels of sulfur and high levels of nitrogen, or both. In addition to these, there are also oxides in the atmosphere from human activity and even those can affect the acidity of rainwater (Park 2013). Radojević and Bashkin (2006) as well as authors Feyen, Shannon, Neville (2009) report that pH parameter and conductivity in precipitation water down in fresh samples using electrochemical methods.

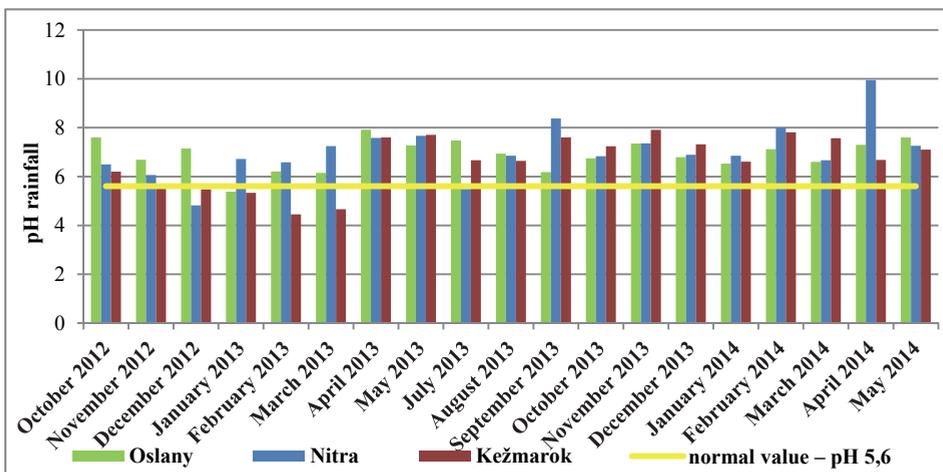


Fig. 3. pH parameters measured in 3 locations, yellow line represents pH 5.6
Rys. 3. Odczyn wody opadowej z trzech punktów, kolorem żółtym oznaczono wartość pH 5,6

Conductivity can be used as a benchmark measurement for the total concentration of inorganic constituents of water. Its value increases with increasing mineral content in the water. Fresh distilled water has a conductivity of from 0.0005 to $0.002 \text{ mS}\cdot\text{cm}^{-1}$, older distilled water 0.002 to $0.004 \text{ mS}\cdot\text{cm}^{-1}$, rain water ranges from 0.003 to $0.06 \text{ mS}\cdot\text{cm}^{-1}$, fresh water 0.05 to $1.5 \text{ mS}\cdot\text{cm}^{-1}$ and waste water more than $10 \text{ mS}\cdot\text{cm}^{-1}$ (Radojević & Bashkin 2006).

For most countries in the United States included in the national monitoring network for the measurement of conductivity was observed rainfall typical value $0,025 \text{ mS}\cdot\text{cm}^{-1}$. In Ishiushi, Japan were detected fairly representative conductivity values of $0.014 \text{ mS}\cdot\text{cm}^{-1}$ set out in the snowfall. It was also shown that the melted ice and snow in winter have almost the same conductivity as rainfall in summer (Farzaneh & Chisholm 2009). Within conductivity measurements of collected rainfall we reached similar results in our experiment, since modus conductivity in the area Oslany reached $0,020 \text{ mS}\cdot\text{cm}^{-1}$, $0.030 \text{ mS}\cdot\text{cm}^{-1}$ in Nitra and $0,030 \text{ mS}\cdot\text{cm}^{-1}$ in the area Kežmarok. Conductivity in the Nitra area reaches a minimum value of $0.01 \text{ mS}\cdot\text{cm}^{-1}$, a maximum of $0.2 \text{ mS}\cdot\text{cm}^{-1}$ and the average value of $0.06 \pm 0.055 \text{ mS}\cdot\text{cm}^{-1}$. In Kežmarok was a the minimum $0.01 \text{ mS}\cdot\text{cm}^{-1}$, maximum $0.27 \text{ mS}\cdot\text{cm}^{-1}$ and the average of $0.074 \pm 0.069 \text{ mS}\cdot\text{cm}^{-1}$. The locality Oslany reached a minimum $0.02 \text{ mS}\cdot\text{cm}^{-1}$, maximum $0.13 \text{ mS}\cdot\text{cm}^{-1}$ and the average of $0.062 \pm 0.038 \text{ mS}\cdot\text{cm}^{-1}$ (table 1). During the reported period, there were two significant variations compared to other values. These were measured in the area of Kežmarok (07.08.2013 to 09.06.2013 and 06.10.2013 to 11.05.2013) of $0.27 \text{ mS}\cdot\text{cm}^{-1}$ and $0.21 \text{ mS}\cdot\text{cm}^{-1}$. The above deviations were probably caused by organic compounds origin.

