

Field Experimental Studies of the Leaching of Humic Substances from the Peat Soils and Estimation of their Role in Dissolved Iron Transportation

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Abstract

A field experiment on humic substances and dissolved iron transportation from the water catchment area was conducted in the spring time. The studies were carried out on a small runoff site (2x1m) filled with peat layer of 50 cm deep.

During the snowmelt, exclusively a subsurface runoff was formed. The values of distribution characteristics of two main fractions of humic substances - humic and fulvic acids - between the solid phase of peat and water runoff were obtained. It has been shown that the process of complexing with fulvic acids significantly expands migration limits of iron in the dissolved phase. By means of thermodynamic modeling it has been found that the water pH value and the concentration of fulvic acids are the limiting factors for iron's existence in a dissolved phase.

A methodology has been proposed to predict emission of humic substances and iron into water runoff of the Pripjat River (Ukraine).

Keywords: plot scale, emission, humic acids, fulvic acids, iron, thermodynamic modeling

Rezumat. Studii experimentale pe teren privind percolarea substanțelor humice din turbării și estimarea rolului lor în transportul fierului dizolvat

Un experiment pe teren privind substanțele humice și transportul minereului de fier dizolvat din apă într-un bazin hidrografic a fost realizat în perioada de primăvară. Studiile au fost efectuate pe microparcele (2x1m), cu un strat de turbă de 50 cm adâncime.

Pe parcursul topirii zăpezii, s-a format și scurgerea intermediară. S-au obținut valorile distribuției caracteristice pentru două fracții principale de substanțe humice - humici și acizi fulvici între faza solidă și lichidă a scurgerii din turbă. S-a demonstrat că procesul de complexare cu acizi fulvici, extinde semnificativ limitele de migrare ale fierului în faza dizolvată. Prin intermediul modelării termodinamice s-a constatat că valoarea pH-ului apei și concentrația de acizi fulvici sunt factorii limitativi pentru existența fierului într-o fază dizolvată. A fost propusă o metodologie pentru predicția emisiilor de substanțe humice și a fierului în scurgerile lichidă a râului Pripjat (Ucraina).

Cuvinte-cheie: scara parcelei, emisie, acizi humici, acizi fulvici, fier, modelarea termodinamică

Introduction

Drinking water supply in Ukraine is provided mainly from the surface water sources. The Dnipro River, the largest river in Ukraine and the third water catchment in Europe, is used for drinking water supply for more than 30 million citizens. Dnipro flow is regulated within the Ukrainian territory and the river represents a cascade of six reservoirs. The construction of Dnipro cascade has led to changes in the river chemical and hydro-biological regimes. The upper Kyiv Reservoir, due to its location, plays the role of the main barrier in the cascade, and at the same time, it is one of the major sources of drinking water supply for 4 million residents of Kyiv, the capital of Ukraine.

The Kyiv Reservoir has specific water chemistry: high content of organic matter and water color, high content of iron, high level of eutrophication, decrease of minimum oxygen level resulting in fish mortality.

The Pripjat River is the main factor determining the chemical characteristics of the Kyiv Reservoir water (Osadcha & Osadchyi 2001, 2002a, 2000b).

Pripjat is the first large tributary forming 27% of the Dnipro water flow. The positive moisture balance, plain ground, and high water table favour the development of wetlands across its basin. A huge amount of organic matter of humic origin comes to the surface water every year affecting its chemistry.

Regional climate changes that have been observed over the last decades had a significant impact on the characteristics of the spring floods of the Pripjat River, causing an increase in winter runoff, which affected the chemical composition of the river (Grebina, 2013; Osadcha & Osadchyi, 2013).

Organic water pollution caused by the increased inflow of humic substances considerably aggravates the problem of providing high-quality drinking water for cities, for which the Dnipro River is the main source of drinking water. Humic substances considerably complicate water treatment process, as during water disinfection they form secondary chlororganic compounds with carcinogenic properties (Radlinger & Heumann, 1997).

The Pripjat River basin is located on the trans-boundary territory. 57% of the area is on the

Ukrainian territory and 43% - in Belarus. The origin of the river, its upper course, and outflow into the Kyiv Reservoir are located on the Ukrainian territory. Despite the fact that the monitoring of hydrological regime of estuarine areas was launched at the end of the XIX century, the existing datasets are very scattered, repeatedly were interrupted, with recording stations changing their coordinate referencing, and after the Chernobyl accident in 1986 much of the data has become the property of various departments. Monitoring the content of organic matter of humic nature is carried out only when implementing specific research projects.

