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ATMOSPHERIC DEPOSITION AS A SOURCE OF NITROGEN AND PHOSPHORUS LOADS INTO THE RZESZÓW RESERVOIR, SE POLAND

This paper reports a study on the contribution made to the loading of the Rzeszów reservoir with nitrogen and phosphorus by atmospheric wet deposition, in relation to the whole-year mass balance. Emissions of pollutants were found to influence the chemistry of wet atmospheric deposition, this being particularly evident in the case of phosphorus compounds. In the case of nitrogen, more than 60% of its total is in inorganic form, while dissolved phosphate-phosphorus accounts for only 10–60% of the total for the element. The calculated atmospheric loads of nutrients (A_{load}) exert an insignificant influence on the overall mass balance for the Rzeszów reservoir. After comparison with earlier data, atmospheric deposition was found to account for less than 0.5% of the mean annual input in the case of nitrogen, and for less than 4% in the case of phosphorus. Nevertheless, a short-term impact may be important, in the course of precipitation, 15% of nitrogen and 25% of the phosphorus is being supplied to the reservoir from the atmosphere.

1. INTRODUCTION

It is well known that an increase of nitrogen and phosphorus loads to lentic waters observable over the last few decades is the primary reason for the eutrophication and degradation of natural as well as man-made lakes (BOMBÓWNA [2], BILLEN et al. [1], HILLBRICHT-ILKOWSKA [5]). The disposal of crudely and inadequately purified sewage combines with diffuse losses following improper practices involving manure and fertilizer use in representing the basic reasons for eutrophication. The importance of loading from nature, e.g. via the nitrogen flux in soil and soil runoff, has became steadily less important as the years have passed (BILLEN et al. [1], HERUT et al. [4]). A second source of the nutrients passing into surface waters is atmospheric deposition. Indeed, an increase in loads of phosphorus and especially nitrogenous compounds from the atmosphere is to be observed, and can be linked with emissions of gases from

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point sources (e.g., the production of thermal and electrical energy and industry), as well as the diffuse sources mainly connected with traffic. Natural syntheses of oxides of nitrogen in the atmosphere also have an impact on values for the loads (KUFEL [12], KOPÁČEK et al. [7], HERUT et al. [4], KUHN [13]).

It appears that the contribution of A_{load} to whole-lake mass balances varies. In conditions of oligotrophy, the A_{load} may well be the source of the majority of nutrients (LO and CHU [14]), while in eutrophic conditions its contribution is less important (KOSTECKI [9]). However, land development also has a major influence on the sizes of loads. In catchment areas in which forest predominate the A_{load} is considerably lower than would be the case in a developed basin, since emission sources tend to be absent (JASSBY et al. [6], PŁUŻAŃSKI et al. [15]). Atmospheric loads of nitrogen and phosphorus are of great importance in mass balances where lake catchment area (CA) is slightly greater than lake area (LA), regardless of land development. The greater the value of the CA:LA ratio, the greater the contribution made by A_{load} to the whole-lake nutrient mass balance. The significance of atmospheric loads also becomes greater thanks to nitrogen and phosphorus from the atmospheric supply making its way directly to the euphotic zone of waterbodies, in which biological productivity is most intensive. This is all the more important in the supplied waters since mineral and hence available forms predominate (JASSBY et al. [6], KUFEL [12], KOPÁČEK et al. [7], HERUT et al. [4]).

The aim of the work was to study concentrations of nitrogen and phosphorus forms in wet atmospheric deposition in the city of Rzeszów, and to estimate the contribution of nutrient loads from the atmosphere to the N and P mass balances in the Rzeszów reservoir.

2. STUDY SITES

The Rzeszów reservoir was built in 1974 near the city centre. Within the precincts of the direct catchment area there are two huge sources of gaseous and particulate emissions: an industrial power station and incineration plant. In turn, within a distance of 5 km there is another power station and within 40 km a few chemical plants. The Rzeszów reservoir is a small and shallow man-made lake on the Wisłok River in south-eastern Poland. Its water depth has decreased considerably over thirty years of exploitation, eutrophication has been observed and aquatic plants have started growing fast across what was previously an open water surface (KOSZELNIK and TOMASZEK [10]). The reservoir is silting up, its volume having decreased from 1.18 M m^3 to 0.5 M m^3 and its mean depth from 1.5 to 0.5 m (KOSZELNIK et al. [11]).

