Original Research

Effect of Land Use and Lake Presence on Chemical Diversity of the Łyna River System

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Abstract

This paper presents results of three years of geochemical research carried out in the upper Łyna catchment in NE Poland. Water in the system is of Ca^{2+} - HCO_3^- - SO_4^{2-} type and reflects mainly the impact of chemical weathering of bedrock. The results indicate that natural components such as Ca^{2+} and HCO_3^-, derived from mineral weathering, dominate chemical composition of the Łyna River system, reaching 90%. However, agricultural input is clearly visible for ions such as Na and K. Under natural conditions their content usually reaches 4.3 and 1.2, respectively, while in the agriculture-dominated subcatchments in the study area the proportion of Na^+ and K^+ reached 8.3 and 4.1 mg L^{-1}.

Besides land use pattern, the main factors modifying riverine transport of the dissolved substances along watercourses are open lakes. They play an important role as sinks for the ions in agricultural areas. The highest decrease in concentration was stated for K^+ by 50%, Na^+ by 36%, SO_4^{2-} by 25%, and Ca^{2+} by 20%. Retention of solutes in lakes is highly dependent on the location within the river catchment and water table area. The largest reservoirs in the region are capable for the retention of 8-12% of the river input. Based on changes in water quality parameters, the Łyna River profile was divided into three distinct zones: headwater zone, middle zone with lakes and lower zone with anthropogenic influences.

Keywords: river, water quality, load, catchment, land use, open lakes

Introduction

The intensive interest in water quality deterioration has induced efforts to understand behavior of both the aquatic environment and its associated hydrological characteristics. The chemical composition of water is a function of hydrogeochemical processes acting within the catchment area [1, 2, 3]. There are numerous factors such as climate, tectonics, topography and lithology, etc., that either individually or in combination influence the natural flux of dissolved ions [4, 5, 6, 7]. Physical and chemical characteristics of a stream are controlled by the interaction of precipitation [6, 8, 9], surface and groundwater runoff [2, 10] with the matrix of catchment characteristics [11, 12, 13, 10].

The presence of open lakes located on the river course modifies the chemical composition of running water. Lakes are often referred to as cleaning basins for rivers because they trap most water constituents [14, 15]. As it was pointed out by Hillbricht-Ilkowska [16], a river in the denudation – accumulation system may be one of the factors controlling the evolution of lake ecosystems.

Monitoring of rivers and streams tells first about the functionality of the whole river catchment concerning its water and matter cycles [6, 13]. Systematic monitoring in a catchment allows for evaluation of the factors related to spatial variations (catchment morphology and land use) and seasonal variations (e.g. temperature). Although en-

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vironmental attributes of a catchment and land use distribution are often used in factor analyses in water quality assessment [5, 10, 17, 18], few studies have considered the stability of flow regime during the sampling period [12, 19]. When the flow remains relatively constant during a period of investigation, the sampling can be used to study the spatial variability of stream chemistry.

In the following, we focus on the Łyna River upstream of Olsztyn city, which represents variations in dissolved ion fluxes in a typical post-glacial catchment the under temperate climatic conditions of middle Europe. Numerous lakes in the area, a significant share of permeable soils and woodland area contribute to the attenuation of flood waves and hydrological inactivity of the river.

In this paper the chemical composition of surface water, geochemical processes controlling water chemistry and spatial variations in flux of solutes are examined. The basic aim of the study includes description of the physical-chemical properties of water in the Łyna River system with the background of differentiated land use and the presence of natural water reservoirs (open lakes) in the post-glacial landscape. The assumption that the kind and amount of material flowing through the catchment reflects all geomorphologic processes taking place within the river catchment was tested further, taking into account the level of anthropogenic activities.

Methods

The Łyna River was investigated during 1998-2000. Sampling was carried out on a monthly basis over a period of three years, from November 1997 to October 2000 at 24 sampling sites located through the upper Łyna catchment (Fig. 1). Twelve sites (L-1 ÷ L-11) are on the Łyna River watercourse and the rest are on the main tributaries and were selected according to land use pattern and distribution of lakes. All of the sites were chosen to reflect the spatial variations in the chemical composition of water with special emphasis on the effect of agricultural and woodland landscapes in the catchment (Table 1). The 5 sub-catchments are of similar soil cover and size but have different distribution of lakes and different land-use patterns.

Electrical conductivity (EC) and pH were measured at the sites using portable conductivity- and pH-meters. Five-liter water samples were collected in polyethylene bottles from various parts of the river basin as well as along the Łyna River watercourse (Fig. 1). The analyses included the most important cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}), anions (Cl^{-}, SO_4^{2-}, HCO_3^{-}), total dissolved matter (TDM) and ash. Laboratory analyses followed the standards described by Hermanowicz et al. 1999 [20]. The charge balance between cations (TC) and anions (TA) < 5% confirms the

