

Determination of Concentrations of Chemical Components in Precipitation over Nonindustrialized Regions in the Vicinity of Gdańsk

Ż. Polkowska, M. Grynkiewicz, A. Przyjazny¹⁾, J. Namieśnik*

Department of Analytical Chemistry, Chemical Faculty, Technical University of Gdańsk, 80-952 Gdańsk, Poland

¹⁾ Kettering University, Flint, MI, USA

Received 12 August, 1999

Accepted 23 August, 1999

Abstract

This paper presents the results of determination of concentrations of chloride, sulfate, phosphate, ammonium, sodium, potassium, calcium and magnesium ions along with total nitrogen, pH and electrolytic conductivity for precipitation collected in nonindustrialized regions near Gdansk (Poland).

A station used for the collection of samples of precipitation consisted of two substations, one of which was located in a deforested area (clearing), while the second was situated in a spruce forest. The samples were collected over a period of one year, from March 2, 1996 to February 1, 1997.

Concentrations of chloride, sulfate, phosphate, nitrate and ammonium ions and of total nitrogen were determined spectrophotometrically. Sodium, potassium and calcium ions were determined using flame photometry while magnesium ions were determined by atomic absorption spectroscopy. pH and electrolytic conductivity of the samples were also measured.

Keywords: deposition; precipitation; throughfall; sampling; analysis

Introduction

Air, water and soil are elements of the environment that are interrelated and strongly interact among each other. Chemical compounds emitted into the atmosphere combine with rain or snow, fall to the earth and become pollutants of water and soil. On the other hand, volatile chemical compounds that entered lakes and rivers and became their pollutants may become atmospheric pollutants if they evaporate.

Recently, in many countries more and more attention is being paid to the control of quality of the environment. This is associated with an increase in environmental pollution not only on a local scale but also on an international scale. In 1995, precipitation in Poland was examined in Cracow and the Cracow district, Turzanski et al. [1], and in the Karkonosze Mountains, Twarowski [2].

Air pollution results from relatively high levels of emission of dusts and gases from industrial sources and transportation in Poland as well as from the inflow of pollutants from abroad. The pollutants emitted to the atmosphere in the Gdansk district are mostly associated with the power industry. Vehicle exhaust is also a significant source of air pollution. The location of industrial plants in the Tricity area (Gdansk, Sopot, Gdynia) also contributes to this problem.

The ions most commonly determined in precipitation (also in throughfall) include chloride, nitrate, sulphate, ammonium, calcium, magnesium, sodium and potassium. Ion chromatography (IC), Udisti et al. [3], Lacaux et al. [4], Hansen et al. [5], Asbury et al. [6], Decet [7], Oikawa et al. [8], Doscher et al. [9], Li et al. [10], Tartari et al. [11], Marchetto et al. [12], Sanusi et al. [13], Avila et al. [14], Balestrini et al. [15] or spectrophotometry Hansen et al. [5], Marchetto et al. [12], and Amezaga et al. [16] are typically used for their determination. The cations, except for ammonium, can be determined by atomic absorption

* Corresponding author

spectroscopy Udisti et al. [3], Lacaux et al. [4], Hansen et al. [5], Decet [7], Asbury et al. [6], Oikawa et al. [8], Li et al. [10], Sanusi et al. [13], Avila et al. [14]. Flow injection analysis (FIA) has also found use in the determination of concentrations of chloride, nitrate, sulphate and ammonium ions, Lovblad et al. [17]. If the detection limit of a given method is insufficient for these determinations, a preconcentration step has to be included in the analytical procedure, Namiesnik et al. [18].

Table 1 presents a comparison of selected ion levels found in this study with literature data for various regions of the world.

This paper presents the study of determination of concentration and deposition of pollutants in precipitation (throughfall) over nonindustrialized regions in the vicinity of Gdansk.

Experimental

Climate in the Sampling Zone

Gdansk voivodeship lies in north central Poland in temperate climatic zone. Air masses circulate along meridian direction: the inflow of Arctic air masses causes cooling in spring and summer. The annual precipitation totals range from 550 to 600 mm.

Sample Collection

The sampling station was located in the Stara Pila forest district in Rumia. It consisted of two substations: PL 10 and PL 11. The exact location of the station is shown in Figure 1.

Samples were collected manually, once a month, over a period of one year from March 2, 1996 to February 1, 1997.

