

# MASS BALANCE OF WATER QUALITY PARAMETERS IN SMALL BASINS

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The aim of this contribution is to evaluate and analyze nutrients and other chemical substances in rain-, surface, and soil water, in the three experimental microbasins operated by the Institute of Hydrology, SAS, with different vegetation cover and land-use practices. The period of observations covered the years 1991–1993. Another objective of our research was mass balancing of pollutants found in the precipitation water and in the runoff from the three model microbasins.

## Material

Water quality observations in three experimental microbasins near Povazska Bystrica were commenced by the Institute of Hydrology, Slovak Academy of Sciences in 1986. In the Rybarik, Lesny and Cingelova microbasins, which are characterized by different land-use practices (forested, agricultural) seven water quality variables (pH, EC,  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , Cl<sup>-</sup>, and  $\text{SO}_4^{2-}$ ) were monitored. The water samples were taken from: (i). rain water; (ii). stemflow under the tree canopy; (iii). the organic–humus topsoil layer; (iv). drainage water; and (v) surface water.

From 1991 to 1993 the water quality analyses were extended to cover additional species ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Zn}^{2+}$ ) and water hardness and alkalinity. In 1991, 276 samples were taken and analyzed, in 1992 the number of analyzed samples increased up to 289, and in 1993 there were 117 samples analyzed.

## Methods

Mass balancing of nitrates in the water cycle of a drainage basin (e.g. hydrologically closed basin) is defined in this study as a difference between its input by atmospheric water (precipitation) and output of the basin (runoff) for chosen time intervals (Pekarova and Miklanek 1999). The total annual balance of the selected substances in the water cycle of the basins can be expressed as follows

$$L_{Dif} = L_{Prec} - L_{Run} \quad (1)$$

where:

$L_{Prec}$  - input load from precipitation (total deposit) [ $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ ];

$L_{Run}$  - output load in the stream water [ $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ ];

$L_{Dif}$  - difference between input and output loads (mass balance) [ $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ ].

The total deposit (both dry and wet)  $L_{prec}$  in the basin was calculated from daily precipitation  $P$  over the three basins, and from measured concentrations of chemical substances  $C$  in the precipitated water. Annual deposit of substances  $L_{prec}$  [ $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ ] was calculated as:

$$L_{Prec} = \sum_{i=1}^p P_i C_i \quad (2)$$

where:

- $i$  – number of samples from precipitation water in a year;
- $p$  – number of precipitation events;
- $P_i$  – precipitation depth at the time of sampling [mm];
- $C_i$  – substance concentration in  $i$ -th sample [ $\text{mg}\cdot\text{dm}^{-3}$ ].

The annual volume of substances in runoff from a unit area (Konicek et al, 1997; Pekarova *et al*, 2005; Baca and Konicek, 2003) can be expressed as:

$$L_{Run} = \sum_{i=1}^{12} C_i \cdot R_i k \quad (3)$$

where:

- $C_i$  - substance concentration in stream water in  $i$ -th month [ $\text{mg}\cdot\text{dm}^{-3}$ ];
- $R_i$  - monthly runoff depth [mm];
- $k$  - conversion constant.

## Results

### Calculation of the precipitation deposit

For the sake of the mass balance in the precipitation water of the forested microbasins, it was necessary to determine the amounts of water captured by interception during the individual months of the vegetation season (Halmova *et al.*, 2006). The interception amounts in the Lesny microbasin (hornbeam forest) fluctuated between 15% in September to 51% in August; and in the Cingelova microbasin (spruce forest), from 32% in March to 58% in August. For the Lesny microbasin, in the months November through March, 8% was subtracted from the open area rainfall amount as the stemflow. The annual deposit  $L_{prec}$  by precipitation in 1992 was calculated according (2) and is shown in table 1.

In the Rybarik agricultural microbasin, the depositions are fairly higher, except for  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ , while these were higher in the Cingelova basin. Most of the quality variables show lower depositions in the Lesny basin. Difference has been observed in the case of potassium, when rainfall water in the forested basins is enriched by this element compared to the agricultural basin. Potassium is washed out from the vegetation tissues, mainly the leaves during the throughfall through the tree canopy (Konicek and Roncak, 1992; Roncak, 1993; Skrivan *et al.* 2004; Fisak 2006).

