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BIOGEOCHEMICAL MULTIFUNCTIONALITY OF WETLAND ECOTONES IN LAKELAND AGRICULTURAL LANDSCAPE

ABSTRACT: The study was focused on the analysis of the effect of the nutrient loads from cultivated and fertilized watershed on the ion balance in wetland ecotones. The investigations were carried out in Masurian Lakeland (NE Poland) in small (0.2 ha) fens dominated by cattail association. Wetland ecotones constitute an effective biogeochemical barrier in respect to nitrates. However, they do not protect lakes against other eutrophication factors arising as the result of multifunctional character of biogeochemical processes in the wetland environment under pression of nutrients of fertilizing origin. The eutrophication of waters can be enhanced by increased amounts of potassium, phosphates, and dissolved organic nitrogen moving out from wetland ecotones.

KEY WORDS: mire, elements, throughflow, agricultural landscape.

1. INTRODUCTION

The interest of ecologist in biogeochemistry of the wetland ecosystems is mainly connected with their function as sinks for inflowing loads of nutrients, mainly nitrogen and phosphorus (Waughman and Bellamy 1980, Nichols 1983, Brinson *et al.* 1984, Peterjohn and Correll 1984, Kruk 1990). The wetlands can act as source and transformers for throughflowing matter (Mitsch and Gosselink 1993). They constitute complex, interactive biogeochemical system (Golterman 1995).

In the light of the above, not only presentation of balance of nutrients is an important objective of wetland studies, but also the demonstration of interactions between key elements suppllying wetlands. This demonstration allows for the better recognition and control of wetlands acting as systems of secondary treatment of wastewater (Tilton and Cadlec 1979), or the filter of mineral substances of fertilazer's origin from agricultural areas (Kruk 1990, 1996). This seems to be very important, due to position of ecotones between watershed and lakes and rivers, which these systems occupy in landscape (Hillbricht-Ilkowska 1995).

The study aims to show and discuss a number of dependencies between the loads of ions flowing through small wetlands, situated among arable fields, supplied by considerable amount of nutrients from the watershed. The investigations focus on the demonstration of interactive character of the ion throughflow by these specific ecotones connecting agrosystems with subsurface waters supplying lakes and rivers. The analysis of interrelationships between major constituents of waters passing by the mires shows that these ecosystems fulfil multifactorial role in cycling of matter in the landscape.

2. STUDY AREA

The study was carried out in two small mires, situated in depressions without run-off in the Mazurian Lakeland, near the town of Mikołajki (Fig. 1) in the years 1982 – 1984. The wetlands were surrounded by arable fields, which were fertilized as follows (approximate data): 56–100 kg N ha^{-1}, 17–45 kg P ha^{-1}, 100–114 kg K ha^{-1}, 20–40 kg SO_4^{2-} ha^{-1} and some certain amounts of Mg and Ca (Traczyk *et al.* 1985).

Mire no 1 is a small object, 0.051 ha in area, situated within Lake Jorzec watershed (Fig. 1). The fen is covered almost completely by cattail rushes (*Typhetum latifioliae* Soo 1927) and its bed was made up of clayey-silty warp, below which is a layer of well-decomposed alder peat. The surface water of the mire had seasonal character and water level changes were considerable. The drainage area of the fen (1.032 ha) is a slope used as arable field and made up in its surface by loamy sands. The watershed/mire area ratio amounts 20.

Mire no 2 is larger (0.183 ha) and is situated near Lake Inulec (Fig. 1). The wetland is covered by two plant associations: willow shrubberies *Salicetum pentandro-cinerea* Almq. 1929 (Pass. 1961) and cattail rushes *Typhetum latifioliae* Soo 1927. The bed is made up of clayey-silty warp and covers slightly decomposed sedge peat. The mire had a seasonal surface water with high ampli-

Fig. 1. The location of the studied wetland ecotones and the scheme of its hydrologic system. 1. wetland with *Typphetum latifoliae*, 2. wetland with *Salicetum pentandro-cinerea*, 3. subsurface inflow from watershed into wetland, 4. subsurface outflow from the wetland.

tude of water level changes in the first year of study, but was subjected to artificial drainage in the second year. The watershed, 1.278 ha of area, is dominated by arable fields and the watershed/mire area ratio amounts 7. The soil in the watershed is made up of light loams and loamy sands.

