# Experimental Research and Mathematical Modeling of Nutrients Release in a Small Watershed

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# Experimentelle Forschung und mathematische Modellierung des Nährstoffaustrags an einem kleinen Einzugsgebiet

## 1 Introduction

The problem of water body eutrophication due to the incoming of nutrients (mainly nitrogen and phosphorus compounds) to the aquatic environments remains one of the most relevant for water quality issues. While point sources of nutrients are controlled in Ukraine through legislation, diffuse pollution practically is not estimated. Meanwhile, a considerable number of studies had shown the main contribution of diffuse sources, especially from agricultural lands, to elevate nutrients concentration (Khrisanov & Osipov, 1993; Behrendt et al., 2000; De Klein & Koelmans, 2011). Arable lands within Ukraine cover more than 70 %; therefore, this factor is expected to be the dominant source of nutrient pollution.

A number of models (ARM, CREAMS, SWAT etc.) have been created to successfully simulate the leaching of nutrients from watersheds. Wide use of these models in Ukraine is restrained by lack of a significant amount of input parameters.

Thereby, development of reliable and, at the same time, sufficiently simple methods to assess natural leaching of

### Zusammenfassung

Die Quantifizierung des Nährstoffaustrags in Flüsse ist für viele wissenschaftliche und praktische Fragestellungen wichtig. Während der Schneeschmelzperiode wurde in einem Feldexperiment die Nährstoffauswaschung untersucht. Dabei wurde ein zehnfacher Austrag von Stickstoff N gegenüber Phosphor P festgestellt. Die Mobilisierung beider Stoffe ist eng mit den hydrologischen Eigenschaften verknüpft. Während Stickstoff sowohl im Direktabfluss wie auch im Zwischenabfluss vorkommt, ist Phosphor hauptsächlich in zweiterem enthalten. Im Beitrag wird ein Algorithmus zur Beschreibung der N und P Mobilisierung vorgestellt. Die Modellgüte erreichte dabei einen Nash-Sutcliffe Koeffizienten von 0.7 bis 0.86. Die Methode kann bei ungenügender Datenlage hinsichtlich N und P angewandt werden.

**Schlagwörter:** Stickstoff, Phosphor, Plot Skale, Simulation.

### Summary

Quantification of nutrients emissions into rivers is important for many scientific and practical purposes. The field experiment was carried out at the small plot scale during a snowmelt period to understand the characteristic of nutrients export from the watershed. It is observed that emission of nitrogen is 10 times higher compared to phosphorous. Both nitrogen and phosphorus release is closely related to the hydrological parameters. While nitrogen is almost evenly distributed between direct flow and interflow, phosphorus comes mainly with the last. The algorithm for simulation of N and P release during snowmelt conditions was presented. The simulation accuracy was assessed based on Nash-Sutcliffe coefficient, which resulted in 0.7 and 0.86 for N and P, respectively. The presented method can be used for basins with insufficient or complete absence on N and P concentrations.

**Key words:** Nitrogen, phosphorus, plot scale, simulation.

nutrients from catchment areas and establishing the limits of variability of their concentrations is an important task for the river basin management in Ukraine.

Our studies have been focused in the evaluation of the ecological problem concerning long-term and seasonal nutrients variability in a small catchment, especially mineral compounds of nitrogen ($N_{min}$) and phosphorus ($P_{min}$), the characterization of their pathways and the quantification of their delivery into streams. The practical line of this study was to develop a method to quantify annual nutrients export in the shortage or even absence of observational data.

## 2 Study area and methods

The Holovesnya river catchment has been selected as the best representing of slowly disturbed basin and contained monitoring site. It is the small right tributary of the Desna river, which flows into one of Europe's largest rivers, the Dnieper.

The Holovesnya river is located in the Northern of Ukraine on the south-western spurs of the Central Russian Upland is rugged with ravines and gullies (Fig. 1). The surface area is 29.5 km$^2$; absolute elevation varies between 180–200 m a.m.s.l. and presents a mean slope of 6 %. The basin lies in a mixed forest zone. About 30 % of the basin area is cultivated while the remaining part is covered by forest with dominance of oak, pine and meadows.

Average annual precipitation is relatively high (670 mm), which 70 % falls in the warm season. The hydrological response of the watershed is reflected in sharp spring floods, ranging from 50 to 70 % of the total runoff, and low water regimes in winter and summer. Summer is often disrupted by rain floods.

