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Inorganic Pollutants Deposition in Gdańsk Region in Relation to the Critical Load Concept

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Abstract

The deposition of acidifying compounds in Gdańsk region has been investigated. Bulk wet (in the open field), and throughfall (in the forest) stand, depositions were measured from 1994 till 2001. The deposition of sulphates, nitrates and ammonium salts has been analysed. The obtained results are compared with the critical deposition for sulphur and nitrogen related to the Gdańsk region. It has been stated that exceeding critical load was not observed for sulphur, while it was observed for nitrogen.

Keywords: atmospheric deposition, acidifying pollutants, critical load

Introduction

A very broad range of air pollutants represented mainly by acidifying compounds have a toxic or specific capacity to damage living organisms or other structures. They enter atmosphere through various pathways, undergo a chain of reactions, and then they are deposited onto surfaces, causing environmental damage.

Acid deposition originating mainly from anthropogenic emissions of sulphur dioxide and nitrogen oxides is damaging acid-sensitive aquatic systems, soils and forests in large areas of Europe. In the case of forests these effects show up in defoliation and reduce the vitality of trees. The vitality of many forests is still decreasing (not necessarily due to acidification); however, the long term effects on soil may be more important. In sensitive areas acidification leads to increased mobility of heavy metals, causing groundwater pollution and soil degradation.

Ammonia emissions reduce the acidity of rainwater, but can increase the threat of soil and watercourse acidification. If ammonium is converted into nitrate in the soil or in water as a result of nitrification, then it can be considered to be equivalent to a divalent acid. Thus, the effect of ammonia emissions in nature can be acidifying. The main source of ammonia is agriculture: fertilisers and volatilisation from animal manure.

As it results from data published in [1] the main sources of sulphur dioxide emission in Europe are the energy sector (about 61%) and industry (22%), while the main sources of nitrogen oxide emissions are transport sector (60%), energy production (21%) and industry (14%). Depositions of acidifying gases have decreased since about 1985 due to undertakings in the energy sector (introduction of the emission control equipment) and in the transport sector (the introduction of exhaust catalysts). In southern Poland the maximum of sulphur deposition was observed in 1980 (about 9 g/m^2 [2]), while in 1995 it was about 3 g/m^2 [1].

Acidification of soils will continue as long as critical loads are exceeded, which is still happening in a large sector of Europe. A critical load is defined as " the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on the ecosystem structure and function" [3]. The most widely

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used definition of a critical load has been developed by the UN/ECE Working group on Nitrogen Oxides [4]: "Critical load is a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge".

Criteria for "significant harmful effects" are set in relation to effects on terrestrial and aquatic indicator organisms. Critical loads are determined separately for different receptors such as soils and lakes and they are calculated for sulphur, acidifying nitrogen and eutrophying nitrogen (the eutrophying effects of nitrogen are associated with increased leaching of nitrogen to groundwater, streams and lakes and changes in forest ecosystems).

Since acidification is caused by deposition of both sulphur and nitrogen, the amount of sulphur deposition that an ecosystem can tolerate will also depend on the level of nitrogen deposition and vice versa. If the level of nitrogen deposition is known (based for example, on model calculations), conditional critical loads for sulphur may be derived. Similarly, the critical loads for nitrogen are derived when sulphur deposition is known. The critical load may vary widely within and between areas and also may vary from year to year.

The critical load concept has been found valuable for the development and implementation of control strategies for transboundary air pollutants. The purpose of determining critical loads is to set goals for future deposition rates of acidifying compounds such that the environment is protected. The concept was already used by Canadian authorities in the early 1980s and it has been further applied in the Nordic countries [5]. For example, in Finland the critical load of atmospheric pollutants was estimated for forest soil and surface waters with respect to acidifying sulphur and nitrogen compounds [4]. For forest soil it was estimated as a criterion according to which acidification was permitted only to the level where the calcium-to-aluminium molar ratio stays above 1. In such a case, the soluble aluminium concentration does not reach a harmful level. The deposition of base cations (K, Ca and Mg), the weathering of base cations from minerals, as well as the uptake of nitrogen and base cations by trees, were taken into account in calculating the critical load [5].