In view of the above mentioned, it is crucial to study emission of organic substances into the Pripjat River and prognosticate quantitative characteristics of their inflow into the Kyiv Reservoir in order to provide proper management of water resources in the Dnipro River basin and to ensure high-quality drinking water supply for the Ukrainian people.

The aim of this study was to examine the peculiarities and establish quantitative parameters of leaching of organic matter of humic nature and iron from the wetlands, as well as to evaluate the role of certain processes influencing the migration of iron with the river runoff.

Materials and methods

The research was conducted at the experimental base of the Ukrainian Hydro-Meteorological Institute (UHMI), located in the forest-steppe zone of Ukraine 130 km from Kyiv.

Experimental site

An experimental plot of 2 m² in area (1x2 m) was established on the left-bank slope of the Ros River valley within a small catchment of the Boguslavka River.

The plot was bordered by a concrete ledge driven 100 cm into the soil and extending 10 cm above the soil. The slope of the plot was 2°. A water inlet unit equipped with a canopy to exclude direct input of rainfall was arranged at the lower end of the plot in a pit 1 m deep. Discharge pipes were installed at a depth of about 10 cm and near the water retaining layer. This allowed to separate physically the surface and subsurface runoff. Water samples were collected in 10 liter plastic containers (Fig. 1).

During the summer, the soil cover of the plot was removed to a soil freezing depth of 50 cm. The resulting pit was covered with water retention layer, on top with tightly laid pieces of peat, sliced in 50 x 50 cm squares from the basin of the Pripjat River.



Fig. 1: Small experimental plot - General view of the plot

The composition of the peat was predominantly (96%) represented by the organic matter of humus nature formed by the decomposition of plant residues. The content of the main fractions of humic substances (HS) were as follows: humic acids (HA) - 696 mg·g⁻¹, fulvic acids (FA) - 265 mg·g⁻¹. The total reserve of humic substance at the plot amounted to 1789 kg (1295 kg of HA and 494 kg of FA) (Fig. 2).

The plot, prepared in such way, was left until winter. A mantle of snow about 1 m high was formed of on it during the cold period.

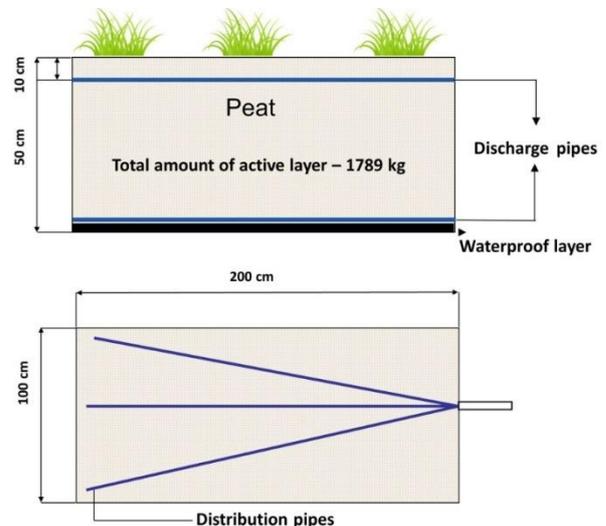


Fig. 2: Cross section and top view of the plot

Snowmelt-Runoff Simulation Experiment

The experiment was started when the air temperature produced a runoff from the collected snow.

The samples of water runoff were collected manually at the outlet of the plot. Sampling frequency depended on the intensity of the flow and the sample's volume should have been at least 2

liters, as was determined by the specifics of the chemical analysis. The acquired samples were filtered through a membrane filter (0.45 μm) and placed in a refrigerator.

Chemical analysis

The filtered samples were analyzed to determine the pH value, water color, the content of HCO_3^- , SO_4^{2-} , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{3+} , and humic substances (HS). The latter were analyzed to determine the content of their two main fractions: humic (HA) and fulvic acids (FA). All analytical procedures were performed in accordance with Nabyvanets et al. (2007).

The resulting data on the volume of water runoff and the content of individual components in it were interpolated with an hourly discreteness.

Results and discussions

Water runoff

During the snowmelt, a water runoff was generated, which lasted 292 hours to exhaust the snow storage. Surface runoff was absent, and the volume of subsoil runoff was 473 liters, which corresponded to a water depth of 237 mm (Fig. 3).

