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Research Article

Chosen anions and cations in the precipitation over the coastal  
zone of the Gulf of Gdańsk

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Gdańsk, pH, precipitation, wet deposition

**Abstract**

The study of the chemical composition of precipitation was carried out from November 2002 till October 2003, in the urbanized area of the Gulf of Gdańsk. About 88% of the collected samples showed acid value, and the average pH was 5.14. The highest acid values were found in summer when sulfates were the dominant ions. The highest concentrations of nitrates were noted between autumn and spring, and the precipitation pH was less acidic than in summer. The coastal station at the Gulf of Gdańsk was characterized by more effective neutralization of precipitation in the heating season as compared to the other urbanized areas. It was found that the neutralization process in the coastal zone was much more intense due to the sea salt particle presence in aerosols rather than in gaseous ammonia. The most intensive neutralization of

precipitation was observed between late autumn and spring. In May, when offshore winds dominated, the values of neutralization coefficient (NF) for  $\text{Na}^+$  and  $\text{NH}_4^+$  were 1.3 and 0.2, respectively. It was evidenced that the specific combination of meteorological parameters (velocity and direction of wind, humidity and temperature of air) had a significant influence on the chemical composition of precipitation.

## INTRODUCTION

Precipitation can be defined as a heterogeneous solution. It includes inorganic and organic chemical compounds of natural and anthropogenic origin. The chemical composition of precipitation provides information on the sources and reactions of gases and aerosols in the atmosphere. Some substances dissolved in precipitation, especially anthropogenic ones, could be good indicators of atmospheric pollution. Although rainwater is the most effective scavenging factor in the atmosphere, it causes re-entry of chemical compounds (by their deposition at soil or water surface) to the cycle of elements in an ecosystem (Richter and Lindberg 1988). The load of substances introduced to the ground with precipitation depends primarily on their atmospheric concentrations, the presence of substances affecting physicochemical conditions and meteorological conditions, such as precipitation level, air temperature and relative humidity, atmospheric pressure, wind direction and velocity.

Sulfur and nitrogen oxides and also sulfate ions could react with atmospheric water drops, which results in the presence of strong sulfuric and nitric acids followed by the formation of acid aerosols. Acid precipitation has adverse effects on land and water ecosystems. The ecological disturbance includes chemical degradation of soils, surface and ground waters together with the loss of their buffering properties, damage or death of great areas of agriculture and forest, corrosion of metal constructions and buildings (Kvaalen *et al.* 2002). Due to atmospheric  $\text{CO}_2$ , even in "clear air" precipitation pH is acidic, and the mean pH of unpolluted precipitation is *ca.* 5.6 (Seinfeld and Pandis 1998). In an atmosphere contaminated with nitrogen and sulfur compounds, the acidity level depends on the presence of neutralizing substances, such as  $\text{NH}_3$ ,  $\text{CaCO}_3$  and hydroxide (Flues *et al.* 2002).

The coastal zone of the Gulf of Gdańsk is affected by anthropopression. The degree of atmospheric pollution could be influenced by local and dispersed emission sources situated in the Tri-City agglomeration (traffic arteries, petroleum refining industry, shipyards and harbours, agriculture) and transfrontier atmospheric pollution. Although acid precipitation has affected Baltic countries for decades (EMEP 2004), there are only a few studies considering the complex chemical analysis of atmospheric precipitation in the coastal zone of the southern Baltic, especially in the Gulf of Gdańsk. Therefore, a long-term scientific project was undertaken in 2002 at the Institute of

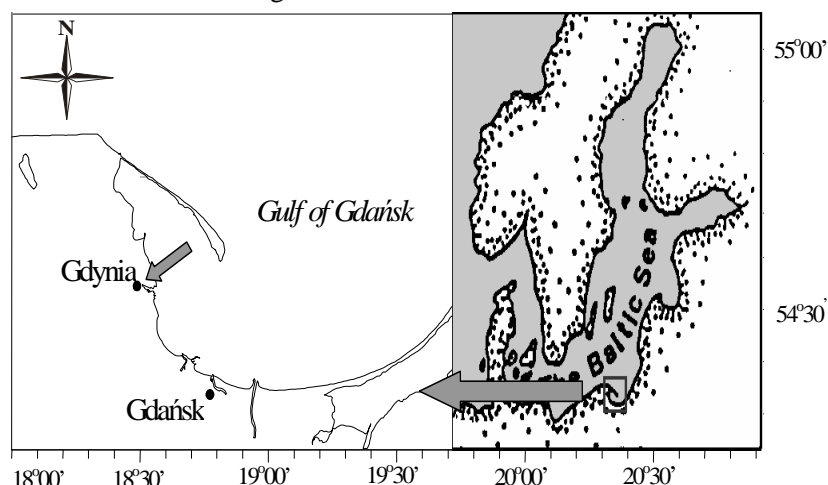
Oceanography, University of Gdańsk. It is aimed at the characterization of chemical composition of atmospheric precipitation and the determination of its causes and effects observed in the coastal zone where land and sea conditions could influence physicochemical processes that occur in the atmosphere.