3. MATERIALS AND METHODS

Between June 2004 and May 2005 inclusive, ten samples of fresh precipitation wa-

ter (rain, or snow in February) were taken from a station located next to the reservoir. The samples of water were collected in a dish (30 cm in diameter) and diluted with deionised water. In turn, the June 29th measurements also entailed analysis of the short-term variability in nutrient concentrations in the precipitation water, 3 samples being taken over a 4h period. Water filtered via a glass-fibre membrane was made subject to spectrophotometric determinations in respect of phosphate phosphorus ($P-PO_4^{3-}$), nitrate nitrogen ($N-NO_3^-$), nitrite nitrogen ($N\text{-}NO_2^-$) and ammonium nitrogen ($N-NH_4^+$) concentrations. In addition, non-filtered samples were subject to determinations for total phosphorus (TP) and total nitrogen (TN) concentrations. All methods employed were after HERMANOWICZ et al. [3], with the exception of TN, for which the method after KOROLEFF [8] was used, on account of the sample volume being less than that needed for the standard Kjeldahl method. The difference between TN and concentrations of the three mineral forms of nitrogen is equal to total organic nitrogen (TON).

The intensities of precipitation for the city of Rzeszów – data items indispensable in calculating loads – were obtained from the site of the Voivodship Inspectorate for Environmental Protection in Rzeszów, the balance making use of a relationship holding that 1 mm of precipitation is equal to a deposition of 1 dm^3 of water per square metre of reservoir surface area. Mass deposition was calculated at seven-day intervals, while concentrations between sampling weeks were approximated using the least squares method.

4. RESULTS AND DISCUSSION

The results of the reported study are shown in table 1. Low values for $N\text{-}NO_2^-$ concentrations were noted in the water collected. Values were close to those reported for surface waters, the mean being 0.032 mg N dm^{-3}. The nitrate nitrogen average was 1.0 mg N dm^{-3} though the range was from 0.4 to 1.6 mg N dm^{-3}. Clear seasonal variations were observed during the period analysed. The June-to-January period had brought about an increase, followed by a decrease before there was a rise in the nitrate concentration once again since April. Concentrations of $N-NH_4^+$ were higher than those observed in surface waters and slightly lower than those for nitrate, the mean being 0.64 mg N dm^{-3} and the range 0.7–1.29 mg N dm^{-3}. Seasonality was also observed, with the highest concentrations observed in spring and summer and the lowest in winter. Total nitrogen contents in the collected waters varied markedly from 0.8 to 3.1 mg N dm^{-3}, though the mean value was 1.98 mg N dm^{-3}. Inorganic forms of nitrogen accounted for more than 60% of the TN, while seasonal variation in TN results from nitrate and ammonium variability, as well as in line with negligible variability in organic nitrogen contents, from 0.22 to 0.41 mg N dm^{-3} (mean 0.33 mg N dm^{-3}).

Phosphate phosphorus concentrations ranged from 0.01 to 0.34 mg N dm^{-3}, while the mean value was 0.05 mg P dm^{-3}. In the case of TP, the mean concentration was twice as high, amounting to 0.1 mg P dm^{-3} (the range being 0.03–2.5 mg P dm^{-3}). In the case of both indexes, the highest content was noted in January (see table 1). The concentration of TP was also high in May, but did not result from the content of dissolved phosphate due to lesser concentrations of P–PO_4^{3-} in spring. Except in January, the variation in P–PO_4^{3-} was not significantly different from that in TP, concentrations being higher in fall and winter, and below 0.1 mg P dm^{-3} during spring and summer.

