

LOADS OF SELECTED CHEMICAL COMPONENTS DELIVERED BY PRECIPITATION AND FLOWING AWAY FROM WRONOWIEC MICROCATCHMENT

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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 partly built-up microcatchment with agriculture and animal farming dominating in its land-use pattern. The research was conducted in the hydrological years 2000 and 2001 within the microcatchment of the Wronowiec watercourse, 1.60 km² in area, situated 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 results obtained corroborated the thesis that atmospheric precipitation constitutes an important source of non-point pollution. The loads of components carried away by outflow were larger than those delivered by rainfall, except manganese and phosphates for which the former were smaller than the latter. The results provided a further evidence to prove that rural settlement and animal farming with poor sanitation contribute substantially to the pollution of outflow waters.

Keywords: microcatchment, precipitation, outflow, loads, chemical components

INTRODUCTION

Besides draining water from the area of a catchment, watercourses transport rock- and soil-weathering products. They carry also dissolved substances supplied by underground waters, municipal and industrial sewage discharges and surface runoffs [Żmuda et al. 2001, Szewrański et al. 2004]. Precipitation, whose role in shaping the quality of surface waters was long underestimated, has an important part in delivering chemical components to such waters [Szymańska 1990, Rajda et al. 1995].

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The study aimed to determine the loads of selected chemical components deposited by precipitation and carried away by outflow waters from the area of an agricultural microcatchment used also for animal farming and housing purposes.

MATERIAL AND METHODS

The research was conducted from November 1999 to October 2001 within the area of the Wronowiec microcatchment situated in the western part of the Małopolska province, in the Wadowice county near the town of Andrychów.

The microcatchment has an area of 1.60 km² and is closed by a gauging section on the watercourse (4th order) which is the right-bank tributary of the Skawa river. The microcatchment lies within the 318–426 m a.s.l. hypsometric range and has the average land slope of 7.4%.

The soils are mostly silts and clayey silts, and only in some places silty clays and loams. Agricultural land covers 130.11 ha, of which arable land accounts for over 64% and grassland for ca 33%, the rest is under orchards. Forests and tree plantations constitute ca 10% of the catchment area and occur along the main watercourse and in pieces of land with greater slopes.

Besides private farms there is also a horse, cattle (ca 285 head) and poultry (30 000 head) farm in the area. The farm employs an indoor management system for cattle. Slurry is used for fertilising the farm's grassland, and farmyard manure is used on arable land. Mineral fertiliser rates on private farms (ca 2.50 ha each) range between 90 and 120 kg NPK · ha⁻¹. Such farms use also farmyard manure, slurry and household wastes for fertilisation purposes.

In order to determine the volume of water flowing away from the catchment area, a complex weir of a triangle-trapezoid type was built in the gauging section. The water level was read once a day (or three times a day in the periods of a sudden water rise) from a staff gauge installed by the weir. Using the rating curve, the mean daily discharges were determined (in dm³ · s⁻¹) and then converted into outflow indices (in mm). To measure the amount of rainfall, a precipitation station equipped with a water catcher and Hellman's pluviometer was established within the Wronowiec catchment.

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 by standard procedures 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 or carried away by outflow. The load of each component (in kg · 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 320 m a.s.l. were compared with the multiannual mean from the meteorological station located in Andrychów (340 m a.s.l.), 1.5 km from the microcatchment.

The precipitation totals differed between the hydrological years (Tab. 1). In 2000, the precipitation was 247 mm lower than in 2001, with the difference to the disadvantage of the former being only 11 mm for the winter half-year and as much as 236 mm for the summer half-year. As the mean annual precipitation total for the two-year period of observations was 144 mm higher than the multiannual mean, this period may be considered as wet. The first year with the rainfall only 20 mm higher than the multiannual mean counted as an average year in precipitation terms, while the second year, whose precipitation total was 267 mm higher than the mean, could be treated as very wet. The winter period (November–April) accounted for 40.0% of the annual total in the first year and for 32.5% in the second year. The winter halves of both hydrological years were wet. The summer periods (May–October) followed the pattern of the respective hydrological years, being 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
1961–1980*	\bar{P}	310	606	916
2000	P	374	562	936
	H	288	230	518
2001	P	385	798	1183
	H	272	389	661
Mean – Średnia 2000–2001	P	380	680	1060
	H	280	310	590

