ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 34 no. 4 pp. 3 - 12 2008

PL ISSN 0324-8461

IDENTIFICATION OF "HOT-SPOT" IMISSION EVENTS REFLECTED IN RAIN PRECIPITATION CHEMISTRY BASING ON ION CHROMATOGRAPHY ANALYSIS AND SELF-ORGANIZING MAPS CLASSIFICATION

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Keywords: Dupniański Stream catchment, bulk precipitation chemistry, ion chromatography, self-organizing maps, "hot-spot" imission events.

Abstract: The present study deals with the application of self-organizing maps (SOM) to identification of "hot-spot" imission events reflected in bulk precipitation chemical profiles basing on ion chromatography analysis. An experiment was conducted in the period between January 1999 and December 2003 at the Dupniański Stream catchment (Silesian Beskid) area to collect both analytical measurements (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe, Mn and Zn), pH and meteorological parameters (prevailing wind direction). A classification of rainwater samples according to identification of strong imission events was performed basing on Kohonen's algorithm. SOM approach allows to identify strong, temporal impact of remote pollution sources located in the vicinity of the Polish – Czech Republic border and indicates cyclical impact of remote pollution sources located in highly industrially developed Katowice and Bełchatów regions.

INTRODUCTION

Atmospheric precipitation chemistry is one of the major factors shaping the trophic conditions in a given woodland ecosystem. Atmospheric pollution may affect indirectly in a form of acid rains the health of forest ecosystems or the chemical balance of surface waters and soils. Time and space diversification of the atmospheric precipitation amount, and therefore of the quantity and quality of chemical species in rain water, is caused by the presence of the atmospheric pollutants, their mutual influence and direction and scavenging behavior of air masses. The results obtained more often by a long-term monitoring programs require an identification of pollution profiles, "hot-spots" events as well as an assessment of the impact of local and cross-border pollution sources and the direction of air mass inflow. Therefore the application of sophisticated data-mining techniques linked with an analysis of atmospheric conditions may play a meaningful role in the assessment of the effect of atmospheric transport of pollution on air quality [25]. Quite good assessment is often accomplished despite of great number of variables involved: data from various periods for many elements affected by various factors (wind speed and directions, temperature, distance from main sources – natural or/and artificial) [2].

The aim of the study is to explore long-term monitoring data set from the Dupniański Stream catchment (Silesian Beskid, Southern Poland) and to demonstrate the opportunities offered by self-organizing maps algorithm in identification of "hot-spot" imission events reflected in rain precipitation chemistry basing on ion chromatography analysis. The main objective is to reveal the relationship between chemical composition of bulk precipitation and seasonality (winter and growing period) or specific meteorological conditions and "hot-spot" imission events which enables definition of air pollution sources.

MATERIALS AND METHODS

Sampling site and sampling procedure

The Dupniański Stream catchment (DSC) of 1.68 km^2 area is located in southern Poland in the Silesian Beskid Mts. (49°34'N, 18°50'E) not far from the main industrial centers. This region of the Polish part of the Carpathian Mountains is affected by air pollution [3, 16, 17]. The catchment is covered with Norway spruce (*Picea abies* Karst) stands of different ages growing on dystric cambisols developed on Istebna sandstone. The studies were conducted in 1999–2003 following methods described in the ICP-Forest Manual [8] and by Małek [16]. A bulk precipitation sampler (BP) was installed in the middle of the catchment at an elevation of 725 m a.s.l. During the growing season, from 1st May to 30th October (the same year), samples of bulk precipitation directly reaching the catchment were collected from collectors (5 units with 15 cm inlet diameter each) installed in an open area 0.5 m above ground level, connected to a plastic tube with an outlet joining a container and a measuring device installed in a bunker. In winter season, from 1st November (the previous year) to 30th April (the following year) six collectors (polyethylene, chemically neutral snow bags with 15 cm inlet diameter each) were installed at 1.3 m above ground level in the open area. Those samplers were placed at a distance of 120–150 m from the forest edge. The sampling was performed on the first day of each month. Meteorological data concerning the study period (1999–2003) were obtained from the Institute of Meteorology and Water Management [9] and Feliksik and Durło [5].