The paper presents the results of a one-year study carried out in Gdynia, 1 km away from the shoreline of the Gulf of Gdańsk. The precipitation was analyzed for the presence of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$  and  $\text{Na}^+$  ions and their changes in winter and vegetation seasons when the precipitation level and chemical composition could affect the rate and range of eutrophication process.

#### MATERIAL AND METHODS

The investigations into the chemical composition of precipitation were carried out on the roof of the building of the Faculty of Biology, Geography and Oceanology (University of Gdańsk) in Gdynia (Fig. 1). The measuring set was positioned 20 m above the ground, over the tree canopy. The sampling period ranged from November 2002 till October 2003, and precipitation types (rainfall, snowfall or snowfall with rainfall) were determined. The basic meteorological data used here were precipitation level, wind velocity and direction, air humidity and temperature, and atmospheric pressure. The period of collector exposure depended on precipitation time and a minimum volume of precipitation sufficient for chemical analyses.

Precipitation samples were collected in a polyethylene bottle (1 dm<sup>3</sup>) and a funnel (20 cm in diameter) made of the same material. Both elements were connected with a Teflon ring.



**Fig. 1.** Location of the sampling station and the sampling set used for precipitation collection.

The collecting bottle and the funnel surface were at first etched with 1M HCl, then washed frequently with deionized milli-Q water and dried at 80°C. The analyses were carried out following the procedures recommended by HELCOM (Granat *et al.* 1992). In accordance with Gordon *et al.* (1995), the samples were not filtered as pH and conductivity measurements were made immediately after sampling. The samples were immediately weighed for volume determination and precipitation level was estimated. Snowfall samples were melted thoroughly at room temperature. The pH values were measured with a glass electrode (ERH-11 type). The pH meter (WTW) was calibrated before with two standard solutions of 7.00 and 4.00 pH values. Conductivity was measured with a salinometer (inoLab Cond Level 1) at 20°C.

The sample aliquots for chemical analysis were kept in polyethylene bottles at 4°C in the refrigerator to preserve them from sunlight and retard the rate of microbial growth and biochemical processes. The samples were stored not longer than two weeks.

The concentrations of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NH}_4^+$  ions were determined by colorimetric methods, and  $\text{Na}^+$  ions by atomic absorption spectrometry (Analyst 300, Perkin Elmer). Chloride ions were determined in the reaction, which yields a yellow complex ( $\text{Fe}[\text{CSN}]_3$ ) in the presence of perchloric acid (EMEP 1977). Ammonia was determined by the indophenol method based on the formation of an indophenol blue pigment in the reaction of phenol and hypochlorite in the presence of ammonia in an alkaline medium (pH 8-11.5) (Lewandowska and Falkowska 2004). Nitrates were reduced in the presence of hydrazine in an alkaline medium followed by the formation of a coloured diazo compound with sulfanilic acid and N-(1-naphthyl)-ethylenediamine dihydrochloride (PN 1992a). Sulfates were precipitated from a barium perchlorate solution in the presence of ethanol, and the excess of barium ions yielded a yellow complex with thorin (PN 1992).

Sample dilution was taken into account while calculating ion concentrations in precipitation. The relative standard deviation at low (high) ion concentrations were:  $\text{Na}^+$ : 0.16 (11.03%);  $\text{Cl}^-$ : 0.69 (9.69%);  $\text{NO}_3^-$ : 0.77 (13.93%);  $\text{SO}_4^{2-}$ : 0.26 (5.29%) and  $\text{NH}_4^+$ : 0.37 (6.08%). Detection limits (LOD = 3SD) for the reference sample were:  $\text{Na}^+$ : 0.003 mg l<sup>-1</sup>;  $\text{Cl}^-$ : 0.132 mg l<sup>-1</sup>;  $\text{NO}_3^-$ : 0.168 mg l<sup>-1</sup>;  $\text{SO}_4^{2-}$ : 0.867 mg l<sup>-1</sup> and  $\text{NH}_4^+$ : 0.132 µmol l<sup>-1</sup>. Volume-weighted mean concentrations of ions in precipitation in several months were expressed as µeq l<sup>-1</sup>, according to the equation:

$$C_M = \frac{\sum P_i C_i}{\sum P_i} \quad (1)$$

where:

$P_i$ : the precipitation amount collected at each sampling period (mm)

$C_i$ : the corresponding concentration

$P_i C_i$ : the total collected amount per unit area and month

The values of chemical compound fluxes ( $\text{mg m}^{-2}$ ) washed by precipitation were estimated every month from the equation:

$$F = \frac{CV}{S} \quad (2)$$

where:

$C$ : ion concentration ( $\text{mg l}^{-1}$ )

$V$ : sample volume ( $\text{dm}^3$ )

$S$ : collector area ( $\text{m}^2$ )

45 rainwater samples were analysed in the study. A multivariate statistical technique, *i.e.* PCA with normalized varimax rotation was applied for the results of all measurements. Neutralization factors (NFs) were derived from a formula by Possanzini (1988):

$$\text{NF}(X)(\mu\text{eq l}^{-1}) = X / (\text{SO}_4^{2-} + \text{NO}_3^-) \quad (3)$$

where:

$X$ :  $\text{NH}_4^+$  or  $\text{Na}^+$  concentrations.