T a b l e 1

Concentrations of analysed indexes in atmospheric waters in mg N(P) dm^{-3}, and molar N:P ratio

Date	N–NO_2^-	N–NO_3^-	N–NH_4^+	TON	TN	P–PO_4^{3-}	TP	N:P
18.06.2004	0.021	0.90	0.74	0.22	1.86	0.12	0.20	21
29.07.2004	0.034	0.40	0.48	0.32	1.20	0.02	0.03	89
26.08.2004	0.024	0.53	0.40	0.37	1.30	0.02	0.03	140
26.10.2004	0.028	1.60	0.77	0.33	2.70	0.04	0.06	100
15.12.2004	0.027	1.30	0.67	0.33	2.30	0.06	0.07	73
05.01.2005	0.056	1.60	0.44	0.36	2.40	0.34	2.50	2
16.02.2005	0.010	0.40	0.07	0.33	0.80	0.01	0.04	44
07.03.2005	0.014	0.60	0.36	0.34	1.30	0.05	0.16	18
11.04.2005	0.074	1.40	1.29	0.41	3.10	0.08	0.13	53
10.05.2005	0.030	1.30	1.20	0.30	2.80	0.01	1.26	5
Mean	0.032	1.00	0.64	0.33	1.98	0.08	0.45	58
Maximum	0.074	1.60	1.29	0.41	3.10	0.34	2.50	140
Minimum	0.010	0.40	0.07	0.22	0.80	0.01	0.03	2
Std. Dev.	0.019	0.49	0.38	0.05	0.79	0.10	0.81	47

The emission of pollutants influences the chemistry of wet atmospheric deposition into the Rzeszów reservoir. This is evident for phosphorus in particular. Undissolved forms discharged with dusts prevailed over dissolved phosphorus compounds during the cold months, when heat-generating plants are operating most intensively. There are increased values for N–NH_4^+ in analysed atmospheric waters by comparison with other N-derivatives in surface waters. A significant impact on the content of ammonium ions in both air and precipitation is exerted by diffuse sources connected with refrigeration and industry. Breeding and emissions from soil may also be of great importance. The dynamics and levels noted for ammonium nitrogen probably result from seasonality and the overlapping of whole sources. When short-term variations in concentrations were observed, the highest values for nitrogen and phosphorus compounds were found to characterize the first hour of precipitation (figure 1). This results from the content of TON, because nitrate and ammonium nitrogen concentrations were initially and further on more stable, within 0.4–0.6 mg N dm^{-3} and 0.3–0.6 mg N dm^{-3}, respectively. The TN

content decreased in the course of the precipitation event, from 1.7 mg N dm^{-3} in the first hour to 0.8 mg N dm^{-3} after four hours of atmospheric deposition. A similar situation applied in the case of phosphorus. P–PO$_4^{3-}$ was at 0.13 mg P dm^{-3} initially, but by the fourth hour it was only at 0.1 mg P dm^{-3}. For TP the decrease was more marked, from 0.4 mg P dm^{-3} to 0.04 mg P dm^{-3}.
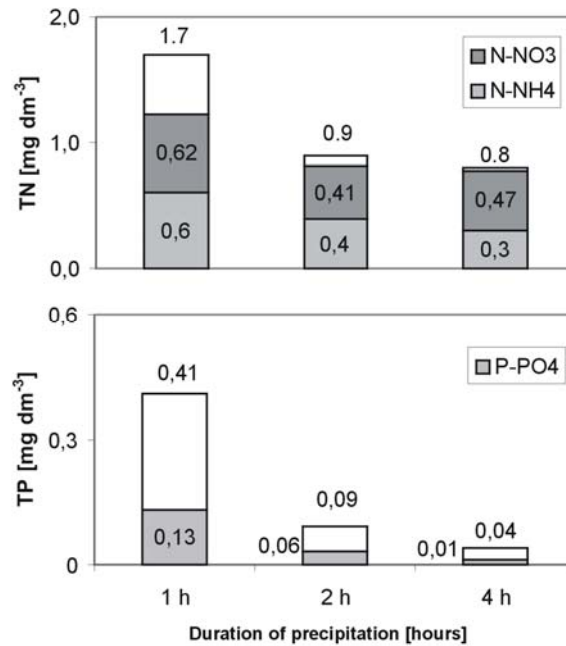