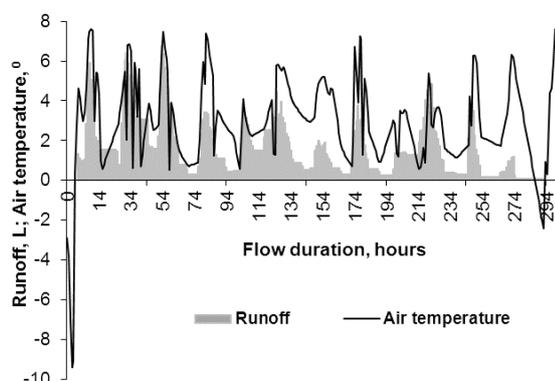


Fig. 3: The dynamics of air temperature and volume of water runoff during the snow melting process on a small runoff plot

It is well known that the rain-induced and spring floods in wetlands' formations are predominantly influenced by filtration flows of atmospheric precipitation through the active layer of peat. The peat that was used in the experimental plot almost entirely consisted of products from the humification of organic residues (96%). Their colloidal dispersion properties account for the high moisture-retaining capacity of the substrate, which can be up to 2000%. In other words, peat is capable of holding the moisture 20 times more of its own dry weight (Moore & Bellamy, 1974; Lishtvan et al., 1979).

The high degree of peat hydrophilicity is associated with the dominance of active polar carboxyl and hydroxyl groups of COOH^- and OH^- in the composition of humic substances, causing the colloidal particles to engage in ion exchange reactions.

Typically, the rate ratio of total runoff to total air temperature (R) decreased with time (Fig. 4). Peat is extremely sensitive to changes in humidity. Its water yield is not a constant characteristic, but depends to a great extent on the preliminary water saturation level. At the initial stage of moistening the peat deposit, a significant proportion of the water is retained by capillary forces in the pores and cracks in the solid skeletal content of the peat, providing sufficiently high water yield of the peat mass. This was observed during the first 3 days of runoff formation. Given the extended watering of the peat mass, the proportion of physicochemical moisture associated with the colloidal particles has increased, thereby lowering water yield of the peat.

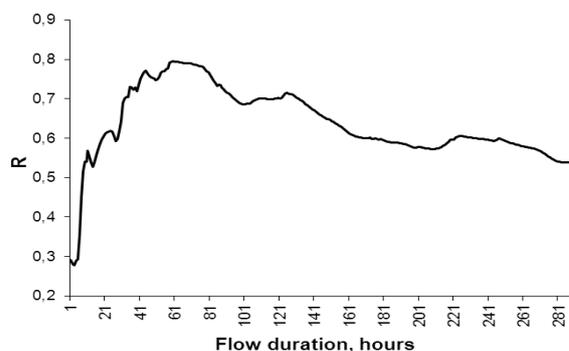


Fig. 4: Change in the ratio of total runoff to total air temperature - R ($^{\circ}\text{C}$), during the formation of the water runoff

Emission of humic substances

The water runoff stimulated HS leaching from the peat thickness. FA dominated within the two investigated HS fractions in the emission runoff, which is typical of natural waters. HA concentration in the water runoff varied between 12–44 $\text{mg}\cdot\text{L}^{-1}$, FA – 144–443 $\text{mg}\cdot\text{L}^{-1}$. It is known that the solubility of HS depends on the size and configuration of its molecule (Popov, 2004). Despite the general HS structure principles, which contain an aromatic core in the center of their molecules being surrounded by peripheral aliphatic chains of carbohydrates and polypeptides, the molecules of HA and FA have significant individual differences. They differ in ratios of aromatic and peripheral aliphatic structures, as well as in different contents of functional groups (predominantly hydroxyl and carboxyl). Higher mobility and reactivity of FA, compared to HA, is due to their lower molecular weight and higher

composition of functional groups. The HA ratio of aromatic and aliphatic carbon is higher than in FA, and the composition of the basic functional groups is significantly lower (Sposito, 1981).

No any significant relationship was found between HS concentrations in subsoil runoff and water expenditures. This is due to turbulent-diffusion nature of HS discharge and is described in detail in our previous work using a one day case-study of HS runoff (Osadcha & Lutkovsky, 2013). Several phases can be singled out in the process of interaction between the solid ground and water runoff. In the first phase, the increase in water expenditure is accompanied by an increase in the concentration of the dissolved substances due to their diffusion from the soil covering until it reaches an equilibrium state between the contacting layer of soil and water.

