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BUDGETS OF ELEMENTS IN A LOWLAND FORESTED WATERSHED: THE COMPARISON OF WATERSHED WITH AND WITHOUT THE STREAM

ABSTRACT: It was shown that hydrochemical properties of stream waters and subsurface (spring) waters and the budgets of elements in a lowland forested watershed calculated on the basis of these properties could differ significantly. The hydrochemical differences concerned the content of dissolved phosphorus, particularly in mineral form, nitrate, ammonium, potassium and manganese. In the dynamics of monthly elemental budgets, visible differences in the course of retention and leaching of nitrate and dissolved organic nitrogen were noted between stream and spring watersheds. The stream environment can modify average monthly budgets in the forested watershed of such elements as SO_4–S and Na by increasing its leaching but of NO_3–N, NH_4–N and Mn by increasing retention level.

KEY WORDS: forested watershed, element budget, subsurface outflow, stream, hydrochemistry.

1. INTRODUCTION

The method of study of forested ecosystems and biogeochemical processes occurring in them which employs calculations of watershed element budgets is used to define the degree of stability and the biogeochemical role of these systems on a landscape scale (Bormann and Likens 1993). The method makes it possible either to follow the impact of such important global processes as “acid rains” (Wright *et al.* 1988, Probst *et al.* 1990) or to assess the impact on intraecosystem nutrient cycling of increased input of elements from the atmosphere (Likens *et al.* 1971, Zimka 1989, Feger 1995).

In investigations concerned with the flow of elements through watershed systems, the study scheme based on atmospheric input and stream output plays a dominant role. This scheme was widely employed particularly in studies of forested watersheds in mountain and highland areas (Likens *et al.* 1977, Andersson and Olsson 1985, Swank and Crossley 1988, Hornung *et al.* 1990). However, the application of that watershed scheme to studies of lowland areas, particularly in post-glacial landscape is beset with inconveniences. These are connected, first of all, with the lack of well-defined hydrogeological relations, the occurrence of lakes and undrained peatlands as areas of initial outflow and also slight slopes. These conditions create a possibility of stream water infiltration into the stream bed and aquifer with significant effect for water budget and nutrient dynamic (Fetter 1988, Allan 1998). The biogeochemical independence of natural, slow-flowing lowland streams in relation to subsurface watershed waters seems to be greater the more differentiated the community functioning in the stream and the more complicated water – deposit relations are. This concerns specially the dynamics of nitrogen and phosphorus (Ford and Naiman 1989, Triska *et al.* 1993). Naturally, the interpretation of watershed budget calculations in these circumstances becomes difficult.

In the light of the above facts, the pausity of published data concerning the relations between watershed surface and subsurface waters should be stressed. Several questions arise in this context. Does a small lowland stream act as a direct transmission path for elements supplied from the watershed? So, could an assumption widely accepted for highland watersheds be adopted for lowland watersheds? What are the relations between hydrochemistry of stream waters and subsurface waters supplying the stream? How do these relations affect element budgets in the whole watershed?

The main objectives of this work were to study the elemental budget of a forested watershed of a stream section by comparing two watershed study schemes:

1. In the first scheme – watershed of stream section with stream, the watershed element retention was calculated as the difference between the sum of atmospheric input and inflow from upper watershed in relation to stream outflow. In this scheme the watershed was treated as ecotone system transporting elements from upper part of watershed.

2. In the second scheme – watershed without stream, the retention was based on the difference between input from the atmosphere and outflow of subsurface waters from a spring drained the part of studied watershed. The data on outflow from it were extrapolated into the whole terrestrial area of watershed.

The study watershed represents a hydrological system typical of young glacial areas. The study stream, outflowing from lakes and wetlands and supplied by seepage and spring waters, has not created a mature valley system till now. The watershed is covered mainly by oak – hornbeam wood. However, there are forested wetlands along the stream particularly near its outlet.

It should be noted that the budget of elements in watershed systems is a sensitive indicator of biogeochemical changes in terrestrial ecosystems caused by man's impact and simultaneously show the influence of the watershed on lakes and rivers as water recipients. The watershed is widely accepted as a basic unit in landscape ecology and is treated as an object of monitoring and investigations on ecosystem transformations secondary to global changes. In view of the role of watersheds, the methodology of element flow through these systems seems to be more and more important.

2. STUDY AREA

The investigations were carried out in North – East Poland, about 5 km southwest of the town of Mikołajki in the Masurian Lakeland (Fig. 1). Its geographical location is 21°30' E and 53°50' N and the lowest point is at an altitude 116 m. The study area was located in a small northern part of the Puszcza Piska forest in the Masurian Landscape Park. The typical lakeland landscape of the study watershed is made up of hills and hummocks divided by peaty depressions. The region is characterized by a dense network of lakes, which together with watercourses create quite complicated hydrological systems. The climatic conditions could be defined as temperate with some properties of a continental climate, such as a long winter period and a considerable yearly amplitude of mean temperatures. The mean long-term yearly sum of precipitation amounts to 580 mm and the most rainy month is July (Bajkiewicz-Grabowska 1989).

The investigations were carried out in a 36 ha watershed of the lower section of the Lisunka stream which is the part of 402 ha watershed of whole Lisunka stream (Fig. 1). Lisunka is a 2.2 km long stream flowing from lake Lisunie, through small Lake Żabie and into Lake Gardyńskie (Fig. 1), located within the Krutynia River drainage basin.The stream section under study is 450 m long with a mean slope of 9‰. The stream flow takes place in a channel of 1–1.5 m width with a bed of sands and gravel. The stream meanders near the outlet and organic deposits in the bed are visible.

The watershed of the low section of the Lisunka has a definitely hummock type of relief amounting to 34 m. The relief is built by moraine hills of quite significant relative heights (up to 31 m) and hillside slopes up to 20%. Loamy and sand-loamy deposits predominate on the surface. Phytosociologically, the area belongs to the association *Tilio Carpinetum* Traczyk 1962 (Polakowski *et al.* 1997). However, communities containing the black alder *Alnus glutinosae* (L.) Gaernt. on wet organic soils have been formed in the southern part of the watershed on the surface of Lake Gardyńskie terrace and locally among hummocks.

