

## Changes of water quality in the Łutownia and Perebel rivers in the Białowieża Primeval Forest

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**Abstract.** The aim of the study was to determine changes in water quality, including chemistry of outflow from two rivers: Łutownia and Perebel located in the Białowieża Primeval Forest.

Water chemistry was investigated once in every three months in the years 2011–2014. Catchments differed in forest cover and habitat types. The results of the analysis of river waters were compared with the limit values for each class of water quality as settled by the legal standards.

It was found that the quality of the water in rivers declined due to high concentrations of carbon and nitrogen organic forms.

In general, there was observed a decrease of the concentration of organic nitrogen and an increase of the concentration of mineral nitrogen, especially in the Perebel catchment area.

**Keywords:** water quality, water chemistry, river, the Białowieża Primeval Forest

### 1. Introduction

It is believed that water conditions are amongst the most important factors shaping the ecosystem of the Białowieża Forest and determining its condition and durability. This applies to both the quantity and the quality of water. Water resources in the forest are steadily diminishing, and one of the main reasons for this phenomenon is the increase in air temperature. Consequently, ground water is at lower levels, streams and small water reservoirs are drying up, soils have less moisture and organic matter is mineralising. It was already pointed out several years ago that the trend of drying habitats poses a threat to the sustainability of the ecosystems in the Białowieża National Park (BNP).

The research conducted in 2009–2010 showed that the water quality in the rivers and reservoirs of the BNP and the groundwater need to be improved (Pierzgalski et al. 2010). The water quality in the Narewka, the largest river in the BNP, is defined as ‘bad’ by the standards of the Water Framework Directive of the European Union, and poor water quality is a particularly serious threat to the functioning of aquatic ecosystems.

Research was also carried out in the Białowieża Forest on the sources contributing to the chemical composition of

the Narewka River to identify them, assess the intensity of their impact and classify them (Miniuk 1998; Skorbiłowicz et al. 2008). A zone that negatively affects the water chemistry of the Narewka was defined, which included the town of Białowieża, Białowieża Forest and agricultural areas (down river, outside of the Białowieża Forest). It has been shown that the river’s water quality is affected by peat marsh areas, which emit some forms of nitrogen (ammoniacal and nitrite nitrogen) as a result of the mineralisation of soil formations.

The aim of the research performed during the period of 2011–2014 was to determine the changes in the quality and diversity of the chemistry of the water flowing in the two rivers– the Łutownia and Perebel – in the Białowieża Forest (Malzahn et al. 2015).

### 2. Study subjects

The river basins of the Łutownia and Perebel differ in terms of forest cover and types of forest habitats occurring within their borders (Table 1). The Łutownia River is a left-bank tributary of the Narewka River, which flows into the Narew. The Łutownia has several tributaries, most of which periodically dry up. Two tributaries, Krynica and

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Dubitka, flow throughout the year. The catchment area of the Łutownia has a high degree of forest cover – 92%. The villages of Teremiski and Buda in a mid-forest clearing and agricultural fields and pasture in the north-western part of the basin form the non-forested area of the basin. The Perebel River is a right-bank tributary of the Leśna Prawa River and, through the Bug River, is also part of the Narew River Basin. The forest cover of the basin is 66%. Non-forest land is located in the upper part of the catchment, mostly consisting of the rural villages of Długi Bród, Zabagonie, Piaski and Witowo. Coniferous forest habitats dominate in the Perebel River Basin, which were partially drained in the past. In 2005, several small weirs were built in its riverbed to slow down the outflow of water from the catchment area. The Perebel is an important source of water for the Topiło Reservoir.

### 3. Materials and research methods

Water samples to assess water quality were collected on a quarterly basis in the hydrological years of 2011–2014 at two fixed locations (next to water gauges):

- from the Łutownia River at the Pogorzelce profile,
- from the Perebel River at the Topiło profile.

Analyses of the physicochemical properties of water samples were performed at the Laboratory of Natural Environmental Chemistry of the Forest Research Institute. The scope of the analysis, research methods and applicable standards and procedures were as follows:

- pH level – potentiometric method (PN-C-04642-7:1999),
- electric conductivity (EC) – conductometric method (PN-EN-27888:1999),
- concentration of anions: chlorine ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), sulphate ( $\text{SO}_4^{2-}$ ), phosphate ( $\text{PO}_4^{3-}$ ) – ion chromatography (IC) method (PN-EN ISO 10304-1: 2009),
- concentration of ammonium cation ( $\text{NH}_4^+$ ) – IC method (PN-EN ISO 14911:2002),
- concentration of the elements: Ca, Mg, Na, K, Fe, Al, Mn, Zn, Cu, Cd, Pb – inductively coupled plasma atomic emission spectroscopy (ICP-OES) (PN-EN ISO 11885:2009),
- concentration of dissolved organic carbon (DOC) – infrared spectrophotometry (PN-EN 1484:1999),
- concentration of total nitrogen bound (TNb) – chemiluminescence method (PN-EN 12260: 2004).

The results of the analysis of river water were compared to the limits established in the ‘Regulation of the Minister of the Environment of 22 October 2014 on the method of classifying the status of the surface water of a body of water and environmental quality standards for priority substances’ (Journal of Laws 2014, item 1482).