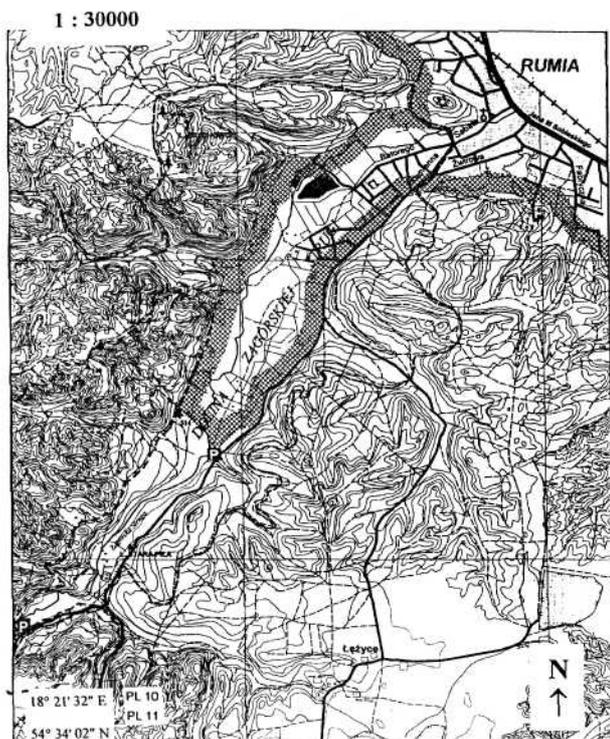


Fig. 1. Location of sampling stations.

Substation PL 10

Substation PL 10 was located in a clearing. The samples collected there were used to determine wet deposition, i.e. pollutants washed by rain from the atmosphere. The station

Table 1. Levels of selected ions in throughfall.

No.	Location, year, author	Selected ions	Concentration [mg/dm ³]
1	Spain Catalonia Holm Oak Forest 1983 – 1994 Avila et al. [14]	Na ⁺	1.37
		K ⁺	0.398
		Ca ²⁺	6.06
		Mg ²⁺	0.342
		NH ₄ ⁺	0.367
		NO ₃ ⁻	1.87
		SO ₄ ²⁻	4.56
2	Israel Pine Forest Oak Forest 1989 – 1992 Singer et al. [19]	SO ₄ ²⁻	11.66-27.02
		SO ₄ ²⁻	7.15-14.16
3	The Netherlands 1983 – 1985 Draaijers et al. [20]	Na ⁺	0.023-0.177
		K ⁺	0.207-2.601
		Ca ²⁺	0.034-0.266
		Mg ²⁺	0.013-0.116
		NH ₄ ⁺	0.032-0.173
		NO ₃ ⁻	0.031-0.112
		SO ₄ ²⁻	0.029-0.254
4	Puerto Rico Montane Forest 1984 – 1985 Asbury et al. [6]	Na ⁺	10.17
		K ⁺	1.14
		Ca ²⁺	1.56
		Mg ²⁺	1.31
		NH ₄ ⁺	0.097
		NO ₃ ⁻	0.905
		SO ₄ ²⁻	7.97
		Cl ⁻	17.68
		PO ₄ ³⁻	0.011
5	Equatorial Africa The Moyombe Forest 1986 – 1987 Lacaux et al. [4]	Na ⁺	0.255
		K ⁺	0.078
		Ca ²⁺	0.186
		NO ₃ ⁻	0.533
		SO ₄ ²⁻	0.504
6	USA North Carolina The Mt. Mitchell Area Forest 1986 – 1988 Lin et al. [21]	Na ⁺	0.07-0.54
		K ⁺	0.01-0.19
		Ca ²⁺	0.05-1.03
		Mg ²⁺	0.01-0.19
		NH ₄ ⁺	0.20-4.39
		NO ₃ ⁻	0.85-12.9
		SO ₄ ²⁻	2.18-33.6
7	Germany The Oak Ridge Forest	Na ⁺	0.144
		K ⁺	0.059
		Ca ²⁺	0.40
		Mg ²⁺	0.046
		NH ₄ ⁺	0.432
		NO ₃ ⁻	2.17
		SO ₄ ²⁻	3.89
Cl ⁻	0.817		

Table 1. Continuation

No.	Location, year, author	Selected ions	Concentration [mg/dm ³]
	Gottingen Forest 1987 Lindberg et al. [22]	Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺ NH ₄ ⁺ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻	0.253 0.257 0.36 0.059 0.918 2.98 4.27 0.348
8	Denmark Klosterhede 1989 The Netherlands Speuld 1993 Hansen et al. [5]	Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺ NH ₄ ⁺ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺ NH ₄ ⁺ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻	85.5 17.0 10.2 14.1 17.3 48.4 82.1 172.3 18.2 20.0 9.0 4.4 47.0 128.0 150.0 30.0
9	Spain Posadero Manzanal Durango Orbio 1993 - 1994 Amezaga et al. [16]	Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺ NH ₄ ⁺ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻	5.15 0.50 3.17 0.78 1.14 1.65 4.50 6.77
10	Italy Bogni di Masino Alpe Culino 1994 - 1996 Balestrini et al. [15]	Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺ NH ₄ ⁺ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻ Na ⁺ K ⁺ Ca ²⁺ Mg ²⁺ NH ₄ ⁺ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻	0.23 1.56 0.88 0.18 0.27 7.96 1.97 0.50 0.32 2.93 1.28 0.25 0.27 14.0 2.45 0.89
11	Lithuania 1994 - 1995 Sopauskiene and Jasineviciene [23]	Na ⁺ K ⁺ Ca ²⁺ NH ₄ ⁺ NO ₃ ⁻ SO ₄ ²⁻ Cl ⁻	0.41-1.21 1.16-3.08 0.74-0.93 1.00-2.02 2.17-3.19 5.16-9.87 1.53-3.78