The concentrations of non-sea-salt sulfate ions ( $\text{nssSO}_4^{2-}$ ) were calculated according to Sievering *et al.* (1990):

$$\text{nssSO}_4^{2-}(\text{mg l}^{-1}) = \text{SO}_4^{2-} - (\text{Na}^+ \cdot 0,059) \quad (4)$$

## RESULTS AND DISCUSSION

### *Chemical characterization of precipitation samples*

Among anions, nitrate, sulfate and chloride showed the greatest concentrations (Table 1). Nitrate dominated in the cold period whereas high concentrations of sulfate and chloride were noted throughout the whole year. However, higher concentrations of both ions were observed in the vegetation season as compared to the other periods. Sodium and ammonium ions were most abundant in winter. Their concentrations were several times lower as compared to those of the  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ions.

In summer, the contribution of non-sea-salt sulfate ( $\text{nssSO}_4^{2-}$ ) dissolved in rainwater remained at a level of 85%. The main source of those ions in the atmosphere is the oxidation of anthropogenic  $\text{SO}_2$  and DMS from natural land origin (big forest complexes-Seaside Landscape Park) and from the sea surface

**Table 1**

Monthly averages of physical and chemical parameters in precipitation samples collected over Gdynia between November 2002 and October 2003 (normal font – average values and summary H, italic font - minimum and maximum values)