Chemical analyses

The main inorganic components of bulk precipitation – anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) were determined directly by ion chromatography (IC) according to the current standards PN-ISO 10304-1 [21] and PN-ISO 14911 [22]. The ion chromatograph Dionex-320 (Dionex Corp., Sunnyvale, CA USA) was coupled with double piston GP40 IC Pump, CD20 IC Conductivity Detector and Dionex PeakNet (ver 5.11) software. In particular, the anions in the calibration solution and bulk precipitation samples were analyzed using analytical column of a type Dionex IonPac AS17 Analytical Column (250 x 2.0 mm i.d.) with IonPac AS17 Guard Column (50 x 2.0 mm i.d.) and ASRS® ULTRA Anion Self-Regenerating Suppressor. The mobile phase was a mixture of 3.5 mmol/dm^3 Na_2CO_3 and 1.0 mmol/dm^3 $NaHCO_3$ and had a flow rate 0.25 cm^3/min. The column temperature was 30°C and the pressure was 6.20 MPa. In both cases (anions and cations) an injection was accomplished by dose loop ($15 \cdot 10^{-6}$ dm^3) operating in room temperature. The analysis of cations was carried out using analytical column IonPac CS12A (250 x 2.0 mm i.d.) with IonPac CG12A Guard Column (50 x 2.0 mm i.d.) and CSRS® ULTRA Auto Suppressor working in recycle mode. The mobile phase was 18 mM methanosulphonic acid and had a flow rate of 1.0 cm³/min. The column temperature was 30°C and the pressure was 11.37 MPa. An example of chromatogram used for quantitative determination of cations in bulk precipitation sample is shown in Figure 1, while for anions in Figure 2.

Peak#	Component's name	Retention time [min]	Amount $[mg/dm^3]$	Peak area	Peak height
1	chloride	6.10	1.21	329157	15451
2	nitrite	7.10	0.58	55698	1606
3	nitrate	9.70	0.23	33577	1237
4	sulphate	13.80	9.12	1890757	46777

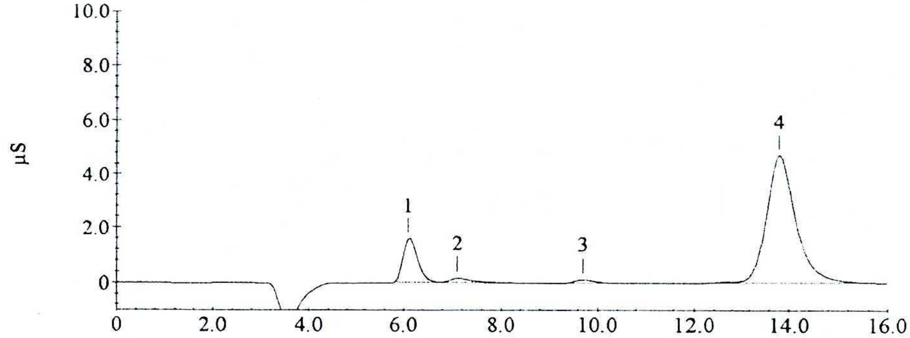

Fig. 1. An example of chromatogram used for quantitative determination of anions in bulk precipitation samples collected at the Dupniański Stream catchment in the period between January 1999 and December 2003

Peak#	Component's name	Retention time [min]	Amount $[mg/dm^3]$	Peak area	Peak height
1	sodium	4.95	0.87	390140	19012
2	ammonium	5.73	0.44	116340	4796
3	potasium	7.12	0.39	113469	4629
4	magnesium	11.02	0.52	233115	7224
5	calcium	12.88	2.93	1243111	23560