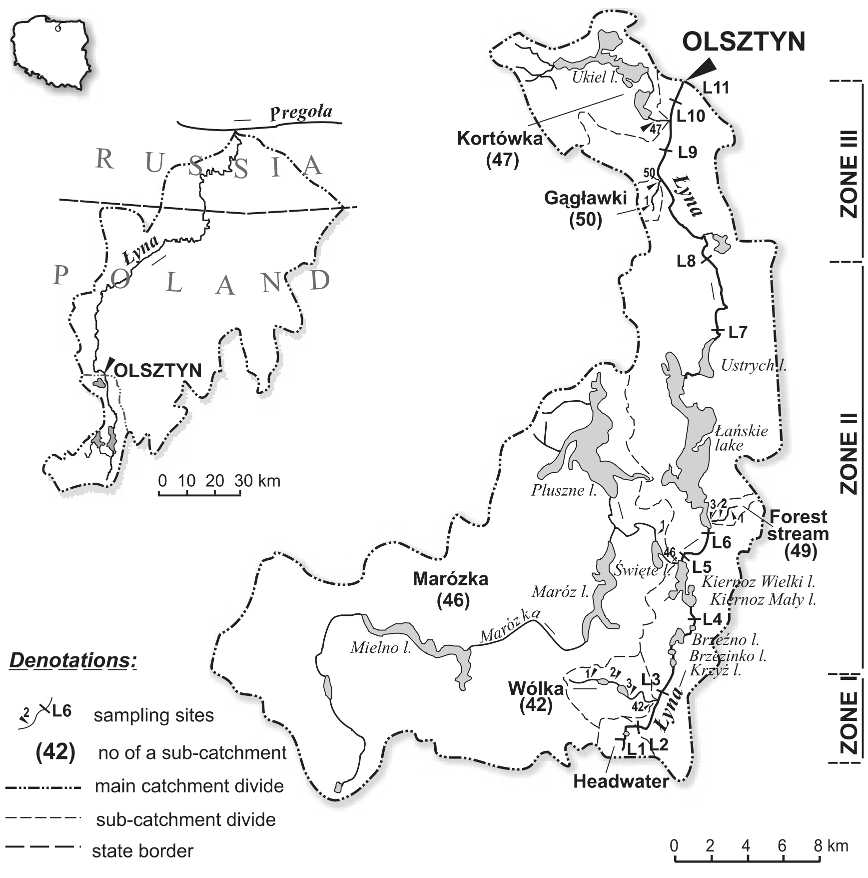

Fig. 1. Location of the upper Łyna catchment and its internal structure. Arrows and names with numbers indicate investigated sub-catchments. See description of the zones in the text.

Table 1. List of sampling sites along the Łyna River and its tributaries.

Sampling sites on the Łyna watercourse				Sampling sites on the Łyna's tributaries				
No	Site	Km of the river	Catchment area [km^2]	No	Site		Km of the stream	Catchment area [km^2]
L-1	Headwaters	264	5.0	42-1	Wólka	Headwaters	9.8	1.6
L-2	Headwaters	263	5.8	42-2		Bolejny	6.8	3.9
L-3	at the Wólka	259	21.9	42-3		Wólka Orłowska	1.5	9.0
L-4	above lakes chain	256	39.5	42		Outlet to Łyna	0.1	13.8
L-5	Kurki	250	358.6	46-1	Marózka	Szwaderki	7.1	269.1
L-6	inflow to Łańskie l.	248	373.1	46		Outlet to Łyna	0.9	307.8
L-7	outlet from Łańskie l.	237	437.7	49-1	Forest Stream	Source area	2.7	2.6
L-8	Ruś	220	474.4	49-2		Middle part	1.1	3.8
L-9	Bartąg	214	508.4	49		Outlet to Łańskie l.	0.1	4.0
L-10	Olsztyn Pozorty	211	567.7	50-1	Gągławki	Upper part	1.4	5.7
L-11	Olsztyn weir	207	601.7	50		Outlet to Łyna	0.2	11.8
L-12	Redykajny*	202	1786.4	47	Kortówka – outlet to Łyna		0.1	42.5

*) the sampling site located south of Olsztyn city, where the Wadąg river enters the Łyna. Due to the large catchment area, is not shown in the Fig.1.

analytical precision of the data and it also implies that the contribution to the solute load by ions not measured in the present study is negligible.

Water levels in the Łyna River were recorded at two sites: at L-5 located above Łańskie lake where continuous measurements were registered by a reference D-Diver (Ejkelkamp, the Netherlands) and at L-11 located in Olsztyn, where everyday measurements were conducted at the broad-crested weir. The water levels were transformed into run-off by use of a rating curve. Discharges of water at other sites were measured simultaneously with the time of sampling. The methods depended on the volume of outflowing water. In most cases an electromagnetic flow velocity sensor (Valeport, UK) was used and the discharge was calculated using the velocity-area method. Low discharges (< 5.0 l s^{-1}) were determined by the volumetric method.

Fluxes of dissolved determinants were calculated as a product of the concentration and corresponding discharge. Annual loads were calculated using the method presented by Webb et al. [21] for calculating river load:

$$\text{Total load} = K\ \Sigma[C_i\ Q_i/ns],$$

where: K is a conversion factor to take into account the period of record, Q_i is the mean discharge for the period of record, Q is the mean discharge for the period between samples, C_i is the instantaneous concentration associated with individual samples and ns is the number of samples.

Net retention of a given substance in a lake was calculated on the basis of mass balance computed as the difference between the total annual input to the lake (river supply plus atmospheric deposition) and the annual export from the lake. The total annual load of a substance was converted into the unit loading of the lake and expressed in kg per 1 m^2 of water table area.

The comparisons of hydrochemical parameters between the sampling sites were performed using one-way analysis of variance followed by Duncan's test as a *post hoc* procedure. The hydrochemical information was recorded in MS an Excel spreadsheet and processed using the statistical software STATISTICA 6.0 PL (StatSoft, Inc., Tulsa USA).

Study Area

The object of investigation is the upper Łyna catchment located in the western part of the Mazury Lake District in northeastern Poland. The area is famous for its natural character: numerous lakes, river valleys deeply incised into the terrain and prevailing forested areas. It was judged representative of the post-glacial landscape. The Łyna River belongs to the largest watercourses in the region. Its total catchment area is 7126 km^2, but 5719 km^2 of its area is within Polish borders. For this paper the study area was limited to upper part: upstream from the source area to Olsztyn. The basin covers 601.7 km^2 and the main river length is 57 km.