Table 1. Annual deposition  $L_{prec}$  of chemical substances in the studied microbasins in 1992 [ $\text{kg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ ]

Basin	$\text{NH}_4^+$	$\text{NO}_2^-$	$\text{NO}_3^-$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Cl}^-$	$\text{Na}^+$	$\text{K}^+$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$
Rybarik	13.6	1.4	30.6	148.2	18.1	33.3	5.2	6.4	175.7	234.7
Lesny	13.6	1.4	11.3	81.6	10.7	17.6	3.3	19.6	152.3	117.9
Cingelova	15.0	1.6	20.6	131.2	15.3	22.6	7.0	18.4	202.6	207.2

## Calculation of wash-out amounts

The amount of substances transported by the streams out from the basins  $L_{Run}$  [kg·ha<sup>-1</sup>·y<sup>-1</sup>] was calculated from concentrations measured in stream water  $C$  and from monthly runoff depths  $R$  in 1992. The annual amount of substances washed out by the streams in 1992 is depicted in Table 2 for the three basins. Higher amounts of substances are released from the Rybarik agricultural basin, whereas lower values were observed in the Lesny forested basin. If we compare the two forested basins we can notice a higher wash-out rate in the Cingelova basin compared to the Rybarik microbasin, with the exception of  $NH_4^+$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $Na^+$ .

Table 2. Annual wash – out  $L_{Run}$  in the stream water in the studied microbasins in 1992 [kg·ha<sup>-1</sup>·y<sup>-1</sup>]

Basin	$NH_4^+$	$NO_2^-$	$NO_3^-$	$Ca^{2+}$	$Mg^{2+}$	$Cl^-$	$Na^+$	$K^+$	$SO_4^{2-}$	$HCO_3^-$
Rybarik	1.4	0.2	90.5	161.0	27.4	53.0	11.9	4.4	221.9	138.9
Lesny	0.81	0.03	4.72	82.99	20.1	12.1	8.28	1.3	114.5	118.6
Cingelova	0.33	0.03	43.2	129	17	12	7.38	1.6	118.6	148.9

## Balance of water quality parameters in experimental microbasins

The results of the balance of water quality parameters in the three microbasins are indicated in table 3. One can assume that the wash-out of the substances in the agricultural basin is higher than in the input. Only  $NH_4^+$ ,  $NO_2^-$ ,  $K^+$  and  $HCO_3^-$  accumulate in the basin. The wash – out of most substances, mainly nitrates, sulphates and chlorides contributes to deterioration of the stream water in the Rybarik agricultural basin. Conversely, the analyzed substances are accumulated in forested basins, except for  $Mg^{2+}$  which is washed out in both forested basins (elevated wash-out rate in the Lesny basin). The Lesny basin releases elevated amounts of  $Ca^{2+}$ ,  $Na^+$ , and  $HCO_3^-$ ; and the Cingelova basin releases higher amounts of  $NO_3^-$ .

Table 3. Balance of chemical substances  $L_{Diff}$  in the studied microbasins in 1992 [kg·ha<sup>-1</sup>·y<sup>-1</sup>]

Basin	$NH_4^+$	$NO_2^-$	$NO_3^-$	$Ca^{2+}$	$Mg^{2+}$	$Cl^-$	$Na^+$	$K^+$	$SO_4^{2-}$	$HCO_3^-$
Rybarik	12.2	1.2	-59.9	-12.8	-9.3	-19.8	-6.6	2.0	-46.3	95.9
Lesny	12.7	1.4	6.6	-1.4	-9.3	5.5	-5.0	18.3	37.8	-0.7
Cingelova	14.7	1.5	-22.6	2.3	-1.7	10.6	-0.4	16.8	84.0	58.3

## Conclusions

The highest transport of the observed substances comes from the agriculturally utilized microbasin Rybarik, while lower amounts were observed in the Lesny microbasin. Comparing the two forested basins, the higher transport rate is in the Cingelova basin, with the exception of  $NH_4^+$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $Na^+$ , when the transport from Lesny microbasin was slightly higher or balanced.

Most of the observed substances are washed out from the agriculturally utilized microbasin. Accumulation was observed only in  $NH_4^+$ ,  $NO_2^-$ ,  $K^+$  and  $HCO_3^-$ . Release of the majority of the monitored substances, mainly nitrates, sulphates and chlorides, deteriorates the runoff water quality in the Rybarik microbasin. Conversely, in the forested microbasins, majority of the monitored substances are captured. However, an exception has been observed in  $Mg^{2+}$ , which is released from both of the forested microbasins; from the Lesnybasin at considerably higher rates than from the Cingelova microbasin. In the Lesny basin, a loss of  $Ca^{2+}$ ,  $Na^+$ , and  $HCO_3^-$  was observed; whereas in the Cingelova basin a fairly high loss of  $NO_3^-$  has been found.

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