contained a sampler consisting of a 5 l polyethylene bottle and a funnel 20.3 cm in diameter. Inside the funnel was a smaller funnel covered with polyethylene gauze (mesh size 2 mm x 2 mm) to prevent larger solid contaminants from entering the bottle. In winter the mesh size was larger (4 mm x 4 mm) while in summer it was smaller. During periods of heavy snowfall, the bottle and the funnel were replaced with a 5 l polyethylene bucket 21 cm in diameter. The sampler was placed on a stand 1.5 m above ground. The summer sampler was used during the period March 30, 1996 - November 2, 1996, while the winter sampler was used from March 2, 1996 to March 29, 1996, and from November 3, 1996 to February 1, 1997. Samples from substation PL 10 were taken directly to the laboratory, where their volume was measured, followed by preparation and analysis.

Substation PL 11

Substation PL 11 was located in the 60-year-old spruce forest. Such a location allowed us to collect so-called throughfall, i.e. deposition washing off the pollutants accumulated in tree crowns. This is the sum of wet and dry deposition, Westling et al. [24]. The station contained 10 samplers placed in a 30 x 30 m square. The samplers consisted of a 2 l polyethylene bottle and a funnel 15.5 cm in diameter. Plastic gauze (mesh size 2 mm x 2 mm) was placed at the end of the funnel stem to prevent solid contaminants from entering the bottle. The samplers were placed on a stand 50 cm above ground. Winter samplers consisted of 5 l polyethylene buckets 21 cm in diameter. The samplers were placed 65 cm above ground. Summer samplers were used from March 30, 1996 to November 2, 1996, while winter samplers were used from March 2, 1996 to March 29, 1996 and from November 3, 1996 to February 1, 1997. Samples from substation PL 11 were transferred to a 20 l polyethylene bucket and their volume measured. Next, a 2 l representative sample was collected. If a funnel was contaminated with bird faeces, the sample was rejected.

In both cases the samplers were additionally equipped with polyethylene sacks of 2 l and 8 l capacity. As a result, bottles did not have to be rinsed with distilled water after each sample collection. The bottles were wrapped in aluminum foil, which prevented evaporation of water during collection of precipitation. Shielding from solar radiation also inhibited algae growth. Samplers of similarly simple designs were used by Reimann et al. in 1994 in Russia, Finland and Norway [25], by Niirnberg et al. in the years 1980-1982 in Germany [26] and by Asman et al. in 1980 in Holland [27].

The samples were then transported to the laboratory, filtered through a medium qualitative filter paper (format 450 x 560 mm, PPH "POCh" S.A. Gliwice, Poland) using polyethylene funnels and stored in polyethylene containers in a refrigerator at about 4°C.

Apparatus

Concentrations of chloride, sulphate, phosphate, ammonium ions and of total nitrogen were determined spectrophotometrically using a Merck model SQ-118 photometer (Germany). This device has already been widely used for

the monitoring of quality of potable and surface waters, Polkowska et al. [28], Namiesnik et al. [29].

Sodium, potassium, and calcium ions were determined using a Carl Zeiss model Flapho-4 flame photometer (Germany). Magnesium ions were determined by AAS using a Carl Zeiss model IN spectrophotometer (Germany).

pH measurements were carried out using an Elmetron model CX-315 computer-controlled pH meter (Poland). Conductivity was measured using a Radelkis model OK-102/1 conductometer (Hungary).

Results and Discussion

The investigations provided information on the quantity of precipitation over a 12-month period (Table 2). The results of determinations of individual components (SO_4^{2-} , Cl^- , NO_3^- , NH_4^+ , PO_4^{3-} , N_{tot} , Mg^{2+} , K^+ , Na^+ , Ca^{2+} , pH, electrolytic conductivity) were tabulated. Table 3 refers to substation PL 10, and Table 4 - to substation PL 11. Electrolytic conductivity was measured to estimate the content of inorganic ions. Table 5 lists limits of detection of individual components.

Table 2. Volume of precipitation [dm^3] collected at individual substations.