The investigation area embraces the upper Łyna catchment with its diversified internal structure defined by the system of 5 sub-catchments (Fig. 1). Among them, the

Table 2. Land use of the sub-catchments in the upper Łyna catchment.

Sample point No	Catchment	Catchment area km^2	Forests		Lakes and wetlands		Build-up areas		Arable lands	
			km^2	%	km^2	%	km^2	%	km^2	%
42	Wólka	13.8	4.3	31.2	1.5	10.9	1.9	13.8	6.1	44.2
46	Marózka	307.8	120.4	39.1	19.9	6.5	23.1	7.5	144.4	46.9
49	Forest Stream	4.0	3.7	92.1	0.1	1.9	0	0	0.2	6.0
50	Gągławki	11.8	4.21	35.7	0.41	3.5	0.2	1.7	6.9	59.1
47	Kortówka	42.5	24.7	58.1	5.4	12.7	6.2	14.6	6.2	14.6
L-11	Łyna	601.7	295.7	49.1	42.3	7.03	70.4	11.7	193.3	32.1

Marózka River is the largest, both in terms of discharge (on average 1.74 $m^3 s^{-1}$) and catchment area (307.8 km^2). The Łyna River may be treated as the northwards axis of its catchment, although its western part is bigger and has a more developed channel system than the eastern part.

The relief of this area is a product of deglaciation during the Pomeranian Phase of the Vistulian period, and of the morphogenetic processes in the Holocene. The central and southern parts of the catchment lie within the outwash plain crossed by four sets of end moraines.

The deposits, composed of a great variety of glacial sediments with a very high sand content, occupy the largest area of the upper Łyna catchment. Organic deposits in the alluvial valley directly influence the physical-chemical properties of river water. The dominant soils in the catchment are brown earths. In river valleys there are patches of alluvial soils proper while podzols can be found in the woodland. About 50% of the moraine plain (mostly loamy sands and fine sandy loams) is potentially arable land. Gleysols and peat-lands, partly used as perennial grasslands, dominate in valleys and other depressions.

A characteristic feature of the catchment is the mosaic land-use pattern that confirms the main forms of the young-glacial relief. The catchment of the upper Łyna River may be classified as woodland-agricultural (Table 2). Forests cover 50.0%, arable lands 32.5% and lakes 7.0% of the area. Cities, other settlements and roads are clustered mainly in the northern part of the catchment and cover 12.0% of the catchment area. Forests prevail on the hilly southern section where a mosaic moraine–hilly landscape dominates. They form a compact widespread woodland cover along both sides of the Łyna River valley from the very south to Ruś village (L-8), including a catchment of the Forest stream (49 site). From L-8 to the closing profile L-11, agriculture and urban areas prevail. Larger patches of fields and grasslands characterize the western part of the catchment including the Wólka stream (42), Marózka River (46) and Gągławki stream (50).

The three years under analysis: 1998, 1999 and 2000 represent average climatic years in relation to the period of 1951-2000 [8]. The mean multi-annual air temperature was 7.1°C, and within the study period it ranged from 7.1--7.6 °C. Average annual precipitation was about 617 mm and, during the investigation period, about 594 mm.

The hydrologic regime of the Łyna River is typical of the temperate zone. Like other rivers of the region, the Łyna has a hydrologic regime supplied by groundwater, rain and snow. The most frequent causes of high discharge are rain and snow, as well as mid-winter and spring thaws. The annual average discharges of the Łyna at Olsztyn varied between 3.78 $m^3 s^{-1}$ and 4.15 $m^3 s^{-1}$ over the three years. The dominance of winter half-year over summer results from not only the distribution and intensity of precipitation but also, to a large extent, from the morphology of the river catchment.

High water capacity of the soil, numerous lakes, especially those included in the direct river flow, make the upper Łyna River system hydrologically inactive. During the study period, maximum discharge (Q_{max}) noticed at the Olsztyn gauge reached 7.26 $m^3 s^{-1}$. In only 8 of flood waves, the increase in discharge from the start of the flood to the peak exceeded 0.5 $m^3 s^{-1}$. The ratio of Q_{max}/Q_{min} during the study was 3.16 and the variability coefficient $cv = 20\%$. The hydrological character of the riverine system with its typical discharge scale and dynamics was representative enough to study the mechanisms and magnitude of river transport under different modes of supplying the Łyna River.

An integral part of the Łyna River system is open lakes (Table 3). The lakes, fed directly by the river, take up 30% of the length under investigation. The river length between lakes Krzyż and Ustrych is occupied in 65% by a chain of 7 lakes. The biggest of them is Łańskie lake, taking 10% of the river's length. Its capacity ($168 \cdot 10^6$ m^3) amounts to almost two years the Łyna river's outflow volume.

Worth noting is the fact that, thanks to the deepest lake, the river is recharged there not only with shallow groundwater directly but also deeper water-bearing horizons, each with its individual duration of the hydrological cycle. In this case the groundwater supply should be considered as a considerable external source of matter in the river-lake system. Hydrogeological survey in the region [22] showed that Łańskie lake is crossed even by three groundwater horizons near the Lalka peninsula. Two of them lie in the Quaternary deposits at depths of

Table 3. Morphological characteristics of lakes on the upper Łyna course.

Lake	Lake area [ha]	Catchment area [km^2]	Depth [m]		Capacity [$x10^3$ m^3]	Retention time [years]
			avr	max		
Krzyż	8.8	21.7	1.5	2.1	102.4	0.007
Brzezinko	6.3	24.6	1.4	2.5	97.2	0.008
Duże Brzeźno	36.1	27.9	2.4	4.6	830.3	0.05
Kiernoz Mały	54.0	39.5	2.9	11.4	1549.0	0.07
Kiernoz Wielki	85.0	358.6	3.3	15.4	2901.8	0.04
Łańskie	1042.0	414.1	16.0	53.0	168047.3	1.83
Ustrych	93.1	437.7	5.5	11.6	5141.9	0.06

Table 4. Mean (*x*) and standard deviation (±*SD*) of chemical composition of the Łyna River and its tributaries. All units are given in mg L^{-1} except for pH and EC µS cm^{-1}.