The above-mentioned regulation as well as its earlier versions from 2008 (Journal of Laws 2008, No. 162, item 1008) and 2011 (Journal of Laws 2011, No. 257, item 1545) on the method of classifying the status of surface water were introduced in Poland to implement Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the

**Table 1.** Characteristics of research catchments in the Białowieża Primeval Forest

| Characteristic of catchment     | Unit                | River    |         |
|---------------------------------|---------------------|----------|---------|
|                                 |                     | Łutownia | Perebel |
| Length of the river             | km                  | 14.8     | 4.7     |
| Catchment area                  | km <sup>2</sup>     | 119.5    | 17.5    |
| Density of river network        | km·km <sup>-2</sup> | 0.563    | 0.736   |
| Altitude of river source        | m a.s.l.            | 164      | 162     |
| Altitude of hydrometric profile | m a.s.l.            | 150      | 158     |
| Forest cover catchment          | %                   | 91.6     | 65.9    |
| Coniferous habitats             | %                   | 9.9      | 31.1    |
| Broadleaved forest habitats     | %                   | 73.5     | 24.5    |
| Riparian forests                | %                   | 8.2      | 10.3    |
| Fresh habitats                  | %                   | 64.0     | 43.3    |
| Wetland habitats                | %                   | 27.6     | 22.6    |
| Fields and meadows              | %                   | 8.4      | 34.1    |

field of water policy, that is, the Water Framework Directive (WFD). The primary and fundamental objective of the WFD is to prevent water pollution and achieve good water quality by defining and implementing measures within integrated programmes of water management in the Member States of the European Union.

#### 4. Results and discussion

The results of the analysis of water taken from the rivers are presented in Tables 2 and 3. Amongst the physicochemical elements tested that had limits set for water quality in subsequent regulations on the status of the surface water of a water body were pH, EC and concentrations of  $\text{SO}_4$ , Cl,

Ca, Mg,  $\text{N-NH}_4$ ,  $\text{N-NO}_3$ . DOC was also analysed, and its level was compared to permissible concentrations of total organic carbon (TOC). Amongst the indicators characterising oxygen conditions and organic pollution, the regulation defines limits only for TOC. The obtained DOC results can be compared to the limit values of TOC, keeping in mind that according to data in the literature, the amount of TOC is mostly made up of DOC, whilst only a small part is suspended organic carbon.

In addition, amongst the water quality indicators studied from the group of particularly harmful substances to the aquatic environment were the concentrations of Zn, Cu and Al, and from the chemical indicators of water quality were the concentrations of Cd and Pb.

**Table 2.** The results of physicochemical analysis of water samples from the Łutownia river in 2011–2014 and limits for class I and II of water quality

| Quarter / Year | EC<br>$\mu\text{S}\cdot\text{cm}^{-1}$ | pH      | H        | Cl   | $\text{SO}_4^{2-}$ | S- $\text{SO}_4^{2-}$ | $\text{NO}_3^-$ | N- $\text{NO}_3^-$ | $\text{PO}_4^{3-}$ | P- $\text{PO}_4^{3-}$ | $\text{NH}_4^+$ |
|----------------|--|---------|----------|------|--------------------|-----------------------|-----------------|--------------------|--------------------|-----------------------|-----------------|
| II / 2011      | 260                                    | 7.76    | 0.000017 | 2.79 | 7.10               | 2.37                  | 0.461           | 0.104              | 0.000              | 0.000                 | 0.078           |
| III / 2011     | 353                                    | 8.19    | 0.000006 | 2.33 | 5.71               | 1.91                  | 0.321           | 0.073              | 0.084              | 0.028                 | 0.072           |
| IV / 2011      | 393                                    | 8.20    | 0.000006 | 4.03 | 16.20              | 5.41                  | 0.000           | 0.000              | 0.000              | 0.000                 | 0.008           |
| I / 2012       | 354                                    | 7.62    | 0.000024 | 3.81 | 15.86              | 5.29                  | 0.785           | 0.177              | 0.000              | 0.000                 | 0.008           |
| II / 2012      | 332                                    | 7.69    | 0.000020 | 2.09 | 4.97               | 1.66                  | 0.249           | 0.056              | 0.000              | 0.000                 | 0.109           |
| IV / 2012      | 236                                    | 7.97    | 0.000011 | 3.63 | 4.67               | 1.56                  | 0.661           | 0.149              | 0.000              | 0.000                 | 0.028           |
| I / 2013       | 157                                    | 9.28    | 0.000001 | 1.63 | 7.27               | 2.43                  | 1.626           | 0.367              | 0.000              | 0.000                 | 0.031           |
| II / 2013      | 291                                    | 7.96    | 0.000011 | 2.68 | 8.17               | 2.73                  | 0.035           | 0.008              | 0.000              | 0.000                 | 0.045           |
| III / 2013     | 384                                    | 7.51    | 0.000031 | 2.65 | 5.88               | 1.96                  | 0.336           | 0.076              | 0.046              | 0.015                 | 0.041           |
| IV / 2013      | 188                                    | 8.26    | 0.000005 | 3.00 | 11.10              | 3.70                  | 0.687           | 0.155              | 0.000              | 0.000                 | 0.016           |
| I / 2014       | 302                                    | 8.42    | 0.000004 | 2.26 | 5.11               | 1.71                  | 1.453           | 0.328              | 0.000              | 0.000                 | 0.019           |
| II / 2014      | 264                                    | 8.01    | 0.000010 | 1.98 | 3.90               | 1.30                  | 0.347           | 0.078              | 0.000              | 0.000                 | 0.114           |
| III / 2014     | 281                                    | 7.93    | 0.000012 | 9.15 | 27.53              | 9.19                  | 0.229           | 0.052              | 0.000              | 0.000                 | 0.047           |
| IV / 2014      | 202                                    | 7.48    | 0.000033 | 5.49 | 23.75              | 7.93                  | 0.229           | 0.052              | 0.000              | 0.000                 | 0.037           |
| <b>Min.</b>    | 157                                    | 7.48    | 0.000001 | 1.63 | 3.90               | 1.30                  | 0.000           | 0.000              | 0.000              | 0.000                 | 0.008           |
| <b>Max.</b>    | 393                                    | 9.28    | 0.000033 | 9.15 | 27.53              | 9.19                  | 1.626           | 0.367              | 0.084              | 0.028                 | 0.114           |
| Mean           | 286                                    | 7.86    | 0.000014 | 3.39 | 10.52              | 3.51                  | 0.530           | 0.120              | 0.009              | 0.003                 | 0.047           |
| Stand.dev.     | 73                                     |         | 0.000010 | 1.94 | 7.52               | 2.51                  | 0.486           | 0.110              | 0.025              | 0.008                 | 0.035           |
| Coeff.of var.  | 26%                                    |         | 74%      | 57%  | 72%                | 72%                   | 92%             | 92%                | 267%               | 267%                  | 74%             |
| Limit I        | 1000                                   | 6.0-8.5 | -        | 200  | 150                | -                     | -               | 2.2                | 0.2                | -                     | -               |
| Limit II       | 1500                                   | 6.0-9.0 | -        | 300  | 250                | -                     | -               | 5.0                | 0.31               | -                     | -               |