* precipitation recorded at the Andrychów meteorological station – opady zanotowane na stacji meteorologicznej IMGW w Andrychowie

In the first year of research, the total annual outflow was 143 mm lower than in the second year, but in both years it accounted for over 55% of precipitation. On average, the outflow in the summer half-year was 30 mm higher than in the winter period. However, in the first year the outflow in summer was 58 mm lower than in winter and constituted almost 41% of total precipitation, whereas in the second (very wet) year the former was higher than the latter by 117 mm and accounted for nearly 49% of precipitation. On average, in the winter half-year ca 74% of precipitation flowed away, whereas in the summer half-year it was 46% (Tab. 1).

Component loads

The annual Mg^{2+} , Mn^{2+} and $Fe^{2+/3+}$ loads, delivered by precipitation to the microcatchment, were small and ranged from 0.59 to 2.49 kg per hectare. The loads of $N-NH_4$, $N-NO_3$, PO_4^{3-} , Cl^- , Ca^{2+} and K^+ were of several kilograms to over ten kilograms per ha, while those of SO_4^{2-} reached several dozen $kg \cdot ha^{-1}$. The components delivered in largest amounts were total suspended solids and dissolved substances (Tab. 2).

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

Tabela 2. Roczne i okresowe ładunki składników ($kg \cdot ha^{-1}$) 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	137.3	69.3	51.8	92.7	189.1	162.0
	2001	55.3	61.4	106.2	199.8	161.5	261.2
$N-NH_4$	2000	4.48	4.95	8.19	13.79	12.67	18.74
	2001	2.95	4.64	8.88	1.98	11.83	6.62
$N-NO_3$	2000	6.74	11.79	10.23	9.46	16.97	21.25
	2001	2.74	3.75	3.36	3.65	6.10	7.40
PO_4^{3-}	2000	0.40	1.64	4.95	2.85	5.35	4.49
	2001	1.46	0.83	3.84	2.62	5.30	3.45
Dissolved substances Substancje rozpuszczone	2000	112.1	1038.4	96.8	1005.6	208.9	2044.0
	2001	146.4	963.4	250.8	1210.5	397.2	2173.9
SO_4^{2-}	2000	37.33	188.75	33.28	128.22	70.61	316.97
	2001	24.05	168.77	35.15	172.58	59.20	341.35
Cl^-	2000	14.18	75.76	0.56	77.03	14.74	152.79
	2001	6.16	60.35	2.25	47.82	8.41	108.17
Ca^{2+}	2000	–	–	–	–	–	–
	2001	5.09	164.44	6.36	171.77	11.45	336.21
Mg^{2+}	2000	–	–	–	–	–	–
	2001	1.42	25.43	1.07	25.57	2.49	51.00
K^+	2000	–	–	–	–	–	–
	2001	2.15	12.71	4.61	18.58	6.76	31.29
Mn^{2+}	2000	1.05	0.84	0.72	0.82	1.77	1.66
	2001	0.69	0.59	0.84	0.12	1.53	0.71
$Fe^{2+/3+}$	2000	0.29	0.55	0.30	0.65	0.59	1.20
	2001	0.09	0.69	0.97	0.45	1.06	1.14

In winter half-years, which had similar precipitation totals, the inflow of the components, except PO_4^{3-} and dissolved substances, was larger for the first year. By contrast, the loads deposited by precipitation in summer half-years, except those of $N-NO_3$ and PO_4^{3-} , were greater for the second year in which the precipitation total of the summer period was 42% higher than in the first year (Tab. 2).

Comparing the loads supplied in the winter and summer halves of the first year, it can be seen that the former, except for N-NH_4 , N-NO_3 , PO_4^{3-} , were larger than the latter, despite the ca 50% higher precipitation total of the summer period (Tab. 2). In the second year, having an over twice higher precipitation in summer than in winter, the amount of precipitation markedly affected the loads of components: the ones delivered in summer, except for Cl^- and Mg^{2+} , exceeded those deposited in winter (Tab. 2).

