

LOADS OF SELECTED CHEMICAL COMPONENTS DELIVERED BY PRECIPITATION AND FLOWING AWAY FROM WŁOSIEŃ STREAM CATCHMENT

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Abstract. The study determined the loads of selected chemical components deposited by precipitation and flowing away from the area of a small catchment used for agriculture and animal farming. The research was conducted in the hydrological years 2000 and 2001 in the Włosień stream catchment located in the western part of the Małopolska province. Water for analyses was sampled twice a month and examined for the concentrations of total suspended solids, ammonium and nitrate nitrogen, phosphates, dissolved substances, sulphates, chlorides, calcium, magnesium, potassium, manganese and iron. Those values and the measured values of precipitation and outflow were used to compute the loads of the respective components. The mean annual loads of N-NH_4 , PO_4^{3-} , Mn^{2+} and $\text{Fe}^{2+/3+}$ did not exceed $2 \text{ kg} \cdot \text{ha}^{-1}$, those of N-NO_3 approximated $10 \text{ kg} \cdot \text{ha}^{-1}$, those of Mg^{2+} and K^+ were of ca $20 \text{ kg} \cdot \text{ha}^{-1}$, and the loads of Cl^- exceeded $50 \text{ kg} \cdot \text{ha}^{-1}$. The other components were removed in greater amounts: SO_4^{2-} and Ca^{2+} – over $100 \text{ kg} \cdot \text{ha}^{-1}$, and total suspended solids – over $200 \text{ kg} \cdot \text{ha}^{-1}$. The largest loads carried away by water were those of dissolved substances – $791 \text{ kg} \cdot \text{ha}^{-1}$. The loads of components delivered by precipitation were smaller than the loads carried away by outflow, except for ammonium nitrate, phosphates and manganese. A comparison of the results of this research with the findings from other studies confirmed that the agricultural and animal-farming use of a catchment contributes to the pollution of surface waters: the component loads flowing out of the area of the Włosień catchment were larger than for the catchments not brought under pressure from the keeping of farm animals.

Key words: catchment, precipitation, outflow, loads, chemical components

INTRODUCTION

Water is in constant movement, circulating between the atmosphere, land and oceans on the earth, and causing various substances to migrate. Chemical components can enter the water at each point in this cycle. The levels of such components in surface waters depend

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on natural and anthropogenic factors. The sources of natural substances are rocks, virgin soils, humus, and to some extent also precipitation [Pawlik-Dobrowolski 1990, Rajda et al. 2001]. Anthropogenic pollution, connected with human existence and economic activity, results from the discharge of municipal sewage, disposal of sewage from animal farms, improper application of organic or mineral fertilisers and plant protection chemicals in agriculture, vehicle and industrial emissions, etc. [Kopeć and Krzanowski 1994].

The study aimed to determine the loads of selected chemical components delivered by precipitation and carried away by outflow waters from the area of a catchment with an agricultural and animal-farming land-use pattern.

MATERIAL AND METHODS

The investigations were carried out from November 1999 to October 2001 in the Włosień stream catchment situated in the Wieprz district in the Małopolska province. The catchment has an area of 7.04 km² and is closed by a gauging section on the stream Włosień. The watercourse is the right-bank tributary of the Siarnica stream – the left-bank tributary of the Wieprzówka river flowing into the Skawa river. The catchment lies within the 268–340 m a.s.l. hypsometric range and has a mean land slope of 4.1%.

The area under study has silty soils. Agricultural land covers 555.37 ha, of which arable land constitutes over 68% and grassland 32%. Forests and plantations covering ca 16% of the catchment area are located along the main watercourse and its tributaries.

Built-up areas are concentrated close to asphalt roads at a considerable distance from the main watercourse. Farms have no sewerage system; the household sewage and liquid wastes from farm facilities are collected in containers and distributed over the fields after harvest.

Animals are kept not only on private farms (ca 2.5 ha each) but also on a commercial farm possessing 600 ha of land, of which ca 70 ha is located within the study area. The land is used as pastures for grazing ca 240 cattle head. Mineral fertilisation (NPK) at a rate of 250 kg · ha⁻¹ is there supplemented with slurry. Mineral fertiliser rates on private farms vary between 90 and 120 kg NPK · ha⁻¹. Such farms use also organic and liquid manure and domestic sewage.