Period of sample collection	Number of days	Substation PL 10	Substation PL 11
02-03-96 to 03-02-96	28	2.40	15.70
03-02-96 to 03-30-96	28	0.33	0.98
03-30-96 to 04-27-96	28	0.80	1.66
04-27-96 to 06-01-96	35	4.00	17.10
06-01-96 to 06-29-96	28	1.90	5.90
06-29-96 to 08-03-96	35	0.30	6.05
08-03-96 to 09-07-96	35	4.80	15.50
09-07-96 to 10-05-96	28	2.98	12.20
10-05-96 to 11-02-96	28	1.65	5.78
11-02-96 to 12-07-96	28	1.86	2.04
12-07-96 to 01-04-97	28	1.02	5.38
01-04-97 to 02-01-97	28	0.27	0.53

On the basis of experimental results deposition could be calculated using the following relations:

- precipitation per unit area was found from the following equation:

$$P = \frac{v \cdot 10^4}{n \cdot \pi \cdot r^2} \quad [\text{mm}]$$

where:

v - volume of collected precipitation [dm^3]

n - number of funnels

r - radius of a funnel or a bucket [cm]

P — precipitation volume per unit area [mm]

- deposition of individual ions was calculated from the following equation:

$$D = \frac{c \cdot P}{10^2} \quad [\text{mg}/\text{m}^3]$$

where:

c - concentration [mg/dm^3]

D - deposition [mg/m^3]

Periods of sample collection were 28 or 35 days. In order to compare data for different months, Figures 2-6 show the results in terms of 30-day deposition calculated from the following equation:

$$P_{30} = \frac{P \cdot 30}{n_d} \quad [\text{mm}/30 \text{ days}]$$

where:

P - precipitation collected over a period of n_d days [mm]

n_d - number of days of sample collection [days]

P_{30} - 30-day precipitation [mm/30 days]

$$D_{30} = \frac{D \cdot 30}{n_d} \quad [\text{mg}/(\text{m} \times 30 \text{ days})]$$

where:

D_{30} - 30-day deposition [$\text{mg}/(\text{m} \times 30 \text{ days})$]

D - deposition over a period of n_d days [mg/m].

Table 3. Concentrations of sulfates, chlorides, nitrates, ammonium, phosphates ion, total nitrogen, magnesium, potassium, sodium, calcium ions in [mg/dm^3], pH and electrolytic conductivity (cond.) in $\text{^}\mu\text{S}/\text{cm}$ in samples of precipitation collected at substation PL 10.

Sample collection period	$\text{SO}_4^{2-}\text{-S}$	Cl^-	$\text{NO}_3^- \text{-N}$	$\text{NH}_4^+ \text{-N}$	PO_4^{3-}	N_{tot}	Mg^{2+}	K^+	Na^+	Ca^{2+}	pH	Cond.
02-03-96 – 03-02-96	0.39	0.98	1.62	1.18	0.04	2.80	0.14	0.25	0.50	4.11	4.70	18
03-02-96 – 03-30-96	3.78	3.40	1.90	3.70	0.52	5.60	1.00	0.54	2.26	5.47	5.90	63
03-30-96 – 04-27-96	0.85	0.24	0.42	0.18	0.04	0.60	0.02	0.59	0.03	3.13	6.80	26
04-27-96 – 06-01-96	2.47	0.78	2.99	1.01	0.01	4.00	0.03	0.59	0.10	2.50	6.16	17
06-01-96 – 06-29-96	3.86	1.10	3.26	0.64	0.04	3.90	0.02	0.26	0.20	3.13	4.58	18
06-29-96 – 08-03-96	1.70	1.00	2.09	0.59	0.36	2.68	0.02	0.51	0.12	3.11	6.10	27
08-03-96 – 09-07-96	0.90	1.30	3.09	1.51	0.04	4.60	0.02	0.84	0.05	3.13	6.27	9
09-07-96 – 10-05-96	0.07	0.70	0.90	0.70	0.04	1.60	0.19	0.36	0.60	3.75	5.44	11
10-05-96 – 11-02-96	0.14	1.10	1.94	0.16	0.01	2.10	0.08	0.17	0.25	0.85	5.02	15
11-02-96 – 12-07-96	0.19	1.80	2.70	0.82	0.01	3.60	0.53	0.27	0.05	1.67	4.73	20
12-07-96 – 01-04-97	0.92	3.00	5.48	0.12	0.23	5.60	0.19	0.43	0.43	0.87	5.95	7
01-04-97 – 02-01-97	–	3.40	4.68	2.02	0.20	6.70	0.29	0.55	0.05	0.67	4.91	23

Table 4. Concentrations of sulfates, chlorides, nitrates, ammonium, phosphates ion, total nitrogen, magnesium, potassium, sodium, calcium ions in [mg/dm³], pH and electrolytic conductivity (cond.) in $\mu\text{S/cm}$ in samples of precipitation collected at substation PL 11.

