

Simulation of humic substances diffuse runoff during a snowmelt event at the experimental plot scale

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Simulation des diffusen Transports von Huminstoffen bei Schneeschmelze am Plotstandort

1 Introduction

Full-scale experiments on small catchments and plots provide an important possibility to study patterns of diffuse runoff of substances. Obtained quantitative parameters can be successfully used to simulate leaching of substances from the surface of the whole catchment area. This approach was applied for humic substances (HS), which contribute from 50 to 90 % of dissolved organic matter (DOM) composition of the Ukraine surface waters. In high colour waters of the forest zone HS are the dominating group (LINNIK *et al.*, 2004). The prevailing part of HS (71–83 %) income to rivers during a snowmelt period (OSADCHA, 2011; OSADCHA

& OSADCHYY, 2001). HS significantly influence the ecological state of water because of oxygen condition deterioration, pH decreasing, as well as changing equilibrium of carbonate-calcium and oxidative-reductive. HS enhance migration parameters of trace metals and organic pollutants in natural waters by creating stable complexes (TIPPING, 2004). They bind from 40 to 70 % of metals in the forms of organic complexes (LINNIK, 2003).

The Dnieper river, the largest in Ukraine and the third catchment in Europe, is used as a drinking water supply for > 30 millions of citizens. High contents of HS lead to significant obstacles for water treatment because drinking water quality doesn't reach the national standards. HS also

Zusammenfassung

Im Zuge einer physikalischen Modellierung des Schmelzabflusses am Standort Boguslav in der Region Kyiv (Ukraine) wurde der Transport von gelösten Huminstoffen (HA) und Fulvinsäuren (FA) untersucht. Dabei wurde das Hauptaugenmerk auf die Huminstoffe, den Hauptbestandteil der organischen Substanzen in den Oberflächengewässern der Ukraine, gerichtet. Ein Algorithmus zur Simulation der Verteilung und der Mobilisierung während der Schneeschmelzvorgänge wurde entwickelt, der auf der mathematischen Beschreibung des Massentransfers für verschiedene Phasen beruht. Die Güte der Simulation nach Nash-Sutcliffe lag bei 0,96 für HA und bei 0,89 für FA.

Schlagerworte: Plot-Skala, Abflusssimulation, Huminstoffe, Huminsäuren, Fulvinsäuren, Versickerung.

Summary

The physical modelling of snowmelt runoff was carried out on the experimental runoff plot, located in Kyiv region (Ukraine) in Boguslav experimental site, to study features of dissolved humic (HA) and fulvic (FA) acids leaching from a catchment. Among investigated components the main attention was paid to the humic substances as a prevailing part of organic matter in surface water of Ukraine. The quantitative parameters of their distribution in the system "solid phase-water" were established. The algorithm for simulation of humic substances release during snowmelt conditions was developed. It was based on the mathematical description of a component mass transfer in separate runoff phases. The accuracy of simulation was assessed on the basis of Nash-Sutcliffe coefficient, which was 0.96 and 0.89 for HA and FA, respectively.

Key words: Plot scale, runoff, simulation, humic substances, humic acids, fulvic acids, leaching.

led to important social problem. In Ukraine, chlorination of drinking water leads to formation of secondary chloric derivatives of HS with carcinogenic properties (RADLINGER et al., 1997; PACIOLA et al., 1999). Thus, forecasting of HS leaching is quite urgent for Ukrainian rivers. So the main objectives of the research were: (1) to develop basis for simulation of HS mass transport from non-point sources; (2) to provide inputs for the model.

2 Methodology

An experimental study was carried out at the research runoff plot of the Boguslav experimental site, located 100 km south from Kyiv. The characteristic soil is spodosol. The banked up plot with area of 400 m² has V-shaped water intake flume. A hook gauge house was buried in the earth. The snow layer of 11 cm was accumulated at the plot during the winter. When air temperature increased, the runoff started and was observed until snow storage ended. Every day observations represented a separate phase of a flow. Runoff water was collected in continuous mode. Sampled water had been filtered through membrane filter (pore size 0,45 µm). To extract HS, 0.5–1.0 l filtrated water was passed through columns filled by ion-exchange DEAE cellulose (SIROTKINA et al., 1974, 1985). Received eluate was acidified to pH = 2, kept on a water bath for 2 hours ($t = 70\text{--}80\text{ }^{\circ}\text{C}$) and settled for 24 hours to divide HS into two basic fractions: humic acids (HA) and fulvic acids (FA)

