INTRODUCTION

River ecosystems are a crucial element of both local and global ecosystems. The environmental safety of rivers, influenced by natural and anthropogenic processes at local and regional levels, is essential for the well-being of populations residing in river basins [Posthuma et al., 2020; Malovanyy et al., 2016; Bhattacharjee & Dutta, 2022; Shmandiy et al., 2017]. The environmental safety of river ecosystems is closely tied to the presence of organic pollutants with hydrocarbon composition. Catastrophic oil spills and the release of oil-based products have far-reaching implications for the stability and health of river ecosystems [Adams et al., 2020; Shevchenko et al., 2021; Loboiichenko et al., 2021a]. The sources and magnitude of hydrocarbon pollution in surface water are on the rise due to the advancement of emerging technologies like shale oil and shale gas extraction methods [Lazaruk & Karabyn, 2020], as well as the occurrence of catastrophic events such as floods. These events contribute to the introduction of localized hydrocarbon pollution sources into watercourses [Starodub et al., 2018]). Rivers located in proximity to drinking water intakes are particularly susceptible to hazardous spills of hydrocarbon compounds. Such incidents have the potential to disrupt the water supply of multiple settlements simultaneously. Therefore, maintaining a constant monitoring regime for water quality in river systems is imperative to ensure their environmental safety [Chowdury et al., 2019; Odnorih et al., 2020; Park et al., 2020; Loboiichenko et al., 2021b].

Furthermore, in the event of catastrophic hydrocarbon inflows into river systems, there exists a potential risk of emergencies that can lead to the disruption of drinking water supply systems in settlements [Dodman et al., 2022].

The Stryi River is one of the most important watercourses in the western region of Ukraine. It serves as a source of water supply, facilitating the flow of water to the cities of Lviv, Truskavets, and Drohobych.
The Stryi River basin is situated on a heterogeneous and complex geological basement known as the Carpathian flysch. The rivers within the Stryi basin experience a notable frequency of floods throughout the year, primarily attributed to brief, yet intense precipitation during the warm season, rapid snowmelt during winter thaws in the mountains, and overall snowmelt during springtime. The river flow exhibits both seasonal variations and long-term fluctuations. Considering the long-term cyclic fluctuations in river flow as well as the dynamic spatial and temporal patterns they exhibit, is a crucial and practical consideration in hydrological and water management calculations. This aspect is significant in terms of ensuring water supply to diverse sectors of the economy, estimating flow rates for rivers with limited observation data, and enabling predictions of catastrophic hydrometeorological events to a certain extent [Pochaievets & Rozlach, 2014].

It is well-established that the rivers in the Carpathian region experience an annual occurrence of 3 to 8 floods, exhibiting varying levels of intensity [Romashchenko & Savchuk, 2002; Susidko et al., 1998].

Having analyzed the complete water availability cycle, encompassing high and low water phases over a span of 29 years, it becomes evident that, on average, there were 6 channel-destroying floods characterized by catastrophic consequences, 14 channel-destroying floods, 77 channel-forming, 98 channel-controlling and 32 channel-preserving floods in the basin. In total, there were approximately 100 active and around 120 passive floods [Pochaievets & Rozlach, 2014].

Obviously, during such floods, water overflows from the floodplain onto the terraces, leading to the influx of localized pollutants from the river terraces into the water flow. To accurately predict the parameters of hydrocarbon migration within the river water flow, it is imperative to employ a suitable mathematical model that incorporates key parameters governing pollutant migration. Additionally, this model should be user-friendly and applicable in emergency scenarios.

Among the various hydrocarbon pollutants, the authors focused specifically on benzene (C₆H₆) due to its high carcinogenicity [Loomis et al., 2017], limited biodegradability [Rusyn et al., 2003] and significant prevalence of aromatic hydrocarbons in the oils of the Carpathian oil and gas province [Sirenko et al., 2017].

This study aimed to predict the migration parameters of hydrocarbon pollutants on the example of benzene (C₆H₆) due to its continuous linear flow into the watercourse of a mountain river.

MATERIALS AND METHODS

To accomplish the objectives of the study, theoretical methods (analysis, synthesis, comparison), field (profile, morphological analysis) and experimental (observation, gravimetric) methods were employed.

Field studies were conducted on two sections of the Stryi River, which is a right tributary of the Dniester River within the Black Sea basin. The fieldwork involved a comprehensive description of the outcrop of alluvial sediments, with profile and morphological methods used to identify different horizons. The main criteria used for diagnosing genetic horizons included variations in color, changes in particle size distribution, layer density, and rock structure. Natural outcrops along the Stryi River, partially cleared by the research team, were used to identify the genetic horizons of the floodplain terrace. The survey section spanned a length of 500 meters and was situated on the left bank of the Stryi River, approximately 2000 meters away from the confluence of the Opir River with the Stryi.