The loads of the components under study were more dependent on their concentrations than on precipitation totals, as indicated not only by higher loads in the winter half of the first year of research, but also by the annual values which, except for dissolved substances and iron, were bigger in the first year despite its 21% lower precipitation total. The most substantial difference (over 178%) was shown by N-NO_3 deposition, the other differences ranged between ca 1% (PO_4^{3-}) and over 75% (Cl^-). The loads of dissolved substances and iron were bigger in the second year, by 90 and 80% respectively, than in the first year (Tab. 2).

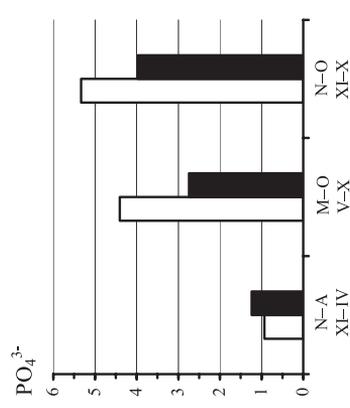
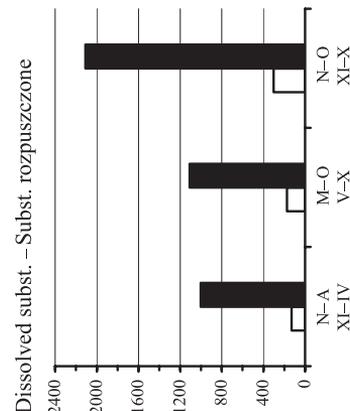
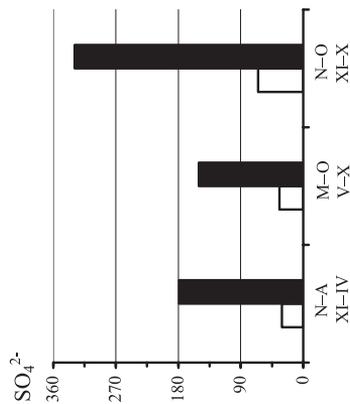
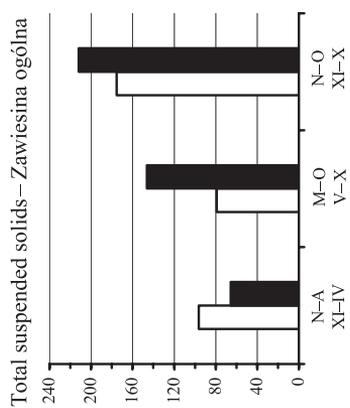
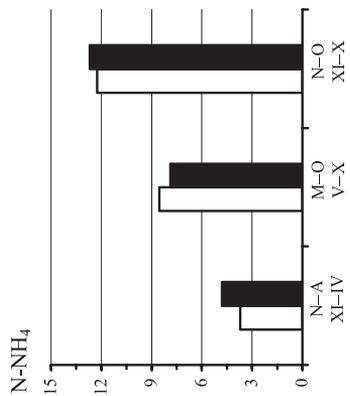
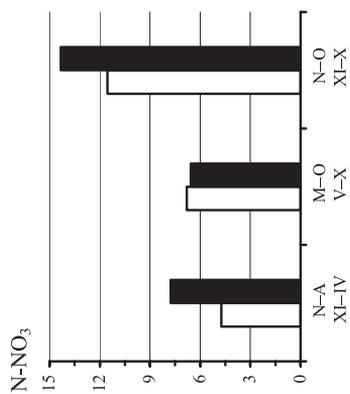
The annual loads of the components carried away by outflow from the microcatchment area differed widely. Those of Mn^{2+} and $\text{Fe}^{2+/3+}$ did not exceed 2 kilograms per hectare, the loads of N-NH_4 , N-NO_3 and PO_4^{3-} were between several and ca $20 \text{ kg} \cdot \text{ha}^{-1}$, whereas those of Mg^{2+} and K^+ reached several dozen kilograms. The loads of the other components, carried away from the catchment, had higher values: suspended solids and Cl^- – over 100 and $200 \text{ kg} \cdot \text{ha}^{-1}$ respectively, SO_4^{2-} and Ca^{2+} – over $300 \text{ kg} \cdot \text{ha}^{-1}$, and were highest (ca $2000 \text{ kg} \cdot \text{ha}^{-1}$) for dissolved substances (Tab. 2).