3. METHODS

The water flow paths through the mire system was determined using a number of hydrogeological methods. The slope of the sub-surface water table was determined by measuring water levels in piezometers and using geodetic theodolite. Ground permeability in and around the fens was measured using data concerned the rise curves of an artificially lowered water level, as proposed by Pisarkov (Wieczysty 1982). With these data it was possible to identify inflow and outflow zones and profiles and subsequently calculate the water flow volume using the formula of Darcy (Pazdro 1983). These data and concentration of ion in subsurface inflow and outflow waters were required for the determination of inflow and outflow ion loads into and out of the mires (see details in Kruk 1990). The atmospheric input was neglected.

Ion balance is equal to the difference between the inflow and outflow of a given ion and could be positive or negative. The positive balance indicate a reduction or decrease of ion load during its flow through the mire (accumulation, retention or discharge into atmosphere as a gas), while a negative balance shows an increase in ion load as a result of losses via subsurface outflow of the ion from the mire.

Subsurface water was sampled once a month over a period of two years (May 1982 – May 1984). The samples were obtained from PVC piezometers installed in the inflow and outflow zones, long enough to comprise over 80–100% of the waterflow section. Prior to the sampling, any water was removed from piezometer and the water which subsequently flew in was sampled for chemical analysis (Kruk 1990). A volume of 3–5 litres of water obtained in this way was then filtered and evaporated at 60° C. Each sample of water was poured into two separate evaporating dishes. Salicylic acid (1–2 mg) was added to one dish to lower pH to below 3, and a similar quantity of NaOH was added to the other, what raised pH to above 11 (Stachurski and Zimka 1984). The ammonium ion concentration was obtained by determining total nitrogen with a CHN gas chromatography apparatus (Carlo Erba). First, total nitrogen was determined in the deposit left following evaporisation of the sample with salicylic acid, which prevented the release of ammonia during evaporation. The ammonium ion concentration was determined by subtracting the nitrogen concentration value in the sample with an addition of NaOH from the total nitrogen concentration. It was assumed that entire ammonium nitrogen would volatilize as gas at pH about 11 (Stachurski 1988). Concentration of phosphates was determined using stannous chloride method, chloride was determined using potentiometric method, while nephelometric method was used to determine sulphate ions (Standard methods for the examination... 1981). Concentration of nitrate ions was determined using potentiometric method. The flame photometry and the atomic absorption method were employed in the case of the metal ions K, Ca, Mg and Na examination (Standard methods for the examination... 1981).

The variables subjected to the regression analysis comprise 42 monthly measurements of the loads of ions inflowing into both fens from the watershed and ions inflow-outflow balances. The statistical analysis was based on the premise that during the study period (with a exception of artificial drainage in mire no 2) both objects had enough in common to allow inflow and outflow data from this period to be combined into series forming the variables (Kruk 1996).

4. RESULTS

The flow of mineral elements through wetlands studied in the conditions of agricultural landscape in Mazurian Lakeland performs the number of characteristic features. First of all, the inflows of calcium and other ions washed out from fertilizers as anions SO_4^{2-}, Cl^- i NO_3^- were considerable (Table 1). The positive balance of nitrates became visible – almost 290 kg $ha^{-1}yr^{-1}$ of NO_3^- was removed from the flow by wetland which constitute 95% of inflow. On the contrary, in case of potassium, outflow exeed inflow more than 2.5 times. The throughflow of

Table 1. Loads of inflow, outflow and balance of elements flowing through the mires in agricultural landscape (mean values ± standard deviation). N = 3. In kg $ha^{-1} year^{-1}$

Element	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-	SRP	DON
Inflow	11.7 ±4.9	207.1 ±120.4	2060.9 ±1259.3	201.9 ±114.3	20.7 ±17.7	305.1 ±213.3	1249.4 ±751.3	615.6 ±406.1	0.15 ±0.06	12.2 ±4.7
Outflow	42.7 ±31.7	154.1 ±90.4	1684.1 ±1165.5	168.2 ±116.8	11.4 ±5.2	15.2 ±12.1	1049.7 ±823.8	626.4 ±480.9	0.23 ±0.15	17.7 ±15.4
Balance (In – Out)	– 31.0 ±26.9	53.0 ±42.8	376.7 ±171.8	33.7 ±3.6	8.7 ±13.7	289.9 251.2	199.7 ±107.0	– 10.7 ±98.3	– 0.08 ±0.10	–5.5 ±12.8
Balance in % of inflow	*– 265*	*26*	*18*	*17*	*43*	*95*	*16*	*– 2*	*– 53*	*–45*