To establish the volume of water flowing away from the area of the Włosień catchment, the water level was measured by using a staff gauge installed at the gauging section of the watercourse. The rating curve was drawn on the basis of flow velocity measurements made with an electronic current meter and the levelling measurements of the gauging section at various levels of water in the stream. Using the rating curve, the mean daily discharges were determined (in dm³ · s⁻¹) and then converted into outflow indices (in mm). A precipitation station equipped with a water catcher and Hellman's pluviometer was established within the catchment to measure the amount of rainfall.

Surface water for laboratory analyses was sampled twice a month. Precipitation water was sampled from containers placed under the catcher. Both kinds of water were examined using standard methods for total suspended solids, ammonium nitrogen (N-NH₄), nitrate nitrogen (N-NO₃), phosphates (PO₄³⁻), dissolved substances, sulphates (SO₄²⁻), chlorides (Cl⁻), calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺), manganese (Mn²⁺) and iron (Fe^{2+/3+}) [Hermanowicz et al. 1999].

The results of the precipitation and outflow measurements and laboratory tests provided the basis for computing the loads of components deposited by precipitation and carried away by outflow. The load of each component (in $\text{kg} \cdot \text{ha}^{-1}$) was calculated as a product of the monthly volume of precipitation or outflow and the mean monthly concentration of the component. The annual and semi-annual (winter and summer) loads for individual years and the means from the two-year research period were considered.

RESULTS

Precipitation and outflow

The amounts of precipitation measured at the experimental station situated at an altitude of 298 m a.s.l. were compared with the multiannual mean from the meteorological station located at Gierałtowiec (285 m a.s.l.), 5 km from the catchment.

The precipitation totals differed between the hydrological years (Tab. 1). In 2000, the annual total was 310 mm lower than in 2001, with the difference between the winter half-years being only 54 mm and between the summer periods, 256 mm. The mean annual precipitation total for the two-year research period was higher than the multiannual mean by 150 mm, therefore this period can be considered as wet [Kaczorowska 1962]. The first year, whose precipitation total was 5 mm lower than the multiannual mean, counted as an average year, while the second year, with precipitation 305 mm higher than the mean, was very wet. The winter period (November to April) accounted for 36.6% of the annual total in the first year, and for 31.6% in the second year. In precipitation terms, the winter half-year was average in 2000 and wet in 2001. The summer period (May to October) followed the pattern of the respective hydrological year and was average in 2000 and very wet in 2001.

Table 1. Mean precipitation totals (mm) in multiannual period (\bar{P}) and study period (P), and mean outflows (mm) in study period (H)

Tabela 1. Średnie sumy opadów (mm) w wieloleciu (\bar{P}) i w okresie badań (P) oraz średnie odpływy (mm) w okresie badań (H)

Years – Lata	Parameter Parametr	Period – Okres		
		N–A – XI–IV	M–O – V–X	N–O – XI–X
1961–1990*	\bar{P}	311	556	867
2000	P	316	546	862
	H	188	191	379
2001	P	370	802	1172
	H	216	290	506
Mean – Średnia 2000–2001	P	343	674	1017
	H	202	241	443

* precipitation recorded at the Gierałtowiec meteorological station – opady zanotowane na stacji meteorologicznej IMGW w Gierałtowiecach

In the first year of research, the annual outflow index was 127 mm lower than in the second year, but in both years it constituted ca 43% of precipitation. On average, the outflow in the

summer half-year was 39 mm higher than in the winter period. In the first year, however, the outflow in summer was higher only by 3 mm than in winter and accounted for almost 35% of precipitation, while in the second (very wet) year, the former was higher by 74 mm than the latter and constituted 36% of precipitation. On average, about 59% of precipitation flowed away in the winter half-year, compared to 36% in the summer period (Tab. 1).

Component loads

The annual PO_4^{3-} , Mg^{2+} , Mn^{2+} and $\text{Fe}^{2+/3+}$ loads per unit area, delivered by precipitation to the catchment, were small and ranged between 0.30 and 2.04 kg. The loads of N-NH_4 , N-NO_3 , Cl^- , Ca^{2+} , K and SO_4^{2-} reached several to several dozen kilograms per hectare. The largest loads deposited by precipitation were those of total suspended solids and dissolved substances – both of the order of hundreds $\text{kg} \cdot \text{ha}^{-1}$ (Tab. 2).