Parameter	Łyna		Tributary channels of the Łyna river									
			Wólka		Marózka		Gągławki		Kortówka		Forest Stream	
	x	±SD	x	±SD	x	±SD	x	±SD	x	±SD	x	±SD
pH	7.76	0.44	7.66	0.36	7.83	0.52	7.52	0.39	7.66	0.58	7.62	0.36
EC	369	38	452	36	345	26	541	52	417	58	417	20
TDM	301	86	375	89	281	87	418	79	307	82	348	83
Ash	192	75	241	82	174	80	279	77	201	76	225	64
Ca^{2+}	54.1	5.2	65.2	7.1	51.3	4.5	74.3	7.3	55.4	6.7	67.8	5.9
Na^+	5.66	1.57	5.72	1.37	5.18	0.65	10.06	3.58	10.90	3.35	3.45	0.61
K^+	1.88	0.79	2.77	1.04	1.77	0.30	4.73	1.63	4.42	1.06	0.77	0.59
Mg^{2+}	5.74	1.81	6.01	1.79	5.63	1.76	6.13	2.26	6.08	1.92	4.72	2.18
HCO_3^-	141	18	175	16	133	21	187	16	148	25	168	9
Cl^-	15.1	3.7	16.7	3.4	15.4	2.1	20.8	4.2	21.3	5.7	10.3	3.5
SO_4^{2-}	43.2	11.4	51.9	13.5	47.1	11.1	70.6	16.5	46.7	13.2	53.4	10.7

EC- Electrical Conductivity, TDM- Total Dissolved Matter

4 m and 26.5 m, whereas the third one is in the Tertiary deposits at a depth of 49 m below water table of the lake (124.90 m a.s.l.).

Results

The Łyna river water is neutral-to-alkaline in nature (pH = 7.1 – 8.4), like most of the other postglacial watercourses [11, 12, 15]. Almost two thirds of the substance transported along the channel system is in mineral form (Table 4).

The analyses showed HCO_3^- and SO_4^{2-} were the dominant anions and they constituted on average 64% and 26% of the total anions (3.90 mmol L^{-1}), respectively (Fig. 2). Chlorides contributed around 11% of the total sum of anions. The cation chemistry indicated that calcium was the major cation, constituting 77% of the total sum of cations (TC) that amounted to 3.71 mmol L^{-1}. Calcium was followed by Mg^{2+} (13%), Na^+ (7%) and K^+ (2%).

More than 93% of all samples were represented by the Ca^{2+} - HCO_3^- - SO_4^{2-} type, while in the remaining 7% of samples Ca^{2+} was replaced by HCO_3^- (HCO_3^- - Ca^{2+} - SO_4^{2-}). The type is characteristic for young-glacial lake lands built of forms rich in calcium carbonate.

Electrical conductivity (EC) in the Łyna River varied between 260-457 µS cm^{-1} (Avg. 369 µS cm^{-1}). The widest range of electrical conductivity (359-637 µS cm^{-1}) was observed in water of rural areas (the Gągławki stream), while the most stable was water in the forested catchment (346-443 µS cm^{-1}). The presence of lakes along the Marózka watercourse decreased values of electrical conductivity when compared to the unpolluted Forest stream catchment (Table 4). In winter (XI-IV) electrical conductivity was usually higher (Avg. 380 µS cm^{-1}) than in summer (Avg. 369 µS cm^{-1}). EC values showed statistically significant correlation with all studied ions and total dissolved matter (TDM). The closest relationships were noted between EC and Ca^{2+} and HCO_3^- (respectively: r = 0.75 and r = 0.72, at $P \leq 0.001$). However, they were less interdependent in agricultural sub-basins (Fig. 3).

The quality of water samples from the Łyna River corresponded to the natural character of its basin. A plot of the ionic concentration versus downstream distance (Fig. 4, 5) showed changes in the stream chemistry, not only as a function of the river length and its catchment area. Change in land use of the tributaries' catchments is responsible for the increasing trend of solute concentration downstream (e.g. the Wólka stream and the Łyna River confluence at L-3 site, see Fig.1). One may see in Fig. 4 that ion concentrations along the Łyna profile show maximum concentrations beneath the reaches of the streams from agricultural areas. This suggests that the increasing trend of ionic concentration is related more to land use than elevation or lithology. The increase in the elements originating from man's activity showed changes in the molar ratios of Na^+ in relation to Cl^- and K^+ along the Łyna profile (Fig. 5).

In contrast to the Forest stream catchment, three of the Łyna river tributaries (the Wólka, Gągławki and Kortówka streams) and the lower section of the Łyna River are strongly influenced by human activity: cultivated areas and the density of the population.

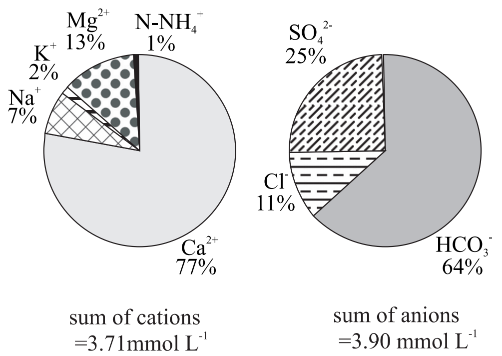

Fig. 2. Average ionic composition of surface water in the Łyna River catchment.