Sample collection period	SO ₄ ²⁻ -S	Cl ⁻	NO ₃ ⁻ -N	NH ₄ ⁺ -N	PO ₄ ³⁻	N _{tot}	Mg ²⁺	K ⁺	Na ⁺	Ca ²⁺	pH	Cond.
02-03-96 – 03-02-96	5.26	2.30	3.00	2.61	0.17	5.60	2.00	1.06	1.00	5.30	3.70	63
03-02-96 – 03-30-96	15.20	11.60	8.54	8.16	0.94	16.7	2.50	7.75	6.40	7.12	4.50	110
03-30-96 – 04-27-96	8.57	9.90	4.12	5.68	0.71	9.80	0.08	2.57	0.40	3.75	3.40	31
04-27-96 – 06-01-96	7.77	2.48	3.90	1.70	0.06	5.60	0.08	3.73	0.94	3.75	4.01	44
06-01-96 – 06-29-96	11.00	4.30	5.48	0.96	0.30	6.80	0.10	5.87	1.21	3.75	4.10	41
06-29-96 – 08-03-96	2.50	2.10	2.16	1.10	0.56	3.26	0.09	2.91	1.04	3.47	5.40	28
08-03-96 – 09-07-96	3.20	2.57	3.87	1.93	0.41	5.82	0.07	4.06	0.60	3.38	4.92	23
09-07-96 – 10-05-96	0.10	3.40	1.70	1.06	0.19	2.76	0.24	2.90	0.90	4.38	4.70	27
10-05-96 – 11-02-96	0.59	5.20	6.65	1.05	0.50	7.70	0.09	0.38	0.35	3.33	4.29	65
11-02-96 – 12-07-96	0.92	8.80	5.53	1.27	0.34	6.80	2.25	1.14	0.35	2.95	4.16	50
12-07-96 – 01-04-97	8.60	8.00	8.43	1.97	0.43	10.4	0.24	1.12	1.12	3.94	3.81	21
01-04-97 – 02-01-97	16.3	20.9	19.97	6.03	1.38	26.0	0.85	7.50	0.35	1.67	4.80	86

Table 5. Limits of detection of individual components [mg/dm³].

Individual components	Limit of detection
Cl ⁻	1
NO ₃ ⁻	0.2
PO ₄ ³⁻	0.06
NH ₄ ⁺	0.01
SO ₄ ²⁻	3
Na ⁺	1
K ⁺	0.5
Ca ²⁺	1
Mg ²⁺	0.02
N _{tot}	0.5

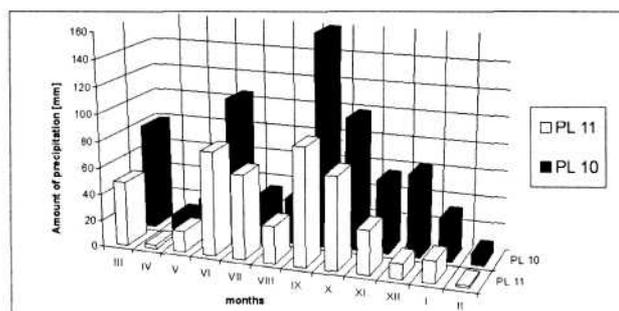


Fig. 2. Amount of precipitation [mm/30 days] in the clearing (substation PL 10) and in the forested area (substation PL 11) from March 2, 1996 to February 1, 1997.

The above calculations provided information on the amount of pollutants falling per unit area over a period of 30 days. The D₃₀ values can be compared because they all refer to the same time period.

Extended studies aimed at the determination of sulphates, nitrates, ammonia, phosphates, total nitrogen, magnesium, potassium, sodium, calcium, acidity, electrolytic conductivity and other characteristics in collected samples of precipitation were carried out during the period from

March 2, 1996 to February 1, 1997. The following conclusions can be drawn on their basis:

a) precipitation volume - higher precipitation was observed for substation PL 10, located in the clearing; the largest value was obtained in September and the smallest in February;

b) sulphates - the highest concentrations were observed in the forested area (substation PL 11) from January to June, i.e. in winter and spring (5.26 - 15.20 mg/dm³), (Spain 4.50 - 4.56 mg/dm³ [16, 14], Israel 7.15 - 27.02 mg/dm³ [19], Lithuania 5.16 - 9.87 mg/dm³ [23]);

c) chlorides - higher concentrations were observed in the forested area (substation PL 11), and the highest concentrations were found in March and April (spring) and in late autumn and winter (November, December and January - 8.00 - 20.9 mg/dm³), (Puerto Rico 17.68 mg/dm³ [6], Spain 6.77 mg/dm³ [16]);