Critical loads have been aggregated for Europe on 50x50 (or 150x150) km x km grid-squares [6]. They may be compared with measured or modelled deposition rates. The criterion for calculation of these critical loads is not universally accepted, and experiments show that common forest tree species may not be particularly sensitive to certain chemical changes in soils. However, there is a broad agreement that acid inputs in excess of critical loads is the only measure of such depletion available on the European scale.

It has been found that the critical acidifying load for forest soils in the most sensitive areas of Finland was less than 20 meq/m^2/year.

The critical load was compared to the level of acidifying deposition and it was found that the deposition level was too high in many areas, e.g. in southern Finland, the exceedance of the acidifying critical load was about 20-50 meq/m^2/year (and even more) [5].

An exceedence is recorded whenever a deposition that exceeds a critical load is observed or calculated. An important limitation of basing emission reductions on large--scale exceedances in 150x150 km^2 grid-squares is that locally, within a large grid area, the deposition may vary considerably, so the actual exceedances in local ecosystems may be significantly different from those based on estimates of average deposition.

The spatial patterns of exceedances of the critical load for sulphur and nitrogen have been presented in [1]. It has been shown that maxima for sulphur (more than 2000 eq/ha) are observed in areas close to the main emission sources in Central Europe (including southern part of Poland), eastern UK and few other places. In parts of Scandinavia, where emissions are quite modest, the number of exceedances is rather large due to the small buffering capacity of the soil. In the Mediterranean region the buffering capacity is much larger, so the critical loads are higher and there are far fewer exceedances.

In the northern part of Poland the exceedances are much lower, and in the Gdańsk region it is less than 40 eq/ha for sulphur and about 40-200 eq/ha for acidifying nitrogen. The highest exceedances are observed for eutrophying nitrogen (200-400 eq/ha) [1].

If one compares the spatial distribution of emission of sulphur and nitrogen with the exceedances pattern, it is evident that there is a relation between them. For instance, in regions with the maxima of exceedances the emissions of sulphur and nitrogen in1995 were about 50,000 tons per year and even more. In the Gdańsk region these emissions did not exceed 10,000 tons yearly per 50x50 km grid square [1]. Analysis of the dry deposition of sulphur dioxide in Poland shows that there are seasonal differences [7]. For example, in Gdańsk region the sulphur dioxide deposition during summer is about 4-8 mg/m^2/day, while during winter it is about 8-12 mg/m^2/day. For nitrogen oxides the relevant values are 0.4-0.6 mg/m^2/day and 0.2-0.4 mg/m^2/day, respectively [7].

The investigations described in this paper are the results of co-operation between BAQA[1], IVL[2] and the Chemical Faculty of Gdańsk University of Technology. It has been shown [9] that the wet and dry deposition of sulphur and nitrogen to forest ecosystems in Southern Sweden is greater than most systems tolerate. Thus, the aim of this study was to evaluate the content of acidifying components in precipitation in Gdańsk region and compare the results with relevant data from Southern Sweden.

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Experimental Procedures

Site Location and Sampling Procedure

Monitoring station PL1 is situated in a mature spruce (Picea abis) forest stands 20 km from Gdynia (Fig. 1) in the forest district of Stara Piła, Poland. It consists of two field sampling substations: PL10 and PL11.

Substation PL10 is used to determine wet deposition (bulk wet), i.e. pollutants washed out from the atmosphere by rain or snow, and is located in the clearance, close to spruce forest. The summer equipment consists of a funnel (20.5 cm in diameter) mounted on a 5 l polyethylene bottle, placed on a wooden pole with the opening 1.5 m above the ground. The funnel contained a smaller one at the bottom, with a netting attached on the top, which is used for prevention of sample contamination. Winter samplers in both substations consists of 5 l polyethylene buckets (21 cm in diameter) instead of the bottles and funnels. Buckets were mounted on the same poles as the summer equipment.