The Holovesnya river has 12.6 km length and is equipped with gage for water level at U-notch. Aside from this, the site has full records of water balance and meteorological observations.

The time series covered the period between 1956–2012 but the chemical data set was uncompleted, due to the limited number of samples (2–4 per year).

Additionally an event-based field experiment was carried out at a small experimental plot to understand better the streamflow generation process and nutrients export. This plot of 2 m$^2$ was previously prepared.

The soil surface layer was removed to a freezing depth of 0.4 m (annual average value), a waterproof layer was laid and the soil surface layer was then replaced. Plastic tubes for runoff collection were positioned near the surface and confining layer. These manipulations allowed us to separate physically the fast direct flow and the slow interflow during the snowmelt event to establish the relative importance of different hydrological pathways in nitrogen and phospho-

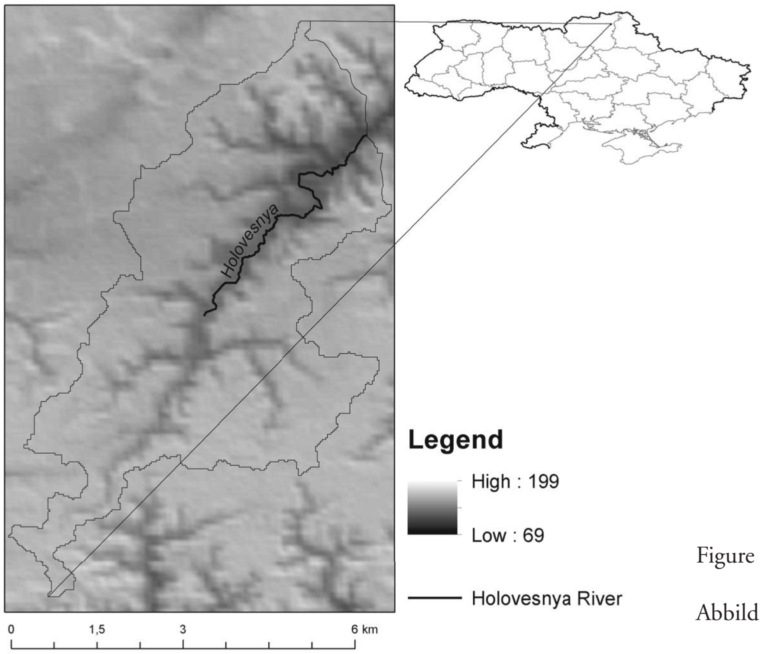

Figure 1: Location and topography of the Holovesnya river catchment

Abbildung 1: Lage und Topographie des Holovesnya Einzugsgebiets rus delivery from land to water. With the temperature increasing the snow began to melt, the runoff process started to form and lasted for 644 hours. Snowmelt water was collected manually depending on the water volume. Samples were filtered through 0.45 µm membrane and analyzed for mineral nutrients compounds ($NH_4^+$, $NO_2^-$, $NO_3^-$, $PO_4^{3-}$). Concentrations of nitrogen and phosphorus were measured photometrically according standard procedures (Nabyvanets et al., 2007).

The experimental study of nutrients leaching was accompanied by mathematical modeling based on the transportation-box approach, presented in detail in Osadcha & Lutkovsky (2013). It was assumed that a quasi-stable equilibrium between solid and liquid phases of soil was reached before the runoff. It was disturbed by water flow. Representing the leaching of nutrients in the form of consistently realized phases of runoff, the governing model equation was:

Formel $$\frac{dC_{sol}}{dt} = k_{mass}(C^*_{sol} - C_{sol}) - k_w C_{sol}$$

where $C_{sol}$ – concentration of $N_{min}$ or $P_{min}$ in runoff water, $k_{mass}$ – constant of diffusion exchange velocity between interaction layer and subjacent layer with concentration of $N_{min}$ or $P_{min}$ in solution $C^*_{sol}$; $k_W$ – washing rate or retardation factor (min $^{-1}$).

## 3 Results and discussion

### 3.1 Trends and year variability

Results of the long-term monitoring showed considerable variation of the studied components in the Holovesnya river water. However, since 2000 the mean values of nitrogen and phosphorus decreased and now vary in narrower limits (Fig. 2). The similar trends of N and P decrease were also verified in other rivers in Ukraine. This fact was attributed to the sharp decline in agricultural production occurring after the Soviet Union disintegration. Besides, the restructuring of economy has led to a significant reduction in greenhouse gas emissions. Release of $NO_x$ compounds to the atmosphere decreased from 2197 t/year in 1990 to 1057 t/year in 2010 and continues to decline (United Nations Framework Convention, 2010).