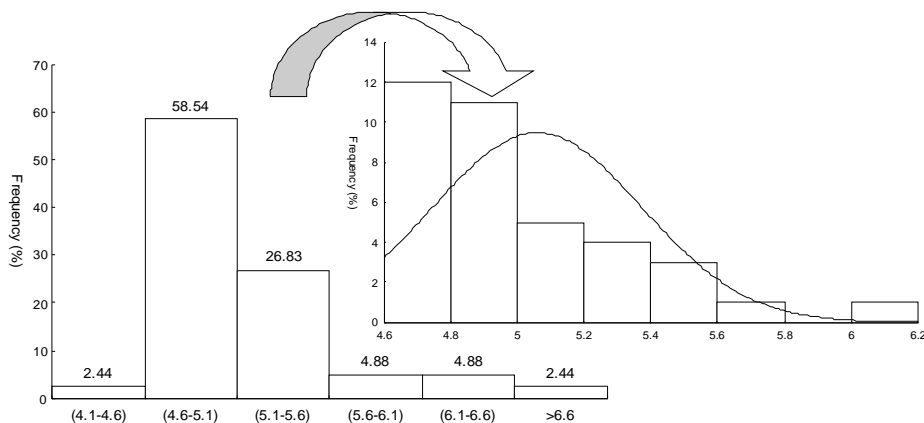
Month-year/n	H (mm)	pH	κ (μS cm <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	V <sub>w</sub> * (m s <sup>-1</sup> )	T (°C)	Rh (%)
				(μeq l <sup>-1</sup> )							
XI-02/2	8.51 <i>(0.59-7.92)</i>	5.31 <i>(5.23-5.38)</i>	-	21 <i>(18-51)</i>	21 <i>(20-22)</i>	283 <i>(134-294)</i>	157 <i>(30-167)</i>	155 <i>(154-172)</i>	2.21 <i>(1.87-6.10)</i>	4.52 <i>(3.57-(-5.47))</i>	-
XII-02/3	12.43 <i>(0.79-6.49)</i>	5.33 <i>(5.11-5.59)</i>	83.20 <i>(76.60-89.80)</i>	57 <i>(24-82)</i>	24 <i>(23-33)</i>	114 <i>(92-260)</i>	143 <i>(79-160)</i>	185 <i>(140-207)</i>	1.79 <i>(1.46-6.30)</i>	-2.69 <i>(-3.09-(-2.28))</i>	-
I-03/4	32.45 <i>(3.30-17.57)</i>	5.30 <i>(5.05-6.45)</i>	39.58 <i>(19.40-53.20)</i>	31 <i>(16-47)</i>	210 <i>(13-415)</i>	90 <i>(62-182)</i>	83 <i>(58-153)</i>	212 <i>(16-290)</i>	2.21 <i>(1.98-6.90)</i>	-	-
II-03/2	1.14 <i>(0.36-0.78)</i>	5.00 <i>(5.00-5.00)</i>	137.60 <i>(112.40-162.80)</i>	189 <i>(168-210)</i>	413 <i>(324-454)</i>	169 <i>(145-181)</i>	212 <i>(13-304)</i>	184 <i>(166-193)</i>	1.58 <i>(1.47-8.20)</i>	-1.84 <i>(-2.93-(-0.70))</i>	81.04 <i>(77.36-100)</i>
III-03/3	7.70 <i>(2.08-5.61)</i>	5.15 <i>(4.80-5.50)</i>	62.30 <i>(52.20-72.40)</i>	18 <i>(8-46)</i>	313 <i>(270-428)</i>	150 <i>(125-160)</i>	137 <i>(126-141)</i>	135 <i>(90-152)</i>	2.45 <i>(2.19-9.00)</i>	3.96 <i>(2.61-5.49)</i>	71.38 <i>(36.74-100)</i>
IV-03/4	19.97 <i>(3.01-11.45)</i>	5.23 <i>(5.12-5.58)</i>	26.20 <i>(11.50-40.90)</i>	34 <i>(30-49)</i>	46 <i>(32-100)</i>	177 <i>(73-180)</i>	49 <i>(40-84)</i>	382 <i>(185-434)</i>	2.63 <i>(1.63-10.70)</i>	7.33 <i>(-0.08-12.68)</i>	72.21 <i>(68.63-100)</i>
V-03/3	51.10 <i>(24.88-26.21)</i>	5.59 <i>(4.96-6.21)</i>	34.10 <i>(12.10-40.20)</i>	19 <i>(16-21)</i>	52 <i>(23-83)</i>	313 <i>(285-341)</i>	167 <i>(129-203)</i>	83 <i>(71-161)</i>	1.82 <i>(1.63-7.00)</i>	13.98 <i>(12.45-15.51)</i>	72.06 <i>(66.10-100)</i>
VI-03/5	68.11 <i>(3.95-34.41)</i>	5.58 <i>(4.52-6.62)</i>	22.88 <i>(12.10-40.20)</i>	7 <i>(3-10)</i>	68 <i>(31-95)</i>	121 <i>(97-189)</i>	10 <i>(7-19)</i>	117 <i>(12-181)</i>	2.26 <i>(1.49-6.30)</i>	16.64 <i>(15.19-20.19)</i>	68.07 <i>(60.79-100)</i>
VII-03/5	67.36 <i>(0.85-27.72)</i>	4.92 <i>(4.70-5.78)</i>	11.18 <i>(9.10-23.50)</i>	9 <i>(4-19)</i>	55 <i>(45-84)</i>	173 <i>(151-355)</i>	45 <i>(1-149)</i>	186 <i>(114-262)</i>	1.89 <i>(1.63-5.50)</i>	18.83 <i>(16.87-21.20)</i>	80.48 <i>(74.16-100)</i>
VIII-03/4	48.38 <i>(3.41-32.97)</i>	4.85 <i>(4.80-5.00)</i>	26.58 <i>(20.40-76.30)</i>	20 <i>(7-26)</i>	138 <i>(38-173)</i>	247 <i>(173-291)</i>	39 <i>(8-92)</i>	183 <i>(58-208)</i>	1.92 <i>(1.85-6.20)</i>	18.29 <i>(13.27-18.82)</i>	75.03 <i>(74.19-100)</i>
IX-03/4	7.37 <i>(0.33-5.43)</i>	4.87 <i>(4.80-4.88)</i>	51.55 <i>(26.80-70.10)</i>	10 <i>(3-46)</i>	142 <i>(139-182)</i>	165 <i>(111-189)</i>	54 <i>(37-109)</i>	208 <i>(81-272)</i>	1.81 <i>(1.25-7.70)</i>	15.79 <i>(12.39-18.01)</i>	76.44 <i>(69.56-100)</i>
X-03/6	50.20 <i>(0.70-19.35)</i>	5.00 <i>(4.80-5.25)</i>	23.74 <i>(4.80-26.00)</i>	31 <i>(2-89)</i>	86 <i>(83-166)</i>	193 <i>(165-250)</i>	56 <i>(9-169)</i>	93 <i>(25-189)</i>	2.00 <i>(1.43-6.30)</i>	7.44 <i>(2.06-11.20)</i>	75.40 <i>(61.28-100)</i>
Average	9.14	5.14	35.19	37	131	183	96	170	2.04	9.30	74.68
S.D.	9.24	0.48	29.28	50	123	68	64	90	0.30	7.85	4.26

n - number of samples, H- total amount of precipitation, κ - conductivity, V<sub>w</sub>- wind velocity (\* - was measured for 30 min., at 10 s intervals), T- air temperature, Rh- air humidity, S.D.- standard deviation

(Falkowska and Lewandowska 2004). In the Tri-City and its suburbs, there are many anthropogenic stationary and mobile sources which emit a great amount of pollutants, *e.g.* Sulfur Reloading Plant "Sulfur-Harbour" (yearly reloading of *ca.* 2 million tons of sulfur), Gdańsk Refinery, agriculture and industry plants, harbours, shipbuilding industry, thermal-electric power stations, adjacent boiler plants and communication arteries. Aerosols formed as a result of DMS conversion are the second potentially important source of rainwater sulfate. In the vegetation periods of 1997 and 2000, the process could produce 75-100% of  $\text{nssSO}_4^{2-}$  in aerosols over the Gulf of Gdańsk (Lewandowska *et al.* 2004). Lee *et al.* (2000) also reported a high contribution of marine source to the formation of  $\text{nssSO}_4^{2-}$  fraction in total sulfate mass at the Sochong coastal station situated on the eastern coast of the Korean Peninsula. The source efficiency depended on phytoplankton vital functions. As a result, DMS was released into the atmosphere whereas wind direction and velocity promoted its drift to the land.