d) nitrates - higher concentrations were observed in the forested area (substation PL 11), the largest values being obtained in winter, spring and fall - 5.53 - 19.97 mg/dm³), (Germany 2.17 - 2.98 mg/dm³ [22], Italy 7.96 - 14.0 mg/dm³ [15], Lithuania 2.17 - 3.19 mg/dm³ [23]);

e) ammonium ions - comparable values were observed at both substations: PL 10 and PL 11, the largest values being obtained in winter and spring (1.18 - 8.16 mg/dm³), (USA, North Carolina 0.20 - 4.39 mg/dm³ [21], Lithuania 1.00- 2.02 mg/dm³ [23]);

f) pH values - larger values were observed for water samples collected in the clearing; the highest pH 6.80 was found on April 27, 1996, and the lowest pH 4.58 was found on June 29, 1996; the pH values for water samples collected in the forested area ranged from 3.40 to 5.40;

g) phosphates - comparable values were observed at both substations: PL 10 and PL 11, the largest values being obtained in January, March and April 0.52 - 1.38 mg/dm³;

h) total nitrogen - comparable values were observed at both substations: PL 10 and PL 11, the largest values being obtained in December, January and March, April 9.80 - 26.0 mg/dm³;

i) magnesium - the highest concentrations were observed in the forested area (substation PL 11) in March and November 2.25 - 2.50 mg/dm³ (The Netherlands 4.4 mg/dm³ [5], Puerto Rico 1.31 mg/dm³ [6]);

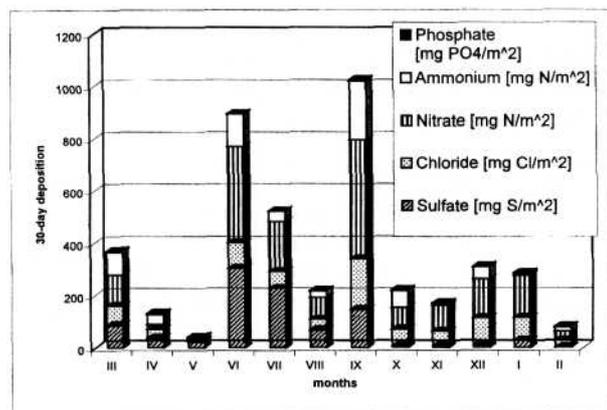


Fig. 3. Phosphate deposition [$\text{mg PCVCm}^3 \times 30 \text{ days}$], ammonium ion deposition [$\text{mg N}/(\text{m}^3 \times 30 \text{ days})$], nitrate deposition [$\text{mg N}/(\text{m}^3 \times 30 \text{ days})$], chloride deposition [$\text{mg Cl}/(\text{m}^3 \times 30 \text{ days})$], sulphate deposition [$\text{mg S}/(\text{m}^3 \times 30 \text{ days})$], in the clearing (substation PL 10) from March 2, 1996 to February 1, 1997.

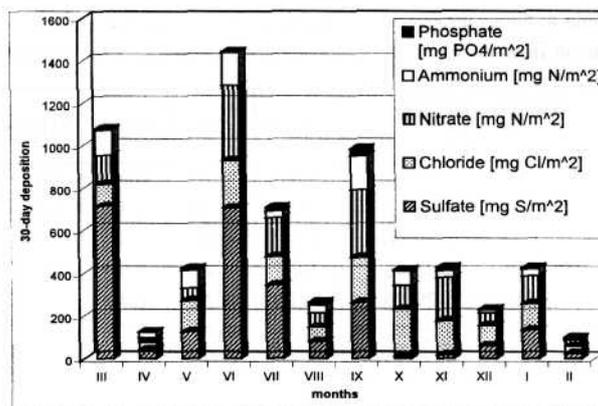


Fig. 5. Phosphate deposition [$\text{mg PO}_4/(\text{m}^3 \times 30 \text{ days})$], ammonium ion deposition [$\text{mg N}/(\text{m}^3 \times 30 \text{ days})$], nitrate deposition [$\text{mg N}/(\text{m}^3 \times 30 \text{ days})$], chloride deposition [$\text{mg Cl}/(\text{m}^3 \times 30 \text{ days})$], sulphate deposition [$\text{mg S}/(\text{m}^3 \times 30 \text{ days})$], in the forested area (substation PL 11) from March 2, 1996 to February 1, 1997.