In the winter half-year, the amounts carried away were for almost all components larger in the first year of research (having a 6% higher winter outflow index) than in the second year: from over 6% (N-NH_4) to over 214% (N-NO_3), only the load of $\text{Fe}^{2+/3+}$ was slightly smaller (Tab. 2). Although the summer half of the second year had a 69% higher outflow index than the same period of the first year, only suspended solids, dissolved substances and SO_4^{2-} were then carried away in larger amounts, whereas the loads of other components were smaller than in the first year's summer period (Tab. 2).

A comparison of the amounts of components carried away from the catchment in the winter and summer half-years differing in the value of the outflow index (a lower summer value in the first year and a much lower winter value in the second year) did not reveal any clear relationship between the removed loads and the outflow volumes. Higher values of loads in the summer period were noted for suspended solids and PO_4^{3-} in both years, for N-NH_4 , Cl^- and $\text{Fe}^{2+/3+}$ – in the first year, and for dissolved substances, SO_4^{2-} , Ca^{2+} , Mg^{2+} and K^+ – in the second year; the other values were higher in winter. The amounts of N-NO_3 and Mn^{2+} were larger in the winter periods of both study years.

The results suggest that the removed loads depended more on the concentrations of the components than on the volumes of outflow. This can be seen not only in the semi-annual values but also in the annual loads which for most components were larger in the first year – from 5% ($\text{Fe}^{2+/3+}$) to over 187% (N-NO_3) – despite its 22% lower outflows. Only the loads of total suspended solids, dissolved substances and SO_4^{2-} were larger in the second year, by ca 61, 6 and 8% respectively, than in the first year.

As regards the means calculated over the two-year research period, the annual loads carried away by outflow were larger than those delivered by precipitation, with the exception of PO_4^{3-} and Mn^{2+} for which the former were lower than the latter by 1.36 and $0.46 \text{ kg} \cdot \text{ha}^{-1}$ respectively (Fig.). The figures for individual years, however, presented