#### Variation of pH - acidification or neutralization

The collected precipitation samples showed acidic values, 4.52-6.62 (Fig. 2). According to commonly accepted classification, the pH of naturally acidic precipitation is above 5.6. The value is a hydrogen ion exponent equilibrated with atmospheric  $\text{CO}_2$  (350 ppm) (Seinfeld and Pandis 1998). In summer, due to



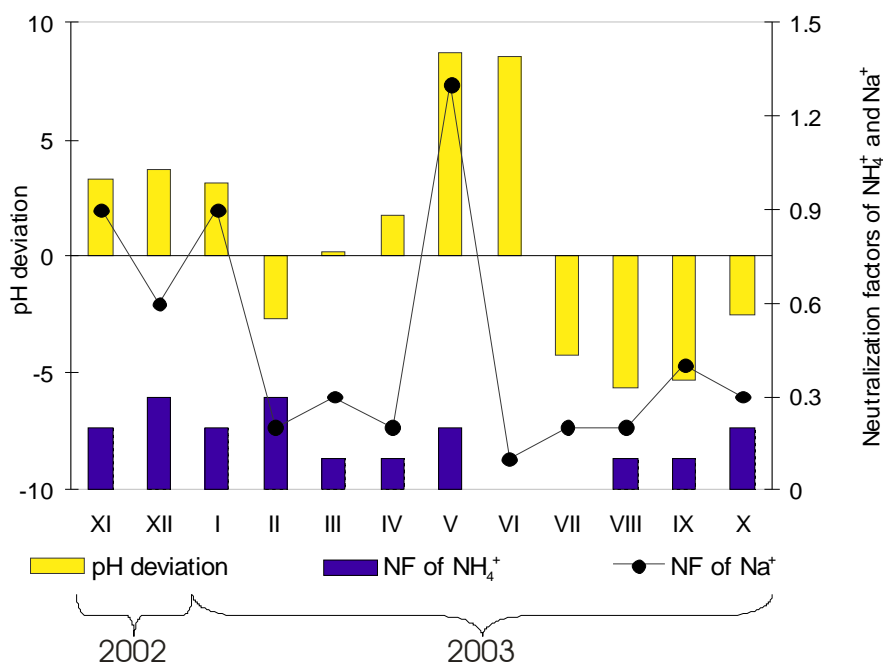
**Fig. 2.** Histograms of precipitation pH values determined in Gdynia (2002/2003).

high photosynthesis intensity,  $\text{CO}_2$  concentration is slightly lower. In winter, however, it increases proportionally to the rate of biomass remineralization (Gratani and Varone 2005). It could be presumed that outside the vegetation season a twofold increase in  $\text{CO}_2$  concentration in relation to the global level will result in a decrease in acidic precipitation pH by 0.15, and the pH will attain a value of 5.45. In summer, on the other hand, a twofold decrease in  $\text{CO}_2$

concentration will produce an increase in pH value to 5.75. However, the above difference is of minor importance on a yearly scale. Irrespective of the accepted classification, only 5 precipitation samples were naturally acidic (Fig. 2). The rest of them (88%) contained acid-forming compounds from anthropogenic sources. Similar results were reported from the middle coast of the Baltic Sea (Łeba - 4.5) (Przybylska 1997), in the Czech Republic - 5.0 (Bridges *et al.* 2002) and Scandinavia (pH below 5.0) (Vuorenmaa 2004).

The annual mean pH of precipitation in Gdynia was 5.14. Monthly mean pH values were always lower than 5.6. Deviation from annual mean pH (Fig. 3) indicates that:

- positive values were noted between late autumn and summer when the concentrations of  $\text{NH}_4^+$  and sea salts were relatively high,
- negative values observed between July and October 2003 point to an increase in precipitation acidity.



**Fig. 3.** Temporal variation of precipitation pH (%) against annual mean pH (the mean value, 5.14, was accepted as 0%) and neutralization factors for  $\text{NH}_4^+$  and  $\text{Na}^+$  ions, calculated from equation (3).