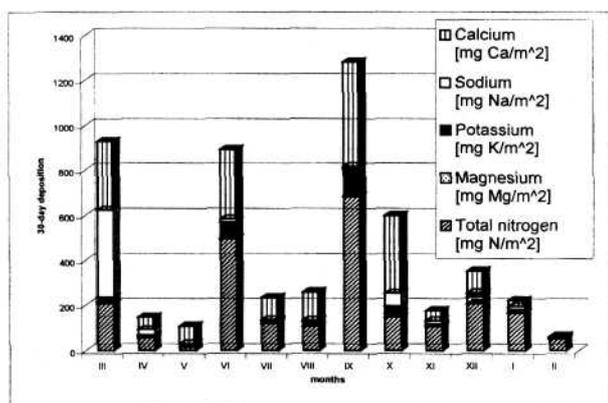


Fig. 4. Calcium ion deposition [$\text{mg Ca}/(\text{m}^3 \times 30 \text{ days})$], sodium ion deposition [$\text{mg Na}/(\text{m}^3 \times 30 \text{ days})$], potassium ion deposition [$\text{mg K}/(\text{m}^3 \times 30 \text{ days})$], magnesium ion deposition [$\text{mg Mg}/(\text{m}^3 \times 30 \text{ days})$], total nitrogen deposition [$\text{mg N}/(\text{m}^3 \times 30 \text{ days})$] in the clearing (substation PL 10) from March 2, 1996 to February 1, 1997.

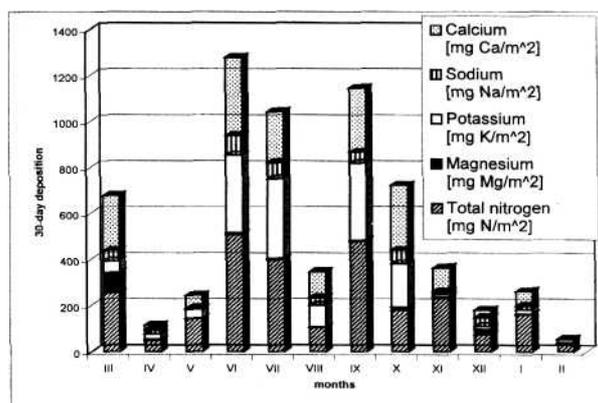


Fig. 6. Calcium ion deposition [$\text{mg Ca}/(\text{m}^3 \times 30 \text{ days})$], sodium ion deposition [$\text{mg Na}/(\text{m}^3 \times 30 \text{ days})$], potassium ion deposition [$\text{mg K}/(\text{m}^3 \times 30 \text{ days})$], magnesium ion deposition [$\text{mg Mg}/(\text{m}^3 \times 30 \text{ days})$], total nitrogen deposition [$\text{mg N}/(\text{m}^3 \times 30 \text{ days})$] in the forested area (substation PL 11) from March 2, 1996 to February 1, 1997.

j) potassium - the highest concentrations were observed in the forested area (substation PL 11), the largest values being obtained in January and March $7.50 - 7.75 \text{ mg}/\text{dm}^3$ (Denmark $17.0 \text{ mg}/\text{dm}^3$, The Netherlands $20.0 \text{ mg}/\text{dm}^3$ [5]);

k) sodium - comparable values were observed at both substations: PL 10 and PL 11, the largest values being obtained in March at substation PL 10 $2.26 \text{ mg}/\text{dm}^3$ (Spain $1.37 \text{ mg}/\text{dm}^3$ [14] and $5.15 \text{ mg}/\text{dm}^3$ [16]);

l) calcium - the highest concentrations were found in autumn at substation PL 11 in March $7.12 \text{ mg}/\text{dm}^3$ (Spain $6.06 \text{ mg}/\text{dm}^3$ [14], The Netherlands $9.0 \text{ mg}/\text{dm}^3$ [5]);

m) electrolytic conductivity was considerably higher for water samples collected in the forested area (substation PL 11) from February to April, the largest value ($110 \mu\text{S}$) being obtained on March 30, 1996.

The largest spread of concentrations was observed for chlorides, sulphates, phosphates, potassium and magnesium ions in water samples collected at substation PL 11. In water samples collected at substation PL 10 the largest concentration spread was found for total nitrogen, nitrates, and ammonium, sodium and calcium ions.

Conclusions

In summary, we conclude that:

- The content of various inorganic ions in precipitation varies with the season of the year.

- The highest contents of inorganic pollutants were detected in water samples collected at the substation located in the forested area (PL 11) in spring and late autumn or winter. This may result from the elution from tree crowns of pollutants deposited there in winter and summer. During spring and autumn raining is heavier and pollutants are washed down from tree crowns.

- The results of selected pollutants determination show a good correlation with results of analysis of the same ions (present in precipitation water sampled from similar areas) obtained by other scientific centres all over the world.

Acknowledgements

During the investigations described in this paper the authors used equipment donated by the League for Envi-

ronmental Protection in Karlshamn (Sweden) whose long-term cooperation with the Faculty of Chemistry of the Technical University of Gdansk is greatly appreciated. The authors would like to thank Professor B. Mędrzycka for her help and for lending some of the equipment used in this study.