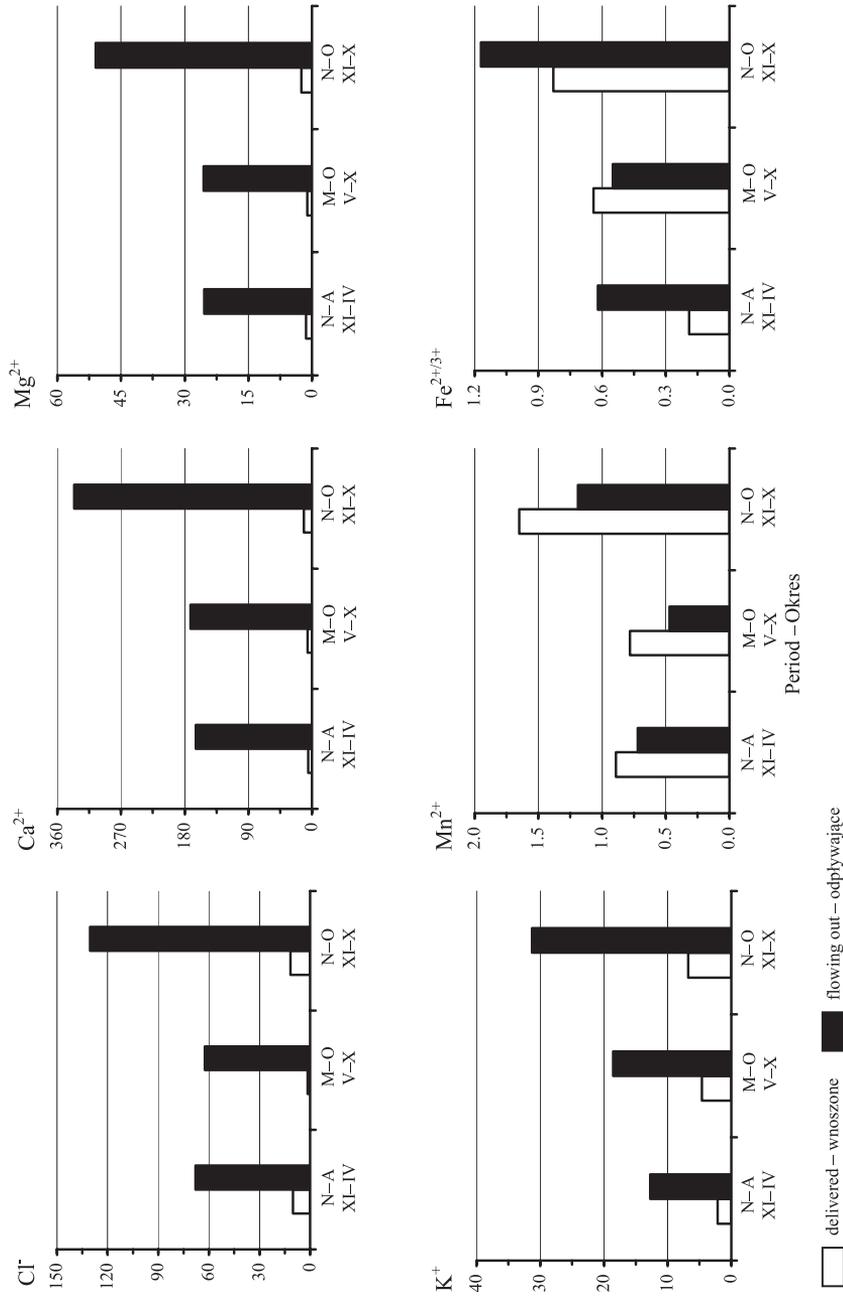


Fig. Annual and seasonal loads of components (kg·ha⁻¹) delivered by precipitation and carried away by outflow (mean of two-year study period)
 Rys. Roczne i okresowe ładunki składniki (kg·ha⁻¹) wnoszonych z opadami i odprowadzanych z odpływami (średnia z dwuletniego okresu badań)

a somewhat different picture: the removal of total suspended solids was smaller than the delivery in the first year, and that of N-NH_4 , in the second year (Tab. 2).

The two-year means for the winter half-year followed the pattern of the annual averages, except for total suspended solids and Mn^{2+} whose deposition in this period was larger than removal by 31 and 0.15 $\text{kg} \cdot \text{ha}^{-1}$ respectively (Fig.). In the summer period, the delivered loads of N-NH_4 , N-NO_3 , PO_4^{3-} , Mn^{2+} and $\text{Fe}^{2+/3+}$ were slightly higher than those carried away: by 0.09 $\text{kg} \cdot \text{ha}^{-1}$ ($\text{Fe}^{2+/3+}$) to 1.66 $\text{kg} \cdot \text{ha}^{-1}$ (PO_4^{3-}) (Fig.).

DISCUSSION

The loads of total suspended solids, flowing away from the Wronowiec microcatchment, are similar to those reported by Szczepański et al. [1999]. Outflow waters carried yearly away 12.68 kg of ammonium nitrate per ha on average, which is several times larger than the figures given by other authors, generally not exceeding 3.0 $\text{kg} \cdot \text{ha}^{-1}$ [Bartoszewicz 1994, Solarska and Solarski 1996, Sarna and Jarzabek 1998, Kanownik 2001, Żmuda et al. 2001]. The amount of ammonium nitrogen delivered annually to the microcatchment area, 12.25 $\text{kg} \cdot \text{ha}^{-1}$, is similar to the amounts found in the regions of Kraków and Zręczycze [Krzemień et al. 1990], Sworzec near Wrocław [Szymańska 1990], and Rzyki near Andrychów [Rajda et al. 1994].

The annual loads of nitrate nitrogen carried away from the microcatchment averaged 13.33 $\text{kg} \cdot \text{ha}^{-1}$. To compare, the loads recorded most often are at a level of several kilograms [Bartoszewicz 1994, Rajda et al. 1995, Solarska and Solarski 1996], in some cases, i.e. in mountain and submontane areas, they may reach even several dozen kilograms [Rajda et al. 1994, Kanownik 2001].