Table 1. Descriptive statistics for the pH, conductivity, soluble substances of rainwater in the monitored sites
Tabela 1. Statystyka opisowa dla pH, przewodności elektrycznej właściwej, substancji rozpuszczonych w wodzie opadowej w monitorowanych punktach

Statistical function	pH			(mS · cm ⁻¹) conductivity			(ppt) soluble substances		
	Oslany	Nitra	Kežmarok	Oslany	Nitra	Kežmarok	Oslany	Nitra	Kežmarok
Average	6.939	6.854	6.611	0.062	0.073	0.074	0.035	0.037	0.047
Error of the mean	0.492	0.608	0.937	0.032	0.043	0.046	0.018	0.019	0.036
Median	7.12	6.85	6.67	0.05	0.06	0.06	0.03	0.03	0.03
Modus	7.48	6.85	7.6	0.02	0.03	0.03	0.02	0.02	0.01
SD	0.614	0.872	1.139	0.038	0.055	0.069	0.023	0.026	0.05
Sharpness	-0.772	-0.566	-0.65	0.639	1.195	2.007	0.909	1.374	1.783
Obliquity	0.515	0.922	-0.876	-0.963	0.649	3.954	0.088	1.628	2.479
Variance margin	2.54	3.56	3.46	0.11	0.19	0.26	0.08	0.09	0.17
Variance is (n-1)	0.359	0.76	1.296	0.001	0.003	0.005	0.001	0.001	0.002
Minimum	5.38	4.82	4.45	0.02	0.01	0.01	0.01	0.01	0.01
Maximum	7.92	8.38	7.91	0.13	0.2	0.27	0.09	0.1	0.18
Sum	145.709	116.51	112.38	1.292	1.24	1.254	0.725	0.623	0.797
Coefficient of variation	0.086	0.123	0.167	0.605	0.736	0.905	0.642	0.685	1.032

The parameter of soluble substances (TDS) was recorded in Nitra area with minimum 0.01 ppt, 0.1 ppt and maximum diameter of 0.037 ± 0.026 ppt. The area Oslany reached minimum of 0.01 ppt, 0.09 ppt and maximum diameter of 0.035 ± 0.023 ppt. The site Kežmarok reached minimum of 0.01 ppt, 0.18 ppt and maximum diameter of 0.047 ± 0.050 ppt (table 1). Overview of each of the measured quantities are shown in figure 4.

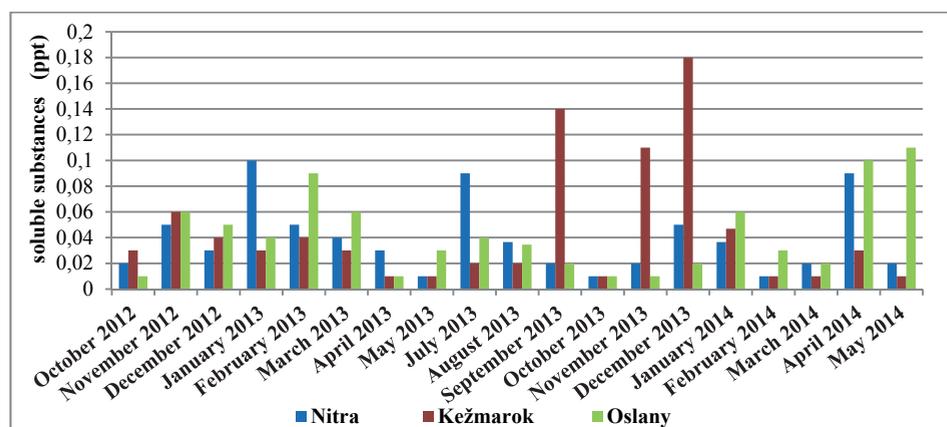


Fig. 4. Overview of total dissolved solids of rainwater in the monitored sites

Rys. 4. Zawartość substancji rozpuszczonych w wodzie opadowej w monitorowanych punktach