Table 2. The correlation of water inflow from watershed (in mm $month^{-1}$) and the loads of NO_3^-, SO_4^{2-} i Ca^{2+} with the budgets of ions throughflowing by the mires in agricultural landscape (in kg ha^{-1} $month^{-1}$). The correlation coeficients R is defined of nonlinear regression equation $y = a + b_1x + b_2x^2$ and the significance level p. (n. s. – not significant)

Budgets		K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	H^+	NO_3^-	SO_4^{2-}	Cl^-	SRP
Inflow of water		0.53	0.64	0.63	0.44	0.90	0.55	0.63	0.25	0.41	0.26
	p	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	*0.01*	n. s.	*0.01*	n. s.
Loads of	NO_3^-	0.65	0.42	0.38	0.20	0.39	0.22	0.99	0.50	0.18	0.10
	p	*0.01*	*0.01*	*0.05*	n. s.	*0.05*	n. s.	*0.01*	*0.01*	n. s.	n. s.
	SO_4^{2-}	0.64	0.50	0.51	0.26	0.82	0.38	0.75	0.27	0.26	0.45
	p	*0.01*	*0.01*	*0.01*	n. s.	*0.01*	*0.05*	*0.01*	n. s.	n. s.	*0.01*
	Ca^{2+}	0.64	0.57	0.59	0.35	0.88	0.47	0.68	0.25	0.48	0.40
	p	*0.01*	*0.01*	*0.01*	*0.05*	*0.01*	*0.01*	*0.01*	n. s.	*0.01*	*0.01*

other elements didn't point at considerable domination of inflow or outflow, however, the negative balance of phosphates and dissolved organic nitrogen should be noted (Table 1). These nutrients, together with potassium, were washed out from mires and were outflowing in subsurface, waters supplying lakes and rivers.

Quite high the watershed/mire area ratio (20 and 7) was relevant to basic role of the water inflow from watershed in nutrient supplying the studied mires. Additionaly, the watershed was fertilized and limed and as result subsurface waters studied shown alkaline properties with average pH 7.7 (unpublished data). The conditions of water inflow and subsidied elements (Ca^{2+}, SO_4^{2-} and NO_3^-) affect monthly balances of ions passing through the wetlands were investigated. The amount of water inflowing into mires influences the balances of the majority of studied ions (at significance level $p<0.01$), but doesn't relates the balances of SO_4^{2-} and SRP (Table 2). Similarly, the inflow of calcium ion correlates significantly with almost all ion budgets, except for sulphate ion (Table 2).

The inflows of nitrates and sulphates, mainly of fertilizer origin, have some separate effect on retention and losses of ions from the mires. They correlate to each other, and the inflow of NO_3^- affect the balance of sulphates even more significantly then components of nitrate fertilizers, that is Na and K ions (Table 3). The loads of NO_3^- from watershed demonstrate high significant correlation also with the balances of nitrates and potassium. The inflow of sulphates affects significantly ($p<0.01$) balances of metals (except magnesium), ammonium, nitrate and phosphate ions and weaker that of hydrogen ion ($p<0.05$) (Table 2).

It is worthly to pay attention to biogeochemical interaction of the balances of such

Table 3 Coefficients of multiple regression equation denoting the relation between the monthly balances of SO_4^{2-} in mires studied (y) with respect to ions inflow from watershed (x). Calculation was made on the basis of a stepwise variable selection (F=4), where the model consists of Ca^{2+}, Mg^{2+}, K^+, Na^{2+}, H^+, NH_4^+, NO_3^-, SO_4^{2-}, Cl^- and SRP inflows. Balance of SO_4^{2-} and inflows of ions were expressed in kg ha^{-1} $month^{-1}$. N = 42

Balance (y)	Coefficient a	Coefficient b of inflow of ions (x_n) *p*	Correlation coefficient
SO_4^{2-}	5.7	2.9 NO_3^- − 3.2 Na^+ + 59.1 K^+	0.70
		0.0000 *0.0001* *0.0013*	

important ions as SRP, NO_3^- and K^+ favorable to eutrophication and H^+ and SO_4^{2-} causing acidification. The balances of nitrate and potassium ions are correlated both with amount of inflowing water and with inflow of elements from fertilizers. But phosphates are significantly dependent on the inflow of calcium and sulphates only (Table 2). The inflow of Ca^{2+} i SO_4^{2-} has the significant effect on the balance of hydrogen ions, however, the exchange of H^+ depends mostly on the amount of inflowing water (Table 2).