Fig. 1. Short-term variations in the chemistry of precipitation

The molar TN:TP ratio (table 1) varied widely from 2:1 in January to 140:1 in August. The ratio changed seasonally, with a maximum noted in summer and a minimum in winter. The N:P ratio varied in water from precipitation points to an excess of nitrogen over phosphorus, especially when high loads of both elements were present. In the water of the reservoir, the N:P ratio varies around a Redfield value of 16:1 (KOSZELNIK and TOMASZEK [10]). Therefore during precipitation, wet atmospheric deposition may increase the N:P ratio in surface waters, creating favourable conditions for oligotrophisation.

The Rzeszów reservoir loadings with nitrogen and phosphorus are as reported in table 2. The maximal load of TN was noted in July (11 mg N m^{-2}d^{-1}), within about 5 mg N m^{-2}d^{-1} of nitrate as well as ammonium. However, in the case of phosphorus in the TP-load of 4.80 mg P m^{-2}d^{-1} only 0.19 mg P m^{-2}d^{-1} was in an available form. The highest mean nutrient loads from the atmosphere into the Rzeszów reservoir were noted in spring, and lower ones during winter. Irrespective of the season, nitrate and

ammonium nitrogen made most of the contribution to the total loads of the element. Nevertheless, an interaction between $N-NO_3^-$ and $N-NH_4^+$ loads was noted. Nitrate loads were twice as great as those of ammonium ions during fall and winter, while in spring and summer loads of both were similar. The contribution of $P-PO_4^{3-}$ to the TP-load was above 65% in summer and only 10–15% between fall and spring. A clear seasonality observed as regards the TN-load arises from the intensity of precipitation (Q_P). Total precipitation from June 2004 to May 2005 was of some 601 mm, ca. 80% of this falling during late spring and summer, when loads of both nitrogen and phosphorus were the greatest. The directly proportional influence of the intensity of precipitation on loads of nitrogen derivatives is confirmed by significant correlations between Q_P and loads of TN, $N-NO_3^-$ and $N-NH_4^+$ (figure 2). These relationships confirm the main influence of mineral forms of nitrogen, too. Nevertheless, in the case of phosphorus no similar relationships were observed.

Table 2

Loads of N and P forms into the Rzeszów reservoir in mg N(P) $m^{-2}d^{-1}$, and precipitation totals (mm) from July 2004 to May 2005

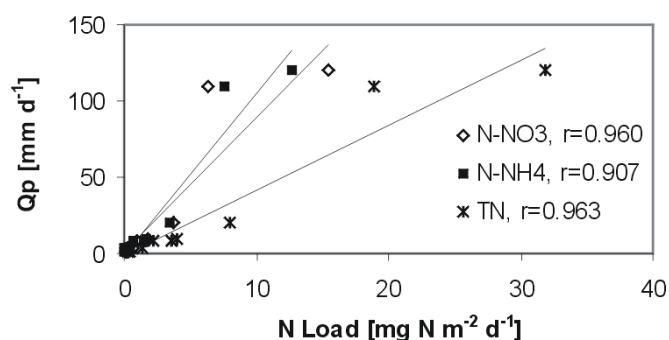|	Period	Precipitation	$N-NO_3^-$	$N-NH_4^+$	TN	$P-PO_4^{3-}$	TP
	VI–VIII	85	2.64	2.16	6.26	0.12	0.18
Mean	IX–XI	19	1.28	0.61	2.18	0.07	0.29
in season	XII–II	8	0.33	0.09	0.54	0.05	0.37
	III–V	45	2.87	2.65	6.36	0.08	1.71
Mean value			1.65	1.24	3.52	0.07	0.50
Maximal value			5.14	4.57	10.86	0.19	4.80

Fig. 2. Relationship between nitrogen loads and precipitation totals (Q_P)