In localities with the same load (Nitra and Oslany), there were measured almost the same values of this parameter. Regarding the burden of study sites by air pollutants, the highest average value in Kežmarok can be explained by the presence of soluble substances in the presence of other substances in precipitation water, which have a predominantly organic nature. An interesting finding is the fact that the conductivity was approximately 1.92 times greater than that of soluble substances. Regression tests depending on the conductivity of soluble substances, showed the coefficient of determination R^2 at 0.626. Dispersion of the values of the correlation field is not large. It refers to a relatively stable growth conductivity values increased from soluble substances. In this regression model, we found a high significance, as Pr value reached 0.005 ($Pr < 0.01$). By testing, we found the average value of conductivity ($0.020 \text{ mS}\cdot\text{cm}^{-1}$) at zero values of soluble substances and increase the

conductivity of $1.25 \text{ mS}\cdot\text{cm}^{-1}$ at increasing the value of soluble substances by one unit of measure (ppt).

The highest value ($0.26 \text{ mg}\cdot\text{l}^{-1}$) for PO_4 in precipitation was recorded in the locality Nitra (mean $0.06 \pm 0.60 \text{ mg}\cdot\text{l}^{-1}$; minimum $0,003 \text{ mg}\cdot\text{l}^{-1}$). The average amounts of PO_4 in the area Oslany were $0.08 \pm 0.05 \text{ mg}\cdot\text{l}^{-1}$ (maximum $0.20 \text{ mg}\cdot\text{l}^{-1}$; minimum $0,007 \text{ mg}\cdot\text{l}^{-1}$). Kežmarok reached the mean value of $0.05 \pm 0.04 \text{ mg}\cdot\text{l}^{-1}$ (maximum $0.14 \text{ mg}\cdot\text{l}^{-1}$, minimum $0 \text{ mg}\cdot\text{l}^{-1}$) (table 2). Trends of $\text{NO}_3^- \text{-N}$ ($\text{mg}\cdot\text{l}^{-1}$) characteristics for monitored areas in comparison with air pollution NO_x measured in automatic monitoring stations (AMS) Nitra and Oslany (Fig. 5). Development heads for to confirmation of our hypothesis that measured values AMS are higher in case of less rainfall. Thereby there is less amount of $\text{NO}_3^- \text{-N}$ contained in rainfall. The air cleans at the expense of the environment by rainfall.

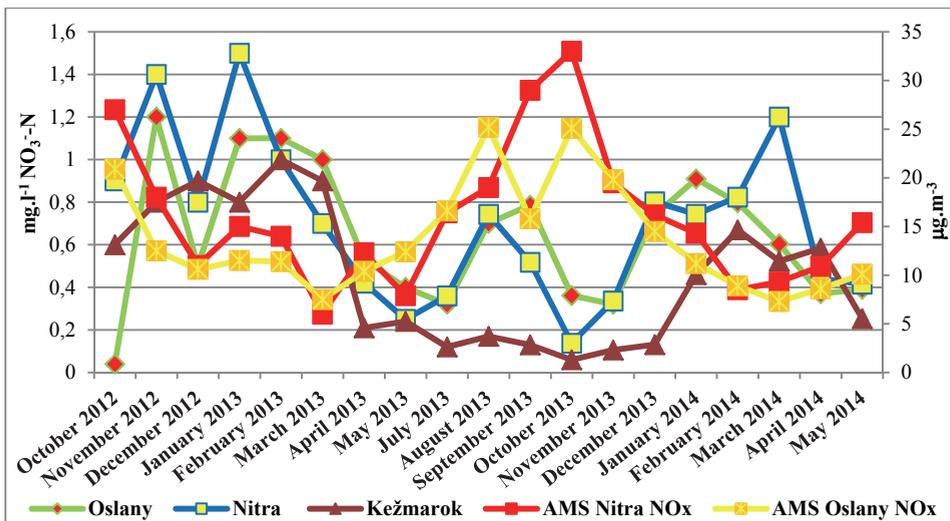


Fig. 5. Trends of $\text{NO}_3^- \text{-N}$ ($\text{mg}\cdot\text{l}^{-1}$) characteristics for monitored areas in comparison with air pollution NO_x