5. DISCUSSION AND CONCLUSIONS

The flow of ions in subsurface waters through minerotrophic peatlands studied is very dynamic in character. Transported ions are subjected to changes of water oxygenation caused by oscillations of water level and cyclic decline of surface water bodies. The ions meet the changes of sorptive properties of geologic medium – from mineral into organic (Gorham 1967, Waugham 1980). Moreover, they are intensively sorbed by biota in vegetative season and outwashed from organic debris in the fall (Boyd 1970, Mason and Bryant 1975).

Taking into account the interactions between ions flowing through midfield mires (Table 2) and the results of former studies (Kruk 1996, 1997), it should be concluded, that inflow of elevated loads of nutrients into these mires, characterized by very unstable conditions, can involve a number of processes important for both mire environment and ecosystem receiving mire waters. Some of these processes are shown in general outline in Fig. 2.

The inflow of nitrates affects the increase of assimilation by plants and, as it meets anaerobic conditions, assimilation by denitrifiers and NO_3^- reduction in denitrification process. These processes manifest in increasing of plant biomass (Wilpiszewska 1990) and the release of nitrogen (as DON) incorporated in decomposed organic substances of plant and bacteria origin (Kruk 1997). This is probably a result of only partly mineralization within conditions of oxygen deficit. The elevated inflow of nitrate ions and denitrification process can cause the mobilization of sulphates realized by oxygenation of sulphides in mineral deposits in mires (Golterman 1995, Lamers *et al.* 1997). However, in long-standing anaerobic conditions, reduction of sulphates takes place and as a consequence sulphur is accumulated as FeS or volatilized (Mitsch and Gosselink 1993). Since, the concentration of nitrate ion in waters inflowing from agricultural watershed is considerable and could cause the oxygenation of sulphides, then NO_3 content in mire waters decreases drastically (Kruk 1996). Probably, mobilization and reduction of nitrates and sulphates are alternately and interdependent ongoing dynamic processes enhanced by agriculture origin inflow of these ions into systems studied.

The elevated loads of nitrates and sulphates from fertilized fields in watershed affect the sulphur cycling in mire ecosystem. The tendency for increasing a hydrogen ion content in mire waters could be a result of this influence (Kruk 1997). Probably, mentioned process acts jointly with other known factor causing acidification of peat soils, namely with nitrification of ammonium ion in aerobic conditions (Zimka and Stachurski 1996). It should be emphasized, however, that any radical action of hydrogen ions on studied mire environment is neutralized by great load of calcium ions in inflow from watershed (Table 1) and its content in mire waters. Calcium acts probably on sorptive complex of mire deposit forcing out an increasing amount of potassium ions, among others (Kruk 1996).