In the second phase, the dynamic washing of contacting layer occurs, when the increase in water expenditure does not affect the concentration of the dissolved substances in the runoff. And in the third phase, is when the water runoff reaches a new soil horizon, the content of the transported substances in the water runoff increases again due to resultant concentration gradient. This phase is usually observed in the descending branch of the hydrograph's runoff. Due to the sequential change of the described phases, the same water flow rate may feature different concentrations of the dissolved substances.

Unlike concentrations, the leaching of HA and FA from the water catchment area depends essentially on the volume of water runoff (Fig. 5). The correlation coefficient between the water runoff and the identified components were 0.91 and 0.97, respectively.

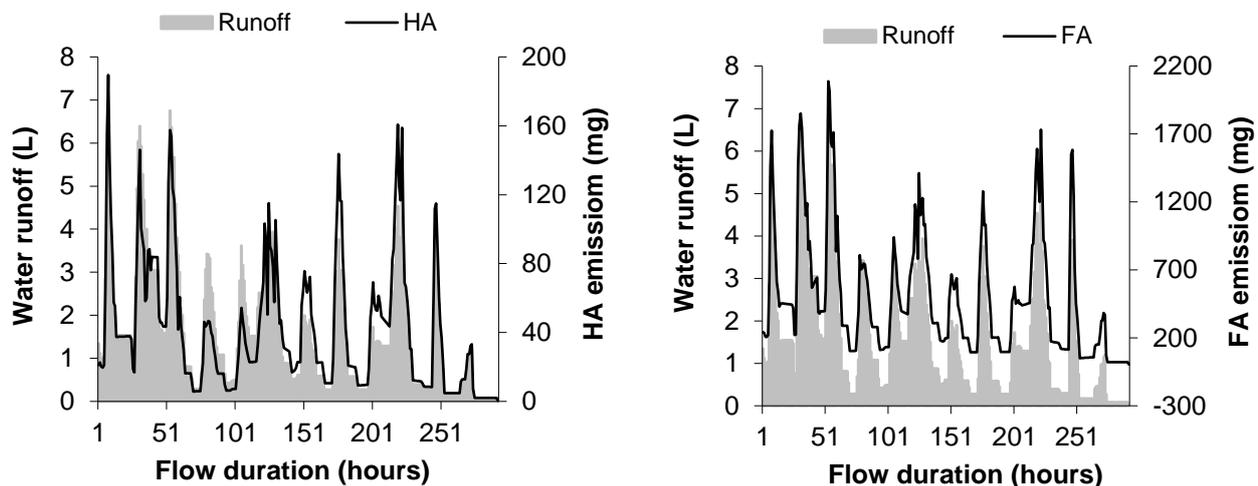


Fig. 5: Emission of Humic acids (left) and Fulvic acids from the packed peat (right) runoff plot during a snowmelt event

As it follows from the mass double curves of HA and FA, dissolution of the former is a homogeneous process. On the contrary, some fractures are observed on HA mass double curve.

Therefore, another laboratory study was conducted to explore conditions and limits of HA solubility in water using HA product. The ratio of the solid to liquid phases in the experiment was 1:100.

The results showed that when HA is contacted with water, not more than 1.8% of the HA mass fraction is dissolved. The process of dissolution of the HA largely depended on the physico-chemical conditions of the environment (Fig. 6).

When ionic strength of the solution increases to $\mu = 0.01$, the dissolved fraction of HA grew to 2.2%, as a result of the substitution reaction from hydrogen ions to alkali metal ions. Further increase

of mineral content in the solution ($\mu = 0.02$) due to higher activity coefficient has led to lower HA dissolubility, whose fraction was reduced to 1.6%. HA is practically insoluble in acidic environment. This is due to the weak acidic properties of HA, whose dissociation constant varies in the range of $pK = 4.8-5.02$ (Popov, 2004).

Accordingly, in a more acidic environment dissociation equilibrium is shifted towards HA undissociated forms and the number of ions involved in ionic interactions is small. Under conditions of water $pH > pK$, HA dissociated forms begin to dominate and their solubility increases. Dissolution of HA under alkaline conditions occurs in two stages, which is due to the initial participation in the dissolving process of carboxyl groups and further – of hydroxyl groups. Furthermore, in an alkaline medium HA molecules unwound and acquire a more

linear structure and, accordingly, more functional groups may enter into ionic interactions.

The study of the molecular weight distribution of dissolved HA showed that their composition is dominated by a low molecular weight HA (molecular

weight <0.25–5 KDa), the composition of which is about 60%. The work Varshal et al. (1979), dedicated to FA study, also noted a decrease in solubility of the FA compounds with the increase of their molecular weights.