Under laboratory conditions, the particle size distribution of sediments was determined using the sieve method. During the simulation of an accidental spill, the concentration of benzene was measured using the gravimetric method.

The determination of benzene (C₆H₆) content was conducted following [MVV № 081/12–0645–09] with some changes in authors’ modification. The method employed for measuring the mass concentration of benzene (C₆H₆), as a representative petroleum product, in surface water, groundwater, and return water involved several steps. Firstly, water and organic matter were extracted from the sample using chloroform. The chloroform was then evaporated, and the residue was dissolved in hexane. Subsequently, a separation process was carried out on an aluminum oxide column to isolate polar compounds, vegetable and animal fats, as well as light hydrocarbons. Hexane was evaporated, and the resulting residue was measured gravimetrically. The mass concentration of petroleum products in the original water sample was determined through calculation methods. Prior to measuring the mass concentration of benzene, it was mixed with rock samples obtained from the first floodplain terrace.

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in a weight ratio of 1:12, followed by thorough mixing. The mixture was then allowed to settle to ensure saturation of the rock with benzene and separation of the liquid phase. The measurement error did not exceed 10% (N = 3).

To determine the diffusion coefficient of benzene in both water and sediments, an experimental spatial hydrodynamic model was employed, in which the sediment samples from the study site were placed. Water and benzene were continuously supplied in a unidirectional manner along the axis of the setup, following the principles outlined in the [Karabyn et al., 2018]. The concentration of benzene in both water and sediments at various points in the system was measured. These measurements allowed for the calculation of the benzene concentration gradient and subsequent determination of the diffusion coefficients using Fick’s law.

The results from mathematical modeling and experimental studies were compared one with one another.

Laboratory studies were carried out at the Environmental Safety Research Laboratory located at Lviv State University of Life Safety (Certificate № RL 091/21 from 30.11.2021). External verification of the results obtained in the university laboratory was carried out in an independent laboratory using infrared spectroscopy, taking every 10th sample for analysis. The sample preparation included extraction of benzene with carbon tetrachloride and chromatographic purification from non-nuclear compounds in an active aluminum oxide column. The amount of benzene was determined using an IRSpect-29 instrument. The device is calibrated with a mixture of decane (56% by volume), isooctane (19% by volume) and benzene (25% by volume). The lower limit of detection is 0.1 mg/dm$^3$. When compared, the result was satisfactory, the error did not exceed the maximum permissible in the method [MVV No. 081/12–0645–09].

Verification of the reliability of the results of mathematical modeling in comparison with experimental data was carried out using the Wilcoxon test [Derrick et al., 2020; Kishore & Jaswal, 2022].

RESULTS AND DISCUSSION

Mathematical modeling is a key method used to predict the spread of oil products in river systems. This approach employs mathematical formulas and algorithms to determine the dispersion of oil products in the river system and their impact on individual components. One of the most common mathematical models of oil spreading in river systems is a system of differential equations. These equations provide a descriptive framework for capturing the movement and dispersion of oil products in the river system, incorporating essential parameters, such as velocity and concentration [Hu et al., 2006; Wang et al., 2023; Robson & Hamilton, 2004].

Most mathematical models for the migration of pollutants in river streams typically overlook the influence of bottom sediments on pollutant movement in the water. However, in the case of mountain rivers characterized by high velocities, turbulent water flow, and narrow cross-sectional dimensions, the interaction between river water and bottom sediments becomes considerably significant. To address this, a mathematical model developed by the authors was employed, initially designed for a single discharge event of pollutants into a water stream [Kuzyk et al., 2023] and adapted to the conditions of continuous linear flow of pollutants.

The mathematical model proposed by the authors comprises two partial differential equations. The first equation describes the processes of pollutant diffusion in water, as well as the phenomena of sorption and desorption in the “water-bottom sediments system”, accounting for the river flow rate. The second equation describes the processes of pollutant diffusion in sediments and the sorption-desorption phenomena in “the sediment-water system”.

\[
\begin{align*}
\frac{\partial C}{\partial t} &= D_w \frac{\partial^2 C}{\partial x^2} - v_w \frac{\partial C}{\partial x} - k_r C + k_w c \\
\frac{\partial c}{\partial t} &= D_r \frac{\partial^2 c}{\partial x^2} + k_r C - k_w c
\end{align*}
\]

where: $C = C(x, t)$ – the concentration of pollutant in the river water, mg/dm$^3$; $c = c(x, t)$ – the concentration of pollutants in the bottom sediments of the river, mg/dm$^3$; $x = 0$ – reference point at time, $t = 0.0$ s; $x$ – the distance from the starting point, m; $D_w$ – the diffusion coefficient of the pollutant in water, m$^2$/s; $D_r$ – the diffusion coefficient of the pollutant in the bottom sediments, m$^2$/s;
$k_w$ – the coefficient of distribution of the pollutant in the “water-bottom sediments” system;
$k_r$ – the coefficient of distribution of the pollutant in the “bottom sediment-water” system;
$v_w$ – the water velocity in the river, m/s.