Most of the physicochemical indicators of the water tested were within the limits set for class I water quality – in terms of pH, conductivity and electrolytic concentrations of  $\text{SO}_4$ , Cl, Ca, Mg,  $\text{N-NH}_4$ ,  $\text{N-NO}_3$ .

Throughout the study period, the pH values of the water ranged between 7 and 8.5 (class I water quality). Only one sample taken from the Łutownia River in the first quarter of 2013 had a pH higher than 9.0, which is above the limit for class II quality (the Regulation's limits for classes III–V have not been set). The EC of water in the two rivers was within 150–450  $\mu\text{S}\cdot\text{cm}^{-1}$ , which is much lower than the limit values for class I water quality (1,000  $\mu\text{S}\cdot\text{cm}^{-1}$ ). Similarly, concentrations of sulphate and chloride ions in the waters of the two rivers were far below the limits for class I water quality.

The maximum concentration of sulphates was observed in water from the Perebel River – 35  $\text{mg}\cdot\text{dm}^{-3}$  (allowable limit of 150  $\text{mg}\cdot\text{dm}^{-3}$ ). The highest concentration of chloride, 9  $\text{mg}\cdot\text{dm}^{-3}$ , was confirmed in the Łutownia River (allowable limit of 200  $\text{mg}\cdot\text{dm}^{-3}$ ). The concentration of calcium in both rivers was similar: 30–80  $\text{mg}\cdot\text{dm}^{-3}$ , with a limit of 100  $\text{mg}\cdot\text{dm}^{-3}$  for class I water quality. Magnesium concentrations were generally higher in the water of the Łutownia River, but measurements for both rivers throughout the study period did not exceed 11  $\text{mg}\cdot\text{dm}^{-3}$ , at an allowable limit of 50  $\text{mg}\cdot\text{dm}^{-3}$ . The concentration of ammonium nitrogen and nitrate nitrogen also did not lower the quality of the water in the rivers. The maximum concentration of ammonium nitrogen was found in the second quarter of 2014 in the Perebel

| $\text{N-NH}_4^+$              | Ca   | Mg    | Na   | K    | Fe    | Al    | Mn    | Cd      | Cu     | Pb     | Zn    | RWO   | TNb  |
|--------------------------------|------|-------|------|------|-------|-------|-------|---------|--------|--------|-------|-------|------|
| $\text{mg}\cdot\text{dm}^{-3}$ |      |       |      |      |       |       |       |         |        |        |       |       |      |
| 0.061                          | 48.5 | 5.74  | 2.31 | 1.20 | 0.293 | 0.006 | 0.001 | 0.00003 | 0.0077 | 0.0613 | 0.027 | 34.17 | 1.79 |
| 0.056                          | 64.8 | 8.77  | 3.06 | 1.02 | 0.084 | 0.003 | 0.014 | 0.00008 | 0.0057 | 0.0468 | 0.035 | 22.06 | 1.75 |
| 0.006                          | 72.8 | 9.71  | 3.65 | 1.36 | 0.030 | 0.007 | 0.006 | 0.00000 | 0.0133 | 0.0019 | 0.050 | 11.50 | 0.82 |
| 0.006                          | 59.9 | 7.61  | 3.49 | 1.27 | 0.301 | 0.011 | 0.021 | 0.00000 | 0.0165 | 0.0004 | 0.048 | 14.33 | 1.26 |
| 0.085                          | 71.3 | 10.56 | 3.74 | 0.80 | 0.039 | 0.006 | 0.201 | 0.00000 | 0.0143 | 0.0014 | 0.034 | 13.57 | 1.23 |
| 0.022                          | 34.6 | 9.90  | 4.04 | 1.87 | 0.015 | 0.005 | 0.006 | 0.00003 | 0.0006 | 0.0021 | 0.028 | 10.64 | 0.64 |
| 0.024                          | 30.9 | 3.19  | 1.41 | 0.79 | 0.039 | 0.013 | 0.012 | 0.00002 | 0.0005 | 0.0038 | 0.033 | 9.48  | 0.81 |
| 0.035                          | 55.9 | 6.65  | 2.84 | 1.47 | 0.111 | 0.012 | 0.001 | 0.00001 | 0.0011 | 0.0028 | 0.033 | 21.86 | 1.02 |
| 0.032                          | 66.1 | 10.52 | 4.88 | 1.66 | 0.012 | 0.007 | 0.002 | 0.00001 | 0.0007 | 0.0067 | 0.050 | 5.80  | 0.42 |
| 0.012                          | 39.7 | 4.67  | 2.40 | 0.90 | 0.130 | 0.007 | 0.006 | 0.00011 | 0.0026 | 0.0006 | 0.019 | 18.57 | 0.93 |
| 0.015                          | 59.4 | 7.58  | 3.43 | 0.88 | 0.045 | 0.005 | 0.003 | 0.00013 | 0.0021 | 0.0023 | 0.035 | 14.61 | 1.02 |
| 0.088                          | 50.0 | 8.12  | 3.70 | 0.97 | 0.029 | 0.001 | 0.178 | 0.00006 | 0.0021 | 0.0021 | 0.011 | 13.36 | 0.86 |
| 0.037                          | 49.3 | 3.81  | 3.87 | 1.67 | 0.311 | 0.012 | 0.017 | 0.00010 | 0.0018 | 0.0025 | 0.028 | 30.54 | 1.55 |
| 0.029                          | 37.4 | 2.84  | 2.88 | 0.33 | 0.162 | 0.013 | 0.010 | 0.00054 | 0.0026 | 0.0014 | 0.019 | 25.78 | 1.29 |
| 0.006                          | 30.9 | 2.84  | 1.41 | 0.33 | 0.012 | 0.001 | 0.001 | 0.00000 | 0.0005 | 0.0004 | 0.011 | 5.80  | 0.42 |
| 0.088                          | 72.8 | 10.56 | 4.88 | 1.87 | 0.311 | 0.013 | 0.201 | 0.00054 | 0.0165 | 0.0613 | 0.050 | 34.17 | 1.79 |
| 0.036                          | 52.9 | 7.12  | 3.26 | 1.16 | 0.114 | 0.008 | 0.034 | 0.00008 | 0.0051 | 0.0097 | 0.032 | 17.59 | 1.10 |
| 0.027                          | 13.7 | 2.70  | 0.86 | 0.42 | 0.111 | 0.004 | 0.066 | 0.00014 | 0.0056 | 0.0191 | 0.012 | 8.29  | 0.40 |
| 74%                            | 26%  | 38%   | 26%  | 37%  | 97%   | 51%   | 194%  | 175%    | 110%   | 196%   | 36%   | 47%   | 37%  |
| 0.78                           | 100  | 50    | -    | -    | -     | 0.4   | -     | 0.00045 | 0.05   | 0.0072 | 1     | 15    | 5    |
| 1.56                           | 200  | 100   | -    | -    | -     | 0.4   | -     | 0.00045 | 0.05   | 0.072  | 1     | 20    | 10   |

