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Petroleum hydrocarbons in soil and water matrices: Testing a new rapid extraction procedure and FTIR spectroscopy for integrated risk assessment in micro- and low-order catchments

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✓ **Abstract.** The aim of the study was to develop a fast and effective approach that would enable subsequent integrated risk assessment in micro- and low-order catchments. The procedure involved an alternative sampling strategy, a rapid one-step cyclohexane extraction, extract purification through florisil, concentration, and analysis using an Agilent Cary 630 FTIR spectrometer equipped with a TumbliIR 100 sampling module, with possible adaptation to 1,000 µm or other commercially available systems to achieve lower detection limits. Validation results showed that for soil matrices (wet soil, bottom sediments) the method provides good internal consistency with a relative standard deviation of approximately 11% ($n = 10$) and a systematic bias of approximately -11.5%, with recovery of 88.5%. The expanded measurement uncertainty is $\pm 24\%$ for soil and $\pm 31.9\%$ for water, which corresponds to typical levels for these environmental matrices. For water matrices (surface and drainage waters, soil washings, percolates) recovery exceeds 94%, systematic bias is small, and precision is at an acceptable level. Model experiments evaluating the effects of the sampling strategy revealed significant systematic shifts: -47% for soil percolate, -43.5% for soil ($w = 45\%$), and -40.3% for water-saturated soil, indicating heterogeneous TPH distribution in samples prior to extraction. Assessment using green analytical chemistry indices via AGREE and AGREEprep tools demonstrated the advantages of the developed procedure over conventional standard methods: the overall AGREE index for the developed method is 0.61 (compared to 0.20-0.33 for the gravimetric method, infrared (IR) method according to the MVI, and ASTM D7678-17. It was established that, within Ivano-Frankivsk,

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concentrations in road dust and roadside soils ranged from $1.6\text{--}2.8 \times 10^3$ mg/kg and locally reached $4.7\text{--}6.5 \times 10^5$ mg/kg, posing high risks associated with stormwater runoff and pollutant discharge into storm drains, eventually entering the Bystritsia Solotvynska River

✔ **Keywords:** sample preparation; method validation; measurement uncertainty; matrix effects; watershed contamination

✔ Introduction

Petroleum hydrocarbons are among the most widespread and environmentally hazardous pollutants in urban and industrial ecosystems. They readily accumulate in soils and surface deposits, are capable of migrating via surface runoff into water bodies, and form persistent contamination hotspots. This issue is of particular relevance for small catchments, where even local pollution sources can rapidly lead to the degradation of the entire hydroecosystem. Under contemporary conditions, there is an increasing need for rapid, reliable, and cost-effective methods for assessing this type of contamination to ensure effective environmental monitoring and risk management.

Petroleum hydrocarbons are incorporated into the environment of urbanised and industrial areas through accumulation on solid surfaces and in soils, as reported by O. Trysniuk *et al.* (2020), as well as in the near-surface geological environment, as noted by E. Kuzmenko *et al.* (2025). They represented one of the main groups of anthropogenic environmental pollutants and are common constituents of street dust and road debris as forms of solid dispersed deposits in urban and industrial areas. Their input into the environment is driven by various sources of anthropogenic pressure, including the operation of petrol filling stations, which is accompanied by emissions of volatile organic compounds and potential leaks of petroleum products into soil and aquatic environments, according to M. Troshyn *et al.* (2025). Additionally, B. Herasymenko (2024) emphasised that accidental leaks from oil and gas pipelines have been identified as a significant source of hydrocarbon input into the soil cover, leading to persistent changes in its physicochemical and biological properties. Military conditions further intensify the scale of petroleum soil contamination, forming new hotspots of ecosystem degradation, as noted by H. Hrytsuliak *et al.* (2025), which necessitates further restoration measures. Under the influence of atmospheric precipitation, they were mobilised by surface runoff and infiltration flows, transported through artificial and natural drainage systems, as well as within soil and rock strata, and, under favourable hydrological and hydrogeological conditions, are dispersed into water bodies or, by forming local or transitory hydrocarbon contamination plumes, create risks for ecosystems of micro- and low-order catchments as a whole. In addition, military strikes by Russia and acts of sabotage caused the destruction of numerous facilities for the storage and transportation of petroleum products throughout Ukraine, which was accompanied by fires and large-scale spills. Unlike fires, which are recognised as an important source of formation and mobilisation of polycyclic aromatic hydrocarbons (PAHs) that enter the

environment through the combustion of organic matter and are subsequently redistributed between the atmospheric, soil, and aquatic compartments, as shown in the review by I. Campos & N. Abrantes (2021), petroleum product spills lead to long-term contamination of the land surface, with a high risk of infiltration into the aeration zone and the formation of persistent degradation zones within the geological environment, as reported by R. Havryliuk *et al.* (2024).

Determination of the total petroleum hydrocarbons (TPH) content in soils and sediments is a key element of environmental contamination assessment and the planning of remediation measures. However, despite the global significance of petroleum contamination of the upper soil and geological environment, existing analytical methods often remain labour-intensive and resource-consuming. As noted by B. Abdykarimov *et al.* (2025), the development of rapid, accurate, and efficient analytical approaches still represents a significant scientific and practical challenge. Despite the high applied significance of the petroleum contamination problem in Ukraine and the urgent challenges associated with the impact of war on the environment, researchers continue to face a number of difficulties in determining petroleum hydrocarbons in various environmental matrices during applied studies. Outdated analytical equipment, the complexity and labour intensity of extraction procedures, as well as potential health hazards for operators limit the possibilities for conducting rapid and reliable measurements. Institutional and laboratory-analytical support of many institutions remains insufficient, which often leads to results with limited accuracy, low reproducibility, and questionable reliability, according to Resolution of the Cabinet of Ministers of Ukraine No. 610-r (2023). The combination of these factors emphasises the need to develop and implement modern, safer, and more effective methods for controlling petroleum product contamination.