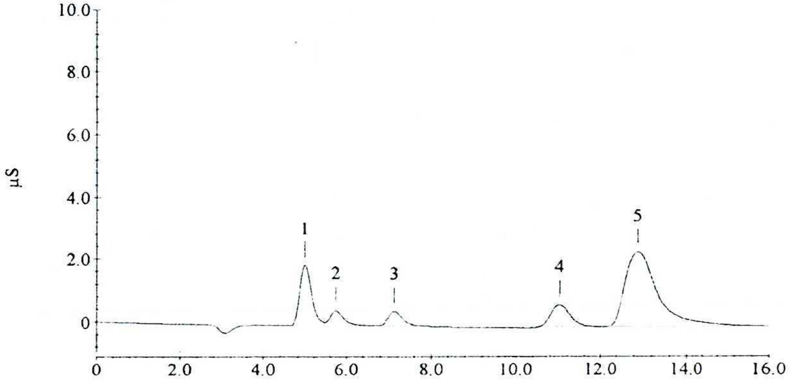

Fig. 2. An example of chromatogram used for quantitative determination of cations in bulk precipitation samples collected at the Dupniański Stream catchment in the period between January 1999 and December 2003

An atomic absorption spectrometer (Varian, Australia) was used to determine Fe, Mn and Zn. A low-pH acid rain sample from southern Ontario (Canada), RAIN.97 – No 409 was, served as a certified reference material (CRM). When the concentration of analytes was below the limit of detection (LOD), the value of one-third LOD was used in the data set due to chemometric requirements [1]. Abandonment of replacement procedure causes a necessity of particular variable elimination and significantly reduces informative abilities of data set.

Self-organizing maps (SOM)

Self-organizing map (SOM) algorithm has been proposed by Kohonen [10] and is a neural-network model that implements a characteristic nonlinear projection from the high-dimensional space of sensory or other input signals onto a low-dimensional array of neurons [13]. The term "self-organizing" refers to the ability to learn and organize information without being given the associated-dependent output values for the input pattern [18]. SOM shares with the conventional ordination methods the basic idea of displaying a high-dimensional signal manifold onto a much lower dimensional network in an orderly fashion (usually a two dimensional space). Interesting SOM applications have been reported mainly in the fields of exploratory data analysis, data mining (evaluation of environmental components, analysis of ecological datasets, water quality assessment or identification and monitoring of complex process states and pattern classification [4, 7, 10, 12, 14, 15, 19, 20, 23, 24, 26, 27]. Theoretical background of SOM approach can be found elsewhere [6, 10–12, 27] and because of this only final set of chosen algorithm components are presented below:

- to perform SOM-based classification a free Teuvo Kohonen toolbox (SOM Toolbox 2.0) was applied [27];
- Kohonen map was chosen as a rectangular grid with number of nodes (n) determined using following formula $n = 5 \times \sqrt{number\ of\ samples}$ [27] and moreover, a hexagonal lattice was preferred because it does not favor horizontal or vertical direction [11], the dimensionality of Kohonen's map was determined as 5 x 8 ($n = 5 \times \sqrt{60} \approx 38.7$);
- grey-scale bar labeled as "d" can be understood in the term of range of the particular species variation, while grey-scale SOM reflects time-depended species abundance;
- in the classification step non-hierarchical K-means classification algorithm was applied; different values of *k* (predefined number of clusters) were tried and the sum of squares for each run was calculated; finally, the best classification with the lowest Davies-Bouldin index was chosen [26]).

RESULTS AND DISCUSSION

In Table 1 descriptive statistics for twelve investigated variables which characterize bulk precipitation samples, while in Figure 3 both U-matrix (unified distance matrix which visualizes distances between neighboring map units) and Kohonen's map reflecting to time-depended species abundance is presented.