**Initial conditions**

1. For the first equation, set the initial condition that indicates the absence of a pollutant in the water:

   \[ C(x, 0) = 0 \]  \hspace{1cm} (2)

2. For the second equation, the initial condition will reflect the fact that there is no pollutant in the sediments at the initial time:

   \[ c(x, 0) = 0 \]  \hspace{1cm} (3)

3. Assume the velocity of water in the river to be constant:

   \[ v_w = \text{const} \]  \hspace{1cm} (4)

4. Assume that the chemical composition of the water in the river and the lithological and chemical composition of the sediments remain constant.

**Boundary conditions**

At the beginning of the calculation, the first-order boundary condition (5) was applied to represent the constant flow of the pollutant into the water at this point using a logistic function, and the absence of the pollutant in the sediments was described by the first-order boundary condition (6):

\[ C(0, t) = C^* \left( 2 \frac{0.5 e^t}{1 + 0.5(e^t - 1)} - 1 \right) \]  \hspace{1cm} (5)

where: $C^*$ – maximum concentration of the pollutant in the water resulting from the discharge, mg/dm$^3$;

\[ c(0, t) = 0 \]  \hspace{1cm} (6)

**Input data of the mathematical model**

Experimentally calculated [Rudobashta & Kartashov, 1993; Sherwood et al., 1975] the diffusion coefficient of benzene (C6H6) in water $1.02 \times 10^{-6}$ m$^2$/s, in a water-saturated pebble-sand mixture (the middle part of the Stryi River) $5 \times 10^{-10}$ m$^2$/s and in a water-saturated sand-clay mixture (estuarine zone of the Stryi River) $4 \times 10^{-10}$ m$^2$/s. The speed in the middle part of the river is 2.0 m/s, and in the mouth – 1.6 m/s.

The distribution coefficients of benzene in the system “water-bottom sediments” ($k_w$) and “bottom sediments-water” ($k_r$) were determined to be 0.50:2.00 for the middle part of the Stryi River and 0.75:1.33 for the estuarine zone of the Stryi River [Kuzyk et al., 2023].

At the study site, the Stryi River channel is characterized by a winding and partially branched structure. It has a depth ranging from 0.5 to 2.9 meters and a flow velocity varying between 1.4–4.6 m/s. The riverbed consists of heterogeneous stones with diameters of 15–25 cm and is covered with a significant amount of pebble sediment. The width of the river ranges from 15 to 60 meters, while the river valley extends up to 650 meters. The river banks exhibit steep slopes, standing 1.5–2 meters above the water level. The Stryi River in the study area features a gentle slope. Within the study area, significant lateral erosion is evident. The geological composition of the study area comprises anthropogenic, alluvial, and Lower Cretaceous sediments, extending to the explored depth. The transfer and accumulation of gravel and pebble sediments in the riverbed and valley can be assessed through monitoring observations obtained from gauging activities. A notable characteristic of the river’s water level regime is the occurrence of floods throughout the year, with no specific seasonal pattern [Volosetskyi & Shpyrnyal, 2013].

**Numerical solution of a mathematical model**

According to the outcomes of mathematical modeling regarding the continuous linear flow of benzene into the Stryi River, the following results were obtained.

At 60 s after the start of continuous flow of benzene into the river system, its maximum
content in water is 0.24933 g/dm$^3$ and decreases to 0 g/dm$^3$ at a distance of 116 m from the discharge source. At 1800 s after the start of continuous flow, the maximum content of benzene is 0.89038 g/dm$^3$ (Figure 1).

From another point of view, the process of benzene migration into the river system can be analyzed by displaying time on the graph along the abscissa axis. At a distance of 1 m from the source of pollution, the maximum content of benzene in water due to its continuous flow is reached 481.1 s after the start of flow of the pollutant and is 0.96186 g/dm$^3$. The maximum content of benzene in bottom sediments on the same section is 0.052921 g/kg (Figure 2).