The available data indicate that dissolved N and P concentrations show a strong and regular seasonal variation. A large part of N and P fluxes occurred during runoff events due to the high runoff volume. Extremely high nutrients export from the watershed is closely related to snowmelt event, since the maximum concentrations arise shortly after winter. Significant rises of N and P content are also originated by heavy rains.

Unfortunately, ongoing monitoring cannot provide information with direct calculation of nutrients fluxes. The limited number of chemical samples (2–4 per year) resulted in a lack of quantitative datasets.

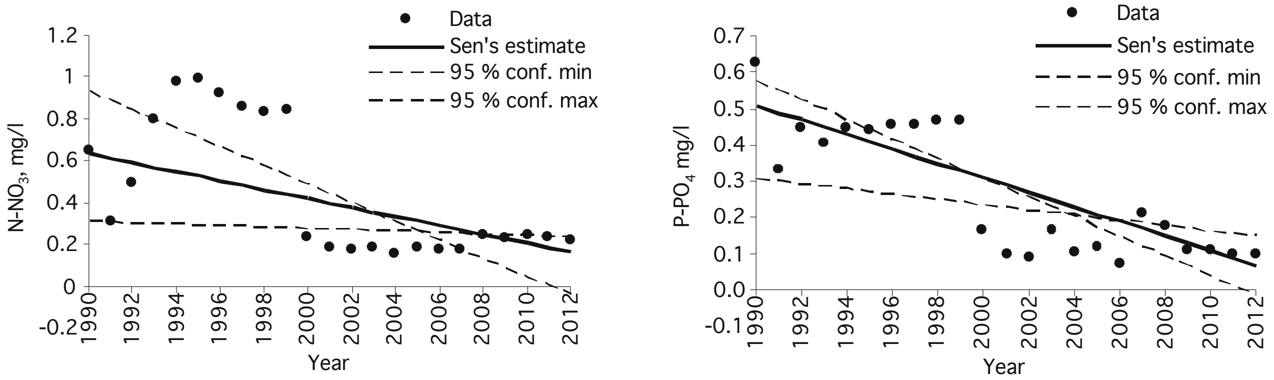

Figure 2: Long-term trends for Nitrate and Phosphate ions in the Holovesnya river for the period 1990–2012, based on the Mann-Kendall test
Abbildung 2: Lanzeittrends nach Mann-Kendall von Nitrat und Phosphat im Holovesnya Fluss für den Zeitraum 1990–2012

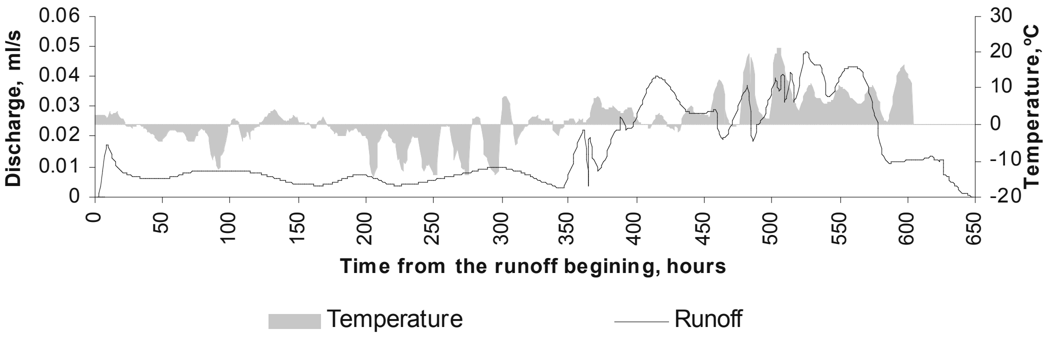

Figure 3: Air temperature and water discharges at the plot during snowmelt experiment
Abbildung 3: Lufttemperatur und Abfluss am Plot während der Schneeschmelze

## 3.2 Experimental approach

The plot scale experiment helped us to assess the relative importance of nutrients processes and pathways as well as to quantify their delivery into the streamflow during the snowmelt. Runoff variability depended on temperature increasing that determined snowmelt (Fig. 3).