Visual assessment of similarities in Kohonen's map pattern for chemical parameters allows to formulate preliminary presumption concerning correlated variables, which was subsequently confirmed statistically as follows ($p = 0.95$, $R_{crit} = 0.25$): Cl^- – NO_3^- (0.80), Cl^- – Zn (0.66), Na^+ – K^+ (0.54), Mg^{2+} – SO_4^{2-} (0.57), Ca^{2+} – SO_4^{2-} (0.38), NO_3^- – SO_4^{2-}

Table 1. Descriptive statistics showing mean, median, minimum, maximum, variance and standard deviation value for inorganic analyte content in bulk precipitation samples collected at the Dupniański Stream catchment in the period between January 1999 and December 2003

Analyte	N	Mean value	Median	Minimum value	Maximum value	Variance	Standard deviation
Cl^- [mg/dm^3]	60	2.04	1.55	0.38	11.92	3.31	1.82
NO_3^- [mg/dm^3]	60	4.18	2.90	0.90	31.33	18.56	4.31
NH_4^+ [mg/dm^3]	60	1.53	1.20	0.14	5.71	1.33	1.15
SO_4^{2-} [mg/dm^3]	60	4.31	3.31	1.22	27.78	15.39	3.92
Na^+ [mg/dm^3]	60	0.85	0.44	0.08	10.55	2.29	1.51
K^+ [mg/dm^3]	60	0.88	0.62	0.05	5.92	0.98	0.99
Ca^{2+} [mg/dm^3]	60	3.29	2.59	0.16	20.55	10.22	3.20
Mg^{2+} [mg/dm^3]	60	0.47	0.25	0.01	3.22	0.45	0.67
Fe [mg/dm^3]	60	0.05	0.02	0.001	0.25	0.003	0.06
Mn [mg/dm^3]	60	0.02	0.01	0.001	0.10	0.0004	0.02
Zn [mg/dm^3]	60	0.10	0.04	0.001	0.79	0.02	0.14
H^+ [µg/dm^3]	60	7.84	2.55	0.01	60.26	145.19	12.05

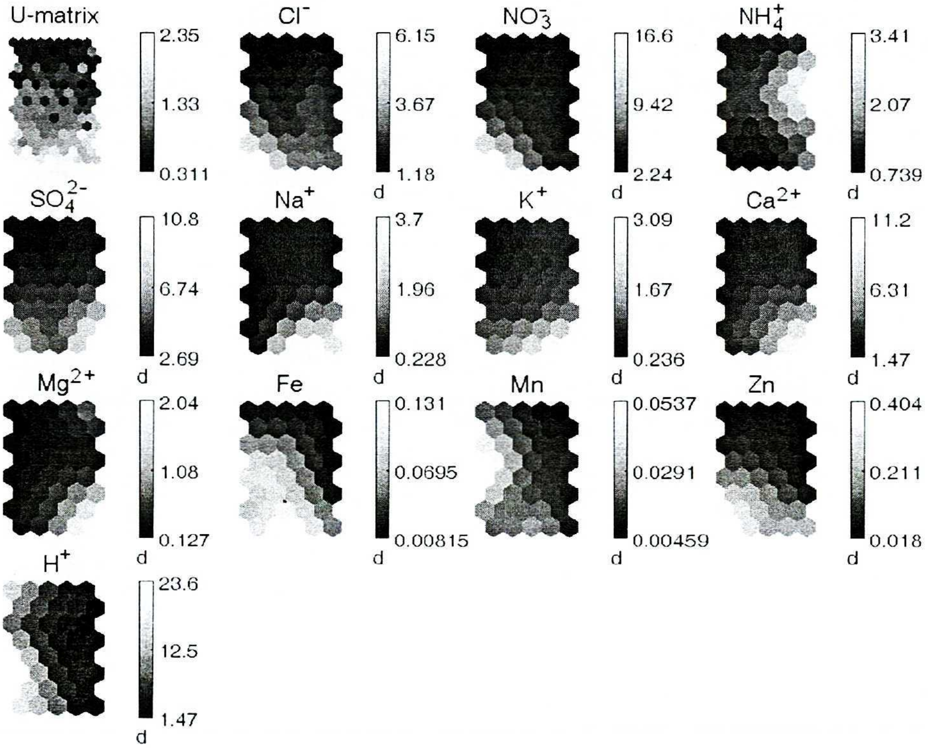

Fig. 3. Visualization of similarities in the unified distance matrix and Kohonen's maps reflecting time-depended species abundance (similarities in the space of objects)