River –  $0.61 \text{ mg} \cdot \text{dm}^{-3}$  (the allowable limit for class I water quality is  $0.78 \text{ mg} \cdot \text{dm}^{-3}$ ). The highest concentrations of nitrate nitrogen in the waters of both rivers occurred in the first quarter of 2013, but they were significantly below the limit of  $2.2 \text{ mg} \cdot \text{dm}^{-3}$ . Also, the concentrations of aluminium, zinc, copper and cadmium did not generally exceed the limits that would result in a lower assessment of water quality.

The factor deteriorating the water quality of the two rivers was the concentration of DOC, most of which exceeded the limit of  $15 \text{ mg} \cdot \text{dm}^{-3}$  (the allowable limit of TOC for class I water quality in streams in natural areas is influenced by peat-forming processes) and, many cases, the limit of  $20 \text{ mg} \cdot \text{dm}^{-3}$  (the analogous limit for class II water quality). Approximately half of the samples taken from the Perebel River and one-third of the samples taken from the Łutownia River had DOC concentrations in the range of  $20\text{--}65 \text{ mg} \cdot \text{dm}^{-3}$ .

On the basis of the tests, the river water can be qualified as

- Class I: Łutownia in 2012 and 2013,
- Class II: Perebel in 2012 and 2014,
- Class III: Perebel in 2011 and 2013 and Łutownia in 2011 and 2014.

In comparing the water chemistry of both streams, we can see that the water of the Perebel River was slightly less alkaline than the Łutownia River's water (average pH was lower by 0.38). At the same time, with small differences in EC (approximately 10%) indicating total water mineralisation, the water from the Perebel River Basin has much higher ion concentrations of phosphate (873%), iron (451%), ammonium (349%), cadmium (238%), aluminium (228%), manganese (217%) and DOC (150%) and somewhat higher concentrations of total nitrogen (138%), sulphate (133%) and chloride ions (120%). The water leaving the Łutownia River Basin has

**Table 3.** The results of physicochemical analysis of water samples from the Perebel river in 2011–2014 and limits for class I and II of water quality