At a distance of 1000 m from the source of pollution, the maximum content of benzene due to its continuous flow is 0.88082 g/dm$^3$ in water and 0.22072 g/kg in bottom sediments (Figure 3).

At 60 s after the start of continuous flow of benzene into the river system, its maximum content in water is 0.18593 g/dm$^3$ and decreases to 0 g/dm$^3$ at a distance of 94 m from the discharge source. At 600 s after the start of continuous flow, the maximum content of benzene is 0.73942 g/dm$^3$ (Figure 4).

At a distance of 1 m from the source of pollution, the maximum content of benzene in water due to its continuous flow is reached 531.4 s after the start of flow of the pollutant and is 0.93444 g/dm$^3$. The maximum content of benzene in bottom sediments on the same section is 0.099854 g/kg (Figure 5).

At a distance of 500 m from the source of pollution, the maximum content of benzene due to its continuous flow is 0.72381 g/dm$^3$ in water and 0.40375 g/kg in bottom sediments (Figure 6).

**Experimental validation of mathematical modeling results**

Using a laboratory installation in the form of a trough filled with bottom sediments and water, and with continuous injection of benzene at a constant concentration, the data regarding the temporal variations in benzene concentration in water were obtained [Karabyn et al., 2018]. The test was performed at different initial concentrations of benzene in water: from 0.05 g/dm$^3$ to 1.2 g/dm$^3$. To demonstrate the verification, the result (Figure 7) is shown with the smallest error at an initial benzene concentration of 1.2 g/dm$^3$. The experimental findings generally support the validity of the mathematical model (Figure 7).

The convergence of the mathematical modeling results with the experimental results was confirmed by means of a one-factor analysis of variance. Thus, the mathematical model is adequate and can be used for forecasting.

**CONCLUSIONS**

The pollution of river systems has severe implications for hydroecosystems, often resulting in significant disruptions across wide areas and
Figure 2. Change in benzene concentration as a result of continuous input of the pollutant at a distance of 1 meter over time in water (C) and bottom sediments (c) of the middle part of the Stryi River

Figure 3. Change in benzene concentration as a result of continuous input of the pollutant at a distance of 1000 meters over time in water (C) and bottom sediments (c) of the middle part of the Stryi River

Figure 4. Change in benzene concentration as a result of continuous input of the pollutant for 60 (C₁) and 1800 (C₂) seconds in water in the area of the estuary of the Stryi River
Figure 5. Change in the concentration of benzene due to its continuous input of the pollutant at a distance of 1 meter over time in water (C) and in bottom sediments (c) in the area of the estuary of the Stryi River.

Figure 6. Change in the concentration of benzene due to the continuous influx of the pollutant at a distance of 500 meters over time in water (C) and bottom sediments (c) in the area of the estuary of the Stryi River.

Figure 7. Change in the concentration of benzene due to the continuous influx of the pollutant at a distance of 1 meter in time in the water of the middle part of the Stryi River (verification and comparison of the results of laboratory experiments and calculation of a mathematical model).
posing a threat to the drinking water supply for local populations. In the occurrence of accidental releases involving substantial volumes of pollutants, such as those arising from military operations or man-made accidents, obtaining prompt and reliable forecasts regarding the movement parameters of pollutants along the river becomes crucial. Mathematical modeling offers a rapid and effective means to generate these forecasts.

The authors have developed a mathematical model to simulate the continuous linear discharge of a pollutant into a water stream. This model comprises two differential equations. The first equation describes the diffusion of the pollutant in water, as well as sorption and desorption processes in the “water-bottom sediments” system. The second equation describes the diffusion of the pollutant in sediments, along with sorption and desorption processes within the “bottom sediment-water” system.

On the basis of the developed mathematical model of pollutant migration, which considers the effect of bottom sediments, relationships have been derived to predict the concentration of a pollutant at a given distance from the pollution source resulting from its continuous linear flow into the water stream of a mountain river. These dependencies enable the estimation of pollutant concentrations at specific distances from the pollution source, considering the time of the pollutant arrival.

The results of the mathematical modeling were experimentally validated, demonstrating acceptable differences between the experimental and theoretical data. This confirms the applicability of the developed mathematical model in predicting the migration of benzene (C₆H₆) in mountain stream water.

The developed model holds potential for predicting the extent of river pollution in emergency scenarios involving the discharge of oil products by environmental inspection personnel, basin management authorities and civil defense units.

REFERENCES


17. Park, J., Kim, K.T., Lee, W.H. 2020. Recent advances in information and communications technology (ICT) and sensor technology for monitoring Water Quality. Water, 12(2), 510. DOI: 10.3390/w12020510