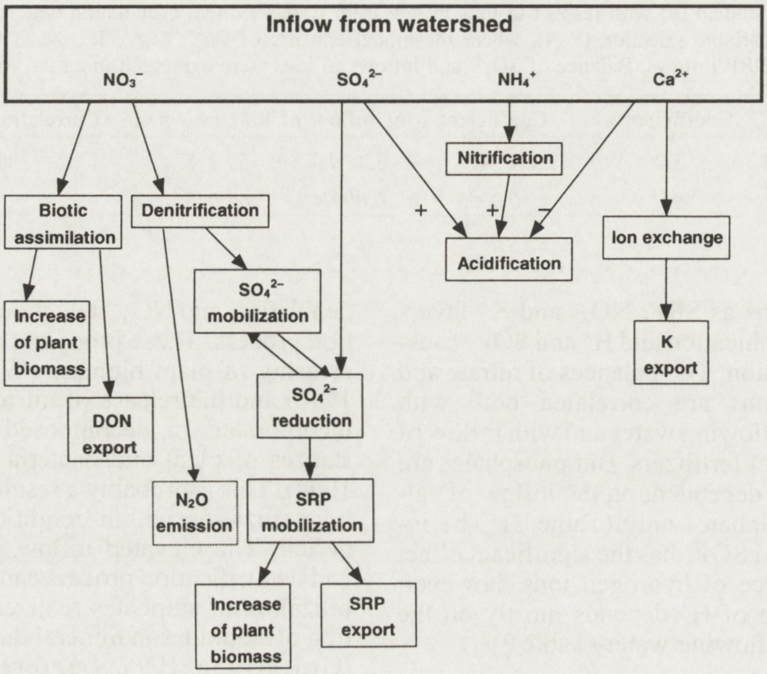

Fig. 2. General outline of biogeochemical processes occured in wetland ecotones subjected to elevated inflow of nutrients from agricultural watershed.

The important effect of increased inflow of sulphate ions on biogeochemical relations in minerotrophic mires seems to be a modification of phosphorus cycling. The moderate increase of SO_4^{2-} inflow causes the change of phosphate balance into positive value (retention), but when sulphate inflow reaches maximum, cleary negative balance is formed, indicating on the phosphorus leaching from the mire (Kruk 1996). The correlation between sulphate inflow and the balance of phosphate in mire waters (Table 2) can be explained by dislodging phosphates from the complexes with Fe by sulphur from sulphates subjected to reduction in anaerobic conditions. This phosphate mobilization from wetland deposits caused by elevated sulphate concentrations is a reason of the phenomenon defined as "internal wetland eutrophication" (Smolders and Roelofs 1995). Indeed, in the view of limited inflow of phosphates from watershed (Table 1), where their excess is sorbed by clay minerals, the possibility of PO_4 mobilization from deposits by reduced sulphur from inflowing sulphates can explain a considerable amounts of phosphorus in mire vegetation biomass (Wilpiszewska 1990). Moreover, leaching of phosphate ions out from mire, stimulated by high level of sulphate inflow, and its transport by subsurface waters can constitute an important factor of eutrophication of lakes. In this situation, sulphates outflowing from arable fields can be recognized as indirect eutrophication factor and located in lake watershed mid-field mire ecotones as the source supplying the phosphorus into the surface water ecosystems (Fig. 2).

6. SUMMARY

The investigations were carried out in Masurian Lakeland (NE Poland) in small fens dominated by cattail association (Fig. 1). The aim of investigations was focused on the analysis of the nutrient loads from cultivated and fertilized watershed on the ion balance flowing by wetland ecotones. The content of nutrients in watershed and wetland waters was considerable.

The characteristic of the relative balances of flowing through ecotone ions, namely Na^+, Ca^{2+}, Mg^{2+}, Na^+, H^+, NH_4^+, SO_4^{2-}, Cl^- and SRP is not very differentiated with tendency to less than 50% of throu-

ghflow reduction. Very visible positive balance (retention) occured only in case of nitrates and significant increase of flow (leaching) in case of potassium ion (Table 1).

Increased inflow of the ions easy released from watershed mineral forms such a nitrogen (nitrate), sulphur and calcium is the result of multifunctional response of biogeochemical system of wetland ecotone (Table 2, Fig 2). The majority of nitrates is retained in vegetation and denitrified, however, the part of NO_3^- could be transformed into dissolved organic nitrogen outflowing outside the wetland (Table 1). The watershed inflow of considerable amounts of nitrates could increase accumulation of sulphur in wetland (Table 3). As a consequence, the increased inflow of SO_4^{2-} could be a reason of positive balance of H^+ ions in wetland waters, strengthening the tendency to acidification of these waters (Table 2). However, the large load of calcium ions from watershed strongly limits this process. Other consequence of increased sulphates inflow to wetland ecotones is its influence on phosphate balance (Table 2) by the possibility of dislodging by SO_4^{2-} phosphate ions from ferrous-organic complexes and leaching phosphate out of mire ecotone, which process could cause eutrophication of subsurface waters and lakes.

Generally, wetland ecotones constitute an effective biogeochemical barrier in respect to nitrates. However, they do not protect lakes against other eutrophication factors arising as the result of multifunctional character of biogeochemical processes in the wetland environment under pression of fertilization originated nutrients. The eutrophication of waters could be strengthened by moving out the increased amounts of phosphates, dissolved organic nitrogen and potassium from wetland ecotones (Fig. 2).

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