(0.41), NO_3^- – Zn (0.65), SO_4^{2-} – Zn (0.47), Na^+ – K^+ (0.54), Na^+ – Ca^{2+} (0.40), Na^+ – Mg^{2+} (0.45), K^+ – Ca^{2+} (0.59), K^+ – Mg^{2+} (0.43), Fe – Mn (0.42) and Fe – Zn (0.44). A complete set of correlation coefficient values is summarized in Table 2. Isolated dependences indicate that in the Dupniański Stream catchment SO_4^{2-} and NO_3^- originating from atmospheric sulphur dioxide and NO_x emission combine with K^+, Ca^{2+}, Mg^{2+} and in the form of salts are deposited on the ground. Moreover, an existing positive correlation between heavy metals (Fe, Mn, Zn) indicate that the investigated area is strongly affected by heavy metals deposition related to ash emission. Monthly averages of analytes' concentration values were clustered basing on the K-means classification approach implemented in SOM toolbox. The number of four significant clusters was determined by the lowest value of the Davies-Bouldin index. Setting-up the monthly average values of analyte's concentration along with the classification results allows to obtain relatively reasonable interpretation of clustering pattern related to both seasonal variation in bulk precipitation chemistry and temporal or cyclical impact of remote pollution sources located in the vicinity of the Silesian Beskid. Clusters I–IV include different number out of totally 60 cases as follows: I – 3 (July 1999, September and October 2000), II – 5 (January 2003, August and September 1999, August 2000 and August 2002), III – 15 (11 from 15 samples collected in growing season) and IV – 37 (25 out from 37 samples collected in winter season). To assess the statistical significance of differences in the means of analyte's concentrations between particular clusters non-parametric Kruskal-Wallis and U Mann-Whitney tests were performed, and adequate p values are summarized in Table 3.

Comparing to other clusters, samples classified as cluster I (CI) characterize the highest mean concentration of Zn (0.38 mg/dm^3) and NO_3^- (18.69 mg/dm^3). Concentration of SO_4^{2-} in CI (8.12 mg/dm^3) is similar to CII (9.30 mg/dm^3). In CI two successive samples were grouped (collected in September and October 2000) and this can indicate a strong, temporary impact of specific pollution source classified as classical "hot-spot" imission event. An assessment of air mass movement trajectories at this time indicate that majority of winds have blown from south and west-south direction [5, 9] and because of this Ostrava-Karvia (located 40 km in southerly direction from DSC) and Triniec (located 15 km in southerly direction form DSC) industrial regions become suspected as possible

Table 2. Ion pair correlation for bulk precipitation samples collected at the Dupniański Stream catchment in the period between January 1999 and December 2003 (bold represents statistically significant values, $p = 0.05$, $n = 60$)

	Cl^-	NO_3^-	SO_4^{2-}	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Fe	Mn	Zn
Cl^-	1.00											
NO_3^-	0.80	1.00										
SO_4^{2-}	0.34	0.41	1.00									
H^+	0.15	0.17	-0.05	1.00								
Na^+	0.01	-0.03	0.07	-0.10	1.00							
K^+	0.26	0.23	0.22	-0.06	0.54	1.00						
Ca^{2+}	0.30	0.13	0.38	-0.21	0.40	0.59	1.00					
Mg^{2+}	0.08	0.02	0.57	-0.22	0.45	0.43	0.68	1.00				
NH_4^+	0.07	0.01	0.09	-0.15	-0.04	0.13	0.11	-0.01	1.00			
Fe	0.19	0.20	-0.04	0.08	0.40	0.21	0.13	0.02	-0.25	1.00		
Mn	0.19	0.13	-0.04	0.34	0.05	-0.02	-0.10	-0.19	0.03	0.42	1.00	
Zn	0.66	0.65	0.47	0.13	0.13	0.24	0.38	0.25	-0.12	0.44	0.19	1.00