Table 2. Annual and seasonal loads of components ($\text{kg} \cdot \text{ha}^{-1}$) delivered by precipitation (LP) and carried away by outflow (LH)

Tabela 2. Roczne i okresowe ładunki składników ($\text{kg} \cdot \text{ha}^{-1}$) wnoszone z opadami (LP) i odprowadzane z odpływem (LH)

Components Składniki	Year Rok	Period – Okres					
		N–A – XI–IV		M–O – V–X		N–O – XI–X	
		LP	LH	LP	LH	LP	LH
Total suspended solids Zawiesina ogólna	2000	56.0	66.8	60.9	88.9	116.9	155.7
	2001	46.0	70.2	127.6	199.4	173.6	269.6
N-NH_4	2000	7.43	0.90	6.63	0.55	14.06	1.45
	2001	3.94	0.35	6.79	0.25	10.73	0.60
N-NO_3	2000	10.01	10.59	4.12	3.52	14.13	14.11
	2001	1.58	3.89	3.08	2.34	4.66	6.23
PO_4^{3-}	2000	0.44	0.44	1.15	0.53	1.59	0.97
	2001	0.22	0.37	0.62	0.95	0.84	1.32
Dissolved substances Substancje rozpuszczone	2000	170.2	337.4	176.3	345.6	346.5	683.0
	2001	91.5	393.3	593.4	504.7	684.9	898.0
SO_4^{2-}	2000	39.77	66.29	39.46	52.53	79.23	118.82
	2001	30.35	68.24	46.74	82.38	77.09	150.62
Cl^-	2000	14.48	24.64	1.62	27.11	16.10	51.75
	2001	4.96	30.29	3.35	27.06	8.31	57.35
Ca^{2+}	2000	–	–	–	–	–	–
	2001	5.56	55.03	7.63	64.20	13.19	119.23
Mg^{2+}	2000	–	–	–	–	–	–
	2001	1.30	10.73	0.74	11.62	2.04	22.35
K^+	2000	–	–	–	–	–	–
	2001	3.03	6.29	4.48	11.49	7.51	17.78
Mn^{2+}	2000	0.75	0.62	0.29	0.15	1.04	0.77
	2001	0.53	0.43	0.46	0.17	0.99	0.60
$\text{Fe}^{2+/3+}$	2000	0.09	0.48	0.21	0.55	0.30	1.03
	2001	0.27	0.66	0.47	1.61	0.74	2.27

In the winter half of the first year of research, despite the lower precipitation total, the delivery of almost all components was greater than in the second year, only that of $\text{Fe}^{2+/3+}$ was smaller. For the summer half-years the pattern was reversed: the amounts of the components, except N-NO_3 and PO_4^{3-} , were larger in the second year in which the precipitation total of the summer period was 47% higher than in the first year (Tab. 2).

As follows from a comparison of the loads delivered in the winter and summer halves of 2000, bigger amounts of N-NH_4 , N-NO_3 , SO_4^{2-} , Cl^- and Mn^{2+} were deposited in the former despite a 73% higher precipitation in the latter (Tab. 2), only the loads of total suspended solids, PO_4^{3-} , dissolved substances and $\text{Fe}^{2+/3+}$ were larger in the summer period. The year 2001, having an over twice higher precipitation in summer, showed a different pattern: the loads delivered in summer, except for Cl^- , Mg^{2+} and Mn^{2+} , were larger than those deposited in winter (Tab. 2).

The loads of the components depended more on their concentrations than on precipitation totals. This was evidenced not only by higher loads in the winter half of the first year, but also by the annual loads which, except for total suspended solids, dissolved substances and iron, were larger in the first than the second year, despite the 26% lower precipitation total of the former. The greatest difference was observed for N-NO_3 : the load deposited in 2000 was three times larger than in 2001. For the other components the differences ranged between ca 5% (Mn^{2+}) and over 93% (Cl^-). The loads of total suspended solids, dissolved substances and iron delivered in the second year were larger by ca 48, 98 and 147%, respectively, than in the first year (Tab. 2).