The supply of the Lisunka stream in the low section is realized by direct drainage of aquifer and by inflows of small wa-

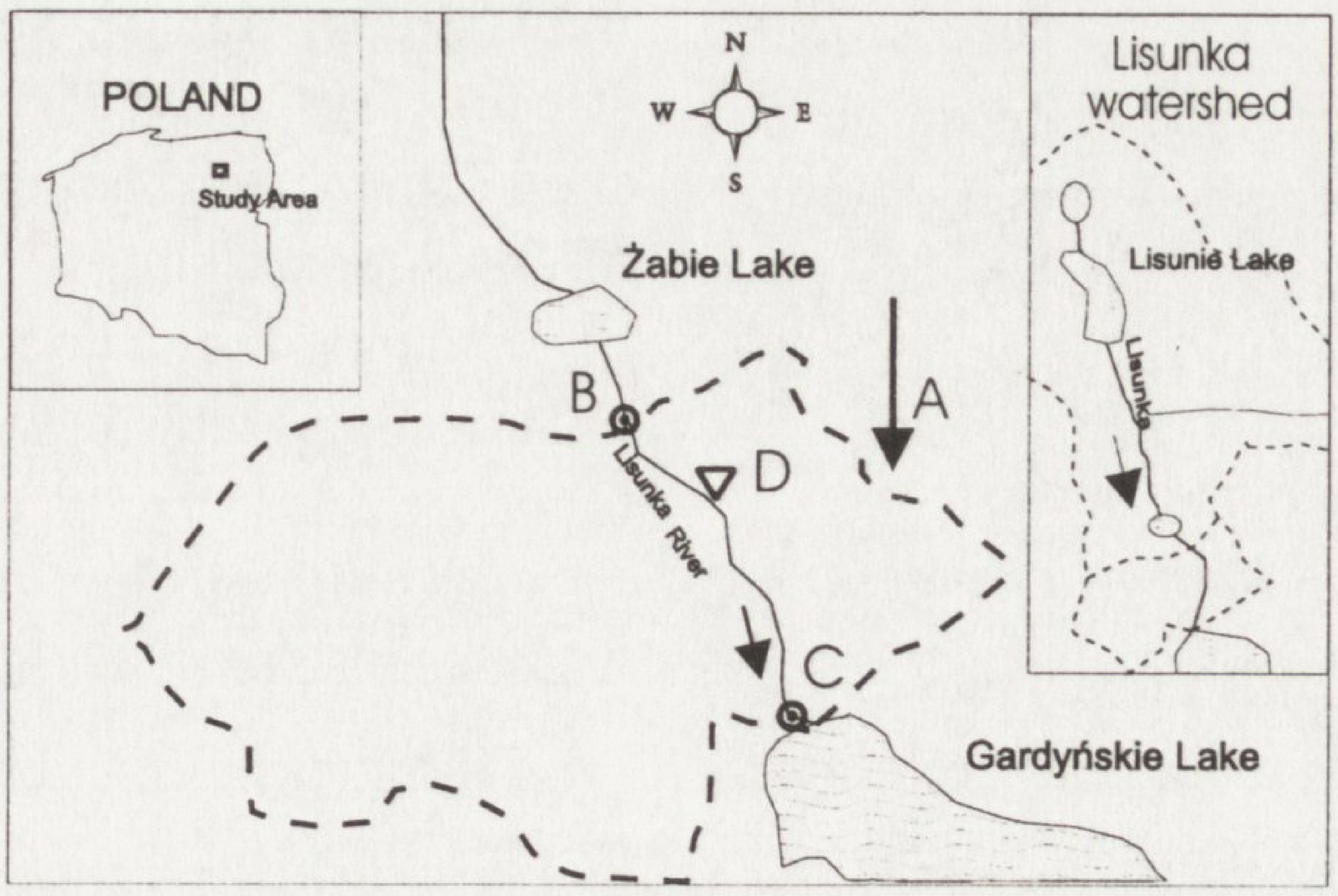

Fig. 1.The location of the Lisunka watershed and it upper and lower parts in Masurian Lakeland, North-East Poland and the scheme of hydrochemical data collection: A – inflow from atmosphere, B – stream inflow into watershed, C – stream outflow from watershed, D – spring outflow.

tercourses outflowing from springs and seepage areas situated under hillslopes at a distance of 1–3 m from the stream. This type of supply is predominant in the upper part of the valley of the stream section. It was in this part, in the eastern bank of the Lisunka, that the outflow from a small underslope spring was selected for hydrochemical investigations (Fig. 1). It is not very productive but highly stable outlet of subsurface waters and it is located under an erosive scarp which undercuts a moraine hillside of a gentle 5% slope. The area drained by the spring contains loamy soils covered by *Tilio Carpinetum* association with diversified tree stand.

3. METHODS

The investigations were carried out in order to provide a quantitative evaluation of element throughflow in the watershed system of stream section. In a widely accepted watershed study scheme (Bormann and Likens 1993), the water and element budgets are calculated generally as the difference between atmospheric inflow and stream outflow from watershed. As the consequence of this assumption, the budget equation of every watershed of stream section should include additional inflow, from upper watershed (Fig. 1). The following structure of the watershed of stream section water budget was proposed:

Precipitation + Stream inflow = Stream outflow + Evapotranspiration ± Storage changes (1)

which is the modification of more general formula of watershed water budget (Jenkins *et al.* 1994, Gutry-Korycka and Soczyńska 1997):

Precipitation = Watershed outflow + Evapotranspiration ± Storage changes (2)

On the basis of the above, two calculation schemes of elemental retention were adopted (Fig. 2). In the first scheme – watershed with stream, the watershed retention of element x was based on the difference between the sum of the inflows from the atmosphere (A) and the stream inflowing from upper watershed (B) and stream outflow (C) according to water budget equation (1):

$$(\text{Retention I})_x = (A_x + B_x) - C_x \quad (3)$$

and in the second scheme – watershed without stream, the watershed retention was based on only one inflow – from the atmosphere (A) and on one outflow – subsurface from the spring (D), which was based on equation (2) and assumed to represent outflow from terrestrial area of the watershed of stream section:

$$(\text{Retention II})_x = A_x - D_x \quad (4)$$

Thus, the two different equations of watershed elemental retention were built around the same area, in the first case (3) with stream and in second (4) without stream (Fig. 1 and 2). These two watershed schemes are comparable in the case of absolute amounts of retention or losses of elements, they concern the same area, but not comparable in relative values (in % to input), due to inclusion of additional inflow and throughflow of stream waters in watershed scheme with stream.