The hydrological response of the plot reached 1.1 $m^3$. About 12 % of the total water volume was generated during the initial period of snowmelt, before temperature raised $0^{\circ}$ C. Supposedly, the superficial layers had not yet thawed during this period. Most of water flow was formed with further warming. This is considered the basic phase and took up 88 % of the total runoff. Distribution of water runoff between their components was as follows: 56 % was overland flow and 44 % was subsurface flow. Based on the conceptual model of stream flow components, the overland flow was identified as direct flow and the subsurface flow as interflow (Doležal & Kvitek, 2004).

During the snowmelt event, 456 mg of $N_{min}$ were delivered into the water. It should be highlighted that nitrogen mass displacement was very similar to the runoff components (Fig. 4): 52 % of nitrogen was released with the direct flow and 48 % with the interflow.

Nitrogen washout curve indicates that 111 mg of nitrogen (24 % of the total flux) were released during the initial flow period with the lower discharges. This could be explained by the peculiarities of nitrogen accumulation in soil. Ammonium ($NH_4^+$), appearing as a result of the ammonification process, is strongly fixed by clay minerals. Opposite nitrification process favors the formation of $NO_3^-$. Nitrate ions have high solubility that causes their geochemical mobility and confirm the fast mass transfer. The solubility of $Ca(NO_3)_2$, $NaNO_3$ and $KNO_3$ at 0 °C is 2010, 727 and 2795 kg/kg $H_2O$, respectively. Keeping in mind that dissolution process is limited by diffusion parameters, $NO_3^-$ dissolution rate would be the maximum at the beginning of the process, when the concentration gradient is the highest.

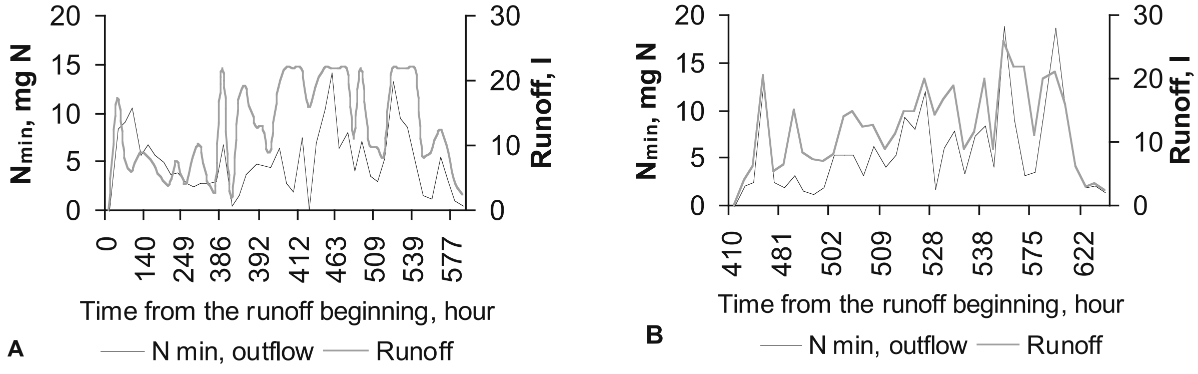

Figure 4: The nitrogen release from the experimental plot during snowmelt: A – direct flow, B – interflow
Abbildung 4: Stickstoffaustrag am Plot während der Schneeschmelze: A – Direktabfluss, B – Zwischenabfluss

Water flow increases at the basic phase, causing the reduction of $NO_3^-$ concentration due to dilution. Data obtained showed that transferring of nitrate compounds is mainly determined by hydrodynamic conditions. An additional hydrograph separation for direct and interflow will not lead to more accuracy when simulating the N fluxes. This conclusion is also confirmed by the Akaike's information criterion, which had similar values in both cases.

In contrast to nitrogen, phosphorus export during snowmelt event was 10 times lower and summed 44 mg. This fact is explained by its low solubility. The main contributor of $P_{min}$ was interflow, which exported about 68 % of P fluxes (Fig. 5).

It is known that only 10 to 20 % of soil phosphates are mobile, while the others are quickly fixed by clay minerals through the sorption process (KHRISANOV & OSIPOV, 1993). Soluble phosphates of calcium, sodium and ammonium are considered to leach at the initial phase. They form about a tenth (3.5 mg) of the total $P_{min}$ flux. At the beginning of the main phase of runoff, phosphates were absent at all, which was associated with the desorption process. A subsequent delivery of phosphate is fully described by a diffusion process.