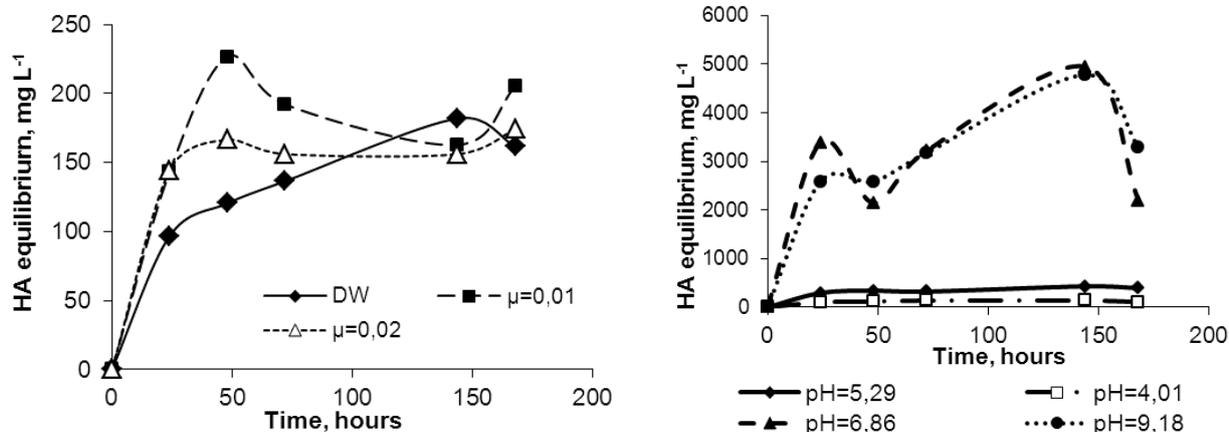


Fig. 6: Humic acids (HA) solubility depending on the (left) ionic strength (μ) and (right) pH of the solution - DW – distilled water

Emission of iron

One of the main components of the swampy massifs in northern Ukraine is iron, whose composition reaches 1.7% in the mineral composition of the peat. Therefore, much attention

in our work was given to the study of trace iron emission from peat thickness.

The experimental data showed that dynamics of iron in snowmelt water was largely determined by both water runoff and FA (Fig. 7). The values of the relevant correlation coefficients were 0.89 and 0.86.

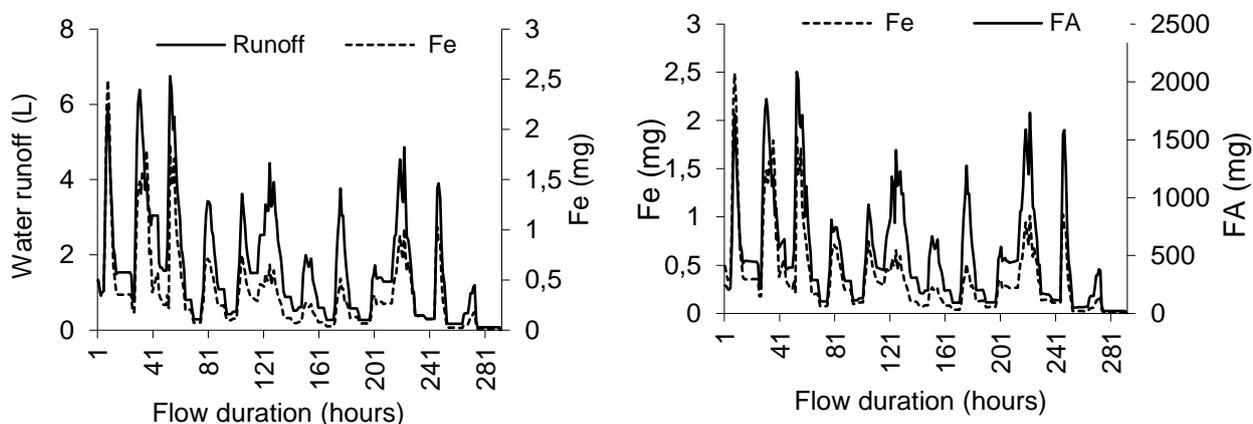


Fig. 7: Chronological graph of (left) iron emission and water runoff (right) emission of iron and fulvic acids from the packed peat soil runoff plot during snowmelt event

Iron belongs to highly unstable elements in the surface water. Like other metals Fe^{3+} is subject to hydrolysis to form slightly soluble compound $Fe^{3+} + 3OH = Fe(OH)_3 \downarrow$.