In autumn, winter and spring, elevated values of precipitation pH as compared to the annual mean were not typical for Gdynia. However, pH of

precipitation events in other urbanized areas, *e.g.* Colmar or Strasburg, was significantly lower in the heating season (Sanusi *et al.* 1996). Other investigations have led to similar findings. Balestrini *et al.* (2000) and Okay *et al.* (2002) noted that precipitation in Italy and Turkey was strongly acidic in the cold half year. The situation in Gdynia was found to be different. Although the results of atmospheric monitoring in the Tri-City (ARMAAG 2004) indicated a marked increase in SO<sub>x</sub>, NO<sub>x</sub> and dust emissions in the cold season, a decrease in acidic precipitation pH was not observed. Such an exceptional situation could be attributed to the presence of precipitation neutralizers. It is highly probable that the process is much more intensive on coarse sea salt particles than on gaseous ammonia (Fig. 3). In winter, when storm winds are common in the surf zone (Table 1), the air is saturated with sea salt that plays a crucial role as a neutralization factor. This was confirmed by NF (Na<sup>+</sup>) values, 0.9 and 0.6 in November and December 2002, respectively.

Within the unusual period observed from autumn to summer, a typical situation was noted only in February. At that time, despite relatively high neutralization factors (0.3 for NH<sub>4</sub><sup>+</sup> and 0.2 for Na<sup>+</sup>), precipitation was acidic. Such a situation was found at the lowest amount of total precipitation (1.14 mm) and highest precipitation conductivity (Table 1). Under such conditions strongly acidic precipitation resulting from the winter emissions of anthropogenically derived pollutants and low neutralizer concentrations could be expected. The data obtained here confirm a long-term trend observed in Gdynia by Owczarek (2000). In next months (March and April 2003), despite the high concentrations of nitrate, sulfate and chloride ions, precipitation was heavier and less acidic than in February.

The pH value of spring precipitation (May and June 2003) was close to the limit value, 5.6. In May, the total precipitation level came up to 51.10 mm, and it was even higher in June (68.11 mm). In addition, heavy rain of 33.4 mm was noted in June. Although in both months the standard deviations from annual mean pH were positive and the highest, they resulted from different reasons. In May, the neutralization factor for Cl/Na<sup>+</sup> was the highest, indicating that neutralization was much more related to sea salt than to NH<sub>3</sub>. In June, however, the observed phenomenon was a consequence of the dilution effect, *i.e.* low nitrate and sulfate concentrations in a high volume of precipitation.

In summer and early autumn, an increased acidity in precipitation was observed though the concentrations of nitrate and sulfate ions were lower as compared to the other seasons. At that period, because of low NH<sub>3</sub> and sea salt concentrations, neutralization of precipitation was not effective. The monthly mean values of neutralization factors calculated for July, August and September 2003 (NF for NH<sub>4</sub><sup>+</sup>= 0.00, 0.01, 0.01, and NF for Na<sup>+</sup>= 0.2, 0.2, 0.4) were

higher than the annual means (NF for  $\text{NH}_4^+$  = 0.10, and NF for  $\text{Na}^+$  = 0.51).

The location of the sampling station in an urban area (Gdynia) and in the vicinity of the surface zone resulted in the influence of both sea and land sources on the basic composition of precipitation. The annual magnitude of ionic species concentration in the precipitation decreased according to:  $\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Na}^+ > \text{NH}_4^+$  (Table 1). Precipitation monitoring over big industrial and urban cities, such as Seoul (Lee *et al.* 2000), Santiago City (Rubio *et al.* 2002) and Strasbourg (Sanusi *et al.* 1996) indicated the dominance of an anthropogenic source for the ions  $\text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+$ . Contrary to this, Al-Momani *et al.* (1995) found high concentrations of sodium and chloride ions at the coastal station in Antalya (Turkey). The concentrations of the precipitation main chemical components were as follow  $\text{Na}^+ > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+$ . The stations in Gdynia and Antalya are located on the sea coast and in urban areas. However, ions of marine origin dominated at the Antalya station surrounded on three sides by the Mediterranean Sea whose salinity is several times higher than that of the Gulf of Gdańsk. Moreover, onshore winds were less frequent in Gdynia. However, during eastern circulation in May 2003, when the onshore wind contribution was 24%,  $\text{Na}^+$  ions were of great importance in the neutralization of precipitation acidity in Gdynia.

### **Statistical analysis**

In order to identify the influence of the examined factors on precipitation acidity, a multivariate statistical technique was applied. The principal components analysis (PCA) indicates that 65.27% of the total variance is explained by the first three components denoted PC1, PC2 and PC3 with eigenvalues greater than unity (Table 2).

Higher score values for the first factor (above 0.8) indicate an inverse proportion between both inorganic nitrogen forms and sodium ions in precipitation and air temperature. At the same time, a direct proportion between the above ions and conductivity was noted. Since ammonia ions occurred at low concentrations, their relationship to sulfate was insignificant, which indicated that  $\text{NH}_3$  played an inconsiderable role in  $\text{H}_2\text{SO}_4$  neutralization. The decrease in  $\text{NH}_4^+$  concentration with temperature increase could be firstly associated with ammonium nitrate dissociation, and secondly, with gaseous ammonia evaporation. Both processes were favoured for most of the year when air humidity was lower than 87% (Dougle *et al.* 1996). It is also most probable that nitrate ions entered into reaction with marine sodium ( $r=0.89$ ,  $*P<0.05$ ,  $n=38$ ), and then were washed out by precipitation. Therefore, the first factor may be attributed to the neutralization of sulfuric acid by sea salt and gaseous ammonia.