The measurements were made at locations shown in Fig. 1. The discharge of the stream was measured at the initial point of the stream section – where it entered the watershed and at the end point

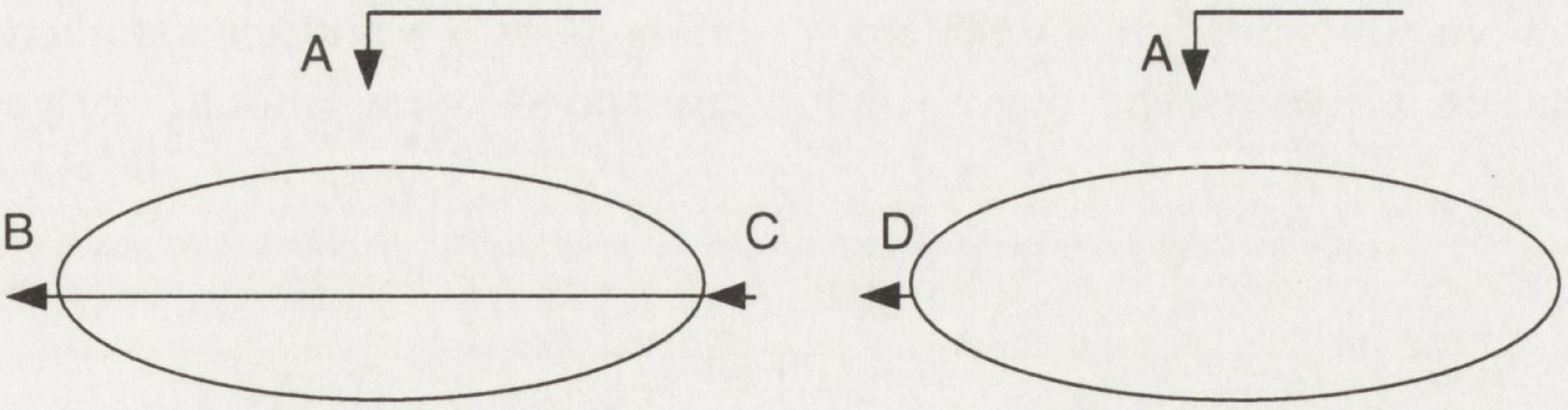

Fig. 2. The presentation of watershed schemes: with stream (left) and without stream (right).
A – inflow from atmosphere, B – inflow from stream, C – outflow by the stream, D – outflow from the spring.

near the outlet of the stream to Lake Gardyńskie – where it left the watershed (Fig. 1). At the first location, measurements were conducted in a 9 m long pipe and at the second point in a 2–3 m cleaned and modelled stream channel. The float method was used in both cases. Flow speed measurement were repeated 3–5 times in order to obtain a credible mean value. These hydrological measurements were carried out once a month and discharge amounts were expressed in mm per month or year, with the 36 ha watershed being a reference area. Data on the atmospheric inflow of water were obtained from a Meteorological Station located in Mikołajki about 2.5 km north-east of the study area.

Simultaneously with hydrological measurements, samples of surface, spring and rain/snow water were collected. Water samples from the stream were collected into 1 l polyethylene containers at two points: where it entered and left the watershed (Fig. 1). Samples of subsurface waters were collected directly from the spring mouth. Precipitation waters were collected into two poliethylene containers with attached plastic funnels. One of them was additionally equipped with a Whatman GF/F mineral filter and a spoonful of salicylic acid. The acid lowered the pH to prevent the liberation of ammonium and development of algae and microorganisms growth in the water collected (Stachurski and Zimka 1984). Samples from this container were used to analyse the content of nitrogen, phosphorus and sulphur forms. The second container was not equipped with either a filter or acid – and the samples from it were used to measure pH and to determine amounts of metals. Samples of rain water were collected from the station located in the Hydrobiological Station of Institute of Ecology, Polish Academy of Sciences – 2.1 km north-east of the watershed. Wet and dry deposits were not separated.

All samples were filtered immediately after collection and their pH were measured. Within 12 hours after collection the concentrations of phosphates were determined by the stannous chloride method, ammonium nitrogen by the indophenol method, sulphate sulphur by the turbidity method with $BaCl_2$ (Standard methods for the examination... 1992) and nitrate nitrogen by the reduction method with sulphanilic acid (Hermanowicz *et. al* 1976). The concentration of total nitrogen was determined by digestion in sulphuric acid (Kjeldahl method) and total phosphorus, by digestion in perchloric acid (Golterman 1969). The differences between concentrations of total and mineral forms of N and P were used to estimate concentrations of organic forms of these elements. The concentrations of dissolved calcium, magnesium, potassium, sodium and manganium were determined using the atomic absorption method (Standard methods for the examination... 1992). The loads of elements in precipitation, inflow and outflow of watershed were calculated by multiplying the amounts of water flow by the concentrations of elements.The loads and budgets of the nutrients studied were expressed as kg ha^{-1} month^{-1} or year^{-1}.

4. RESULTS

4.1. HYDROLOGY

The hydrological parameters monitored in this study: precipitation, stream inflow and outflow, present a quite diversified picture of seasonal dynamics (Fig. 3). First of all, the distribution of precipitation amounts in each year of the study varied considerably. There was a lack of intensive rainfall in summer months (July–August) in the first year of study, but in the next year this period had a high precipitation level amounting to 80–100 mm per month. By contrast, spring was rather wet in 1992, but in the next year it was dry. A considerably higher amount of rainfall was noted in September in the first year (Fig. 3). In general, the rates of evapotranspiration and retention change (indirectly defined) in summer months were similar to the rate of precipitation in these periods. However, in the other months these parameters were characterized by very unstable changes (Fig. 3). It was probably caused by the completion of watershed retention after summer months with a deficit in rainfall (September–November 1992) and by the influence of snow retention, for example in December 1993 (Fig. 3). Dynamics in flow variation in the Lisunka stream were generally associated with the seasonal dynamics of precipitation (Fig. 3).