| Quarter / Year | EC                  | pH      | H        | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | S-SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | N-NO <sub>3</sub> <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> | P-PO <sub>4</sub> <sup>3-</sup> | NH <sub>4</sub> <sup>+</sup> |
|----------------|---------------------|---------|----------|-----------------|-------------------------------|---------------------------------|------------------------------|--------------------------------|-------------------------------|---------------------------------|------------------------------|
|                | μS·cm <sup>-1</sup> | -       |          |                 |                               |                                 |                              |                                |                               |                                 |                              |
| II / 2011      | 189                 | 8.09    | 0.000008 | 4.98            | 12.72                         | 4.25                            | 0.000                        | 0.000                          | 0.000                         | 0.000                           | 0.037                        |
| III / 2011     | 304                 | 7.37    | 0.000043 | 5.37            | 3.66                          | 1.22                            | 0.036                        | 0.008                          | 0.229                         | 0.075                           | 0.099                        |
| IV / 2011      | 239                 | 7.69    | 0.000020 | 2.84            | 17.42                         | 5.82                            | 0.322                        | 0.073                          | 0.134                         | 0.044                           | 0.172                        |
| I / 2012       | 198                 | 7.26    | 0.000055 | 5.81            | 23.80                         | 7.94                            | 0.205                        | 0.046                          | 0.000                         | 0.000                           | 0.032                        |
| II / 2012      | 260                 | 7.94    | 0.000011 | 3.33            | 13.29                         | 4.44                            | 0.996                        | 0.225                          | 0.150                         | 0.049                           | 0.395                        |
| I / 2013       | 263                 | 7.19    | 0.000065 | 6.74            | 35.20                         | 11.75                           | 1.118                        | 0.253                          | 0.000                         | 0.000                           | 0.021                        |
| II / 2013      | 229                 | 7.34    | 0.000046 | 5.25            | 18.84                         | 6.29                            | 0.068                        | 0.015                          | 0.053                         | 0.017                           | 0.042                        |
| III / 2013     | 230                 | 7.47    | 0.000034 | 2.67            | 14.27                         | 4.76                            | 0.573                        | 0.129                          | 0.208                         | 0.068                           | 0.100                        |
| IV / 2013      | 277                 | 8.46    | 0.000003 | 4.59            | 8.49                          | 2.83                            | 0.613                        | 0.139                          | 0.064                         | 0.021                           | 0.019                        |
| I / 2014       | 277                 | 7.99    | 0.000010 | 3.23            | 5.75                          | 1.92                            | 0.398                        | 0.090                          | 0.059                         | 0.019                           | 0.379                        |
| II / 2014      | 224                 | 7.10    | 0.000079 | 2.49            | 5.65                          | 1.88                            | 0.607                        | 0.137                          | 0.000                         | 0.000                           | 0.784                        |
| III / 2014     | 455                 | 7.77    | 0.000017 | 2.81            | 7.88                          | 2.63                            | 0.204                        | 0.046                          | 0.000                         | 0.000                           | 0.033                        |
| IV / 2014      | 262                 | 7.37    | 0.000043 | 3.02            | 15.12                         | 5.05                            | 0.030                        | 0.007                          | 0.156                         | 0.051                           | 0.006                        |
| <b>Min.</b>    | 189                 | 7.10    | 0.000003 | 2.49            | 3.66                          | 1.22                            | 0.000                        | 0.000                          | 0.000                         | 0.000                           | 0.006                        |
| <b>Max.</b>    | 455                 | 8.46    | 0.000079 | 6.74            | 35.20                         | 11.75                           | 1.118                        | 0.253                          | 0.229                         | 0.075                           | 0.784                        |
| Mean           | 262                 | 7.48    | 0.000033 | 4.09            | 14.01                         | 4.68                            | 0.398                        | 0.090                          | 0.081                         | 0.026                           | 0.163                        |
| Stand.dev.     | 66                  |         | 0.000024 | 1.42            | 8.64                          | 2.89                            | 0.366                        | 0.083                          | 0.084                         | 0.028                           | 0.228                        |
| Coeff.of var.  | 25%                 |         | 72%      | 35%             | 62%                           | 62%                             | 92%                          | 92%                            | 104%                          | 104%                            | 140%                         |
| Limit I        | 1000                | 6.0-8.5 | -        | 200             | 150                           | -                               | -                            | 2.2                            | 0.2                           | -                               | -                            |
| Limit II       | 1500                | 6.0-9.0 | -        | 300             | 250                           | -                               | -                            | 5.0                            | 0.31                          | -                               | -                            |

clearly higher concentrations of magnesium (174%), copper (173%), nitrates (133%), potassium (131%) and zinc (118%).

Organic nitrogen is the difference between TNb and the amount of mineral forms of nitrogen ( $N_{\min}$ ), in this case, nitrate nitrogen and ammonium nitrogen. In the equation, it was assumed that the nitrogen in the form of nitrite nitrogen was not present or its concentration was so small that it could be bypassed. This assumption is correct if the water quality has not significantly deteriorated since the tests performed in the spring of 2010 in the Białowieża Forest for the Narewka and several of its tributaries. In these studies, the chemical analyses carried out at 11 measuring sites showed no presence of nitrite nitrogen (Pierzgalski et al. 2010). The concentration of organic nitrogen ( $N_{\text{org}}$ ) was calculated using the following formulas:

$$N_{\text{org}} = \text{TNb} - N_{\min}$$

$$N_{\min} = N_{\text{NO}_3} + N_{\text{NH}_4} \quad (\text{when } N_{\text{NO}_2} = 0),$$

where

$N_{\text{org}}$  is the organic nitrogen,  
 TNb is the total nitrogen bound,  
 $N_{\min}$  is the mineral nitrogen,  
 $N_{\text{NO}_3}$  is the nitrate nitrogen,  
 $N_{\text{NH}_4}$  is the ammonium nitrogen,  
 $N_{\text{NO}_2}$  is the nitrite nitrogen.

The calculated concentration of organic nitrogen was significant, and its amount is depicted in Figures 1 and 2. The concentration of  $N_{\text{org}}$  in the water of the Lutownia River was in the range 0.31–1.62 mg·dm<sup>-3</sup> and in the Perebel River 0.24–2.62 mg·dm<sup>-3</sup>. The organic form of nitrogen dominated for all dates.