Rys. 5. Porównanie linii trendów $\text{NO}_3^- \text{-N}$ ($\text{mg}\cdot\text{l}^{-1}$) do zanieczyszczenia powietrza związkami NO_x w monitorowanych punktach

Table 2. Descriptive statistics for the PO₄⁻³-P, NO₃⁻-N, SO₄⁻² of rainwater in the monitored sites
Tabela 2. Statystyka opisowa dla PO₄⁻³-P, NO₃⁻-N, SO₄⁻² w wodzie opadowej w monitorowanych punktach

Statistical function	(mg·l ⁻¹) PO ₄ ⁻³ -P			(mg·l ⁻¹) NO ₃ ⁻ -N			(mg·l ⁻¹) SO ₄ ⁻²		
	Oslany	Nitra	Kežmarok	Oslany	Nitra	Kežmarok	Oslany	Nitra	Kežmarok
Average	0.079	0.063	0.049	0.7	0.743	0.46	3.692	6.333	0.308
Error of the mean	0.043	0.041	0.033	0.279	0.292	0.296	3.56	7.81	0.484
Median	0.079	0.063	0.04	0.7	0.743	0.46	1.5	1	0
Modus	0.1	0.08	0.09	0.5	0.743	0.8	1	1	0
SD	0.055	0.062	0.042	0.362	0.387	0.335	4.664	15.91	0.821
Sharpness	0.683	2.147	0.969	0.612	0.395	0.282	1.358	3.599	3.163
Oblliquity	-0.02	6.09	0.213	0.579	-0.33	-1.617	0.271	13.21	10.378
Variance margin	0.193	0.257	0.141	1.56	1.362	0.94	13	61	3
Variance is (n-1)	0.003	0.004	0.002	0.131	0.15	0.112	21.751	253.2	0.675
Minimum	0.007	0.003	0	0.04	0.138	0.06	0	0	0
Maximum	0.2	0.26	0.141	1.6	1.5	1	13	61	3
Sum	1.652	1.072	0.834	14.707	12.63	7.82	51.692	88.66	4.308
Coefficient of variation	0.688	0.951	0.839	0.504	0.505	0.706	1.217	2.422	2.572

In the period from 10.06.2013 to 11.05.2013 precipitation appeared nationwide (hit in the short term the whole territory of Slovakia) in this parameter were measured almost identical, while the minimum data (Nitra and Oslany $0.01 \text{ mg}\cdot\text{l}^{-1}$, Kežmarok $0.00 \text{ mg}\cdot\text{l}^{-1}$). Concentrations of phosphorus in natural waters in the form of phosphate ions, is one of the most serious problems in the environment since its contribution in the process of eutrophication is not negligible. The average quantities measured in the waste waters reach as 9, 15 respectively. $30 \text{ mg}\cdot\text{l}^{-1}$ (Radojević & Bashkin 2006). During the whole period of our observations, we conducted 51 analyzes of phosphates in precipitation and none of them limit the phosphate content set out in Annex 2 to the Government Decree 269/2010 is not exceeded.