References

1. TURZANSKI K.P., GODZIK B.: Wet deposition of pollutants in the Cracow region, Proc. Symposium on Chemistry and Effect of Acid Rain on the Environment, Poznan - Jeziory, 10 June 1996, p. 11.
2. TWAROWSKI R.: Acidity and pollution of precipitation in the Karkonosze, Proc. Symposium on Chemistry and Effect of Acid Rain on the Environment, Poznan - Jeziory, Poland, 10 June 1996, p. 61.
3. UDISTI R., BARBOLANI E., PANTANI F., *Ann. Chim.*, 81, 51, 1991.
4. LACAUX J. P., DELMAS R., KOUADIO G., CROS B., ANDREA M. O., *J. Geophys. Res.*, D6, 6195, 1992.
5. HANSEN K., DRAAIJERS G. P. J., IVENS W. P. M. F., GUNDERSEN P., van LEEUWEN N. F. M., *Atmos. Environ.*, 20, 3195, 1994.
6. ASBURY C. E., MCDOWELL W. H., TRINIDAD - PIZARRO R., BERRIOS S., *Atmos. Environ.* 10, 1773, 1994.
7. DECET F., *Boll. Chim. Igien.*, 45, 277, 1994.
8. OIKAWA K., MURANO K., ENOMOTO Y., WADA K., INOMATA T., *J. Chromatogr. A*, 671, 211, 1994.
9. DOSCHER A., SCHWIKOWSKI M., GAGGELER H.W., *J. Chromatogr. A*, 706, 249 1995.
10. LI C. S., HONG Y. T., JENG F. T., *Sci. Total Environ.*, 164, 19, 1995.
11. TARTARI G. A., MARCHETTO A., MOSELLO R., *J. Chromatogr. A*, 706, 21, 1995.
12. MARCHETTO A., MOSELLO R., TARTARI G. A., MUNTAU H., BIANCHI M., GEISS H., SERRINI G., SERRINI-LANZA G., *J. Chromatogr. A*, 706, 13, 1995.
13. SANUSI A., WORTHAM H., MILLET M., MIRABEL P., *Atmos. Environ.*, 30, 59, 1996.
14. AVILA A., ALARCON M., QUERALT I., *Atmos. Environ.* 32, 179, 1998.
15. BALESTRINI R., GALLI L., TAGLIAFERRI A., TARTARI G., *Chemosphere*, 4-5, 1095, 1998.
16. AMEZAGA I., GONZALEZ ARIAS A., DOMINGO M., ECHEANDIA A., ONAINDIA M., *Water, Air, and Soil Pollution*, 97, 303, 1997.
17. LOVBLAD G., HOVMAND M.: IVL Report, Throughfall Monitoring in the Nordic Countries, Swedish Environmental Research Institute, Gothenburg 1994.
18. NAMIESNIK J., LUKASIK J., JAMROGIEWICZ Z.: Collection of environmental samples for analysis, Polish Scientific Publishers PWN, Warszawa, p. 112, 1995.
19. SINGER A., GANOR E., FRIED M., SHAMAY Y., *Atmos. Environ.*, 22, 3881, 1996.
20. DRAAIJERS G. P. J., ERISMAN J. W., SPRANGER T., WYERS G. P., *Atmos. Environ.*, 19, 3349, 1996.
21. LIN N. - H., SAXENA V. K., *Atmos. Environ.*, 2, 517, 1991.
22. LINDBERG S. E., BREDEMEIER M., SCHAEFER D. A., QI L., *Atmos. Environ.*, 8, 2207, 1990.
23. SOPAUSKIENE D., JASINEVICIENE D., *Atmos. Phys.*, 1, 5, 1996.
24. WESTLING O., HULTBERG H., MALM G.: Total deposition and tree canopy internal circulation of nutrients in a strong acid deposition gradient in Sweden, as reflected by throughfall fluxes. In: Nutrient uptake and cycling in forest ecosystems (Eds. L.O. Nilsson, R.F. Huttel and U.T. Johansson) Kluwer Academic Publ., p. 639, 1995.
25. REIMANN C., DE CERIFAT P., HALLERAKER IO H., VOLDEN T., AYRAS M., NISKAVAARA H., CHEKUSHIN V. A., PAVLOV V., *Atmos. Environ.*, 31, 159, 1997.
26. NURNBERG H. W., VALENTA P., NGUYEN D., GODDE M., URANO DE CARVALHO E., FRESENIUS Z., *Anal. Chem.*, 317, 314, 1984.
27. ASMAN W. A. H., SLANINA J., BAARD J. H., *Water, Air, and Soil Pollution*, 16, 159, 1981.
28. POLKOWSKA Z., NAMIESNIK J., WYSOCKA I., GORLO D., *Chem. Inz. Ekol.*, 4, 557, 1996.
29. NAMIESNIK J., POLKOWSKA Z., KONIECZKA P., *Chem. Inz. Ekol.*, 3, 373, 1994.