### 3.3 Modeling approach

The simulation methodology was developed in order to address the gaps in the chemical component data sets. Detailed description of the simulation methodology can be found in our work (OSADCHA & LUTKOVSKY, 2013).

Taking into account that the main mechanisms of $N_{min}$ and $P_{min}$ transfer in the system "solid-water" are the physical processes of convective diffusion and desorption, N and P release during the experiment was simulated by calibrating the minimum number of parameters specified by the dynamic processes. The runoff phenomenon was divided into some periods. At the runoff beginning, chemical compounds are transferred from the top soil layer. The physical basis of their mass transport was described by convection-diffusion basis. In the second phase, when runoff reached peak values in the layer of interaction, it is changed into process of hydrodynamic washing of pore solution. In the third phase, substance concentrations rise again as a result of mass transfer from the lower layers of the soil.

All mentioned phases had been described mathematically (OSADCHA & LUTKOVSKY, 2013) and the dynamics of the nutrients concentration was simulated.

Results of simulated N and P wash out from the experimental plot are presented in Figs. 6 and 7. The accuracy of $N_{min}$ and $P_{min}$ simulation was assessed based on Nash–Sutcliffe efficiency coefficient (MORIASI et al., 2007). Results of $N_{min}$ and $P_{min}$ flow were 0.70 and 0.86, respectively.

The modelling approach was applied to the watershed scale for the Holovesnya river. Daily concentrations of N and P were obtained based only in streamflow data. Finally, simulated and measured discharges of $N_{min}$ and $P_{min}$ were compared.

Nutrients fluxes were found and their reference values were calculated. This approach can be applied for other basins with limited amount of information regarding chemical composition of the water.

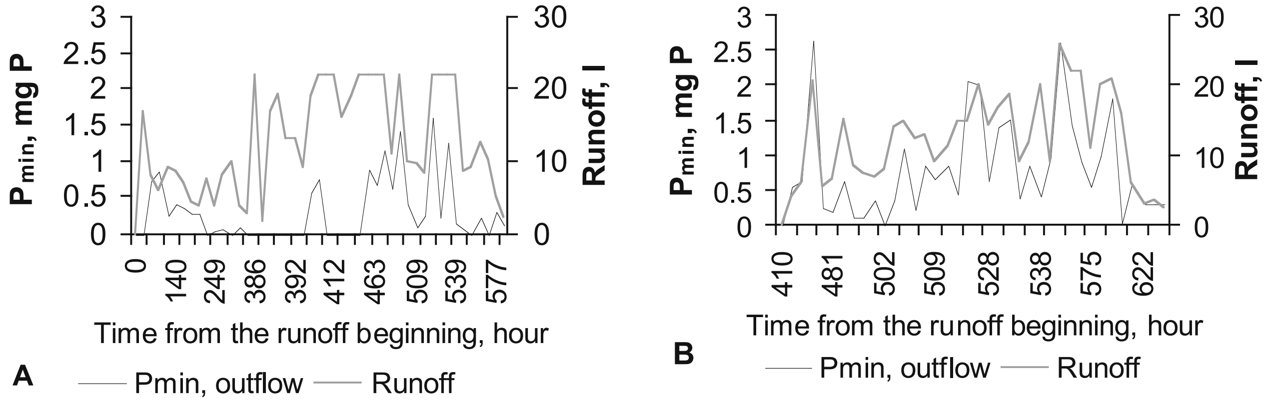

Figure 5: The phosphorous release from the experimental plot during snowmelt: A – direct flow, B – interflow
Abbildung 5: Phosphoraustrag am Plot während der Schneeschmelze: A – Direktabfluss, B – Zwischenabfluss