(MCDONALD et al., 2004]. HA and FA content had been detected spectrometrically according to a calibrating curve in coordinates “Optical density of solutions at $\lambda = 440\text{ nm}$ concentration (HA or FA)”. These HS fractions differ in solubility in water and have essentially diverse behaviour in a water ecosystem. HA perform an accumulation function. They are, as well as bound pollutants, easily sorbed by suspended particles and later pass into the deposits. FA contribute to stabilization of pollutants in dissolved condition because they establish complex compounds and consequently play a transporting role.

The modeling exercise was based on transportation-box approach with the following restrictions. Surface layer of soil with thickness H , and volumetric contents of water q is uniformly watered by melting water with intensity I . At the same time water in the interaction layer is completely intermixed and leaves it as a surface runoff with intensity Q and infiltration with intensity $I-Q$. We assumed that before the runoff a quasi-stable equilibrium was reached between solid and liquid phases of soil which then was disturbed by snow melting. Leaching of organic substances were represented as a consistently realized discharge phase.

3 Results and discussion

Obtained results for the one day runoff are shown in Figure 1.

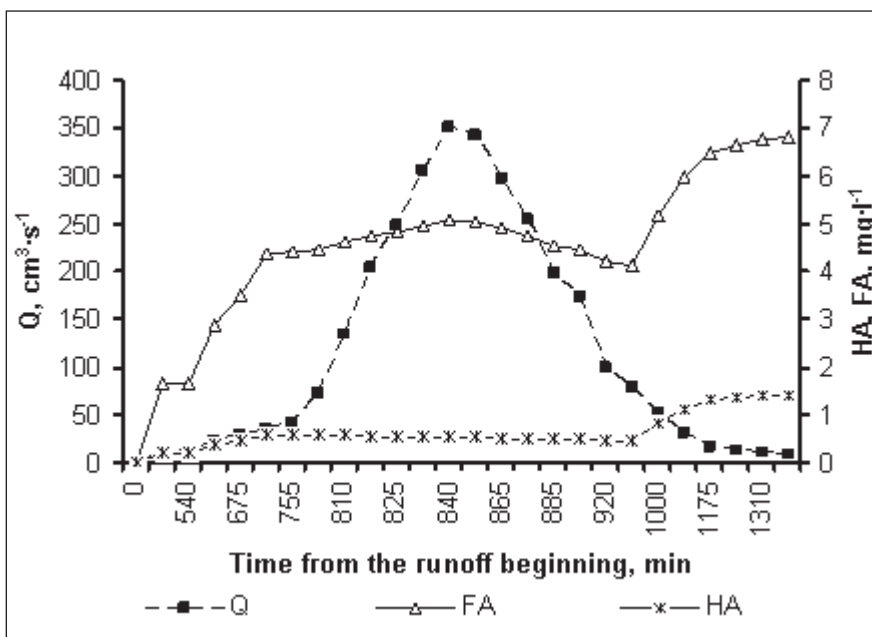
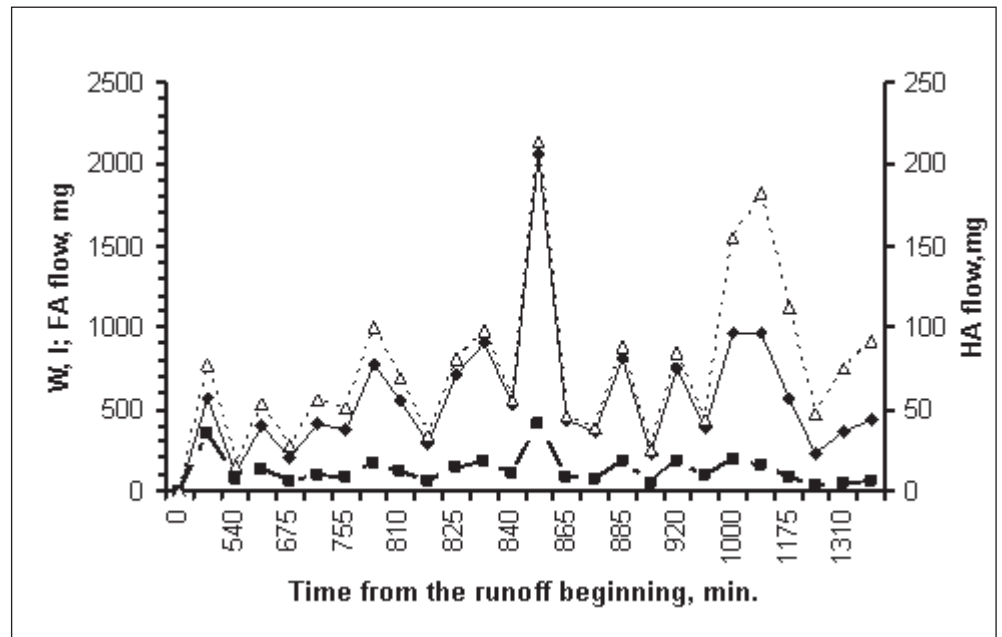