**Table 2**

Principal component analysis of main chemical species concentration and meteorological parameters over Gdynia

<i>Variable</i>	<i>PC1 Neutralization</i>	<i>PC2 Local circulation</i>	<i>PC3 Regional circulation</i>
Total precipitation level (mm)	-0.39	0.64	-0.15
Atmospheric pressure (hPa)	0.50	-0.25	0.57
Wind direction*	0.15	-0.42	0.58
Wind velocity (m s <sup>-1</sup> )	-0.14	-0.65	-0.37
Temperature (°C)	-0.87	0.03	0.24
Relative humidity (%)	0.02	0.87	-0.10
Conductivity (μS cm <sup>-1</sup> )	0.86	-0.04	0.09
pH	-0.12	-0.64	-0.01
NH <sub>4</sub> <sup>+</sup> (μeq l <sup>-1</sup> )	0.86	0.14	0.18
NO <sub>3</sub> <sup>-</sup> (μeq l <sup>-1</sup> )	0.94	0.04	-0.10
Cl <sup>-</sup> (μeq l <sup>-1</sup> )	-0.17	0.00	0.75
Na <sup>+</sup> (μeq l <sup>-1</sup> )	0.84	0.03	0.40
SO <sub>4</sub> <sup>2-</sup> (μeq l <sup>-1</sup> )	0.07	0.25	0.47
Eigenvalue	4.34	2.33	1.88
Total variance [%]	34.7	18.1	14.7

\*- predominant wind direction calculated from Rubinstejn formula (Kostin and Porkowska 1957)

The second factor describes an inversely proportional relationship between pH, air humidity and precipitation level. It could be assumed that precipitation acidity decreased with an increase in air humidity and precipitation level. Such a situation was frequently observed at the coastal station in Gdynia, between May and September 2003, when high air humidity was accompanied by a high volume of weakly acidic precipitation (Table 1). In addition, the precipitation level over Gdynia depended on wind velocity. The higher the wind velocity, the lower the volume of precipitation. Thus, the second factor is correlated with air circulation.

The third factor points at a strong influence of wind direction on the chemical composition of precipitation. The results of principal component analysis showed that the concentration of chloride ions was directly proportional to atmospheric pressure and wind direction. As the sampling station was located in the surface zone and urbanized area, chloride ions probably originated both from marine and land sources, which resulted in high Cl<sup>-</sup> concentration:

- in spring and summer (May, June and July 2003) sea winds dominated and Cl<sup>-</sup> occurred as NaCl. At that time, the molar Cl<sup>-</sup>/Na<sup>+</sup> ratio (1.18) was close to that in sea water, and the correlation between those ions was statistically significant ( $r=0.80$ ,  $*P<0.05$ ,  $n=13$ ),
- in winter (November and December 2002), when east and south-east winds prevailed, chloride ions in the precipitation could be brought from the Gulf of

Gdansk as well as from outside the gulf with terrigenous material. The second source appears to be of greater importance because of the lack of correlation between  $\text{Cl}^-$  and  $\text{Na}^+$  and very strong winds at that time of the year.

### **Wet deposition**

Acid precipitation over Gdynia was observed all the year round. Nitrate, chloride and sulfate showed the highest fluxes in the coastal zone, irrespective of the season. As a result of every precipitation event, the average amounts of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  per  $1\text{m}^2$  of the coastal zone were 71.24 mg; 53.82 mg and 58.14 mg, respectively. Lower loadings were found for  $\text{NH}_4^+$  (2.63  $\text{mg m}^{-2}$ ) and  $\text{Na}^+$  (13.46  $\text{mg m}^{-2}$ ) (Table 3). High deviations from the mean value were noted

**Table 3**

Monthly values of ion deposition in wet precipitation over Gdynia, between November 2002 and October 2003 (normal type-summary value, italic type-minimum and maximum values)