The loads carried away by the outflow water differed between the components. The annual loads of N-NH_4 , PO_4^{3-} , Mn^{2+} and $\text{Fe}^{2+/3+}$ did not exceed $2 \text{ kg} \cdot \text{ha}^{-1}$ on average, those of N-NO_3 amounted to ca $10 \text{ kg} \cdot \text{ha}^{-1}$, those of Mg^{2+} and K^+ were of ca $20 \text{ kg} \cdot \text{ha}^{-1}$, and the loads of Cl^- exceeded $50 \text{ kg} \cdot \text{ha}^{-1}$. The amounts of SO_4^{2-} and Ca^{2+} exceeded $100 \text{ kg} \cdot \text{ha}^{-1}$, and those of total suspended solids were twice as high. The largest loads removed by water from the catchment area were for dissolved substances (several hundred $\text{kg} \cdot \text{ha}^{-1}$; Tab. 2).

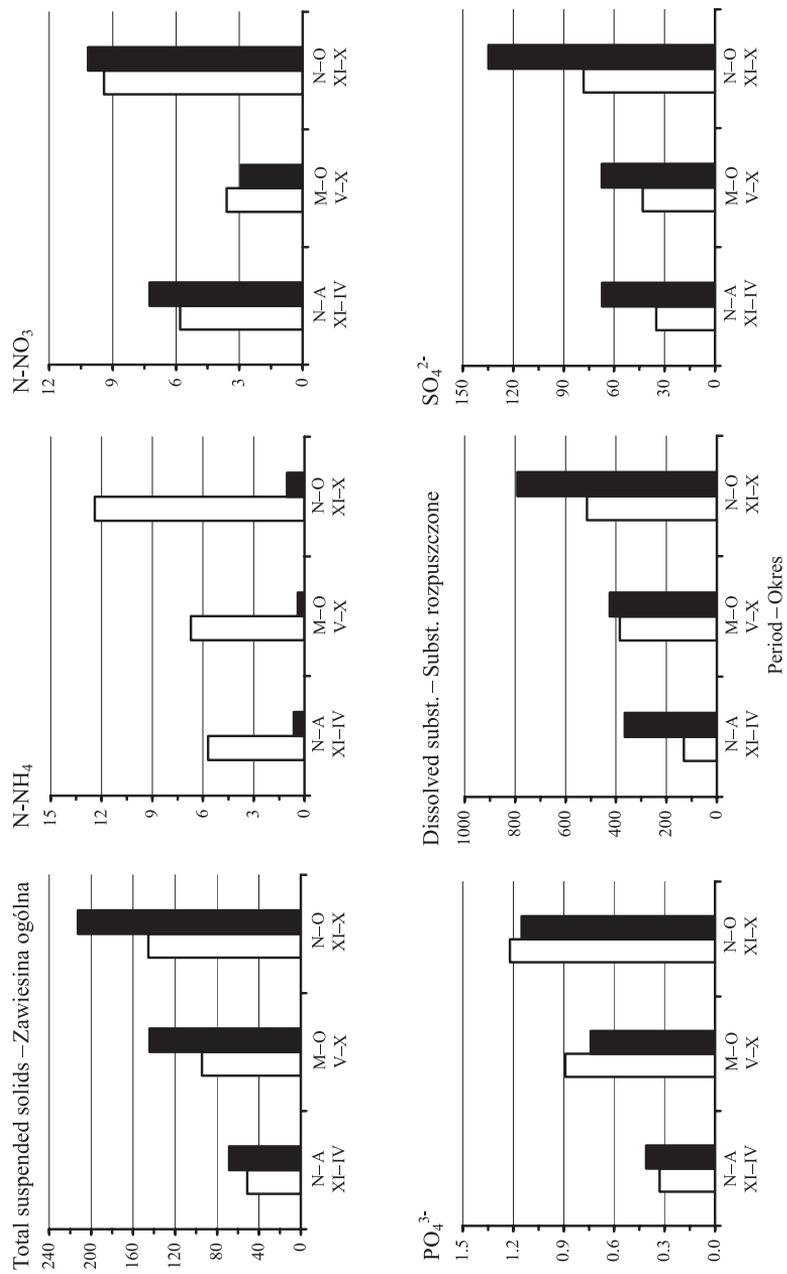
In the winter half-year, the loads of N-NH_4 , N-NO_3 , PO_4^{3-} and Mn^{2+} carried away by water were larger in the first year of research, despite the 13% lower winter outflow index, than in the second year, while the loads of other components were smaller (Tab. 2).