Figure : Discharges (Q), humic acid (HA) and fulvic acid (FA) concentrations in runoff water on 22nd of February 2011
Abbildung 1: Abfluss (Q), Huminsäure- (HA) und Fulvinsäurekonzentration (FA) im Abfluss am 22. Februar 2011

Figure 2: Water, HA and FA fluxes from the research plot for 1 day (22nd of February 2011) of the sampling period
 Abbildung 2: Tageswerte der Wasser-, HA- und FA-Flüsse am Forschungsplot für den 22. Feb. 2011



FA content proved to be considerably higher compared to HA, and concentrations ranged, respectively, within 1.6–6.6 mg·l⁻¹ and 0.2–1.4 mg·l⁻¹. At the same time, content of HA in soils was two times higher than FA (respectively 54 and 27 mg·g⁻¹). This happened due to the different solubility of HA and FA, caused by lower molecular masses of FA and higher content of carboxyl and phenolic functional groups in their structure that determines good solubility of FA (PERDUE et al., 2003). FA is the most mobile part of the HS and their leaching from topsoil can be considered as determinative factor for DOM formation.

Dynamics of water discharge and HS concentrations are different. Water discharge was characterized by bell-shaped curve, while concentrations of HS did not follow the same shape and present three stages: (1) With increasing water discharge, the HS concentrations synchronously increased and both parameters presented close correlation. Then HS concentrations increased rapidly almost up to the equilibrium conditions between the solid and liquid phase. (2) The further water discharge increase practically did not influence HS content. (3) Their concentration increased, on the contrary, at the descending hydrograph branch (Fig. 1).

Daily HS diffuse flow from the surface of the test plot was calculated on the basis of experimental data according to the multiplication of water discharge by the concentration of the HA or FA. Fluxes of HA and FA washing out were respectively 1.9 g and 14.5 g for 1 day of runoff (Fig. 2). It is necessary to underline that the most significant leaching occurred at the maximum limit of the water flow (W). Pair-

wise correlation coefficients for W-HA flow values and W-FA flow values respectively reached 0.7 and 0.8 (significance value set on the basis of Student's T distribution, $p = 0.05$; $r > 0.57$).

Obtained experimental data show good conditions of diffusion that can describe mass transfer in a heterogeneous system. Based on this approach the mathematical simulation of HS runoff was carried out. Results of the full-scale experiment were used to set the parameters.

Being open, the system "catchment area/runoff" is characterized by convective movement of liquid. Correction for convectivity, which value depends on the filtration flow velocity dispersion, was taken into account.

In the first phase, on hydrograph rising, concentrations of HS in runoff are increased due to the diffuse exchange with the porous solution (MUDROCH, 1983):

$$\frac{dC_{sol}}{dt} = k_{mass}(C_{soil}^* - C_{sol}) - k_w C_{sol} \quad (1)$$

where

C_{sol} – runoff concentration of HS, k_{mass} – constant of diffusion exchange velocity between interaction layer L_{int} and layer L_t at depth of ~ 8 cm with a concentration of HS in solution C_{soil}^* ; k_w – washing rate or retardation factor (min⁻¹), for simplification of calculation the leaching process is assumed as a constant with suppressed infiltration $Q \sim I$. k_w calculated according to equation 2:

$$k_w = \frac{I}{H(\rho K_d + \theta)} \quad (2)$$

where

H – thickness of the soil surface layer, θ – volumetric contents of water, I – intensity of water discharge, ρ – soil density, K_d – distribution coefficient of HS in the system “soil-water”.