Throughfall station (substation PL11) is located in a spruce forest and consists of ten collectors with funnels on poles placed in a 30m x 30m square. Rainfall going through the tree conopies washes out pollutants from the needles and branches. Thus, throughfall is a sum of dry and wet deposition. For throughfall sampling, the summer equipment consists of a funnel (15.5 cm in diameter) placed on a 2 l polyethylene bottle. The samplers are placed on a wooden stand with the bottle openings 80 cm above the ground. A nylon netting is applied between the container and the funnel in order to prevent contamination of the sample. During winter the collectors and funnels are replaced by buckets for snow collection. The throughfall samples are combined and analyzed as one representative sample.

The collectors for both bulk precipitation and throughfall are covered with aluminium foil to avoid any undesirable effect caused by sunlight. All samples are collected once a month.

The sampling station has been in operation since October 1994.

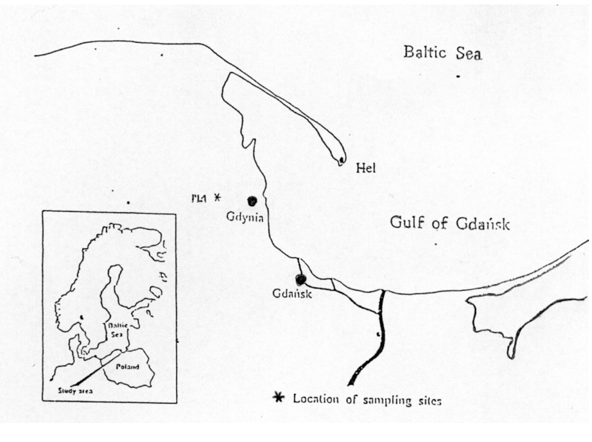

Fig. 1. Location of sampling sites.

Sampling was carried out according to the procedure applied in the EC monitoring system in permanent forest plots [8,9].

There are three factors describing the process of sampling:

- *time*: the samples are collected once a month;
- *sampling*: PL11 samples are well mixed and the one – a representative sample is taken; PL10 is collected and samples separately;
- *storage*: samples are stored in polyethylene bottles in the refrigerator.

Analytical Procedure

The collected volume of precipitation was measured. pH values of samples were analysed. The concentration of sulphates, nitrates, and ammonia nitrogen was determined spectrophotometrically using a HACH DR/2000 Spectrophotometer, a single-beam apparatus controlled by a microprocessor. The instrument provides colorimetrical analysis in the range of visible light. The determination of all ion concentrations were performed against blank tests and using relevant methods.

Concentration of sulphates was determined as a precipitate of barium sulphate (Sulfa Ver 4 reagent was used) and the turbidity measured after reaction was proportional to sulphate concentration. Nitrogen ammonia concentration was determined using the method with salicylate in which 5-aminosalicylate is formed. After its oxidation in the presence of sodium nitroprusside catalyst a blue coloured compound appeared – the amount of which is measured spectrophotometrically. Nitrates were determined by their reduction to nitrites using cadmium. Then, nitrite ion reacts with sulfanilic acid and a diazonium salt is formed. Its amber colour intensity is measured spectrophotometrically.

The analysis results were used for calculation of deposition of particular pollutants for a given area.

Results and Discussion

On the basis of analysis results, deposition was calculated according to Formulas (1) and (2):

$$P = \frac{v * 10^4}{n * \pi * r^2} \qquad (1)$$

where,

P – precipitation volume per unit area [dm^3/ha]
v – volume of collected precipitation [dm^3]
n – number of funnels
r – radius of a funnel or a bucket [cm]

and

$$D = \frac{C * P}{10^2} \qquad (2)$$

where,

D – deposition [kg/ha]
C – concentration [mg/dm^3]