strong emission areas. Cluster II (CII) groups bulk precipitation samples collected mainly in the late growing period for reiterate months (i.e. August 1999, 2000 and 2002). Comparing to other clusters, samples clustered as CII characterize the high concentration of Zn (0.23 mg/dm^3) and SO_4^{2-} (9.30 mg/dm^3) and the highest concentration of alkali cations: Na^+ (4.29 mg/dm^3), K^+ (3.48 mg/dm^3) and Ca^{2+} (10.49 mg/dm^3). Similar to deduction way presented above an assessment of air mass trajectories at this time indicate that majority of winds have blown from north and north-east direction [5, 9]. Such meteorological conditions can be favorable for cross border pollution transport from high industrially developed Katowice and Bełchatów regions, located respectively 70 km and 200 km in northern direction and also highly urbanized Krakow metropolitan area, which is located 80 km north-east from the Dupniański Stream catchment. Such phenomenon indicates possible cyclical impact of remote pollution source caused by annually comparable and repeatable meteorological condition. Opposite to strongly acidic precipitation events related to pollution from Ostrava-Karvia and Triniec (H^+ – 16.31 µg/dm^3) precipitation which occurs simultaneously with wind from north and north-east directions (Bełchatów, Katowice, Krakow) are more alkaline and thus less pressing for woodland ecosystems. During growing season (11 from 15 samples) dominating air masses from north and north-west [5, 9] were related to bulk precipitations highly impoverished, comparing to CII, with alkali cations. On average, concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} were four to six times lower. Comparable amounts of acid-rain precursors with simultaneously lower amounts of alkali metals indicate that

Table 3. Statistical assessment (Kruskal-Wallis test, U Mann-Whitney test) of differences between mean concentration values of inorganic analytes of bulk precipitation samples collected at the Dupniański Stream catchment in the period between January 1999 and December 2003 (bold represents statistically significant values, p = 0.05)

Analyte	Average value				K-W	U Mann-Whitney test					
	CI	CII	CIII	CIV	test*	CI–CII	CI–CIII	CI–CIV	CII–CIII	CII–CIV	CIII–CIV
Cl^- [mg/dm^3]	6.63	2.78	2.01	1.58	$p = 0.0178$	$p > 0.05$	$p < 0.05$	$p < 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$
NO_3^- [mg/dm^3]	18.69	4.82	4.34	2.86	$p = 0.0004$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p > 0.05$	$p < 0.05$
NH_4^+ [mg/dm^3]	0.80	1.58	1.21	1.71	$p = 0.6701$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$
SO_4^{2-} [mg/dm^3]	8.12	9.30	4.00	3.46	$p = 0.0350$	$p > 0.05$	$p < 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$
Na^+ [mg/dm^3]	0.40	4.29	0.35	0.62	$p = 0.0001$	$p < 0.05$	$p > 0.05$	$p > 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$
K^+ [mg/dm^3]	1.44	3.48	0.54	0.62	$p = 0.0003$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p < 0.05$	$p > 0.05$
Ca^{2+} [mg/dm^3]	4.16	10.49	2.53	2.56	$p = 0.02$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p < 0.05$	$p < 0.05$	$p > 0.05$
Mg^{2+} [mg/dm^3]	0.42	1.90	0.26	0.37	$p = 0.0019$	$p < 0.05$	$p > 0.05$	$p > 0.05$	$p < 0.05$	$p < 0.05$	$p > 0.05$
Fe [mg/dm^3]	0.09	0.10	0.10	0.02	$p < 0.0001$	$p > 0.05$	$p < 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p < 0.05$
Mn [mg/dm^3]	0.02	0.02	0.04	0.01	$p = 0.0208$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p < 0.05$
Zn [mg/dm^3]	0.38	0.23	0.15	0.03	$p = 0.0001$	$p > 0.05$	$p < 0.05$	$p > 0.05$	$p < 0.05$	$p > 0.05$	$p < 0.05$
H^+ [µg/dm^3]	16.31	2.67	12.27	6.07	$p = 0.0479$	$p > 0.05$	$p < 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$	$p > 0.05$