The concentration of dissolved HS (C_{sol}) at the first phase of runoff changed according to:

$$C_{sol}(t) = \frac{C_{eq}}{L_{int}} \sqrt{\frac{D t}{\pi}}, \quad (3)$$

where

D – convective diffusion coefficient of HS; $D = k_{diff} + \alpha V_{convective}$, where k_{diff} – molecular diffusion coefficient, α – convective diffusion coefficient, $V_{convective}$ – convective flow velocity.

According to the Fick’s law the driving force for diffusion is a concentration gradient; and speed of this process depends on molecular diffusion coefficient. The latter, in its turn, is defined by molecular mass (MM) of substance. A feature of HS is absence of stable structure, they represent a heterogeneous system of polyelectrolytes with a wide range of MM – from hundreds to hundreds of thousands Daltons (Da). To obtain quantitative information on MM characteristics of HA and FA, an additional gel-chromatography separation was done. On the basis of the obtained molecular-mass distribution (Fig. 3) the weighted-average MM of HA and FA was calculated. For HA it was 19.0 ± 0.22 kDa and for FA – 0.8 ± 0.09 kDa. Possible sorption of HS from a pore solution was not considered.

On the basis of the weighted mean values for HA and FA mentioned above their molecular diffusion coefficients were calculated using empirical formula (4), based on the reference data:

$$D_m = 4,674 \cdot e^{-0,1912\sqrt{M_w}} \quad (4)$$

In the second phase, when runoff reached peak values, process of hydrodynamical washing of pore solution in the interaction layer took place. Concentrations of HS in runoff are described by the following formula (OSNY et al., 1989):

$$C_{sol}(t) = C_0 \exp\left\{-\frac{I \cdot t}{H(\rho K_R + \theta)}\right\}, \quad (5)$$

where K_R – effective distribution coefficient of the substance in the system “soil-water” (SMETTEM et al., 1991), depending on K_d – distribution coefficient of substance between solid and liquid phase.

On the basis of experimental simulation of runoff K_d for HA = $0.125 \text{ l}\cdot\text{kg}^{-1}$, and K_d for FA = $0.00058 \text{ l}\cdot\text{kg}^{-1}$.

In the third phase, observed on the descending branch of the discharge hydrograph, concentration of substances increased as a result of mass transfer from the next layers of soil. The first phase was repeated, but with other parameters of process. Concentration of dissolved substances was determined by the formula:

$$C_{sol}(t) = C_{eq} - \frac{S(C_0 - C_f)}{Q} \sqrt{\frac{D}{\pi t}}, \quad (6)$$