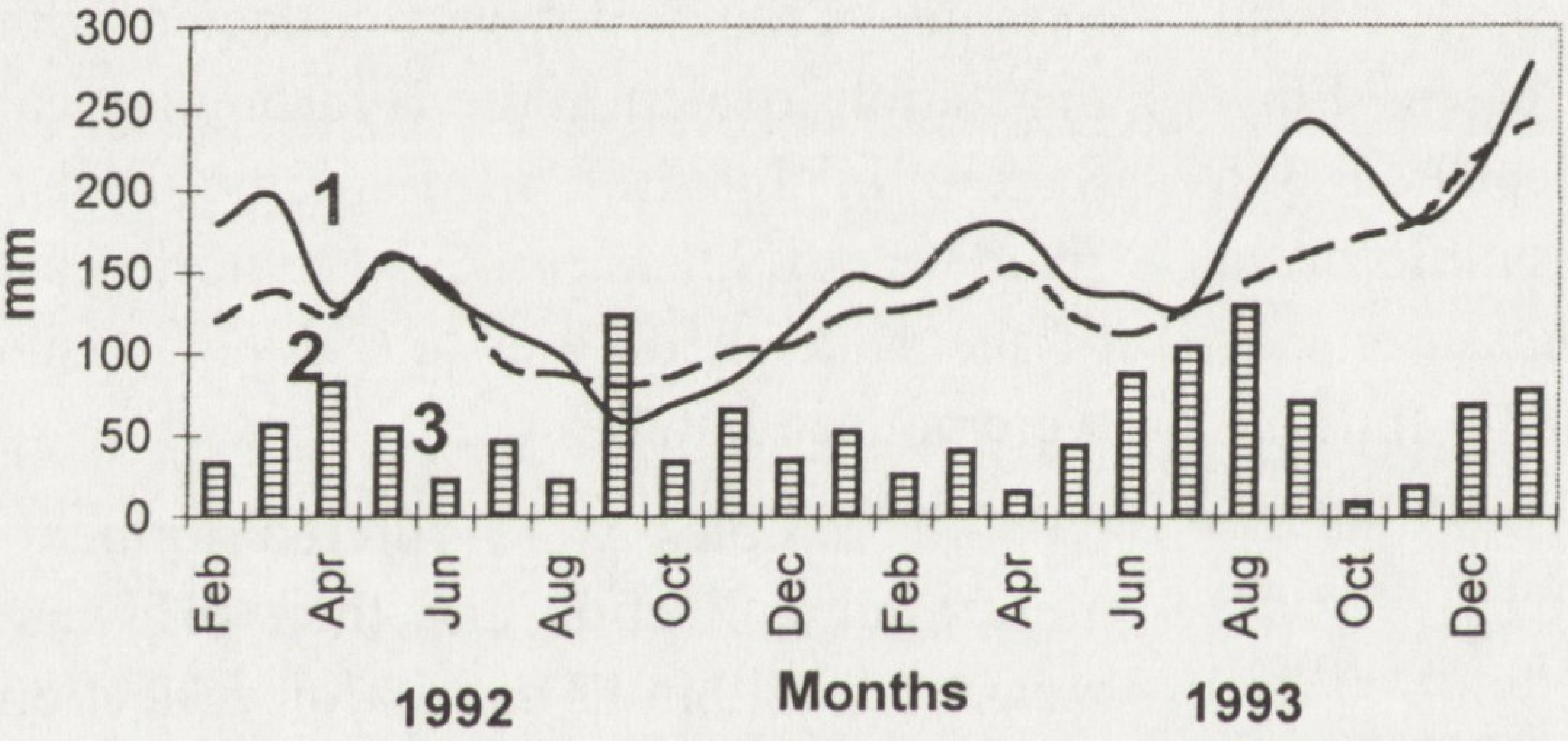

Fig. 3. The hydrology of low section of Lisunka Stream in the period of two years: February 1992 – January 1994: 1 – stream inflow, 2 – stream outflow, 3 – precipitation

The most characteristic phenomenon in stream flow was clear predominance of stream inflow to watershed over stream outflow observed regularly in both autumn seasons with the lowest water states and after months poor in rainfall. Such a course of flow curves indicated that stream water infiltrated into the area of the watershed and by this process was retained in aquifer – in fact, the amounts of retention change (evapotranspiration is low in autumn) were relatively high (Fig. 3).

In spite of the significant differences in the monthly dynamics of individual hydrologic parameters in the first and second years of the study, the sums of precipitation were similar in both years, reaching more than 600 mm (Table 1). But probably, the above differences and, above all, a dry summer in 1992 in contrast to the summer in the next year abundant in rainfall, were the main causes of considerable differences in other components of yearly

Table 1. The components of water budget of the lower section of the Lisunka stream watershed (mm) (compare Fig. 3)

Components of water budget	Year I	Year II
Precipitation	620.9	683.9
Stream inflow	1359.9	1893.2
Stream outflow	1490.2	2214.6
Watershed subsurface outflow	130.3	321.4
Evapotranspiration ± change of storage	490.6	362.5

water budgets in the Lisunka watershed. Both stream inflow into the watershed and outflow from it were, in the second year of study, greater by about 1/3 than in the previous year. In contrast with it, evapotranspiration and retention change values were significantly higher in the first year with a summer rainfall deficit (Table 1). If it is assumed that the difference between surface outflow from the watershed and stream inflow into it arose as a result of side supply of subsurface waters from watershed, this supply in the second year of the study was about 2.5 times greater than in the first year (Table 1).

The hydrology of the forested watershed of the low section of Lisunka stream was dependent on early spring thaws and on changes in precipitation in the summer season. Another characteristic feature was a tendency towards periodic infiltration of stream waters into subsurface waters, which was connected with the completion of watershed water retention after dry months.