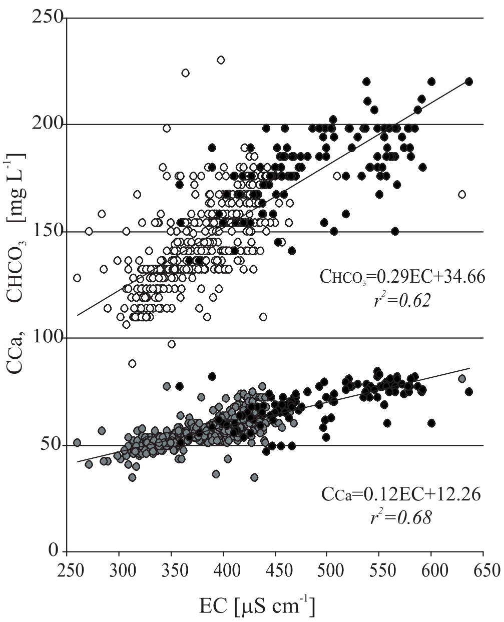

Fig.3. EC vs. HCO_3^- (open circles) and Ca^{2+} (closed circles) concentrations in water of the upper Łyna catchment. Black circles refer to agricultural sub-catchments. Analytical uncertainties are less than the symbol size.

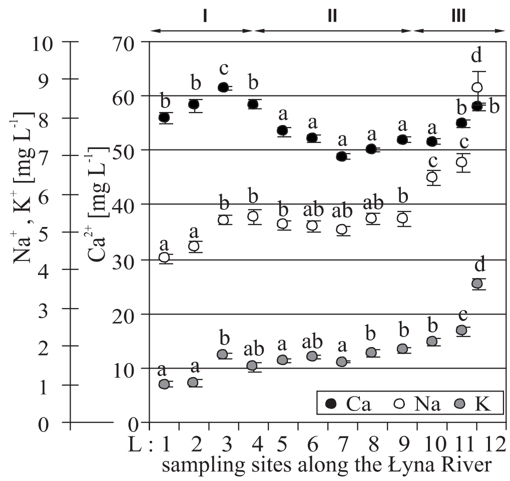

Fig.4. Variation in the main cations concentrations downstream distance of the Łyna River. Vertical bars indicate standard error of mean. The same letters show statistically homogeneous groups of means at $P \leq 0.05$. Horizontal arrows show three geochemical zones (description in the text).

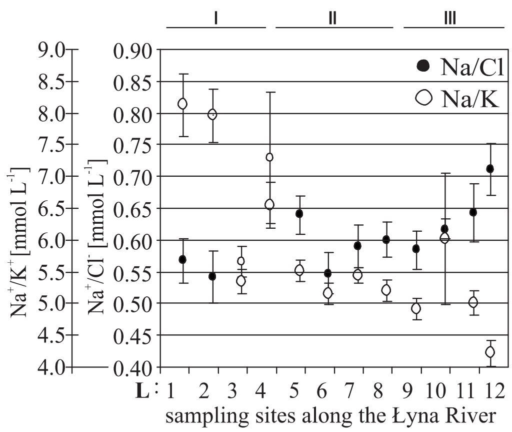

Fig.5. Variation in the ratios of Na^+/K^+ and Na^+/Cl^- along the Łyna River profile. Vertical bars indicate standard deviation. Horizontal arrows show three geochemical zones (description in the text).

Table 5. Average concentrations of mineral compounds [mg L^{-1}] in the three zones of the upper Łyna river profile. The values signed with different letters are significantly different in Duncan test at $P \leq 0.05$.

Compound	Parameter	ZONE I	ZONE II	ZONE III
		Head-waters	Lake chain	Antropogenic
		N=72	N=144	N=144
Ca^{2+}	x	58.22^{c}	51.72^{a}	53.72^{b}
	± SD	5.57	4.25	4.44
Na^{+}	x	4.75^{a}	5.20^{b}	6.63^{c}
	± SD	0.80	0.72	1.88
K^{+}	x	1.33^{a}	1.67^{b}	2.42^{c}
	± SD	0.51	0.39	0.88
Mg^{2+}	x	5.55^{a}	5.49^{a}	6.08^{b}
	± SD	1.91	1.70	1.74
HCO_3^-	x	156.73^{b}	134.69^{a}	136.65^{a}
	± SD	13.03	17.59	14.31
Cl^-	x	14.15^{a}	13.88^{a}	16.88^{b}
	± SD	3.15	2.91	4.34
SO_4^{2-}	x	43.78^{b}	40.18^{a}	46.00^{b}
	± SD	10.35	11.03	11.98

Spatial differences in dissolved matter sources are observed along the Łyna profile when analyzing chemical properties of water (Table 5). Three zones of the dissolved material supply and transport may be distinguished.

ZONE I. The zone covers 7 initial kilometers of the headwater course and it is characterized by the highest ionic composition. The high concentrations of dissolved material result from intensive leaching of the rock (overland flow is about 15 l s^{-1} km^2) rich in calcium carbonate and from the supply of readily soluble compounds in water drained from organic and mineral soil horizons in the bottom of the spring area valley. K and Na ions, which are commonly thought to be of an anthropogenic origin, have the lowest concentrations there: 1.33 and 4.75 mg L^{-1}, respectively. Amounts of Ca^{2+} and HCO_3^- in spring water are expected to be higher (58.22 and 156.73 mg L^{-1}, respectively) due to the nature of residence time of water in contact with weatherable minerals building the Tertiary substratum. Another weathering product as sulphates showed concentrations at the level of 43.78 mg L^{-1}.