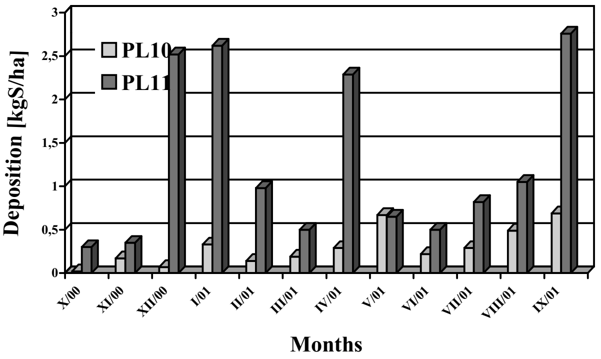

Fig. 2. Deposition of sulphates in 2000/2001.

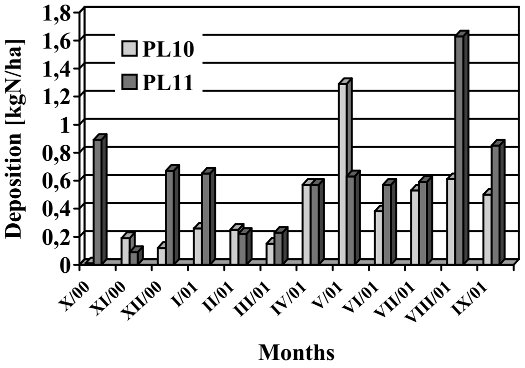

Fig. 3. Deposition of nitrates in 2000/2001.

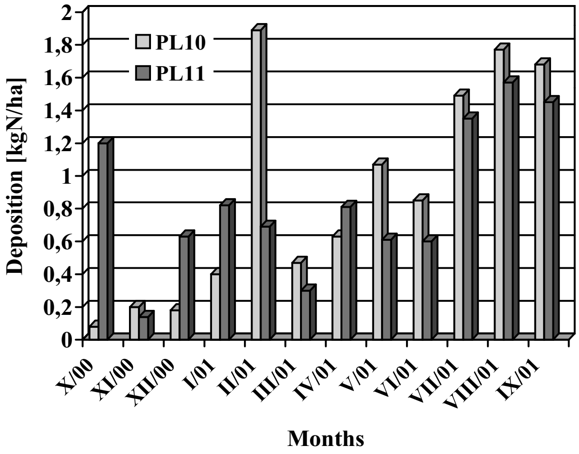

Fig. 4. Deposition of ammonia nitrogen in 2000/2001.

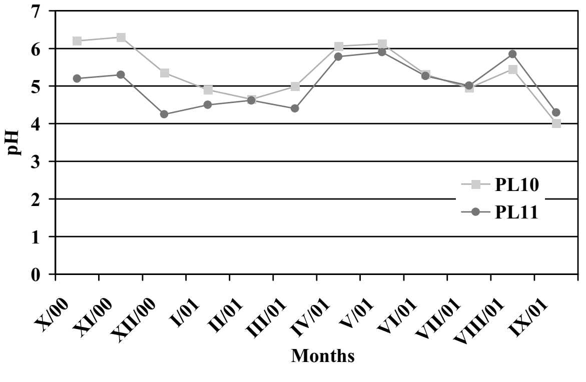

Fig. 5. pH value from the period 2000/2001.

Figs. 2–5 present monthly results from October 2000 to September 2001.

As can be seen from Fig.2 deposition of sulphates from the studied period shows seasonal changes. The highest sulphate deposition value was observed in winter months. The highest value corresponding to PL11 was registered in January and it was equal to 2.62 kg of S per hectare. Such a high throughfall deposition could be explained by high emission of acidic gases from the heating sector. Heat production is still mainly based on coal combustion, thus higher concentrations of sulphur can be found in that period. Previous years show the same tendency was observed in winter and early spring time, too [8].

The monthly deposition of nitrates in the period of October 2000 to September 2001 varies from 0.08 kgN/ha in October to 1.89 kgN/ha in February for PL10, and from 0.14 kgN/ha in November to 1.57 kgN/ha in August for PL11(Fig.3). The results show significant differences, which do not indicate any tendency. Definitely, increasing tendency of nitrates deposition started in July (Fig. 3).