After analysing all of the tested physicochemical indicators, most do not show any trends of change or clear sea-

| N-NH <sub>4</sub> <sup>+</sup> | Ca   | Mg    | Na   | K    | Fe    | Al    | Mn    | Cd      | Cu     | Pb     | Zn    | RWO   | TNb  |
|--------------------------------|------|-------|------|------|-------|-------|-------|---------|--------|--------|-------|-------|------|
| mg·dm <sup>-3</sup>            |      |       |      |      |       |       |       |         |        |        |       |       |      |
| 0.029                          | 50.5 | 3.73  | 3.19 | 0.49 | 0.456 | 0.019 | 0.003 | 0.00020 | 0.0056 | 0.0458 | 0.026 | 45.14 | 2.16 |
| 0.077                          | 65.0 | 3.93  | 2.45 | 0.46 | 1.931 | 0.026 | 0.339 | 0.00108 | 0.0061 | 0.0425 | 0.034 | 65.25 | 2.70 |
| 0.133                          | 43.0 | 4.01  | 2.95 | 0.71 | 0.039 | 0.019 | 0.225 | 0.00000 | 0.0006 | 0.0250 | 0.015 | 16.47 | 1.46 |
| 0.025                          | 35.7 | 3.11  | 2.79 | 0.91 | 0.127 | 0.015 | 0.022 | 0.00000 | 0.0113 | 0.0012 | 0.031 | 19.67 | 1.35 |
| 0.307                          | 47.1 | 3.94  | 3.09 | 0.90 | 0.173 | 0.010 | 0.092 | 0.00010 | 0.0028 | 0.0015 | 0.022 | 19.94 | 1.84 |
| 0.017                          | 53.3 | 4.15  | 3.66 | 1.22 | 1.227 | 0.034 | 0.003 | 0.00022 | 0.0002 | 0.0017 | 0.052 | 30.82 | 1.68 |
| 0.033                          | 48.0 | 3.75  | 3.58 | 0.83 | 0.350 | 0.020 | 0.004 | 0.00004 | 0.0002 | 0.0024 | 0.023 | 32.03 | 1.53 |
| 0.078                          | 41.8 | 3.75  | 3.14 | 0.84 | 0.059 | 0.005 | 0.012 | 0.00008 | 0.0001 | 0.0019 | 0.022 | 5.58  | 0.51 |
| 0.015                          | 54.7 | 3.64  | 3.42 | 0.28 | 0.650 | 0.020 | 0.000 | 0.00022 | 0.0027 | 0.0014 | 0.015 | 31.53 | 1.84 |
| 0.294                          | 55.8 | 3.75  | 2.69 | 0.24 | 0.713 | 0.015 | 0.070 | 0.00018 | 0.0018 | 0.0016 | 0.017 | 43.41 | 2.44 |
| 0.609                          | 41.2 | 1.07  | 1.85 | 2.39 | 0.751 | 0.039 | 0.138 | 0.00020 | 0.0034 | 0.0055 | 0.058 | 18.56 | 1.66 |
| 0.025                          | 75.7 | 10.35 | 4.45 | 1.38 | 0.020 | 0.003 | 0.014 | 0.00001 | 0.0021 | 0.0030 | 0.015 | 7.50  | 0.33 |
| 0.005                          | 44.4 | 3.98  | 3.03 | 0.79 | 0.200 | 0.004 | 0.039 | 0.00014 | 0.0015 | 0.0032 | 0.025 | 7.78  | 0.25 |
| 0.005                          | 35.7 | 1.07  | 1.85 | 0.24 | 0.020 | 0.003 | 0.000 | 0.00000 | 0.0001 | 0.0012 | 0.015 | 5.58  | 0.25 |
| 0.609                          | 75.7 | 10.35 | 4.45 | 2.39 | 1.931 | 0.039 | 0.339 | 0.00108 | 0.0113 | 0.0458 | 0.058 | 65.25 | 2.70 |
| 0.127                          | 50.5 | 4.09  | 3.10 | 0.88 | 0.515 | 0.018 | 0.074 | 0.00019 | 0.0029 | 0.0105 | 0.027 | 26.44 | 1.52 |
| 0.177                          | 10.8 | 2.04  | 0.63 | 0.56 | 0.555 | 0.011 | 0.104 | 0.00028 | 0.0032 | 0.0162 | 0.014 | 17.35 | 0.76 |
| 140%                           | 21%  | 50%   | 20%  | 64%  | 108%  | 62%   | 140%  | 148%    | 107%   | 154%   | 50%   | 66%   | 50%  |
| 0.78                           | 100  | 50    | -    | -    | -     | 0.4   | -     | 0.00045 | 0.05   | 0.0072 | 1     | 15    | 5    |
| 1.56                           | 200  | 100   | -    | -    | -     | 0.4   | -     | 0.00045 | 0.05   | 0.072  | 1     | 20    | 10   |

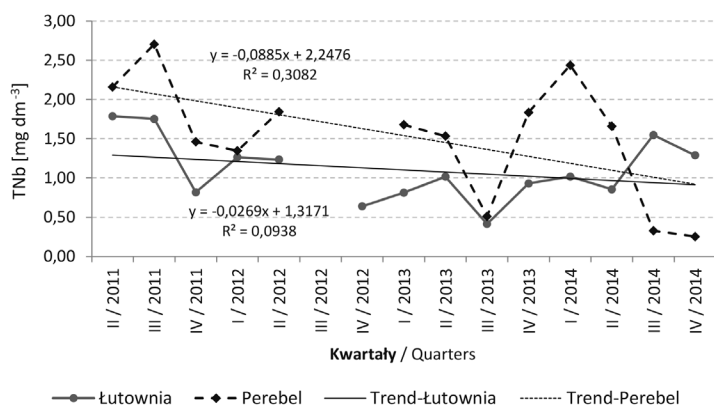
sonal variation. Only TNb concentrations in the Łutownia River water and TNb and DOC in the Perebel River water indicate decreasing trends (Figures 3 and 4). On the basis of the calculations, it can also be stated that the concentration of organic nitrogen is decreasing and the concentration of mineral nitrogen is increasing in both the rivers. In all cases, the changes are occurring more quickly in the water of the Perebel River (the absolute values of coefficients of skewness trend lines are larger), in a catchment area that

has over 30% coniferous habitats, and also more than 30% non-forested land. Although the concentration of DOC in the two rivers is significant, it should be noted that this carbon is derived from natural sources and its concentration does not exceed that found in the other, clean rivers of the Białowieża Forest (Pierzgalski et al. 2010; Malzahn et al. 2014).