However, agricultural interference on the chemical composition of water is noticeable on the 5^{th} km from the Łyna sources, where the river receives solutes from its left-hand tributary, Wólka Stream (Fig. 6). The stream supplied the Łyna River with 2.77 mg of K L^{-1}, 5.72 mg of Na L^{-1}, 16.7 mg of Cl L^{-1}, 51.9 mg of SO_4 L^{-1}. The concentrations of K^+ were by 50% higher, Na^+ by 17% and both Cl^- and SO_4^{2-} by 15% higher in comparison to the Łyna River headwater.

As shown in Fig. 7, due to high overland flow, extremely high annual sediment yield (2.2 t ha^{-1} yr^{-1}) is formed in the headwater area (zone I). Of this the most essential part consisted of such ions species as bicarbonates (1.0 t ha^{-1} yr^{-1}), calcium (0.4 t ha^{-1} yr^{-1}) and sulphates (0.3 t ha^{-1} yr^{-1}).

ZONE II. The second section of the upper Łyna River is almost 20 km long and stretches between sites L-4 and L-8. Ion concentrations and fluxes exhibited a declining trend along the watercourse (Fig. 6, 7). The decreased con-

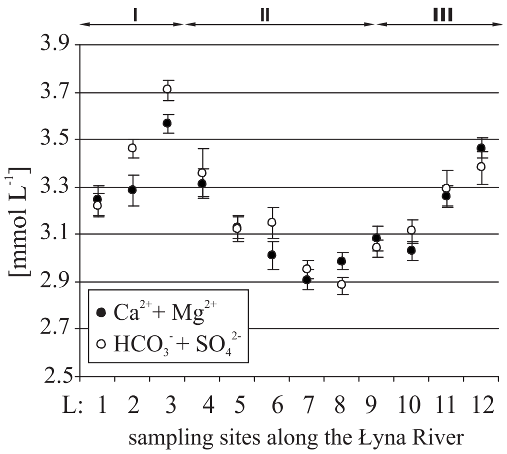

Fig. 6. Changes in sums of Ca^{2+} and Mg^{2+} as well as HCO_3^- and SO_4^{2-} along the Łyna river profile. Horizontal bars indicate ± standard deviation. Horizontal arrows show three geochemical zones (description in the text).

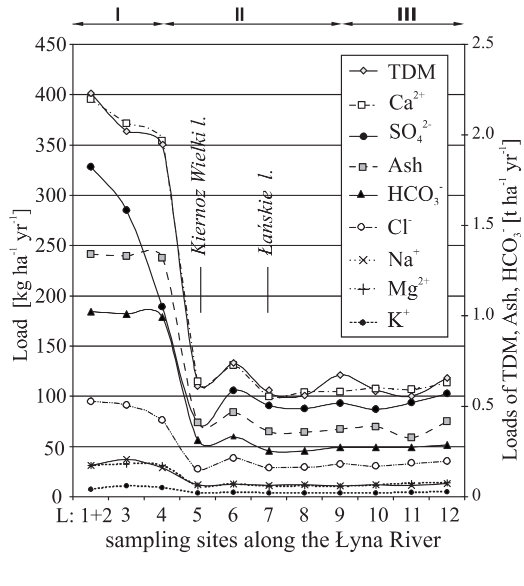

Fig. 7. Changes in annual loads of dissolved substances in kg ha^{-1} along the Łyna River profile. Horizontal arrows show three geochemical zones (description in the text).

Table 6. Changes in main ions concentrations [mg L^{-1}] in relation to land use and lake presence in the Łyna River catchment. The values signed with different letters are significantly different from each other in Duncan test at $P \leq 0.05$.

Compound	Parameter	Land use and lake presence			
		Agriculture		Forest	
		No lakes	With lakes	No lakes	With lakes
		N= 108	N= 108	N= 108	N= 108
Ca^{2+}	x	70.7[c]	56.2[b]	58.7[b]	48.8[a]
	± SD	8.4	8.8	8.8	2.9
Na^{+}	x	8.3[c]	5.3[b]	4.3[a]	5.0[a]
	± SD	3.6	0.7	1.0	0.6
K^{+}	x	4.1[c]	2.2[b]	1.2[a]	1.6[a]
	± SD	1.5	0.7	0.7	0.2
Mg^{2+}	x	6.3[b]	5.6[ab]	5.2[a]	5.6[a]
	± SD	2.2	1.8	2.0	1.8
HCO_3^-	x	180[c]	150[b]	149[b]	123[a]
	± SD	17.8	29.7	20.1	9.3
Cl^-	x	19.4[c]	15.7[b]	12.7[a]	13.9[a]
	± SD	4.3	2.7	3.7	2.5
SO_4^{2-}	x	63.6[b]	47.9[a]	46.0[a]	44.6[a]
	± SD	18.2	12.2	11.4	10.0

centrations in zone II concerned mainly calcium (51.72 mg L^{-1}), sulphate (40.18 mg L^{-1}) and bicarbonate (134.69 mg L^{-1}) ions because they created groups of means significantly lower in comparison to the water classified to zone I (Table 5). The ions of magnesium and chlorides showed no statistical differences between zones I and II. Concentrations of sodium and potassium in zone II created groups significantly higher than in zone I. Along this section, the river water displayed the least variability of mineral-dissolved components.

Weathering losses of the investigated ion species were modified along the Łyna watercourse due to the changes in the catchment areas and the presence of lakes (Fig. 7). The most significant decrease in the weathering yield was stated for site L5 as a result of the delivery of solutes from large catchment of the Marózka River (307.8 km^2). The yields of bicarbonates, calcium and sulphates amounted to 314 kg ha^{-1}, 144 kg ha^{-1} and 73.4 kg ha^{-1}, respectively.