It is also interesting to note the comparatively large differences in concentrations of ammonia nitrogen (Fig.4). The highest concentration of ammonia for PL10, 1.29 kgN/ha, was found in May and for PL11, 1.63 kgN/ha in August, while the lowest concentrations occurred in October (0.01 kgN/ha) in PL10 samples and in November (0.09 kgN/ha) in PL11 samples. The terrestrial ecosystem incorporates the wet and dry-deposited nitrogen as an essential macronutrient source. Between 30% and 60% of the nitrogen deposited on lands is thought to be absorbed by the ecosystem, which could be an explanation in this case.

Rain seems to be called "acid" when its pH is about 5. Considering the seasonal changes of pH of PL10 and PL11, between October 2000 and September 2001, it must be stated that in almost all cases, acid rain occurs (Fig.5).

The results show that pH of precipitation ranges between:

- 4.01 and 6.3 for PL10;
- 4.25 and 5.90 for PL11.

A record high pH of PLl0 was found in November, and of PL11 – in May. The lowest pH of PL10 was found in February and September. The lowest pH of PL11 samples was measured between December and March. It is interesting to note that about 42% of both, throughfall and bulk precipitation, pH was lower than 5.

As sampling and analysis were performed since 1994, a summary of sulphates (SO_4–S), acidifying nitrogen (NO_3–N) and eutrophying nitrogen (NH_4–N) depositions measured at Stara Piła, during the period of 1994–2001 were calculated. Annual deposition is a sum of monthly depositions from October till September. The results are expressed in kilograms per hectare of a given area. The volumes of precipitation, corresponding to each year, are also added.

In Figures 6-9 the annual results of precipitation and depositions are presented in graphical form.

Discussion of Results

As seen in Figs. 2–9, there is a significant difference between results from substations PL10 and PL11. In almost all cases, deposition of particular pollutants measured in the forested area (PL11) is greater than deposition of the same pollutants measured in the open field (PL10), which results from the phenomenon of dry deposition. The exceptions are observed in the case of nitrate nitrogen between 1995 and 1997, when the deposition from the open field exceeds throughfall deposition. A similar situation occurred between 1999 and 2000 in the case of ammonia nitrogen, when NH_4–N deposition from PL10 was higher than the concentration from PL11 substation. The fact that nitrogen deposition in a few throughfall samples is lower than in bulk precipitation indicates nitrogen retention in conopies.

A general observation from Figure 7 is that the deposition of sulphates is decreasing until 2000 and it again increased in 2001. This can be easily noticed in both substations PL10 and PL11. Similar evidence can be seen in nitrate analysis. In spite of the high NO_3–N deposition in 1995/96, a stabilising tendency established till 2001 (Fig.3). In 2001, a large quantity, above 10 kg of N per hectare, was measured. The NH_4–N investigation provides the most conclusive evidence (Fig.9).

Conclusions

The aim of this paper is to discuss a correlation between acidifying pollutants deposition over Gdańsk region and the critical load concept.

A general observation from recent and previous measurements of dry and wet deposition is that highly acidic character of precipitation occurs mainly due to the presence of high concentrations of sulphates and nitrates. Most SO_4–S deposition occurs in the autumn/ winter time. This is perhaps not suprising in view of the fact that the energy sector in Gdańsk region (about 30 km from the field station) is based on coal combustion that provides large emissions of acidifying compounds.

On the basis of analysis of critical loads for different areas [10] it has been stated that in northern Poland where PL10 and PL11 stations are located, the critical annual deposition of sulphur should not exceed 500–1000 eq/ha (16 – 32 kgS/ha) and the critical deposition of nitrogen also should not exceed 500–1000 eq/ha (7-14 kgN/ha). However, in reality these critical values have been exceeded by 200–500 eq/ ha for sulphur (6.4–16 kgS/ha) and by 0-200 eq/ha for nitrogen (0–1.4 kgN/ha). These data relate to the period before 1993 [10].