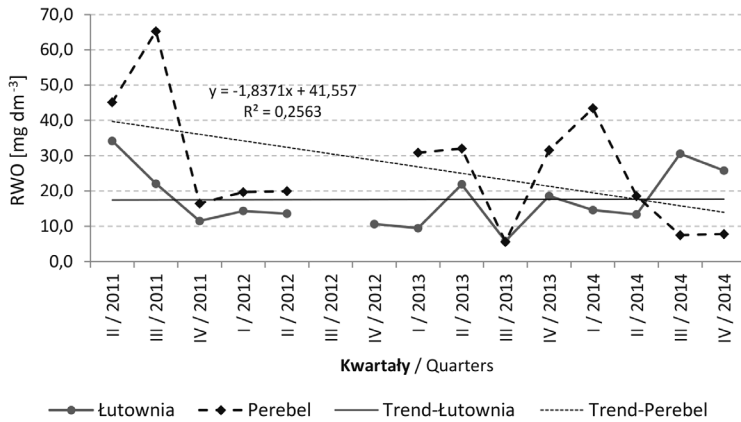
The DOC found in natural waters is made up of about 90% of a complex mixture of humus compounds, star-

**Figure 1.** Concentrations of total bound nitrogen (TNb), mineral nitrogen ( $N_{\min}$ ) and organic nitrogen ( $N_{\text{org}}$ ) in the waters of the Łutownia river in 2011–2014

**Figure 2.** Concentrations of total bound nitrogen (TNb), mineral nitrogen ( $N_{\min}$ ) and organic nitrogen ( $N_{\text{org}}$ ) in the waters of the Perebel river in 2011–2014



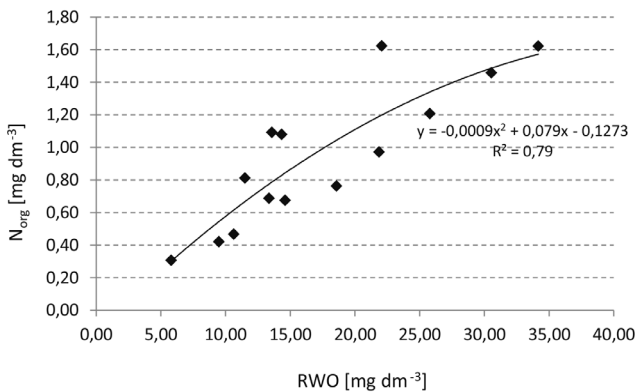
**Figure 3.** Changes in concentrations of total bound nitrogen – TNb (and their linear trend) in the waters of rivers: Łutownia and Perebel in 2011–2014



**Figure 4.** Changes in concentrations of dissolved organic carbon – RWO (and their linear trend) in the waters of rivers: Łutownia and Perebel in 2011–2014

ting with short chain molecule acids to large particles of humic substances (Moore et al. 2003). The formation and movement of DOC in soils is an important process of the transformation of soil organic matter and the carbon cycle between ecosystems. An important source of DOC in river water is peat soil. An increase in the concentration of DOC in surface waters has been observed in both Europe and North America for decades (Sapek 2009), which was not confirmed, however, in this four-year study, perhaps because of a too short period of research.

Of importance to the interpretations made above is the fact that about 20% of the Białowieża Forest has hydrogenic soils. They constitute a separate group of soils in which the bulk of the matter is made up of organic substances, and the joining of humus and minerals resulting from changes in hydrological conditions influences the transformation process of these soils. As a result of dehydration, the organic matter undergoes rapid biological oxidation; its amount gradually decreases and its mineral content increases (Pastuszko 2007).

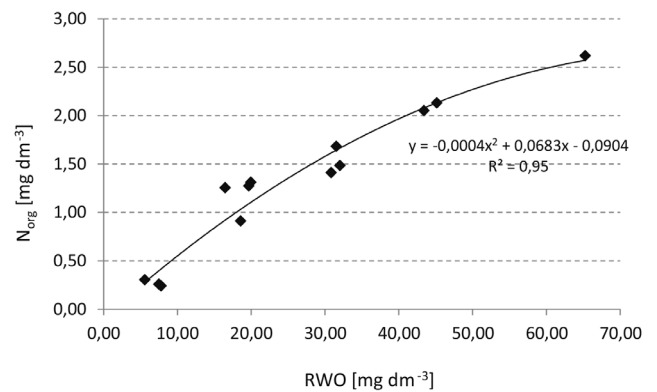


**Figure 5.** The relationship between the concentration of dissolved organic carbon (DOC) and the concentration of organic nitrogen ( $N_{org}$ ) in the waters of the Łutownia river in 2011–2014

Pawluczuk and Gotkiewicz (2003), in studying the peat marsh soils of late-glacial areas in the northeast of Poland, demonstrated that the mineralisation of organic nitrogen compounds varies depending on habitat conditions, especially humidity and the methods by which water is supplied. They showed that in the desiccated soil of outwash plains, mineralisation can be quite extensive, whilst at the same study site, this process was inhibited in heavily moistened soils.

Research in the Biebrza River Valley showed that the wetlands surrounding the river are the main source of the significant quantities of organic nitrogen present in it, with the largest concentrations occurring in the summer. Organic nitrogen enters the river as the main component of organic matter washed out from layers of peat, which also contains organic phosphorus and carbon (Bielak 2009).