Its hydrolysis begins in acidic environment with dominance of $Fe(OH)_2^+$, and at $pH > 6.5$ we observe an almost full hydrolysis of the metal to form a poorly soluble form of $Fe(OH)_3^0$.

At $pH=8$, the amount of dissolved iron Fe^{3+} balanced with hydroxide $Fe(OH)_3^0$ does not exceed $0.2 \text{ mg}\cdot\text{L}^{-1}$.

In real aquatic ecosystems, the concentration of dissolved iron is often greater than the specified value. In particular, in our modeled water runoff, the iron concentration reached $0.62 \text{ mg}\cdot\text{L}^{-1}$.

This phenomenon is due to the complexing process, competing with hydrolysis and increasing iron migration capability. Thus, Osadchyi et al. (2016)

shows that the iron in Dnipro reservoirs is present predominantly in the form of complex compounds with organic ligands. HA and FA are the dominating ligands of organic nature participating in the process of complexing. Due to significant difference in their concentrations in natural waters, metal complex compounds predominate with the latter.

The coexisting forms of iron in the water runoff were examined by a thermodynamic approach using the model MINTQA2 which is built on the equilibrium constant principle. The model database was modified before calculation because of the absence of stability constants for iron and HS (Osadchyi et al., 2003).

The difficulty lay in that the stability constants of metal-HS complexes, identified at certain pH values, are conditional. It is a well-known fact that the average molecular weight of dissolved HS increases with growing pH because of association. Therefore,

stability constants of HS increase with higher pH, which is caused by structural changes of HS, when many of the surface functional groups are acting as additional binding centers.

The stability constants of fulvate complexes with iron, mentioned in the literature, were obtained for pH = 5. However, this pH value is not typical for the surface water. To modify pH into real pH values the following methodical approach was used. Complexing abilities of most metals (as it was found for EDTA complexes) are functionally dependent on their ionic potential. This allowed us to develop the equation and predict the stability constants of HS complexes based on at least one conditional constant (Osadchyi et al., 2016). Calculations of other pH were done according to the equation:

$$\lg\beta_{1(c)} = 0.0667 \text{ pH}^2 - 0.033 \text{ pH} + 5.5.$$

Obtained stability constants are presented in Table 1.

Table 1: Stability constants of complex compounds of iron with fulvic acids under different pH $\lg\beta_{1(c)}$ * - experimental conditional stability constant

Parameter	Stability constants, $\lg\beta_{1(c)}$							
pH	3	4	5	6	7	8	9	10
$[\text{Fe}^{3+}\text{-FA}]^+$	6.0	19.1	7.0*	7.7	8.5	9.5	10.6	11.8
$\text{Fe}(\text{OH})\text{FA}^0$	19.1	19.2	20.1*	20.8	21.6	22.6	23.7	24.9

The data of the chemical composition of subsurface runoff, produced at the experimental plot during snowmelt, was used as input data for thermodynamic modeling of coexisting forms of iron. The calculations were made for water temperature 5°C, pH = 7.6. The composition of HA and FA was 13 and 288 mg·L⁻¹, respectively. Iron concentration ranged from 0.1 to 9.0 mg·L⁻¹. The results showed that, regardless of the concentrations studied, the iron in the aqueous phase almost entirely (99.8-100%) is present in the form of hydroxy-fulvate complex compounds. In neutral and slightly alkaline environments, complex $\text{Fe}(\text{OH})_2^+$, resulting from the hydrolysis, reacts with FA with subsequent formation of highly soluble hydroxy-fulvate complexes. This process significantly increases iron migration capability in aquatic ecosystems.

Within the studied concentration range Fe occupies 15-62% of fulvate ligands (Fig. 8 left).

Using thermodynamic modeling methodology, we defined boundary concentrations of the dissolved iron for the conditions of the surface waters in Ukraine. Forms of iron migration were modeled using concentration 2 mg·L⁻¹, within the range of pH = 6.0-9.5, with FA concentrations variability from 2.5 mg·L⁻¹ to 30 mg·L⁻¹. From Fig. 8 (right) it follows that given pH = 7 and FA concentration being within the range 10-30 mg·L⁻¹, the content of iron in the solution may be from 0.35 to 1.95 mg·L⁻¹. With pH growing to 8.0, the concentration of dissolved Fe is reduced to 0.1-0.8 mg·L⁻¹. Increased pH value resulted in removing of iron from the solution due to hydrolysis.