The report from 1998 [1] shows that sulphur exceedences have decreased and are lower than 40 eq/ha (<1.2 kgS/ha) while for nitrogen it is even higher than earlier (200 – 400 eq/ha, 1.4 – 2.8 kgN/ha).

Comparing the results obtained in our investigations with those discussed above one can state that the wet

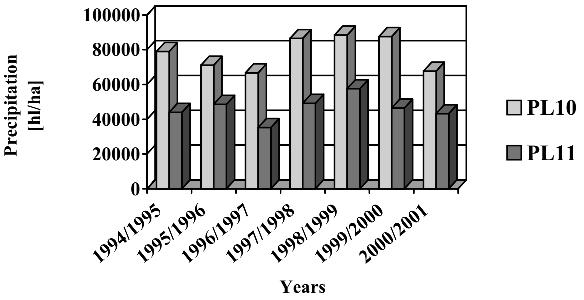

Fig. 6. Annual precipitation in 1994–2001.

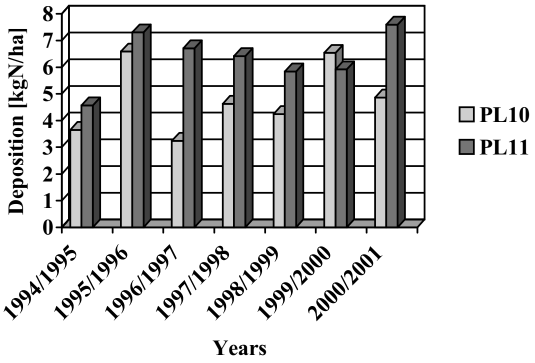

Fig. 7. Deposition of sulphates in 1994–2001.

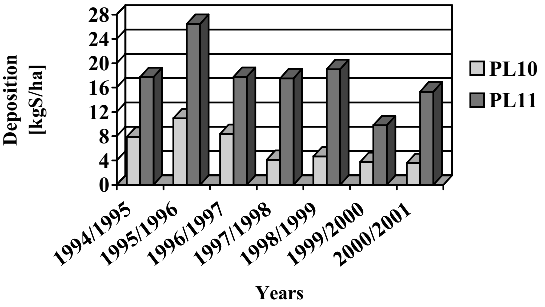

Fig. 8. Annual deposition of nitrates in 1994–2001.

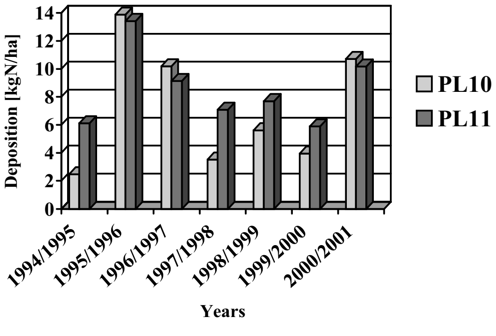

Fig. 9. Annual deposition of ammonium nitrogen in 1994-2001.

deposition of sulphur in the open field (PL10 substation) is much lower (4 – 11 kgS/ha) than the lowest value of critical annual deposition (16 kgS/ha). However, in the forested areas (PL11 substation) the results are much higher (up to 26 kgS/ha) because throughfall represents total – dry and wet deposition. In this case the lowest value of critical deposition is exceeded; however, the upper critical deposition values (32 kgS/ha) are not yet reached.

In the case of nitrogen deposition, the sum of nitrates and ammonium nitrogen exceed the lowest critical deposition value (~7kgN/ha) in each year of the study period (1994 – 2001). In some years even the upper critical deposition value (14 kgN/ha) has been exceeded.

It is evident that in industrial areas the exceedences differ from those in 1993. Thus, the main conclusion from the above analysis is that the efforts are needed in order to decrease the acidifying gas emissions in northern Poland.

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