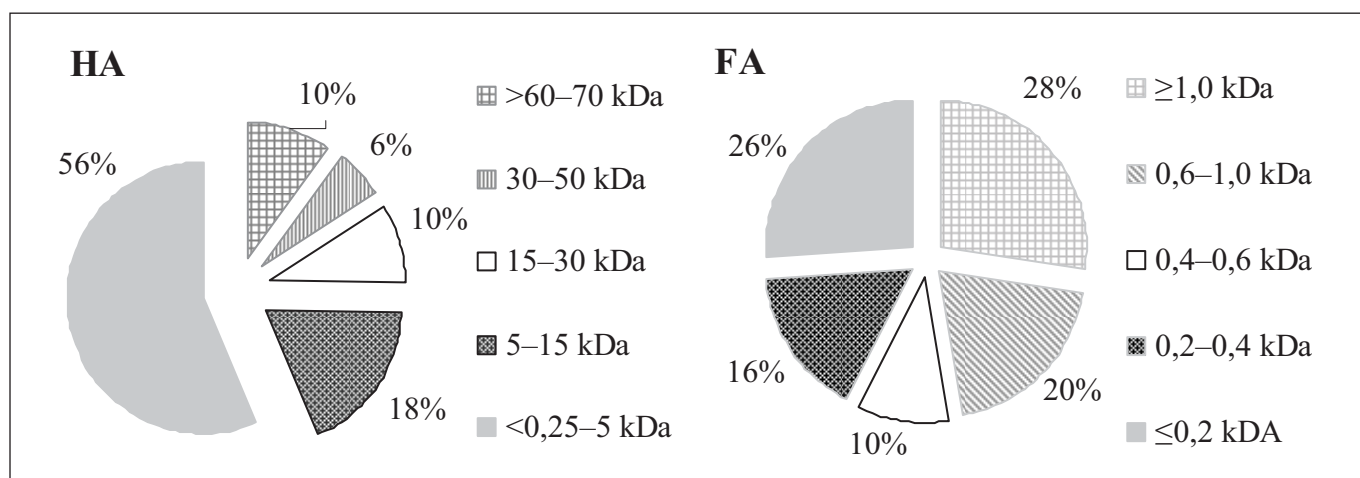


Figure 3: Molecular mass range of HA and FA, %
 Abbildung 3: Molekularmasseverteilung von HA und FA in %

where S_{eq} – equilibrium concentration. For HA it equals to 0.59 mg/l and for FA – 5.06 mg/l, S – area of the experimental runoff plot, C_0 – initial concentration of HS in a layer of interaction, C_{if} – concentration HS on the interface “soil-runoff”, $C_{if} = C_{sor} K_R S_{sor}$ is the concentration of HS in solid phase of interaction layer. Concentration gradient is aligned with the new balance: $C_{sol} = C_{sor} K_R$. Decrease of water discharges in this case reduces the arrival of dissolved substances into water.

The results of simulation for HA and FA washout are shown in Fig. 4.

It is important to note the high degree of correlation between model calculations and the experimental data. Correlation coefficients were $R^2 = 0.82$ for the first and third (diffusive) phases and $R^2 = 0.96$ for washing phase (phase 2). The accuracy of HA and FA simulation was assessed on the basis of Nash-Sutcliffe efficiency coefficient (MORIASI et al., 2007). For HA and FA flow it was 0.96 and 0.89, respectively. Taking into account the high values of the coefficient mentioned above we have come to the conclusion that the suggested model describes processes with sufficient accuracy.

Conclusions

Summing up, this full-scale experiment allowed us to understand better the release from watershed and dynamic of HS, as the main component of DOM, as well as their bound

pollutants. Obtained income parameters were used for simulation of HS snowmelt runoff from the basin of the largest Dnieper tributary, the Pripyt river, whose waters are most enriched in HS. Inner water body processes were not considered at this stage.

References

- AIKIN, G.R., D.M. MCKNIGHT and R.L. WERSHAW (eds.) (1985): Humic substances in soil, sediment and water. Geochemistry, isolation and characterization. New York: John Wiley and Sons.
- LINNIK, P.N., T.A. VASILCHUK and R.P. LINNIK (2004): Humic substances of natural waters and their importance for the water ecosystems (review). Hydrobiological Journal. 40, No. 1, 81–107 (in Russian).
- LINNIK, P.N. (2003): Complexation as the most important factor in the fate and transport of heavy metals in the Dnieper water bodies, Anal. Bioanal. Chem. 376, 405–412.
- OSADCHA, N.M. (2011): Regularities of humic substances migration in surface waters of Ukraine. Author's abstract of Dissertation for a Doc. Habil. degree in Geogr. Sci. Kyiv.
- OSADCHA, N.M., V.I. OSADCHYY (2001): Estimation of dissolved humic substances leaching with runoff of the Pripyat river. Proceeding of the Ukrainian Hydrometeorological institute, Iss. 249, 161–177 (in Russian).