Atmospheric deposition of reactive nitrogen is a very important process in the nitrogen cycle. If there is an increase in nitrogen loading of the atmosphere, nitrogen saturation of ecosystems may occur. In urban areas, the main anthropogenic source of nitrogen compounds in precipitation water is burning of fossil fuels (Brimblecombe et al. 2007). Parameter nitrate nitrogen showed highest value ($1.5 \text{ mg}\cdot\text{l}^{-1}$) in Nitra again (along with the parameters conductivity and soluble substances). The average value in the locality Nitra was $0.74 \pm 0.15 \text{ mg}\cdot\text{l}^{-1}$ (minimum $0.14 \text{ mg}\cdot\text{l}^{-1}$). In Kežmarok the average measured value was $0.46 \pm 0.33 \text{ mg}\cdot\text{l}^{-1}$ (maximum $1.00 \text{ mg}\cdot\text{l}^{-1}$; minimum $0.060 \text{ mg}\cdot\text{l}^{-1}$). In the most heavily loaded area Oslany was reached the average value of $0.70 \pm 0.36 \text{ mg}\cdot\text{l}^{-1}$ (maximum $1.60 \text{ mg}\cdot\text{l}^{-1}$; minimum $0.040 \text{ mg}\cdot\text{l}^{-1}$) (table 2). Problems with the quality of rainwater are described as acid rain. The term includes more acidic than pH of the aqueous solution, it includes the main concerns of sulfuric acid anions (SO_4^{2-}) and nitric (NO_3) (Iqbal & Mido 2010) as well. Acidification is thus involved sulfates and nitrates, which are formed by oxidation of SO_2 and NO_x emissions. These can have natural or anthropogenic origin. The proportion of anthropogenic sources is estimated at over 50% of the SO_2 in over 30% of the NO_x (Schwedt, 2001). The average value $\text{SO}_4^{2-}\text{-S}$ in Oslany reached $3.70 \pm 4.66 \text{ mg}\cdot\text{l}^{-1}$ (maximum $13 \text{ mg}\cdot\text{l}^{-1}$; minimum $0 \text{ mg}\cdot\text{l}^{-1}$); Nitra was $15.91 \pm 6.33 \text{ mg}\cdot\text{l}^{-1}$ (maximum $61 \text{ mg}\cdot\text{l}^{-1}$; minimum $0 \text{ mg}\cdot\text{l}^{-1}$) and in the area of High Tatras region – Kežmarok $0.31 \pm 0.82 \text{ mg}\cdot\text{l}^{-1}$ (maximum $3 \text{ mg}\cdot\text{l}^{-1}$, minimum $0 \text{ mg}\cdot\text{l}^{-1}$) (table 2).

Amount of sulfate sulfur in precipitation at all sites reached relatively low, mostly zero values. Extreme value ($61 \text{ mg}\cdot\text{l}^{-1}$) was recorded in the locality Nitra in 30 days period – from 05 November to 05 December 2013. This was measured in snowfall melted and the temperature reaches 25°C (all analyzes were conducted under the same temperature conditions of 22 to 25°C). The probable cause was a combination of snow layer (rough surface) and airborne dust respectively aerosols of sulfur compounds in the horizontal precipitation. The measured amount was 2.65 times greater than that allowed for the irrigation waters ($23 \text{ mg}\cdot\text{l}^{-1}$). A similar conclusion had been reached by Lange et al. (2003), who gives the example of the German Ore Mountains enrichment of Ca^{2+} , Na^+ , Cl^- , NH_4^+ , NO_3^- , and SO_4^{2-} in mist 6-7 times higher than in the rain. This enrichment is lower than specified in Zimmermann et al. (2003), which highlights the differences contents in fog versus vertical precipitation. For SO_4 it was 9-times, NO_3 13-times NO_3 , Cl 17 times for NH_4 19 times more than in vertical precipitation.

Horizontal precipitation tends to be significantly longer in direct contact with the surface of the vegetation. Fog droplets stay on the leaf 4 times longer while drop (Pahl 1996). Evaporation of intercepted water mist additionally leads to the formation of highly acidic solutions of surface vegetation (Frevert & Klemm 1984). Dominant source of sulphates in Europe is energy, which contributes by 61% in environmental pollution within sulfur compounds (Braniš & Hůnová 2009). In addition to the chemical composition of precipitation in the localities we studied their quantity. Development of rainfall is for better clarity shown graphically in figure 6.