Beneath that site, the magnitude of weathering yield did not change until Olsztyn. However, open lakes as direct recipients of the solutes transported by flowing water, modified the flux. There was stated a discrepancy between the loading of a lake and its water table area. Kiernoz Wielki lake (85 ha) represents reservoirs of the highest loading in the region. The lake is simultaneously loaded by two rivers: Łyna and Marózka with 22 $\times$ 10^3 tons over a year, which reveals 25 kg of solutes per 1 m^2 of water table area, 60% of which is in a mineral form. In the very upper part of zone II, the loading with dissolved matter of three small lakes (Krzyż, Brzezinko and Brzeźno), located between L3 and L4, reached 8 kg per 1 m^2 of water table area. On the contrary, Łańskie lake, having the water table area 12 times as large as Kienoz Wielki lake, received 2.6 kg of TDM per 1 m^2.

In the case of most constituents the export of investigated ions from lakes is smaller than the load. The output from Kiernoz Wielki and Łańskie lakes accounts for 92 and 88 % of the total input (river supply and atmospheric deposition) of TDM to the lakes. But the rule does not concern small lakes located near headwater areas, where the groundwater recharge is very intensive. The calculated mass balance for the group of Krzyż, Brzezinko and Brzeźno lakes showed that the input of each ion was considerably lower than the output. The annual load of exported solutes from the lakes accounted for 167% of the input.

The highest annual net retention of the dissolved matter was characterized by Łańskie lake and amounted to 3091 t yr^{-1}, which reveals 0.3 kg m^{-2} yr^{-1} (Table 7). Łańskie lake stored annually 721 t of HCO_3^- (6% of the input), 664 t of Ca^{2+} (13%), 130 t of Cl^- (12%) 23 t of Na^+ (5%) and 23 t of K^+ (13%) .The only sulphate and magnesium ions showed additional recharge from the lake or its direct catchment. The export of SO_4^{2-} was higher by 3.8% and Mg^{2+} by 1.6%, than the input of the ions to the lake.

The retention of solutes in Kiernoz Wielki lake amounted to 8% (1694 t yr^{-1}, 2.0 kg m^{-2} yr^{-1}). The export of all ions under investigation was lower than the input to the lake. Ion species retained in the lake ranged from 4% of HCO_3^- to 24% of Cl^-.

ZONE III. The zone, again 20 kilometers long, spreads out between site L-9 at Bartąg village and Olsztyn (L-11 and L-12). Water displayed the highest variability of dissolved components. This is indicative of feeding by ground water of quite stable physical-chemical parameters that is overlapped there by agricultural and urban influences. This results in an increase in such a biologically inert compound as chlorides. On the other hand, the decrease in the molar ratio of Na^+/K^+ was significant there (4-5 mmol L^{-1}) in comparison to unpolluted headwaters (8 mmol L^{-1}) and it was caused mainly by considerable input of K^+ (Fig. 5). Except for bicarbonates, water in the zone III differed statistically from the other two groups of means and made a group of the highest means for Na^+ (6.63 mg L^{-1}) and K^+ (2.42 mg L^{-1}), which was marked in Table 5. It is a significant consequence of the enrichment of the Łyna River with the polluted Gągławki stream water. From this place to site L-12 in Olsztyn the river does not recover its good quality due to increasing urban influences.

Concentrations of the substances introduced into the Łyna River system differ not only between catchments of different land use but also within a group of the same land use type. Comparison of water chemistry from agri-

Table 7. External loading and retention of chemical compounds in lakes located along the Łyna River computed for the period 1998-2000.

Compound	Krzyż, Brzezinko and Brzeźno lakes					Kiernoz Mały and Kiernoz Wielki					Łańskie				
	Input*		Retention (+) or Release (-)			Input		Retention (+) or Release (-)			Input		Retention (+) or Release (-)		
	t yr^{-1}	kg m^{-2} yr^{-1}	t yr^{-1}	kg m^{-2} yr^{-1}	%	t yr^{-1}	kg m^{-2} yr^{-1}	t yr^{-1}	kg m^{-2} yr^{-1**}	%	t yr^{-1}	kg m^{-2} yr^{-1}	t yr^{-1}	kg m^{-2} yr^{-1}	%
TDM	4236	7.8	-2846	-5.3	-67	21662	25.5	1694	2.0	+8	26631	2.6	3091	0.3	+12
Ash	2552	4.7	-2400	-4.4	-94	12186	14.3	166	0.2	+1	16752	1.6	1703	0.2	+10
Ca^{2+}	790	1.5	-531	-1.0	-67	4083	4.8	144	0.17	+4	5030	0.5	664	0.1	+13
Na^{+}	75	0.1	-57.4	-0.1	-77	438	0.51	30	0.04	+7	533	0.1	27	0.003	+5
K^{+}	23	0.04	-12.0	-0.02	-52	137	0.16	9.1	0.01	+7	180	0.02	23	0.002	+13
Mg^{2+}	76	0.1	-27	-0.05	-36	399	0.47	25	0.03	+6	442	0.04	-17	-0.002	-4
HCO_3^-	2097	3.4	-1624	-3.0	-77	11911	116	477	0.56	+4	11911	1.2	721	0.01	+6
Cl^-	203	0.4	-131	-0.24	-65	1230	1.45	292	0.34	+24	1555	0.2	181	0.02	+12
SO_4^{2-}	636	1.2	-122	-0.23	-19	3281	3.86	473	0.56	+14	3923	0.4	-313	-0.03	-8

*) includes river and atmospheric supply; **) refers to Kiernoz Wielki lake

cultural catchments with lakes (the Wólka stream, sites: 42-1, 42-2, 42-3, 42) and without lakes (the Gągławki stream, sites: 50-1, 50) showed distinct differences in the ion concentrations although there are similar intensity of agrotechnics and amounts of applied fertilizers as well as similar catchment morphology. As shown in Table 6, lakes are important traps for all ions investigated in these agricultural catchments. The average concentrations of the two groups of means showed statistically significant differences at $P \leq 0.05$. The most considerable ones were observed for potassium ions, whose concentrations at the outflows from lakes amounted to 2.2 mg L^{-1} and were approximately 50% lower in comparison to agricultural areas without lakes.