4.2. HYDROCHEMISTRY

The hydrochemical investigations were concerned with the composition of atmospheric waters, stream waters flowing into and out the study watershed and spring waters supplying the major stream. The composition of waters supplied study watershed from atmosphere characterized by high average concentrations of cations as Ca^{2+}, Na^{+} and as a probably result pH value exeed 7. The elevated concentrations of ammonium and sulphate ions in rain/snow waters should be noted (Table 2). It turned out that the pH values and concentrations of almost all elements analysed in the surface waters of the inflow and outflow were similar and did not differ more than 1.5 times from each other (Table 2).

On the other hand, a greater number of wider hydrochemical differences were observed between stream and spring waters. The mean levels of phosphate and ammonium in subsurface waters were significantly higher ($P < 0.0001$ and $P < 0.005$ respectively) than in stream waters, and in contrast, the mean concentration of nitrate in spring waters was 50–100 times lower than in surface waters (Table 2). Those differences between the mean values of concentrations of N and P organic forms were not significant. Generally, subsurface waters were about 2 times richer in phosphorus and 4–5 times poorer in nitrogen than stream waters and these differences were significant (Table 2).

Table 2. The hydrochemical properties of atmospheric inflow waters, stream inflow waters to watershed, stream outflow waters from watershed and spring waters supplying stream. Means ± standard deviation (n = 24). The levels of significance < 0,05 for differences between hydrochemical properties of stream outflow waters and spring waters were marked (t - test for differences in means from independent populations was used)

Type of waters	pH	PO_4-P	DOP	DTP	NH_4-N	NO_3-N	DON*	DTN*	SO_4-S	Ca	Mg	K	Na	Mn
		μg l^{-1}			mg l^{-1}									μg l^{-1}
Atmospheric inflow	7.1 ±0.3	18 ±13	10 ±12	28 ±18	0.49 ±0.46	0.14 ±0.23	0.51 ±0.80	1.16 ±1.08	0.67 ±0.37	1.56 ±1.19	0,19 ±0,09	0.52 ±0.47	1.78 ±2.40	20 ±17
Stream inflow waters into watershed	8.0 ±0.3	9 ±5	15 ±11	24 ±11	0.04 ±0.02	2.10 ±3.47	0.70 ±0.53	3.52 ±3.49	8.81 ±2.28	75.90 ±13.32	8,33 ±0,79	0.89 ±0.45	4.11 ±1.78	20 ±10
Stream outflow waters from watershed	8.0 ±0.2	12 ±5	17 ±20	28 ±20	0.03 ±0.02	1.26 ±2.29	0.73 ±0.57	2.54 ±2.27	8.77 ±1.48	77.22 ±10.05	8,38 ±0,70	0.88 ±0.23	5.06 ±2.94	16 ±10
Spring waters	7.9 ±0.2	28 ±9	24 ±30	51 ±32	0.06 ±0.04	0.02 ±0.03	0.68 ±0.54	0.70 ±0.57	9.68 ±1.87	79.18 ±12.69	9,03 ±1,46	1.10 ±0.21	5.92 ±2.83	25 ±15
P	*n.s.*	< 0,0001	*n.s.*	< 0.02	< 0.005	< 0.01	*n.s.*	< 0.005	*n.s.*	*n.s.*	*n.s.*	< 0.002	*n.s.*	< 0.05

*n = 18

n.s – not significant.

The types of waters investigated in this study differ not only with respect to mean P and N forms concentrations but also the contribution of particular forms to the total content of these elements. The contribution of the organic P form exceeded the contribution of phosphates in stream waters. However, this relation was reversed in spring water. In the case of nitrogen, the nitrate form was dominant in the watercourse, and dissolved organic nitrogen in subsurface water (Table 2).

As opposed to mineral forms of N and P, no statistically significant differences were recorded between stream and spring waters for pH, sulphate, calcium, magnesium and sodium concentration levels. However, such differences were demonstrated for potassium and manganese – with considerably greater amounts of these elements recorded in waters outflowing from the spring (Table 2).

4.3. ELEMENT RETENTION AND LOSSES

The variability of monthly element budgets (total inflow–outflow) in the Lisunka watershed during the two-year study demonstrated several characteristic properties connected with the seasonal cycle and the distribution of precipitation. The spring periods generally brought retention of mineral phosphorus, but late summer was associated with its leaching (Fig. 4a). The curve of DOP variability oscilated around zero, with an exception in August 1993, when heavy rainfalls quickly leached this form (compare Fig. 3 and 4b). Almost all monthly budgets of NH_4–N were positive with maximum values in spring and summer (Fig. 4c). In the case of other forms of nitrogen: the nitrate and organic, it was difficult to distinguish seasonal tendencies in their mothntly budgets. Attention should be paid to a considerable increase in NO_3–N removed from stream throughflow as a consequence of summer 1992, extremely poor in rainfall. However, this process was not observed in subsurface outflow (Fig. 4d). The cycles of DON retention in spring and leaching in winter were clear–cut, but, as in the case of nitrates, only for monthly budgets calculated on the basis of stream flow (Fig. 4e).

In contrast with the above, visible negative values indicating leaching from the watershed dominated in the monhly budgets of SO_4–S, Ca and Mg. The maximum amounts of leached elements noted during thaws in early spring 1992 and in September 1993 after heavy rainfall were very characteristic. Some weak tendencies towards retention of these elements were observed particularly in the period August–November 1992 after a dry summer (Fig. 4f, g and h). Similar cycles of leaching and retention were also observed in the case of potassium. However, a more clear tendency towards accumulation and a balanced throughflow dominated its monthly budgets (Fig. 4i). The sodium ion was more easily leached than potassium, for example in the winter of 1992 year (Fig. 4j). In contrast with other metals, the monthly budgets of manganese clearly demonstrated an excess of retention of this element in the watershed (Fig. 4k).