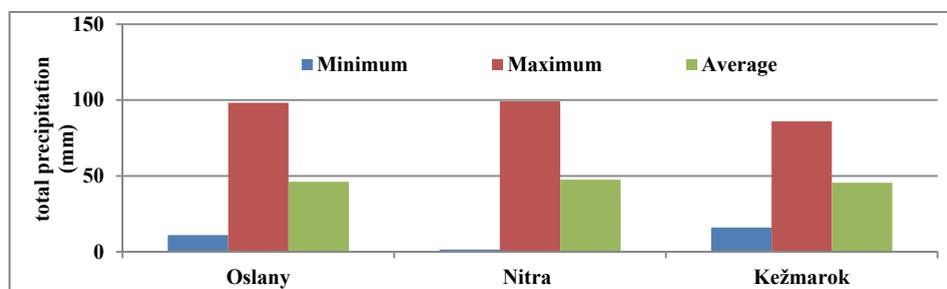


Fig. 6. Precipitation amount in monitored localities

Rys. 6. Ilość opadów atmosferycznych w monitorowanych punktach

This graph displays that rainfall in Nitra, Oslany and Kežmarok was relatively balanced. In Oslany it was 46.12 ± 28.841 mm (maximum 98.2 mm; minimum 11 mm), in the locality Nitra 47.57 ± 27.60 mm (maximum 99.2 mm; minimum 1.5 mm) and area Kežmarok 45.49 ± 23.35 mm (maximum 86.00 mm, 16.00 mm minimum) (Fig. 6).

Within the reporting period, we recorded the rainfall occurrence, which interfered with all three locations simultaneously (e.g. during the period 05.10.2013 - 06.11.2013). We assume that samples of rainwater from these periods should have similar properties based on similar chemical and physical characteristics. Mentioned above, we managed to prove on the basis of the results achieved in the area Oslany and Nitra. In the case of Kežmarok locality, distant around 250 km from Nitra and Oslany, the argument was not proven.

Our results show that rainfall affecting larger areas may have similar chemical and physical properties at regional level (100×100 km).

4. Conclusion

Monitoring of selected rainfall parameters is essential for early detection limit values. The analysis analyzes of precipitation monitor parameters such as temperature, pH, conductivity, TDS, the amounts of the compounds $\text{PO}_4^{3-}\text{-P}$ ($\text{mg}\cdot\text{l}^{-1}$), $\text{NO}_3^-\text{-N}$ ($\text{mg}\cdot\text{l}^{-1}$) and $\text{SO}_4^{2-}\text{-S}$ ($\text{mg}\cdot\text{l}^{-1}$). Trend in reducing concentrations of acidifying compounds (SO_2 , NO_x , CO_2), has resulted in increasing the pH in measured in precipitation. pH reached an average value of 7.12 ± 0.614 in the area Oslany, Nitra 6.85 ± 0.760 and $6.61 \pm 1,139$ locality Kežmarok. Most of the pH values in all the three study areas exceeded the "normal value" pH 5.6. In Kežmarok we monitored in three consecutive periods (from 09.01.2013 to 09.04.2013) pH below 5.6, which is considered as acid rain. This fact may be explained by transboundary impact of industrial activities in Poland. Conductivity of rainwater in the area of Nitra was around 0.06 ± 0.055 $\text{mS}\cdot\text{cm}^{-1}$. The area Kežmarok was found an average value of 0.074 ± 0.069 $\text{mS}\cdot\text{cm}^{-1}$. The site Oslany was a mean value of 0.062 ± 0.038 $\text{mS}\cdot\text{cm}^{-1}$. The parameter TDS was recorded in the locality Nitra average of 0.037 ± 0.026 ppt, in Oslany 0.035 ± 0.023 ppt and location Kežmarok 0.047 ± 0.050 ppt. The highest value (0.26 $\text{mg}\cdot\text{l}^{-1}$) for PO_4 was observed in the locality Nitra (mean 0.06 ± 0.60 $\text{mg}\cdot\text{l}^{-1}$). The average amounts of PO_4 in the area Oslany were 0.08 ± 0.05 $\text{mg}\cdot\text{l}^{-1}$ and

Kežmarok was characterized by the mean value of $0.05 \pm 0.04 \text{ mg}\cdot\text{l}^{-1}$. Parameter nitrate nitrogen showed the highest value ($1.5 \text{ mg}\cdot\text{l}^{-1}$) in Nitra again (along with the parameters conductivity and soluble substances). The average value in Nitra was $0.74 \pm 0.15 \text{ mg}\cdot\text{l}^{-1}$, in Oslany $0.70 \pm 0.36 \text{ mg}\cdot\text{l}^{-1}$ and Kežmarok $0.46 \pm 0.33 \text{ mg}\cdot\text{l}^{-1}$. Amount of sulfate sulfur ($\text{SO}_4^{2-}\text{-S}$) in precipitation at all sites reached relatively low number, typically zero. Rainfall in Nitra, Oslany and Kežmarok was relatively balanced. In Oslany it was $46.12 \pm 28.84 \text{ mm}$; Nitra $47.57 \pm 27.60 \text{ mm}$ and $45.49 \pm$ locality Kežmarok 23.35 mm .