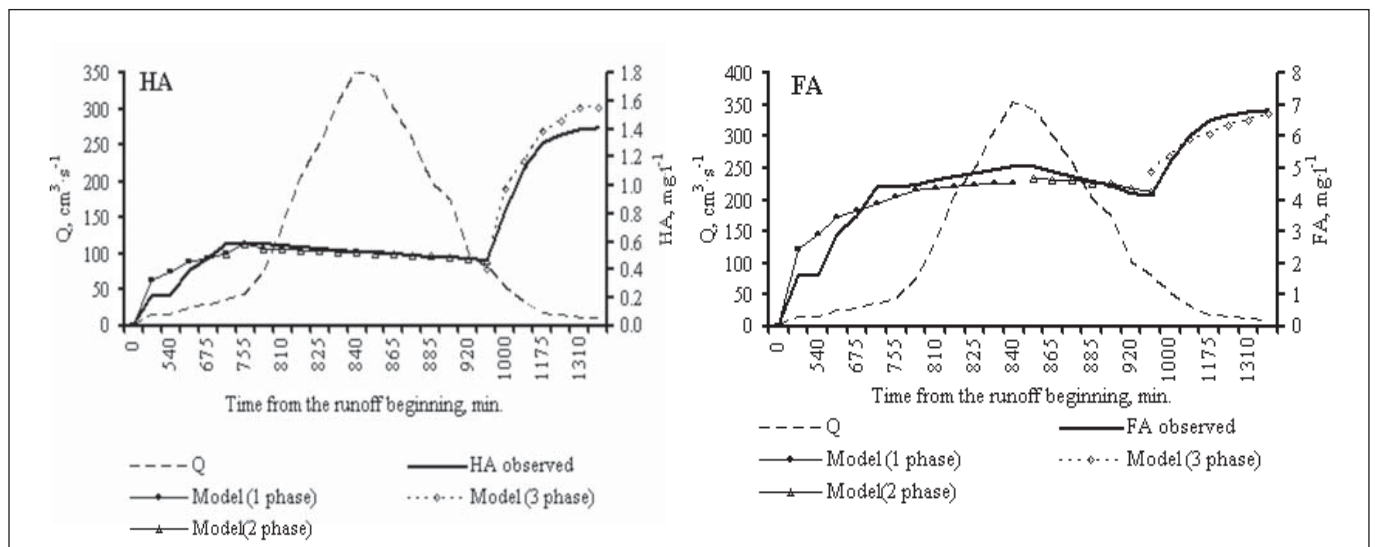


Figure 4: Simulation of HA and FA diffuse runoff at the experimental runoff plot
Abbildung 4: Simulation des diffusen Abflusses von HA und FA am Plotstandort

- MCDONALD, S., A.G. BISHOP, P.D. PRENZLER and K. ROBARDS (2004): Analytical chemistry of freshwater humic substances. *Analyt. Chim. Acta.*, 527, 105–124.
- MORIASI, D.N., J.G. ARNOLD, M.W. VAN LIEW, R.L. BINGNER, R.D. HARMEL and T.L. VEITH (2007): Model Evaluation Guidelines for Systematic Quantification of Accuracy in Watershed Simulations. *Transactions of the ASABE*, 50, Iss. 3, 885–900.
- MUDROCH, A. (1983): Distribution of Major Elements and Metals in Sediment Cores from the Western Basin of Lake Ontario. *Journal of Great Lakes Research*, 9: 2, 125–133.
- OSNY, O.S., K. BACCHI-REICHARDT, L. LIBARDI PAULO and O. MORAES SÉRGIO (1989): Scaling of soil hydraulic properties in the evaluation of hydraulic conductivity determination methods. *Soil Technology*, 2: 2, 163–170.
- PACIOLA, M.D., G. DAVIES and S.A. JANSEN (1999): Generation of hydroxyl radicals from metal-loaded humic acids. *Environ. Sci. Technol.*, 33: 11, 1814–1818.
- PERDUE, E.M. & J.D. RITCHIE (2003): Dissolved Organic Matter in Freshwaters, *Treatise on Geochemistry*. 5, 273–318.
- SIROTKINA, I.S., G.M. VARSHAL, Y.Y. LUR'É and N.P. STEPANOVA (1974): Application of cellulose sorbents and sephadexes for systematic analysis of organic substances in the natural waters. *Journal of Analytical Chem.*, 29: 8, 1626–1633.
- SMETTEM, K.R.J., D.J. CHITTLEBOROUGH, B.G. RICHARDS and F.W. LEANEY (1991): The influence of macropores on runoff generation from a hillslope soil with a contrasting textural class. *Journal of Hydrology*. 122: 1–4, 235–251.
- RADLINGER, G. & K.G. HEUMANN (1997): Determination of halogen species of humic substances using HPLC/ICP-MS coupling. *Fresenius' J. Anal. Chem.*, 359, 430–433.
- TIPPING, E. (2004): *Cation binding by humic substances*. Cambridge: Cambridge University Press.

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