The loads of most components removed in the summer period were larger in the second year having a 52% higher summer outflow index than the first year, only the loads of N-NH_4 , N-NO_3 and Cl^- were lower (Tab. 2).

With almost identical outflows in the winter and summer of 2000 and a 74 mm higher outflow in the summer of 2001, larger loads of total suspended solids, PO_4^{3-} , dissolved substances and $\text{Fe}^{2+/3+}$ were deposited in the summer halves of both years, and larger loads of Ca^{2+} , Mg^{2+} and K^+ , in the second year. The loads of N-NH_4 , N-NO_3 , and Mn^{2+} were larger in the winter of both years, those of SO_4^{2-} in the first year, and those of Cl^- , in the second year (Tab. 2).

As suggested both by the semi-annual and annual loads of N-NH_4 , N-NO_3 and Mn^{2+} , which were higher in the first year despite its 25% lower outflow, the removal of those components was more dependent on their concentrations than on the volumes of outflow. The loads of other components reached higher values at larger outflows.

The means from the whole study period demonstrate that for most components the annual loads carried away by outflow waters were larger than those delivered by precipitation, except N-NH_4 , PO_4^{3-} and Mn^{2+} for which the former were lower than the latter by 11.37, 0.07 and $0.33 \text{ kg} \cdot \text{ha}^{-1}$, respectively (Fig.).