However, calculated loads of nutrients exert only an insignificant influence on the overall mass balance for the Rzeszów reservoir. During a study conducted from 1999 to 2001 (KOSZELNIK and TOMASZEK [10]), an average of 3500 mg N $m^{-2}d^{-1}$ of TN and 280

mg P $m^{-2}d^{-1}$ of TP were supplied to the reservoir. Mean atmospheric deposition of TN and TP (3.5 mg N $m^{-2}d^{-1}$ and 0.5 mg P $m^{-2}d^{-1}$) thus accounted for only 0.1% and 0.2% of the earlier estimated loads, respectively. Following the comparison of the lowest riverine loads reported (2600 mg TN $m^{-2}d^{-1}$ and 120 mg TP $m^{-2}d^{-1}$) with the highest atmospheric loads being noted (10.9 mg TN $m^{-2}d^{-1}$ and 4.8 mg TP $m^{-2}d^{-1}$), the contribution of A_{load} to the whole balance only increased to 0.5% (for nitrogen) and 4% (for phosphorus). Nevertheless, notwithstanding an insignificant A_{load} influence on whole-year nutrient mass balances, a short-term impact was observed. Results from the four-hour-change study show that most of the nitrogen and phosphorus downloaded from the atmosphere into the Rzeszów reservoir came during the first hour of precipitation. Thus, large loads of nutrient are concentrated over a short time – the first hour of precipitation – as distinct from the evenly-distributed (daily as well as seasonal) riverine input (R_{load}). Comparison of the two-hour deposition of TN and TP on July 29th (45 mg N $m^{-2}h^{-1}$ and 6 mg P $m^{-2}h^{-1}$, respectively) to mean R_{load} in the period of 1999–2001 (290 mg N $m^{-2}h^{-1}$ and 23 mg TP $m^{-2}d^{-1}$, respectively) point to a significant increase in the importance of the A_{load} for nutrient mass balances. Loads of TN make up 15% and TP 25% of R_{load}. These lead to a risk of accelerated eutrophication because in A_{load} it is mineral and available forms of nutrients that predominate, especially in the case of nitrogen. Moreover, the A_{load} is supplied directly to the whole area of the euphotic zone of the reservoir, with loss of nutrients being compensated for in this way.

5. SUMMARY

The contribution of atmospheric loads of nitrogen and phosphorus to the whole-year mass balance for the Rzeszów reservoir is insignificant, even when intensive precipitation was observed. Nevertheless, the short-term impact is noticeable and important, because the majority of the nitrogen and phosphorus are supplied to the reservoir during the growing season, when most of the precipitation was noted. Nutrients introduced directly and evenly across the surface of the body of water, and in a form that is biologically available may be quickly consumed, and complement other sources. Sources of gaseous emission located within the catchment area may seasonally influence concentrations and loads of nutrients to the Rzeszów reservoir.

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OPAD ATMOSFERYCZNY JAKO ŹRÓDŁO ŁADUNKÓW AZOTU I FOSFORU
ZASILAJĄCYCH ZBIORNIK ZAPOROWY W RZESZOWIE

W pacy dokonano analizy znaczenia ładunków azotu i fosforu zasilających zbiornik rzeszowski wraz z opadem atmosferycznym w całkowitym bilansie biogenów. Badania prowadzono w cyklu jednego roku. Stwierdzono, że w przypadku azotu obserwowana zmienność ładunków wynika z sezonowości występowania azotu azotanowego i amonowego, które mają największy udział w azocie całkowitym. Rozpuszczalne fosforany stanowiły około 10% fosforu całkowitego od jesieni do wiosny, latem natomiast ich udział wzrastał do ponad 60%. Porównując wyliczone ładunki z ładunkami wnoszonymi do zbiornika przez rzeki, stwierdzono, że udział ładunków atmosferycznych jest nieistotny (0,1–0,2% całości). Jednakże analiza krótkoterminowych zmian składu chemicznego opadu wskazuje, że główna część ładunku atmosferycznego zasila zbiornik w pierwszych godzinach opadu. W związku z tym w momentach intensywnej depozycji atmosferycznej udział opadu atmosferycznego w bilansie masowym azotu i fosforu dla zbiornika rzeszowskiego wzrasta do odpowiednio 15% i 25%.