Partial results of our research will be complemented by additional sites to map the largest territory of Slovakia with the high environment load. The Achieved results confirm that after the rain, the measured values of air pollution are much lower and rainwater pollution is contaminated. Regression tests of the rainwater pollution calculated $R^2 = 0,626$. Dispersion of the correlation is not large, and shows the relatively stable growth in the value of rainwater contamination with an increase of air pollution. The results show that the complicated detection of environment load could be replaced by simple rainwater collection and subsequent analysis. To test the accuracy 24-hour sample collection as well as the 24 hourly values for air pollution is needed, because for monthly interval and for some samples anomalies periodically occurred.

Due to the growing problem of the impact of air pollution on natural ecosystems especially in Central Europe, Great Britain and Scandinavia (Posch et al. 1998), it is necessary to continue to monitor developments and long-term trends in air pollution and chemical precipitation in different types of ecosystems (Stred'anský et al. 2007). Monitoring Atmospheric deposition is important not only for the determination of deposition flows to ecosystems, but also serves as a basis for calculating critical loads of acidity and eutrophication as well as for the validation of other models evaluating the impact of air pollution on the ecosystem. According to recent findings, more than 90% of the population of European cities is exposed to air pollutants, which seriously threatens their health. This finding follows the report Air quality in Europe – 2013 from the workshop of the European Environment Agency (EEA 2013). New scientific findings indicate that human health may be damaged already within the lower concentrations of air pollutants than originally anticipated (EEA 2013).

From the obtained results, we expect prospective benefits and clarify the dynamics of environmental pollution by oxides of sulfur and nitrogen in various locations SR, which we consider significant in terms of geographical and environmental burdens of pollutants. The current situation of certain habitats continues to cause damage to the individual components of the environment. For this reason, we consider as very important to monitor the load and quantify the negative effect, which is the basis to propose corrective measures to improve the current situation.

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Wpływ zanieczyszczenia powietrza na jakość wód opadowych

Streszczenie

Istotne zanieczyszczenie powietrza Słowacji bierze się z ciepłowni i elektrociepłowni, spalarni śmieci, przemysłu chemicznego, transportu, górnictwa odkrywkowego i energii jądrowej. Emisje z tych źródeł wpływają negatywnie na produkcję rolną oraz zmniejszają właściwości gleby poprzez ich zakwaszenie, alkalizację i metalizację. To ma również wpływ hodowlę roślin i zwierząt. Celem pracy było określenie wpływu zanieczyszczenia powietrza na jakość wody deszczowej. W tym celu wybrano trzy punkty monitoringowe: Oslany, Nitra i Kieżmarku. Pierwszy obszar monitorowany – Oslany był położony w pobliżu elektrowni Słowackiej Nováky, który jest jednym z głównych ośrodków przemysłowych i energetycznych z górnictwa węgla brunatnego. Drugi zurbanizowany obszar Nitra jest średniej wielkości miastem regionalnym (87,533 mieszkańców). Ostatnim obszarem badań jest Kieżmark położony w pobliżu Tatr Wysokich reprezentujący obszar o najniższym zanieczyszczeniu powietrza. Analizy wody deszczowej przeprowadzono przy użyciu kolorymetru HI 99300, DR/890, HQ konduktometru 14d i DR 6000 spektrofotometru. Za pomocą tych narzędzi w laboratorium pomierzono parametry takie jak: temperatura, wartość pH, przewodność elektrolityczną właściwą, substancje rozpuszczone, ilość związków $\text{PO}_4^{3-}\text{-P}$ ($\text{mg}\cdot\text{l}^{-1}$), $\text{NO}_3^{-}\text{-N}$ ($\text{mg}\cdot\text{l}^{-1}$) and $\text{SO}_4^{2-}\text{-S}$ ($\text{mg}\cdot\text{l}^{-1}$). Monitorowanie depozycji atmosferycznej jest ważne dla ekosystemów i stanowi podstawę do obliczania ładunków decydujących o zakwaszeniu i eutrofizacji, jak również dla określenia modeli oceny wpływu zanieczyszczenia powietrza na ekosystem. W pracy potwierdzono hipotezę, że zmierzone wartości AMS są wyższe w przypadku mniejszych opadów. Natomiast w wodzie opadowej nie zaobserwowano mniejszej ilości $\text{NO}_3^{-}\text{-N}$. Powietrze oczyszczane jest, ale kosztem środowiska, poprzez opady atmosferyczne. Na podstawie uzyskanych wyników stwierdzono, że zanieczyszczenie środowiska tlenami siarki i azotu jest inne w różnych miejscach. Zaobserwowano, że istotą jest położenie geograficzne. Uzyskane wyniki pozwoliły stwierdzić, że niektóre siedliska są zagrożone. Z tego powodu należy monitorować i oceniać w wodzie opadowej tlenki siarki i azotu w celu zaproponowania środków naprawczych jeśli takie będą musiały być wprowadzone na poprawę zaistniałej sytuacji.