Water in forested areas shows a distinct decrease mainly in the Ca, HCO_3 ions concentrations when it outflows from lakes. However, no significant differences were observed for SO_4 and Cl anions between forested catchments with and without lakes.

The analysis of dissolved sediment yields from sub-catchments of different land use patterns showed that the loading from forested areas amounted to 400 kg yr^{-1} ha^{-1} and from agricultural areas reached 740 kg yr^{-1} ha^{-1}. On the contrary to e.g. headwater areas, in agricultural catchments the yield was more related to high concentrations rather than discharge of water. The matter losses from urban areas stabilized at the level of approximately 600 - 650 kg yr^{-1} ha^{-1}.

Conclusions

This study report on the temporal and spatial variations of major elements in the dissolved matter transported throughout the upper Łyna basin. Twelve sampling sites were monitored from the source of the Łyna River towards a gauge at Olsztyn and twelve more were located over 5 sub-catchments differentiated by land use. The objectives of this study were to describe the transport of major elements in the dissolved form and to define the different inputs that contribute to the water chemistry in order to estimate dissolved fluxes.

The snapshot sampling of the upper Łyna River system within the period of three years embraced different modes of river supply. For this purpose, a specially designed measurement system made it possible to show changes in water chemistry in sub-catchments with different land use pattern. The comparison of catchments with extremely different land use resulted in the detailed characteristic of spatial ion variation.

The obtained data showed that the behavior of investigated riverine system and associated hydrological characteristics are derived primarily from the basin they drain. The character of the young-glacial relief, lithological diversification, drainage density, shape of the valley and channel as well as the land use pattern and lake presence are factors determining the magnitude of material supply to the upper Łyna River and the distribution of its sources.

The hydrochemical profile of the main river of the catchment made it possible to establish three zones of different modes of river channel supply with water and dissolved matter: headwater, middle with open lakes and the lowest zone with anthropogenic influences. Thanks to that division the natural character of the Łyna River headwaters was exposed on the background of natural processes and man's activity that significantly influence water quality down the river. Thus, a very good quality of water in the uppermost zone may be considered as a benchmark of geochemical background for the assessment of water chemistry condition in the region. The analysis of dissolved constituents in water along the Łyna River profile also allowed for an assessment of the importance of the tributary channels as transfers of man-made pollutants.

The most visible changes in the chemical composition of water were found for ions correlated with anthropogenic activity: Na^+ and K^+. The differences in their concentrations showed unequivocally that the source of ions in water from agricultural catchments is mainly chemical weathering of bedrock overlapped by anthropogenic pollution. The rough estimation of proportion between natural ions sources and ions originated from anthropogenic sources is 75% when measured with EC or ash. The share of natural components deriving from mineral weathering (leaching of soil) such as Ca^{2+}, HCO_3^- in water from arable lands is very high and reaches 90%. However, the agricultural input prevails as for such ions as Na^+ and K^+, for which natural part is estimated as 35% and 15%, respectively, whereas Cl^- derives in 50% from natural sources.

The study of dissolved matter chemistry suggests the importance of the reservoir existence for the ion fluxes. Open lakes, taking 30% of the total river length, act as sinks on the watercourse for most particulates due to biogeochemical fixation, sedimentation and resuspension in bottom sediments. This is confirmed by comparison of ionic composition of water in catchments with and without lakes. The results showed that water flowing out from lakes is free from a considerable part of each of the studied ions, especially in agricultural catchments, which confirmed results of the research in the Jorka [15] or Hańcza [16] river systems in the eastern part of the Mazury Lakeland. In this regard, the highest decrease in concentration concerned: K^+ by 50%, Ca^{2+} by 20%, Na^+ by 36%, SO_4^{2-} by 25%. The retention of solutes in lakes is highly dependent on the reservoir location within the catchment and water table area. The largest reservoir in the region, Łańskie lake, is capable of retaining 12% of solutes supplied by sources of different modes: a river, stream and atmospheric deposition, which means the annual retention of more than 3,000 tones of solutes per year. The smallest open lakes located near the headwater were characterized by higher export of solutes than the import due to an intensive recharge by groundwater rich in dissolved matter.

The investigations showed that lakes decrease the annual matter losses from catchments. The presence of Łańskie lake caused a decrease in weathering yield from 760 to 632 kg ha^{-1} yr^{-1}. The role of open lakes as sinks in forested catchments is less clear due to the balance between input and output of the substances of anthropogenic origin (Na^+, K^+, Cl^-). It proves that lakes play a significant role in running water purification, but most of all, in agricultural landscape. However, the problem of the excess of the substance "consumed" by a lake arises. The loss of equilibrium in such water ecosystems may lead to an advanced eutrophication process and degradation of reservoirs.

Presented results on spatial diversity in river water quality reflect one of the basic processes of a contemporary denudation system in the temperate zone. Variability of chemical composition of water is a good indicator of a catchment system in conditions of stable flow regime. The qualitative characteristics of river transport obtained in the research procedure have made it possible to define a base of the mechanism underlying the functioning of the upper Łyna catchment as a present-day regularity in the West Warmia and Mazury young-glacial area situated in the temperate climatic zone.

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