Phosphates were removed in an amount of ca 4.0 $\text{kg} \cdot \text{ha}^{-1}$ per year, which substantially exceeds the values obtained under different conditions. Namely, the annual outflow of phosphates from the Spiskie Foothills is 0.37 $\text{kg} \cdot \text{ha}^{-1}$ [Kanownik 2001], from the Wielickie Foothills – ca 0.35 $\text{kg} \cdot \text{ha}^{-1}$ [Sarna and Jarzabek 1998], from the Mazurian Lake District – 0.22 $\text{kg} \cdot \text{ha}^{-1}$ [Solarska and Solarski 1996], and from the polluted catchment of the Maskawa river – ca 2.0 $\text{kg} \cdot \text{ha}^{-1}$ [Murat-Błażejewska and Sojka 2002].

The loads of phosphates, chlorides, calcium, magnesium and iron flowing away from the study catchment were larger than in other regions of Poland [Solarska and Solarski 1996, Miler and Murat-Błażejewska 1997]. Potassium was removed in a greater amount than in the Mazurian Lake District [Solarska and Solarski 1996], the Spiskie Foothills [Kanownik 2001] and the Beskid Mały Mts [Rajda et al. 1995], but its load was smaller than that carried away by the Wyskoć Rów waters from the Kościńska Plain [Bartoszewicz 1994].

Under the conditions of the Wronowiec microcatchment, greater amounts of manganese, on average, reached this area with rainfall than were carried away by the watercourse. The loads of this component, both in precipitation and outflow, were larger in the winter half-year than in the summer period. This might have resulted from heating houses with coal and slack causing considerable emissions of manganese oxides into the atmosphere.

CONCLUSION

The loads of ammonium nitrogen, nitrate nitrogen and sulphates deposited yearly to 1 ha of the microcatchment area were substantial, which supports the thesis that precipitation is an important source of non-point pollution.

In the year with average precipitation, larger loads of N-NH₄, N-NO₃ and phosphates were deposited in the summer half-year and of the other components, such as total suspended solids, dissolved substances, sulphates, chlorides, calcium, magnesium, potassium, manganese and iron, in the winter period. In the year with a very wet summer, the loads of the components, except for Cl⁻ and Mg²⁺, delivered in this period were larger than those deposited in winter.

The amounts of components carried away from the microcatchment by outflow ranged from ca 1 to over 300 kg · ha⁻¹ per year, and for dissolved substances they exceeded 2000 kg · ha⁻¹. The annual loads of the components important for the environment and agriculture averaged several kilograms (PO₄³⁻), between ten and twenty kilograms (N-NH₄ and N-NO₃), or several dozen kilograms (Mg²⁺ and K⁺) per hectare.

For most components the loads carried away by outflow were greater than those deposited by rainfall. The exceptions were Mn²⁺ and PO₄³⁻ for which the former were smaller than the latter.

The land-use pattern of the Wronowiec microcatchment – agriculture, animal farming and housing – is an important contributing factor to the pollution of waters flowing out of this area: the loads of the components under study were higher than in other regions of Poland.

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ŁADUNKI WYBRANYCH SKŁADNIKÓW CHEMICZNYCH WNOSZONYCH Z OPADAMI I ODPLYWAJĄCYCH Z MIKROZLEWNI CIEKU WRONOWIEC

Streszczenie. W pracy określono ładunki wybranych składników chemicznych deponowanych z opadami atmosferycznymi i odprowadzanych z odpływem z obszaru mikrozwlewni osadniczo-rolniczo-hodowlanej. Badania prowadzono w latach hydrologicznych 2000 i 2001 na terenie mikrozwlewni ciek Wronowiec, o powierzchni 1,60 km², położonej 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. Otrzymane wyniki potwierdziły tezę, że opady atmosferyczne stanowią liczące się źródło zanieczyszczeń obszarowych. Ładunki składników wynoszonych z odpływem okazały się większe od ładunków wnoszonych przez opady; odstępstwem od tej reguły było mniejsze wynoszenie manganu i fosforanów. Uzyskane wyniki potwierdziły, że osadnictwo wiejskie oraz chów zwierząt przy nieuporządkowanej gospodarce wodno-ściekowej przyczyniają się silnie do zanieczyszczenia odpływających wód.

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

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