* K-W test – Kruskal-Wallis test

bulk precipitation related to north-west prevailing wind directions generate serious hazard for health conditions of woodland ecosystem. 25 out from 37 samples, in which air mass movements dominated from west [5, 9], grouped in CIV were collected in winter season characterized, from among of other clusters, by the lowest concentration of Cl^- (1.58 mg/dm^3), NO_3^- (2.86 mg/dm^3), SO_4^{2-} (3.46 mg/dm^3) and heavy metals. Such phenomenon suggests that pollutants emitted in the west of Dupniański Stream catchment may dilute in the atmosphere. Precise explanation of dilution reasons should be connected with analysis of wind direction and wind speed. In general bulk precipitation deposited during winter periods is slightly contaminated comparing to the others.

CONCLUSIONS

1. Self-organizing map approach is an efficient tool for preliminary presumption concerning interrelation between variables in the investigated data set.
2. SOM proves its "resolving power" allowing to identify both cyclical impact of remote sources of pollutants and temporarily "hot-spot" imission events.
3. Chemical composition of bulk precipitation is related to prevailing directions of air masses movement and thus, deduction way based on both analytical measurements and meteorological parameters analysis allows to identify possible emission areas which strongly affect health conditions of woodland ecosystems at the Dupniański Stream catchment.
4. Bulk precipitation samples collected in September 2000, October 2000 and July 1999 characterized by highest concentration of Zn and NO_3^- indicate a strong, temporal impact of pollution source located in the near vicinity of the Polish – Czech Republic border (pollution from Ostrava-Karvina and Trinec industrial regions).
5. Comparing to other clusters obtained by SOM, bulk precipitation samples collected in the late growing period (August 1999, 2000, 2002 and September 1999) indicate cyclical impact of highly industrially developed Katowice and Bełchatów regions as well as highly urbanized Krakow metropolitan area region because of high concentration of Zn, SO_4^{2-}, Na^+ and K^+.

Acknowledgements

This research was supported financially in the framework of project: "Optimization of chemometrical techniques of exploration and modeling results originating from environmental constituent's pollution monitoring" (1439/T02/2007/32). The author would kindly thank to dr inż. Stanisław Małek (Department of Forest Ecology, Forest Faculty, Agricultural University, Krakow) for delivering a long-term monitoring data set and also to dr inż. Grzegorz Durło (Department of Forest Protection and Climatology, Agricultural University, Krakow) for help with assessment of meteorological parameters.

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Received: November 30, 2007; accepted: February 15, 2008.

IDENTYFIKACJA PRZYPADKÓW WYJĄTKOWO WYSOKIEJ IMISJI ODZWIERCIEDLONYCH W CHEMIŹMIE OPADÓW ATMOSFERYCZNYCH NA PODSTAWIE OZNACZEŃ TECHNIKĄ CHROMATOGRAFII JONOWEJ I KLASYFIKACJI TECHNIKĄ SAMOORGANIZUJĄCYCH SIĘ MAP

W pracy opisano możliwości zastosowania algorytmu samoorganizujących się map (SOM) do identyfikacji przypadków wyjątkowo wysokiej imisji odzwierciedlonych w profilach chemicznych opadów atmosferycznych wyznaczonych techniką chromatografii jonowej. Badania prowadzono w okresie od stycznia 1999 do grudnia 2003 na terenie zlewni Potoku Dupniańskiego (Beskid Śląski) gromadząc wyniki oznaczeń analitycznych (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe, Mn i Zn), pH oraz parametrów meteorologicznych (przeważający kierunek wiatru). Klasyfikację próbek opadów atmosferycznych w celu identyfikacji wysokich wartości imisji wykonano poprzez zastosowanie algorytmu Kohonena. Technika SOM umożliwiła wykrycie silnego, incydentalnego oddziaływania odległego źródła zanieczyszczeń zlokalizowanego w pobliżu granicy polsko-czeskiej i wskazuje na występowanie cyklicznego oddziaływania odległych źródeł zanieczyszczeń zlokalizowanych na terenach silnie uprzemysłowionych Katowic i Bełchatowa.