A similar phenomenon is probably occurring in the Białowieża Forest, as studies have found a significant positive correlation between the concentrations of organic carbon and organic nitrogen in the water of both rivers (Figures 5 and 6).



**Figure 6.** The relationship between the concentration of dissolved organic carbon (DOC) and the concentration of organic nitrogen ( $N_{org}$ ) in the waters of the Perebel river in 2011–2014



The climatic conditions of recent years – increased temperatures, droughts and irregular rainfall – are of key significance in the Białowieża Forest for the concentration levels (and changes thereof) of organic carbon and various forms of nitrogen. In this area, after more than 20 unfavourable years, optimal thermal and moisture conditions for the environment of the forest were noted only in 2009–2013 (Malzahn et al. 2014). The increasing intensity of the mineralisation of nitrogen compounds in soils observed in recent years may be an indication of the currently observed effects of climate change on this process (Sapek 2006). This is confirmed by studies showing that an excessive lowering of the groundwater table increases the intensity of mineralisation as well as the thickness of the layers in which this process is occurring (Turbiak, Miatkowski 2003). This results in the release of amounts of nitrogen that exceed the requirements of plants, with this surplus eluted from the soil and dispersed in the environment.

## 5. Conclusions

- The variability of specific chemical characteristics of surface water differed. The coefficients of variation ranged from 21% for concentrations of calcium in the water of the Perebel River to 267% for phosphate concentrations in the water of the Lutownia River.
- In 2011–2014, the water quality of the Lutownia River was determined to be class I and III, whilst the quality of the Perebel River was class II and III because of high concentrations of organic forms of carbon and nitrogen.
- The lower quality of the water in the rivers was impacted by the leaching of large amounts of organic matter from the soil.
- The gradual decline in the concentrations of organic nitrogen, with a simultaneous increase in the concentration of mineral nitrogen (especially in the Perebel River water), testifies to the intensification of the mineralisation of organic matter in the soils of this river basin.

## Conflict of interest

The author declares no potential conflicts of interest.

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## References

- Bielak S. 2009. Ocena i prognoza stanu ekologicznego ekosystemu rzecznoego na obszarze Biebrzańskiego Parku Narodowego. Politechnika Krakowska. Praca doktorska, 1–337.
- Malzahn E., Pierzgalski E., Tyszka J., Janek M., Fronczak E., Stolarek A. 2014. Zmiany warunków klimatycznych i wodnych w środowisku lasów naturalnych Puszczy Białowiejskiej. Maszynopis. Instytut Badawczy Leśnictwa, 1–245.
- Miniuk V. 1998. Chemizm wód powierzchniowych w różnych typach zagospodarowania zlewni na terenie Puszczy Białowiejskiej. *Parki Narodowe i Rezerваты Przyrody* 17(1): 93–115.
- Moore T.R., Matos L., Roulet N.T. 2003. Dynamics and chemistry of dissolved organic carbon in Precambrian Shield catchments and an impounded wetland. *Canadian Journal of Fisheries and Aquatic Sciences* 60: 612–623. DOI 10.1139/F03-050.
- Pastuszko A. 2007. Substancja organiczna w glebach. *Ochrona Środowiska i Zasobów Naturalnych* 30: 83–98.
- Pawluczuk J., Gotkiewicz J. 2003. Ocena procesu mineralizacji azotu w glebach wybranych ekosystemów torfowiskowych Polski północno-wschodniej w aspekcie ochrony zasobów glebowych. *Acta Agrophysica* 1(4): 721–728.
- Pierzgalski E., Tyszka J., Boczoń A., Janek M., Wróbel M., Stolarek A., Pachuta K., Oględzki P., Frąk M., Sikorski P., Komecka L., Czachorowski S., Pietrzak L., Ksepko M. 2010. Operat zarządzania wodami i ochrony ekosystemów wodnych (do Planu Ochrony Białowiejskiego Parku Narodowego). Maszynopis. Instytut Badawczy Leśnictwa, 1–162.
- Rozporządzenie Ministra Środowiska z dnia 20 sierpnia 2008 r. w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych. Dz.U.2008 nr 162 poz. 1008.
- Rozporządzenie Ministra Środowiska z dnia 9 listopada 2011 r. w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych oraz środowiskowych norm jakości dla substancji priorytetowych. Dz.U.2011 nr 257 poz. 1545.
- Rozporządzenie Ministra Środowiska z dnia 22 października 2014 r. w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych oraz środowiskowych norm jakości dla substancji priorytetowych. Dz.U.2014 poz. 1482.
- Sapek A. 2009. Rozpuszczalny węgiel organiczny w wodzie z gleb torfowych na bagnie Ławki. *Roczniki Gleboznawcze* 60(2): 89–101.
- Sapek B. 2006. Wpływ opadu atmosferycznego i temperatury oraz uwilgotnienia gleby łąkowej na uwalnianie i dynamikę mineralnych form azotu. *Woda-Środowisko-Obszary Wiejskie* 17: 29–38.
- Skorbiłowicz M., Skorbiłowicz E., Wojciuk Z., Winiarek P. 2008. Wpływ źródeł antropogenicznych i naturalnych na jakość wód rzeki Narewka. *Ochrona Środowiska i Zasobów Naturalnych* 37: 58–63.
- Turbiak J., Miatkowski Z. 2003. Zawartość mineralnych form azotu w długotrwale odwodnionej płytce glebie torfowo-murszowej i mineralno-murszowej. *Woda-Środowisko-Obszary Wiejskie* 9: 139–151.