As was pointed out in the description of the methods, the budgets of elements in the forested watershed of the lower section of the Lisunka stream were studied using two measurement schemes: the first was based on stream flow, and the second, on subsurface outflow. Generally, the seasonal variability curves of element budg-

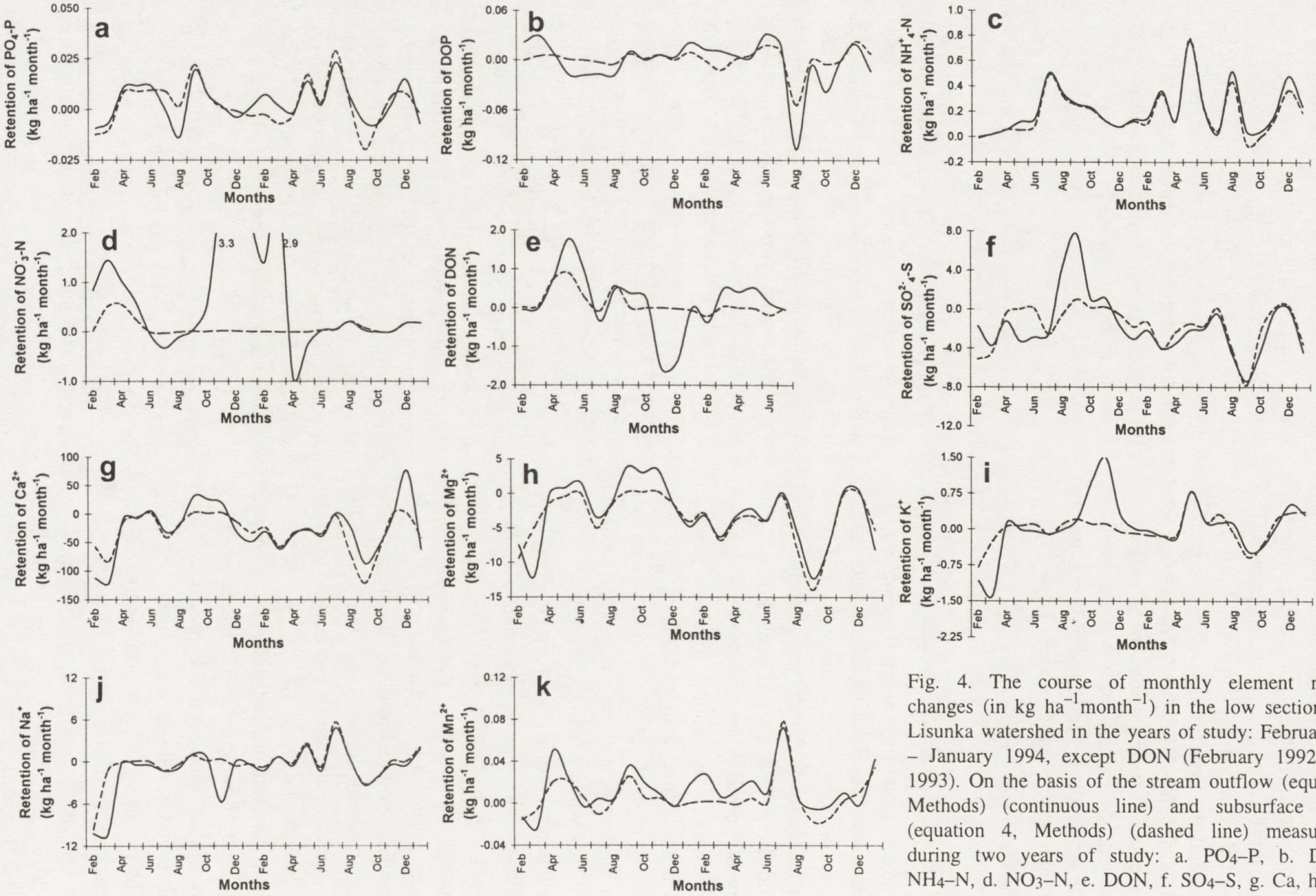

Fig. 4. The course of monthly element retention changes (in kg ha^{-1}month^{-1}) in the low section of the Lisunka watershed in the years of study: February 1992 – January 1994, except DON (February 1992 – July 1993). On the basis of the stream outflow (equation 3, Methods) (continuous line) and subsurface outflow (equation 4, Methods) (dashed line) measurements during two years of study: a. PO_4–P, b. DOP, c. NH_4–N, d. NO_3–N, e. DON, f. SO_4–S, g. Ca, h. Mg, i. K, j. Na, k. Mn

ets calculated on the basis of the two schemes demonstrated in many cases a similar picture (Fig. 4), shown most visibly in the case of NH_4–N, Ca and Mg monthly budget dynamics (Fig. 4c, g, h) and to a lesser degree for the budgets of PO_4–P and Mn (Fig. 4a, k). Similarity between the two study schemes adopted for such elements as DOP, SO_4–S, K and Na varied depending on the year and season. Significant differences in the course of monthly budget values for these elements were noted in the first year of the study, particularly in autumn (Fig. 4b, f, i, j). However, the greatest lack of synchronization in monthly budget variability patterns throughout most of the study period was seen in the case of the nitrogen forms: NO_3–N and DON. The amplitude of watershed monthly budget values calculated on the basis of stream water flow for these nutrients was several times higher than the range of budget variability in the study scheme utilizing subsurface water hydrochemistry (Fig. 4d, e).

The several characteristic differences and similarities between element budgets in the study watershed obtained using the two calculation schemes described above could be observed not only as monthly changes, but in monthly average budgets in study years as well.

In the case of phosphorus forms there are no significant differences in monthly budgets (Table 3). A diversified picture was observed in the case of average monthly watershed budgets for nitrogen forms. NH_4–N budgets were on the similar level in the two study schemes but the watershed with stream retained significantly (P < 0,02) more ammonium ion than watershed of subsurface outflow. The clear-cut difference was demonstrated in the budgets of nitrate nitrogen. The budget of NO_3–N calculated from the scheme using stream flow amounted to 1 kg $ha^{-1}month^{-1}$ and that calculated on the basis of subsurface waters – only to about 0.11 kg $ha^{-1}month^{-1}$, but significant diffrences (P < 0.05) occured only in the first year of study (Table 3). In case of DON, in spite of diversified course of monthly budgets (Fig. 4e), the significant differences in average monthly retention were not shown (Table 3). The monthly retention of total dissolved nitrogen was almost three times greater in watershed with stream than in watershed without it and this difference was significant in the level P < 0.005 (Table 3).