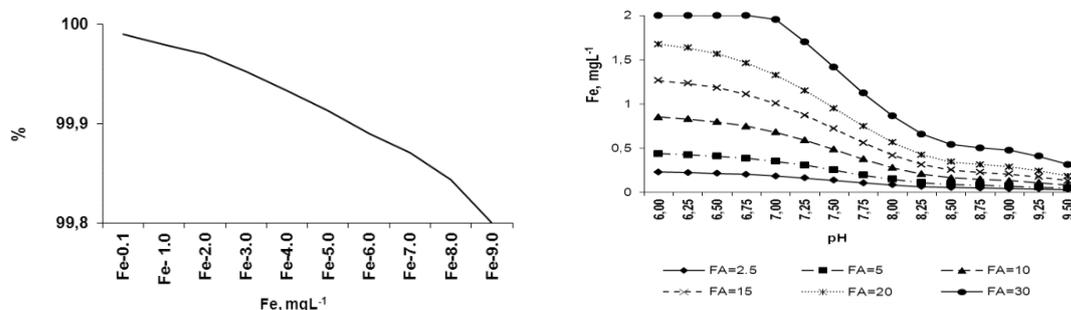


Fig. 8: Forms of iron present in water of subsurface runoff from peat deposits (left) and limits of iron migration (2 mg·L⁻¹) in dissolved state under pH variability within the range 6.0-9.5 and FA concentrations – 2.5-30.0 mg·L⁻¹ (right)

Inflow of humic substances and iron from the water catchment area of the Pripjat River

The following methodology was proposed to estimate the inflow of organic substances and iron from the Pripjat River into the Kyiv Reservoir.

Experimental plots provide information regarding the role of individual factors. A significant drawback is that homogeneous landscape in such plots does not allow for extrapolating the results to the watershed level, featuring cumulative effect of different processes on the runoff water chemistry. 15 different landscape complexes are singled out in the basin of the Pripjat River (Obodovsky et al., 2012). Nonetheless, simulation data on leaching of substances from a peat deposit can be utilized with high reliability to evaluate the inflow of organic compounds from its water catchment area. This

assumption is based on the following facts. The swampiness of the Pripjat Basin area is relatively high, the area of wetlands in the natural state is 6.8 thousand km², combined with drained areas it reaches more than 16.8 thousand km² (approximately 15%) (Fig. 9). Waterlogged areas feature special type of water with the highest concentration of organic substances among water objects, high content of biogenic elements and heavy metals, primarily iron. By contributing to feeding of surface watercourses, swampy waters directly affect the chemistry of the rivers, and this influence is often beyond the waterlogged region (Osadcha & Osadchyi, 2013).

Thus, the wetlands have major contribution to the inflow of organic substances and iron in the basin of the Pripjat River. The influence of other landscapes would be minimal.

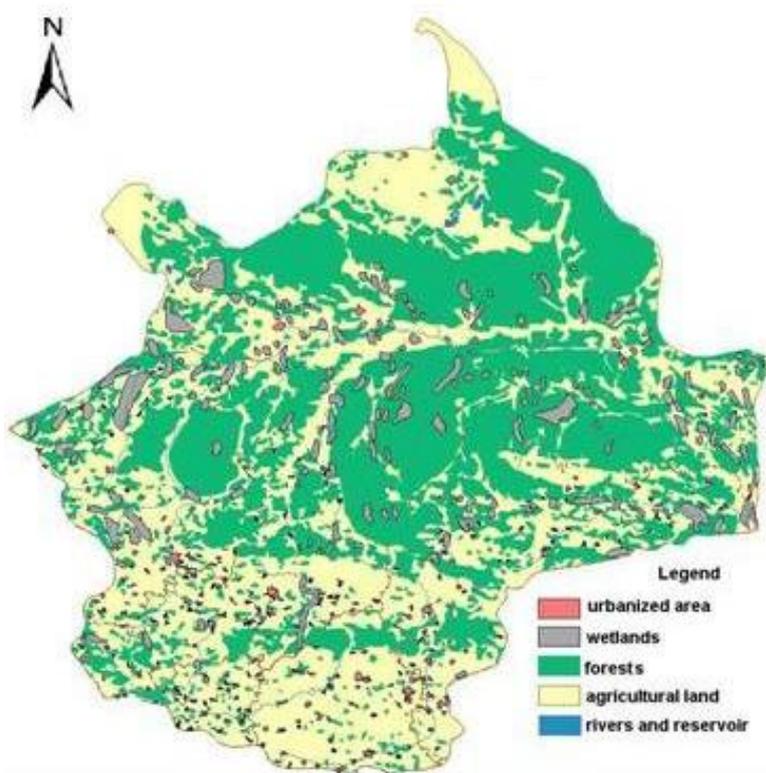


Fig. 9: Land use in the Pripjat Basin

Water runoff generated at the small packed, peat covered plot was 237 mm deep, which almost matched the value of the historical maximum in Pripjat Basin (272 mm, which was observed in 1845). Thus, the entire range of possible changes in water content was covered. As it is known, the concentrations of solute depend on water runoff indicators.