Abstract

Significant air pollutants of Slovakia are heating plants and thermal power plants, waste incinerators, chemical industry, transportation, surface mining and nuclear energy. Emissions from these sources affect agricultural pro-

duction cumulating at soil surface and decrease soil characteristics. This leads to soil acidification, alkalization of soils and metallization, it also causes reduction of yields and descent performance of animals.

In this paper we analyze the impact of air pollution on rainwater quality. For the performance the research we selected three locations: Oslany, Nitra and Kežmarok. The first monitored area was Oslany which is a load area, situated near the Slovak power plant Nováky, which is one of the key industrial and energy centers with lignite mining in the neighborhood. The second researched monitored area is medium-sized regional town (87,533 inhabitants) Nitra representing urbanized area. The last area of research is Kežmarok located near High Tatra representing the area of the lowest air pollution. The analyzes of rainwater were carried out using HI 99300, Colorimeter DR/890, the conductivity meter HQ 14d and DR 6000 spectrophotometer. Using these instruments in the laboratory, we monitored parameters such as temperature, pH, conductivity, TDS (total dissolved solids), the amount of the compounds $\text{PO}_4^{-3}\text{-P}$ (mg.l^{-1}), $\text{NO}_3^{-}\text{-N}$ (mg.l^{-1}) and $\text{SO}_4^{-2}\text{-S}$ (mg.l^{-1}). Monitoring of the Atmospheric deposition is important apart from the determination of deposition flows to ecosystems, but also for serving as a basis for calculating critical loads of acidity and eutrophication as well as for the validation of other models evaluating the impact of air pollution on the ecosystem.

Development heads for to confirmation of our hypothesis that measured values AMS are higher in case of less rainfall. Thereby there is less amount of $\text{NO}_3^{-}\text{-N}$ contained in rainfall. The air cleans at the expense of the environment by rainfall.

From the obtained results, we expect prospective benefits and clarify the dynamics of environmental pollution by oxides of sulfur and nitrogen in various locations SR, which we consider significant in terms of geographical and environmental burdens of pollutants. The current situation of certain habitats continues to cause damage to the individual components of the environment. For this reason, we consider as very important to monitor the load and quantify the negative effect, which is the basis to propose corrective measures to improve the current situation.

Słowa kluczowe:

zanieczyszczenie powietrza, analiza wody opadowej, pH, przewodność elektrolityczna właściwa, substancje rozpuszczone, $\text{PO}_4^{-3}\text{-P}$, $\text{NO}_3^{-}\text{-N}$, $\text{SO}_4^{-2}\text{-S}$

Keywords:

air pollution, precipitation analyzes, pH, conductivity, TDS, $\text{PO}_4^{-3}\text{-P}$, $\text{NO}_3^{-}\text{-N}$, $\text{SO}_4^{-2}\text{-S}$