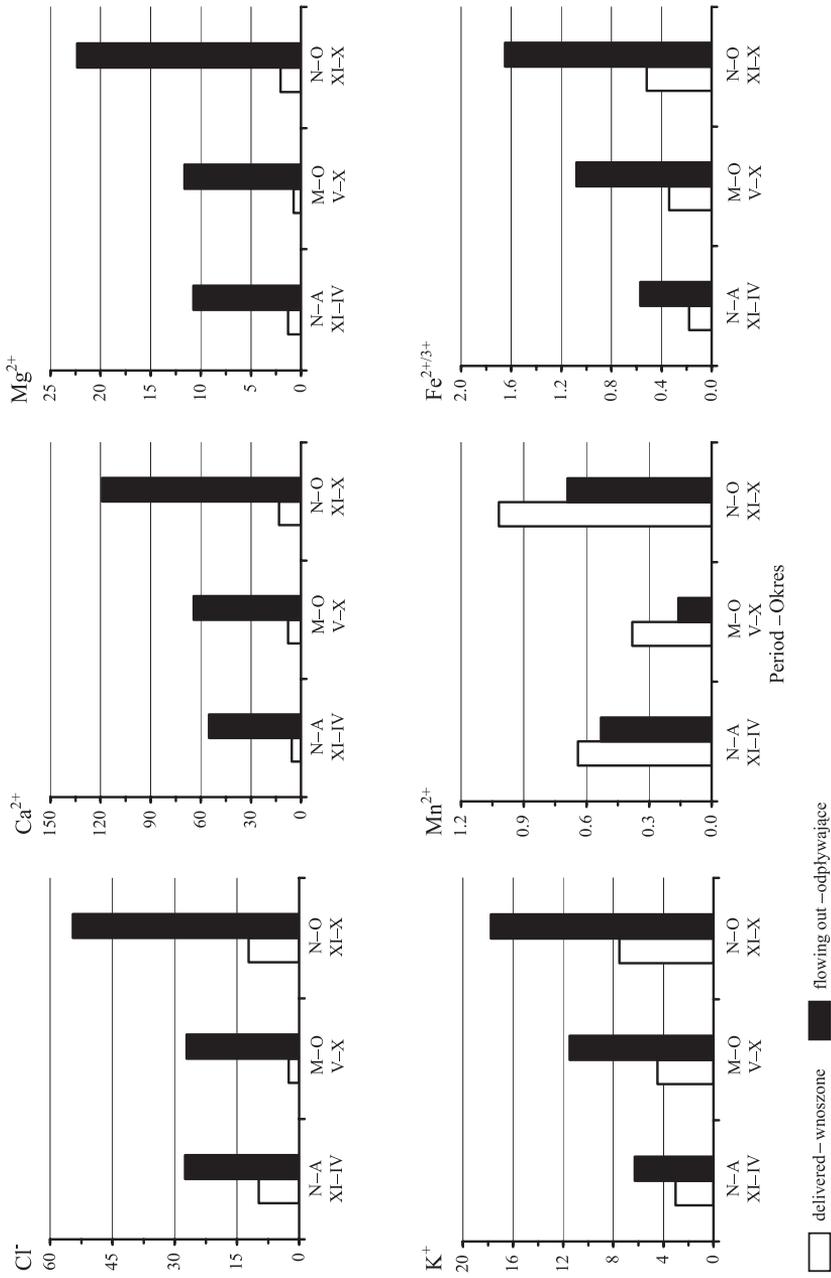


Fig. Annual and seasonal loads of components (kg·ha⁻¹) delivered by precipitation and carried away by outflow (mean of two-year study period)
 Rys. Roczne i okresowe ładunki składników (kg·ha⁻¹) wnoszonych z opadami i odprowadzanych z odpływem (średnia z dwuletniego okresu badań)

The winter results followed a similar pattern with the removed loads being larger than the deposited ones. The exceptions were only N-NH₄ and Mn²⁺ whose amounts delivered in the winter half-year were on average larger than those carried away by 5.06 and 0.11 kg·ha⁻¹, respectively (Fig.). In the summer period, the deposited loads of N-NH₄, N-NO₃, PO₄³⁻ and Mn²⁺ were larger than the removed loads by 0.15 kg·ha⁻¹ (PO₄³⁻) to 6.31 kg·ha⁻¹ (N-NH₄) (Fig.).

DISCUSSION

The amounts of total suspended solids removed yearly from the Włosień stream catchment were similar to those established by Szczepański et al. [1999]. The annual load of ammonium nitrogen, carried away by water, averaged 1.03 kg·ha⁻¹ and was about three times smaller than the value most frequently quoted in the literature [Bartoszewicz 1994, Solarska and Solarski 1996, Kanownik 2001, Żmuda et al. 2001]. The load of 12.40 kg of ammonium nitrogen delivered by water to the unit area of the catchment was similar to the loads measured in the areas of Kraków and Zręczyce [Krzemień et al. 1990], Sworzec near Wrocław [Szymańska 1990], and Rzyki near Andrychów [Rajda et al. 1994].

From the Włosień catchment, water carried away 10.17 kg of nitrate nitrogen per ha on average, which is close to the values usually reported in the literature to be several kilograms per ha [Bartoszewicz 1994, Rajda et al. 1995, Solarska and Solarski 1996]. In the mountain and submontane regions, the removed loads of this component may reach even several dozen kilograms [Rajda et al. 1994, Kanownik 2001].

The average amount of phosphates removed yearly from the study area, 1.15 kg·ha⁻¹, exceeded the levels reported from the Spiskie Plateau (0.37 kg·ha⁻¹) [Kanownik 2001], the Wielickie Plateau (0.35 kg·ha⁻¹) [Sarna and Jarzabek 1998], and the Mazurian Lake District (0.22 kg·ha⁻¹) [Solarska and Solarski 1996]. On the other hand, it was lower than the load removed from the polluted catchment of the Maskawa river (2.0 kg·ha⁻¹) [Murat-Błażejewska and Sojka 2002].

The loads of sulphates, chlorides, calcium, magnesium and iron removed by water were larger than those recorded in other regions of Poland [Solarska and Solarski 1996, Miler and Murat-Błażejewska 1997]. The amount of potassium removed from the catchment was higher than in the Mazurian Lake District [Solarska and Solarski 1996], on the Spiskie Plateau [Kanownik 2001] or in the Beskid Mały Mts [Rajda et al. 1995], but lower than the load carried away by the Wyskoć Rów waters from the Kościańska Plain [Bartoszewicz 1994].

On average, larger loads of manganese were deposited by precipitation in the Włosień catchment than were carried away by the waters flowing out of its area. Larger amounts of this component, both in precipitation and outflow, were noted in the winter half-year. The cause might be seen in the use of coal and slack for heating houses resulting in substantial emissions of manganese oxides into the atmosphere.

CONCLUSION

The annual loads of N-NH₄, N-NO₃ and SO₄²⁻ deposited to 1 ha of the catchment area were substantial, which indicates that precipitation constituted a significant source of non-point pollution.

In the year with average precipitation, larger loads of N-NH₄, N-NO₃, SO₄²⁻, Cl⁻ and Mn²⁺ were deposited in the winter half-year than in the summer period, despite the fact that the precipitation total of the former was about 42% lower. The loads of total suspended solids, PO₄³⁻, dissolved substances and Fe^{2+/3+} were larger in the summer half-year. In the year with a very humid summer having an over twice higher precipitation than winter, the loads deposited in the summer period were for most components, except Cl⁻, Mg²⁺ and Mn²⁺, larger than in the winter half-year.