To account for these differences, the methodology of separation of water runoff into

intervals was used, which was developed by EPA (2007). According to the percentage of exceedance such intervals were divided into: high flows (<10%), moist conditions (10-40%), mid-range conditions (40-60%), dry conditions (60-90%), low flows (> 90%).

Due to the fact that hydrological observations in the mouth area of Pripjat were not systematic, the flow duration curve was developed for the upper Mozyr station, where observations began in 1881.

Runoff characteristics at the main-stream station near the city of Chernobyl were recalculated in accordance with Gorbachova & Khrystyuk (2001).

Segments corresponding to the runoff layer values of individual water content intervals were singled out on a hydrograph's runoff at the experimental plot. Average concentrations of HA, FA and iron (Table 2) were calculated for each of the intervals.

Using the presented data one can get the leaching values of the studied substances for any

period of time (day, month, season, and year) making use of the relation:

$$\text{Load} = \text{Swetlands} \cdot \text{Water depth} \cdot C$$

where: Load – leaching of substances for a given period of time; Swetlands - wetlands area; Water depth – runoff layer of a specified probability, mm; C - concentration of substances.

Table 2: Values of runoff layer and average concentrations of HA, FA and iron for different water content conditions of the Pripyat River, outlet station near the city of Chernobyl

Runoff	Percentage of exceedance, P	Water depth (mm)	HA (mg·L ⁻¹)	FA (mg·L ⁻¹)	Fe (mg·L ⁻¹)
High flows	<10	237	25.8	304.5	0.22
Moist conditions	10-40	151	23.3	289.0	0.24
Mid-range conditions	40-60	114	23.6	284.0	0.30
Dry conditions	60-90	88	23.9	280.9	0.31
Low flow	>90	61	22.9	278.9	0.33

Note: HA= humic acids; FA =fulvic acids; Fe=iron.

The projections of annual inflow of HA, FA and iron into the Kyiv Reservoir with Pripyat waters in years with low water level, average water level and high water level (Table 3) are in good agreement with similar characteristics, obtained during field observations (Osadcha & Osadchyi, 2002a).

Table 3: Annual leaching of HA, FA, and iron with water of the Pripyat River

Period	HA (Kt year ⁻¹)	FA (Kt year ⁻¹)	Fe (t year ⁻¹)
Dry year	9.7	119.2	90.8
Average water level	17.7	213.8	195.5
Wet year	32.2	379.5	376.1

Note: HA= humic acids; FA =fulvic acids; Fe=iron.

Conclusion

A field experiment was conducted on a small runoff plot to study the inflow of organic substances and iron from the peat layer of 50 cm deep during the spring season.

During snowmelt, a saturation excess mechanism of runoff generation was observed, which produced a subsurface runoff 237 mm deep.

The intensity of the runoff decreased with increasing duration of the peat mass moistening.

Spring simulations showed more intensive inflow of dissolved FA than HA. The concentration of HA in the runoff ranged within 12-44 mg·L⁻¹, while the minimum and maximum values of FA content exceeded them nearly by an order of magnitude and amounted to 144-443 mg·L⁻¹.

The results of HA model distribution in a solid-to-water phases system showed that not more than 1.8% of HA mass fraction is dissolved. HA dissolution occurs in two stages, featuring sequential involvement of carboxyl and hydroxyl groups.

The HA emission from the experimental plot depended on the performance of water runoff.

The iron emission from waterlogged areas was determined by water runoff and the presence in it of organic substances. Geochemistry of wetlands significantly improves migration properties of iron due to its binding into strong compounds with humic acids. Iron enters the river in the form of dissolved hydroxy-fulvate complexes. Being one of the most common elements in the earth's crust, iron does not engage all HC potential binding sites, some of which are free to interact with other metals. Calculations using thermodynamic modeling showed that pH value and FA concentration are the main factors determining the migration of iron in a dissolved state.

A methodology has been proposed to calculate the leaching of HC and iron from the water catchment area of the Pripyat River under various water content conditions.

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