The selection of a particular watershed study scheme was not important for the calculation of calcium, magnesium and potasssium budgets (Table 3). The significant differences of average monthly budgets between two study watershed schemes occured in case of SO_4–S, Na and Mn, but only in second year of study. Greater amounts of sulphates were leached from watershed with stream (P < 0.01) and more manganese was accumulated in this system (P < 0.05), however sodium was retained more easily in watershed without stream (P < 0.005) (Table 3).

5. DISCUSSION

The absence of a modifying influence of stream environment on element budget calculations is assumed as a rule in investigations of element budgets in forested watersheds located in mountain and highland areas (Likens *et al.* 1977, Johnson and Van Hook 1989, Probst *et al.* 1990, Mulder *et. al.* 1990). Indeed, fast flowing, well aerated and draining homogenous rock massive, mountain streams have

Table 3. The comparison of average monthly retention of elements in watershed with stream (equation 3) and in watershed without stream (equation 4) in the years of study. Means ± standard deviation (n = 12). t – test for differences in means from independent populations was used. *P* – significance level

PO_4-P	DOP	DTP	NH_4-N	NO_3-N	DON	DTN	SO_4-S	Ca	Mg	K	Na	Mn
g ha^{-1}month^{-1}			kg ha^{-1} month^{-1}									g ha^{-1}month^{-1}
Watershed with stream												
1992												
2.5 ± 9.4	2.3 ± 16.3	4.8 ± 17.3	0.17 ± 0.14	1.02 ± 1.14	0.10 ± 0.89	1.30 ± 0.76	-0.47 ± 3.35	-12.4 ± 23.5	-0.75 ± 2.29	0.05 ± 0.73	-2.36 ± 3.93	10.4 ± 19.8
1993												
4.3 ± 9.1	-5.3 ± 35.2	-1.0 ± 38.3	0.26 ± 0.22	0.31 ± 0.91	*n.d.*	*n.d.*	-2.93 ± 2.11	-14.4 ± 19.9	-2.13 ± 1.86	0.08 ± 0.34	0.07 ± 2.09	16.7 ± 21.3
Watershed without stream												
1992												
3.5 ± 9.0	2.3 ± 4.2	5.7 ± 10.1	0.15 ± 0.14	0.11 ± 0.20	0.20 ± 0.33	0.47 ± 0.43	-1.15 ± 1.87	-10.7 ± 13.1	-1.16 ± 1.43	-0.04 ± 0.25	-0.99 ± 2.67	4.5 ± 12.2
1993												
2.2 ± 11.9	-0.4 ± 18.6	3.7 ± 23.1	0.23 ± 0.22	0.06 ± 0.08	*n.d.*	*n.d.*	-2.34 ± 2.22	-19.8 ± 17.0	-2.33 ± 1.96	0.07 ± 0.35	0.40 ± 2.18	9.1 ± 24.2
P												
1992												
n.s.	*n.s.*	*n.s.*	< 0.02	< 0.05	*n.s.*	< 0.005	*n.s.*	*n.s.*	*n.s.*	*n.s.*	*n.s.*	*n.s.*
1993												
n.s.	*n.s.*	*n.s.*	< 0.02	*n.s.*	*n.d.*	*n.d.*	< 0.01	*n.s.*	*n.s.*	*n.s.*	< 0.005	< 0.05

n.s. – not significant;
n.d. – not determined.

a rather small chance for autonomy of biogeochemical relations. However, with the landscape resembling lowlands more and more, gentler slopes and slower speed of flow, the fact that a stream constitutes a distinct natural system becomes more visible. Consequently, the relation between allochtonous substances supplied from the watershed and the stream's internal environment become more and more complicated – the hydrochemistry of stream water becomes less and less representative of watershed element cycling. One of the most important factors in these conditions responsible for the development of the "structural and functional relationship of biotic and abiotic factors" in a stream (Lampert and Sommer 1996) is its dependece on the supply of subsurface waters (Timm and Ohlenforst 1994). A watercourse typical of lowland areas with postglacial relief, characterized by a moderate slope and supplied by watershed subsurface waters, was selected in this study (Fig. 1). In addition, as became evident from hydrological investigations, stream waters infiltrated periodically into the aquifer (Fig. 3).

The major question in the study was as follows: To what extent can a watercourse with the properties presented above reflect the biogeochemical processes in the lowland watershed? In the accepted watershed scheme of the stream section, aside from the input of elements from atmosphere, the inflow and outflow of elements in the stream occurred. It means that the watershed budget is actually the difference between atmospheric input and subsurface inflow from land to the stream – as a difference between stream inflow and outflow (Fig. 1) and, in addition, the budget of hydrochemical processes inside the stream. This study showed that a lowland stream with a moderate flow speed is able to modify the throughflow of nutrients N, Mn, K, P and, consequently to distort their budgets in a drained watershed.

It should be noted that the two years of study abounded in very diversified meteorological-hydrological situations: apart from periods with a precipitation deficit, months with considerable amounts of rainfall occurred (Fig. 3). An unbalansed course of precipitation in both summer seasons was the most probable cause of differences in amounts of subsurface outflow between the first and second year of the study (Table 1). These differences were also the major source of the mostly irregular and very variable changes of monthly element budgets in the watershed (Fig. 4).

The results of comparisons of the hydrochemical properties of surface and subsurface outflow waters were the first signals indicating the important differences between amounts of surface and subsurface outflow of elements from the watershed studied and between watershed budget schemes as well. The most significant differences in the concentration of elements concerned N and P forms and the K ion, the major nutrients responsible for biomass production. Interestingly, the content of PO_4–P, NH_4–N and K was greater in spring waters than in the stream, the only exception being the concentration of the nitrate ion in the stream, which exceeded several times this parameter in spring outflow (Table 2). The differences in phosphate concentrations could be explained, on the one hand, by an anaerobic environment of subsurface waters conducive to PO_4^{3-} ion dissociation (Gambrell and Patrick 1978), and on the other hand, by strong biotic sorption and complexation with Ca in aerated and alkaline (pH near 8) stream waters (Lindsay 1979). However, greater concentrations of ammonium and potassium ions in spring waters in comparison to stream waters are probably connected with more intensive leaching of these elements directly from forest soils. A considerable range of differences between nitrate concentrations in watercourse waters (high) and in spring waters (low) could be variously explained. It is known that an increase of nitrate concentration in outflow from a forested watershed can indicate disturbances in intraecosystemic nitrogen cycling, caused for example by tree felling (Likens *et al.* 1977), but also as a result of aging of the treestand (Reynolds and Edwards 1995). Other reasons for the presence of excess amounts of nitrates in outflow waters include: intensive aeration and mineralization of soil organic matter or peat (Kruk 1997) and leaching from fertilizers. It is, however, difficult to select a reason responsible for this case, but it should be sought in the upper part of the Lisunka stream which was not studied.