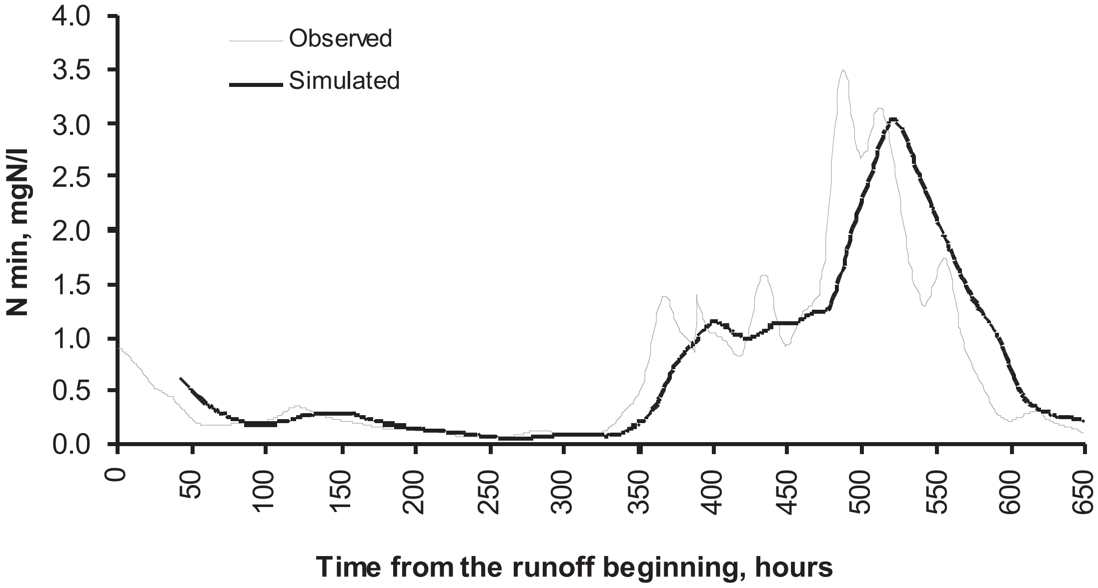

Figure 6: Simulation of soluble nitrogen concentrations in runoff waters using total discharge data
Abbildung 6: Berechnung der lösbaren Stickstoffkonzentration im Flusswasser

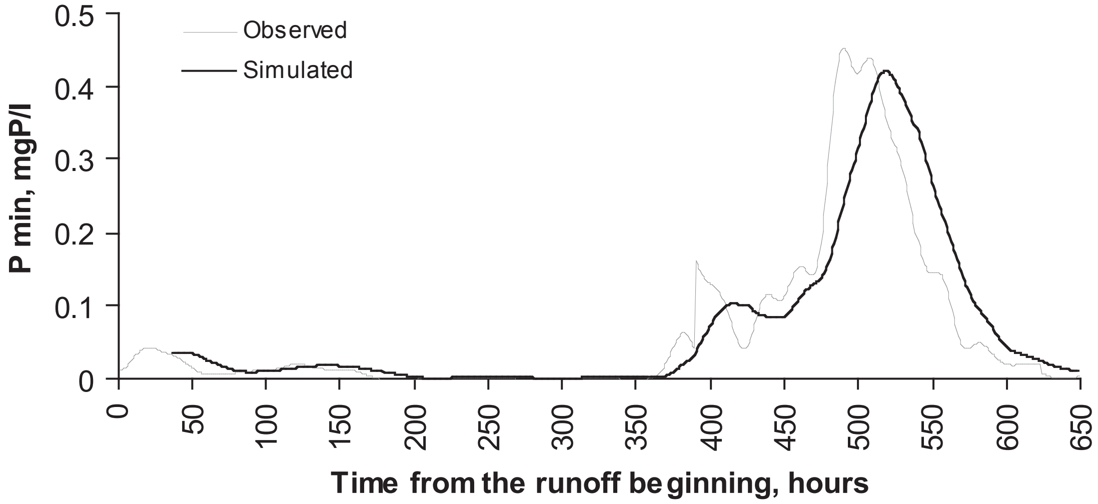

Figure 7: Simulation of soluble phosphorus concentrations in runoff waters using total discharge data
Abbildung 7: Berechnung der lösbaren Phosphorkonzentration im Flusswasser

## 4 Conclusions and further research

Executed full-scale experiments resulted in better understanding of N and P leaching from the watershed during a snowmelt event and allow finding the quantitative parameters of their distribution between solid and liquid phases. Nutrients transfer was mainly determined by the hydrological regime. Combination of discharge and concentration data allowed the quantification of nutrients delivery and enables the comparison of the influence of different nutrients pathways, and inputs to the stream. Estimation of nitrogen release does not require hydrograph separation. While as for phosphorus, which is mainly delivered by the interflow, the hydrograph separation procedure provides more accuracy.

Rainfall events influence on N and P outcomes should be further examined.

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