Month	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{Cl}^-$	$\text{Na}^+$	$\text{SO}_4^{2-}$
	( $\text{mg m}^{-2}$ )				
XI.02	3.2 <i>(0.5-2.7)</i>	11.0 <i>(0.8-10.2)</i>	86.6 <i>(2.9-83.8)</i>	31.3 <i>(0.4-30.8)</i>	64.3 <i>(5.0-59.4)</i>
XII.02	7.4 <i>(1.2-4.0)</i>	18.5 <i>(1.61-9.09)</i>	51.0 <i>(7.4-26.3)</i>	41.4 <i>(1.5-23.9)</i>	111.9 <i>(5.4-64.5)</i>
I.03	17.8 <i>(1.9-9.5)</i>	428.2 <i>(5.1-295.1)</i>	104.6 <i>(10.2-48.3)</i>	62.7 <i>(9.2-23.9)</i>	334.7 <i>(5.4-248.3)</i>
II.03	2.3 <i>(1.1-1.3)</i>	29.5 <i>(1.6-9.1)</i>	6.9 <i>(1.9-5.1)</i>	5.6 <i>(0.1-5.5)</i>	10.2 <i>(2.9-7.3)</i>
III.03	2.4 <i>(0.8-1.7)</i>	151.5 <i>(7.4-22.1)</i>	41.7 <i>(9.4-32.2)</i>	24.6 <i>(6.1-18.5)</i>	50.6 <i>(9.2-41.5)</i>
IV.03	7.4 <i>(2.4-5.1)</i>	42.1 <i>(56.2-95.4)</i>	106.7 <i>(14.3-74.7)</i>	16.5 <i>(5.9-10.7)</i>	270.8 <i>(27.1-243.6)</i>
V.03	1.8 <i>(0.4-1.4)</i>	37.3 <i>(18.8-23.3)</i>	321.4 <i>(54.08-267.32)</i>	124.2 <i>(19.34-78.37)</i>	122.1 <i>(32.00-90.14)</i>
VI.03	13.7 <i>(0.4-6.1)</i>	293.3 <i>(4.5-79.28)</i>	296.4 <i>(23.8-116.8)</i>	16.5 <i>(0.9-8.8)</i>	386.3 <i>(7.8-295.2)</i>
VII.03	24.3 <i>(0.4-16.7)</i>	234.1 <i>(4.5-79.3)</i>	420.2 <i>(6.3-150.9)</i>	70.8 <i>(0.6-45.0)</i>	610.7 <i>(4.7-215.3)</i>
VIII.03	10.4 <i>(1.0-3.4)</i>	421.3 <i>(18.33-357.8)</i>	430.6 <i>(1.3-292.8)</i>	43.5 <i>(0.6-21.2)</i>	430.8 <i>(10.5-324.8)</i>
IX.03	4.2 <i>(0.5-2.1)</i>	65.9 <i>(18.3-47.6)</i>	43.8 <i>(2.3-35.2)</i>	9.4 <i>(0.6-4.7)</i>	74.6 <i>(1.3-52.0)</i>
X.03	8.0 <i>(0.3-2.8)</i>	312.6 <i>(7.3-100.6)</i>	415.5 <i>(4.2-167.5)</i>	65.0 <i>(2.7-37.9)</i>	227.9 <i>(1.1-121.2)</i>
Weighted average	2.63	53.82	58.14	13.46	71.24
Annual sum at 375 mm	103	2045	2326	511	2778
Annual flux after correction for precipitation level h=600 mm	165	3272	3722	818	4445

at the end of August 2003. At that time, the values of nitrate and sulfate fluxes ( $\text{NO}_3^-$  - 357.80  $\text{mg m}^{-2}$ ;  $\text{SO}_4^{2-}$  - 324.78  $\text{mg m}^{-2}$ ) were exceptionally high. The fluxes of the above ions always showed higher values during the vegetation season compared to the other periods. The increase in nitrate fluxes within the period of biggest requirements for nutrients in the Gulf of Gdańsk could intensify the eutrophication process. The results of our experiment indicated that in the hydrological year 2002/2003 *ca.* 62% of total precipitation occurring over the coastal zone of the Gulf of Gdansk was collected. On applying a correction for precipitation level, the annual flux of ion inflow increased and reached the following values:  $\text{SO}_4^{2-}$  - 4445  $\text{mg m}^{-2}$ ;  $\text{Cl}^-$  - 3722  $\text{mg m}^{-2}$ ;  $\text{NO}_3^-$  - 3272  $\text{mg m}^{-2}$ ;  $\text{Na}^+$  - 818  $\text{mg m}^{-2}$ ;  $\text{NH}_4^+$  - 103  $\text{mg m}^{-2}$ .

#### CONCLUSIONS

1. The measurements carried out in Gdynia for a 1-year period showed that all precipitation events were acidic. 88% of the precipitation had a pH of less than 5.6, the value of unpolluted water equilibrated with atmospheric  $\text{CO}_2$ .
2. In the coastal zone of the Gulf of Gdańsk, the degree of precipitation acidity was influenced mainly by the dynamics of the processes that occur in the sea and atmosphere and generate a specific pattern of wind velocity, total amount of precipitation and relative air humidity.
3. The situation observed in Gdynia was found to be different compared to other urbanized areas with typically acidic precipitation during the heating season. This points at an exceptional role of the coastal zone being a source of sea salt, which is much more effective than ammonia in the neutralization of acidic precipitation.
4. The highest fluxes of acid-forming compounds washed out by precipitation were noted in the vegetation season. In particular, as a result of nitrate deposition in wet precipitation, the eutrophication process in the Gulf of Gdańsk might be intensified.

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