To what degree did the above differences in stream and subsurface hydrochemistry influence the watershed element budgets? Generally, in the case of monthly element budgets calculated in two watershed schemes the similiraty of their changes was more or less evident . The influence of hydrologic cycles was very clear here. However in the case of NO_3–N and DON budgets, the similarity of their variability patterns was strongly disturbed (Fig. 4).

The average monthly budgets of dissolved phosphorus forms in both watershed schemes were similar and small in absolute values (Table 3). These results agree with balanced phosphorus budgets in watersheds of hummock areas and highlands (Zimka 1989, Gibson *et al.* 1995). However, not all differences in the course of monthly element budget patterns caused analoguous differences in average monthly budgets. Such a situation was noted in the case of nitrogen budgets. It was shown that there were no visible differences between NH_4–N monthly budgets dynamic (Fig. 4c) in the study watershed schemes but average monthly retention differ significantly (Table 3). A considerable differences between the two watershed schemes occurred in the case of monthly nitrate budgets. The influence of the stream's environment caused an almost ninefold increase in the amount of NO_3–N removed from the throughflow by the watershed according to the scheme based on surface waters (Table 3). The question appears what caused the removal of considerable amounts of nitrate inflowing from the upper section of the stream Lisunka? The most probable reason for this phenomenon was assimilative reduction, particularly by periphyton and denitrification in the hyporheic zone (Triska *et al.* 1993). The average monthly budget differences in the two watershed schemes concerning other elements such as SO_4–S, Mn and Na were probably of geochemical origin: variability of redox conditions, cation exchange in deposits.

It is also worthwhile to pay attention to some inconvieniences connected with the arrangement of the watershed scheme based on subsurface water outflows. The most common are: difficulties with delimitation of the spring drainage area, a possibility of supply from a deeper aquifer and unrepresentativeness of subsurface point outflows in relation to linear stream drainage.

6. CONCLUSION

On the basis of the above analysis of differences in element concentration in stream and spring waters, monthly element budgets dynamic and differences in average monthly retention, the following sequence of elements can be grouped from those strongly to weakly subject to modification by the stream draining the watershed:

NO_3–N, Mn > DON, NH_4–N, K > DOP, PO_4–P, SO_4–S, Na > Ca, Mg

7. SUMMARY

The main objective of the present work was to study element budgets in the watershed of the lower section of the Lisunka stream, located in postglacial landscape in the Masurian Lakeland (N-E Poland), forested mainly by oak-hornbeam association (Fig. 1) and to compare two watershed calculation schemes (Fig. 2):

1. Watershed with stream was based on the hydrochemistry of the stream draining the watershed, and element retention were calculated as the difference between the sum of input from the atmosphere and stream inflow in relation to stream outflow.

2. Watershed without stream, the element retention was based on the difference between input from the atmosphere and outflow of subsurface waters from a spring drained the part of studied watershed. The data on outflow from it were extrapolated into the whole terrestrial area of the watershed.

Thus, the two elemental retention equations were built around the same area of watershed, in the first case with stream and in second without stream, including only terrestrial part of watershed (Figs 1 and 2).

Hydrologic methods aiming to define the major components of a watershed water budget, the method of collection of precipitation and several known methods of determinations of main elements: N and P forms, SO_4–S, Ca, Mg, K, Na and Mn were utilized in the work. The measurements and collection of samples were conducted once a month during two years 1992–1994.

The hydrology of the forested watershed studied was quite diversified in individual years of the investigations and seemed to be strongly influenced by precipitation, especially in summer. There was a periodic tendency towards infiltration of stream waters to the bed, which was connected with the completion of water retention in the aquifer after months with a rainfall deficit, usually in summer or autumn (Fig. 3). In spite of a similar level of precipitation in both years the outflow from the watershed was less than half in the first year (with an extremely dry summer) in comparison to the second year (Table 1).

Statistically significant hydrochemical differences between stream and subsurface outflow waters concerned the amounts of dissolved phosphorus, particularly in mineral form, dissolved total nitrogen and its mineral forms and concentrations of potassium and manganese. These differences, however, were not significant in the case of pH, dissolved organic forms of N and P, sulphate, calcium, magnesium and sodium (Table 2).

The tendencies to remove particularly NH_4–N and NO_3–N from the watershed throughflow and to leach SO_4–S, Ca and Mg from the watershed were clearly visible in the courses of monthly element budgets. However, the budgets of other elements oscillating around a balance between inflow and outflow were subject to the influences of vegetational cycles (P forms, DON) or the amounts of precipitation (Na, K) (Fig. 4). The differences in the courses of budgets calculated on the basis of stream and subsurface outflow waters were very clear-cut in the case of nitrate and organic nitrogen and to a smaller degree for SO_4–S, K, Na and DOP budgets (Fig. 4).

It was shown that the biogeochemical environment of the stream could significantly modify the average monthly budgets of such elements as SO_4–S and Na by increasing leaching, but NO_3–N, NH_4–N, DTN and Mn by increasing retention or removal from throughflow. Simultaneaously, irrespective of which element budget scheme was calculated, based on stream or subsurface water hydrochemistry, no visible differences for P forms and Ca, Mg ions were noted (Table 3).

In the discussion, an interpretation of the element budget differences recorded in the study was undertaken and, on the basis of analysis of differences in element concentrations in stream and

spring waters, monthly budgets dynamic and comparision of average monthly values, the set of elements cycling in a forested watershed can be grouped in the following sequence from those strongly to those weakly subjected for modification by stream:

NO_3–N, Mn > DON, NH_4–N, K >
DOP, PO_4–P, SO_4–S, Na > Ca, Mg

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