The loads delivered by precipitation depended more on the concentrations of the components than on precipitation totals. This was suggested by the larger loads noted in the winter half of the first year of research and by the annual loads which, except for total suspended solids, dissolved substances and iron, were larger in this year despite its 26% lower precipitation total.

The annual loads carried away from the catchment ranged from 1 kg·ha⁻¹ to almost 270 kg·ha⁻¹, and for dissolved substances reached 900 kg·ha⁻¹. From among the components important for the environment and agriculture, N-NH₄ and PO₄³⁻ were removed in very small amounts, while the loads of N-NO₃ averaged ca 10 kg·ha⁻¹, and those of Mg²⁺ and K⁺, ca 20 kg·ha⁻¹.

The removed loads of N-NH₄, N-NO₃ and Mn²⁺ depended more on their concentrations than on the volumes of outflow. This was suggested by their semi-annual and annual values which were higher in the first year despite its 25% lower outflows. The loads of the other components were larger in the year with higher outflows.

For most components the mean annual loads carried away by outflow were larger than those deposited by precipitation. Only for ammonium nitrogen, phosphates and manganese the former were smaller than the latter.

The agricultural and animal-farming pattern of land use in the Włosień catchment contributes to the pollution of waters flowing out from this area. The loads of the components under study were higher than those recorded by other authors in catchments not subjected to the pressure associated with farm animal keeping.

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ŁADUNKI WYBRANYCH SKŁADNIKÓW CHEMICZNYCH WNOSZONYCH Z OPADAMI I ODPLYWAJĄCYCH ZE ZLEWNI POTOKU WŁOSIEN

Streszczenie. W pracy określono ładunki wybranych składników chemicznych deponowanych z opadami atmosferycznymi i odprowadzanych z odpływem z obszaru niewielkiej zlewni o rolniczo-hodowlanym typie użytkowania. Badania prowadzono w latach hydrologicznych 2000 i 2001 na terenie zlewni potoku Włosień w zachodniej części województwa małopolskiego. Próby wody do analizy pobierano dwa razy w miesiącu i oznaczano stężenie zawiesiny ogólnej, azotu amonowego i azotanowego, fosforanów, substancji rozpuszczonych, siarczanów, chlorków, wapnia, magnezu,

potasu, manganu i żelaza. Wartości stężeń oraz zmierzone wartości opadów i odpływów wykorzystano do obliczenia ładunków poszczególnych składników. Wynoszone z obszaru zlewni średnie roczne ładunki N-NH_4 , PO_4^{3-} , Mn^{2+} i $\text{Fe}^{2+/3+}$ nie przekraczały $2 \text{ kg} \cdot \text{ha}^{-1}$, ładunki N-NO_3 kształtowały się na poziomie ok. $10 \text{ kg} \cdot \text{ha}^{-1}$, ładunki Mg^{2+} i K^+ wynosiły ok. $20 \text{ kg} \cdot \text{ha}^{-1}$, a ładunki Cl^- przekraczały $50 \text{ kg} \cdot \text{ha}^{-1}$. W większej ilości wynoszone były SO_4^{2-} i Ca^{2+} – ponad $100 \text{ kg} \cdot \text{ha}^{-1}$ i zawiesina ogólna – ponad $200 \text{ kg} \cdot \text{ha}^{-1}$. Najwięcej z obszaru zlewni odpływało z wodą substancji rozpuszczonych – $791 \text{ kg} \cdot \text{ha}^{-1}$. Ładunki składników wnoszonych przez opady, z wyjątkiem azotu amonowego, fosforanów i manganu, były mniejsze od odprowadzanych z odpływem. Porównanie otrzymanych wyników z wynikami innych badań potwierdziło, że rolniczo-hodowlane użytkowanie zlewni wpływa na zanieczyszczenie wód powierzchniowych: ładunki składników odpływających z obszaru zlewni potoku Włosień były większe niż w przypadku zlewni nie poddanych presji związanej z chowem zwierząt gospodarskich.

Słowa kluczowe: zlewnia, opady, odpływ, ładunki, składniki chemiczne

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