These circumstances emphasise the relevance of developing and implementing analytically reliable and environmentally safe procedures for sampling and determining petroleum hydrocarbons in various environmental matrices, which is a necessary prerequisite for proper diagnosis of environmental conditions, environmental risk assessment, pollution monitoring, and substantiation of environmental protection measures. Accordingly, the aim of the study was to develop and experimentally validate a rapid analytical method for the determination of petroleum hydrocarbons in soils and waters of small catchments using an extraction approach combined with FTIR spectroscopy. The scientific novelty of the study lies in the development and experimental confirmation of the effectiveness of a new rapid

extraction and FTIR spectroscopy procedure adapted to contemporary scientific and practical challenges, which can be effectively and promptly applied for integrated environmental risk assessment in micro- and low-order catchments.

✔ Literature Review

For the quantitative assessment of petroleum hydrocarbon content in water and the environment, their concentration is regulated as the TPH indicator in accordance with EU legislation. TPH represent a generalised term that encompasses several hundred chemical compounds derived from crude oil and composed of carbon and hydrogen atoms, including benzene, toluene, xylenes, hexanes, naphthalene, fluorene, jet fuel, mineral oils, and related substances, as noted by A. Simion *et al.* (2022). In Ukraine, standard methods are used to determine TPH (most often under the term “petroleum products”). For water and soils, classical, normatively established approaches oriented toward reproducibility and compatibility with the state control system remain the most widespread. For aqueous matrices, methods based on extraction with organic solvents followed by gravimetric determination (MVI No. 081/12-0645-09, 2010), IR analysis (MVI No. 081/12-0877-13, 2014), or gas chromatographic analysis (DSTU ISO/TR 11046-2001, 2002; DSTU ISO 9377-2:2015, 2016) are commonly applied. In soils and bottom sediments, Soxhlet or liquid-solid extraction is typically followed by gravimetric analysis (MVI No. 081/12-0116-03, 2004; MVI No. 081/12-0725-10, 2011), IR analysis (DSTU ISO/TR 11046-2001, 2001; MVI No. 081/12-0637-09, 2009), or gas chromatography (DSTU ISO 16703:2007, 2007).

Among the existing methods for measuring petroleum product content, the fluorimetric method using the FLUORAT analyser is very often applied in Ukraine; it is based on extraction of petroleum products from the sample with hexane, optional purification of the extract, and allows determination of the mass concentration of petroleum products in water in the range of 0.005–50 mg/L. Gas chromatography (GC-FID, less often GC-MS) is mainly used in reference and research laboratories for detailed analysis of fractional composition, whereas more “green” approaches (SPME, direct IR probing, express methods) are still implemented on a limited scale and are mostly applied within scientific developments and pilot studies rather than routine state monitoring. This may be due to the still limited availability of modern analytical equipment.

In the reviews by A. Adeniji *et al.* (2017) and Z. Yue *et al.* (2021), the strengths and weaknesses of traditional methods for determining TPH in environmental samples are summarised, with some being more suitable for field screening and others for laboratory analysis. Infrared spectroscopy (EPA 418.1), gravimetry (EPA 1664A), gas chromatography with FID and MSD (EPA 8015, 8270, 625), UV spectrophotometry, immunoassays (EPA 4030, 4035), as well as Raman and fluorescence spectroscopy are discussed; preparation of liquid samples is usually performed by liquid-liquid (LLE) or solid-phase (SPE) extraction, whereas

solid matrices are mainly extracted by Soxhlet. The authors emphasise that IR spectroscopy is gradually replacing other approaches due to the need to eliminate halogenated solvents classified as ozone-depleting and underline the key role of sampling strategy. At the same time, TPH analytical procedures differ substantially in terms of the range of fractions determined and specificity: methods with different extraction efficiencies may yield different TPH concentrations for the same sample, and the use of different calibration standards and extractive solvents complicates result comparability, making a detailed understanding of the applied methodology critically important for correct data interpretation.

A. Imam *et al.* (2019) emphasised the key role of chemical analysis and the importance of using chromatography, spectroscopy, and various sample pretreatment methods for effective monitoring and evaluation of bioremediation experiments. The review by B. Abdykarimov *et al.* (2025) showed that Soxhlet extraction, despite its low environmental friendliness, remains a widespread method for determining TPH due to its high extraction efficiency, whereas more environmentally friendly methods, such as gas chromatography-mass spectrometry with solid-phase microextraction and direct IR probing, reduce solvent use and minimise sample preparation. This review highlighted the need to balance analytical efficiency and environmental sustainability and demonstrates pathways for improving the greenness of methods in forensic and environmental monitoring. J. Płotka-Wasyłka *et al.* (2021) also noted that analytical chemistry is increasingly oriented toward the principles of green analytical chemistry (GAC), especially in sample preparation, with the aim of developing environmentally safe and more sustainable analytical procedures. Critical evaluation of such methods should consider validation criteria, practical and financial aspects alongside GAC principles, as reported by S. Hammad *et al.* (2025).

L. Wang *et al.* (2020) noted that in traditional contaminated-site assessment, soil sampling and transportation of samples from sites are excessively expensive and labour-intensive, whereas the use of portable and accessible field equipment provides a rapid and cost-effective solution to complement complex laboratory analyses. According to the researchers, portable Fourier transform infrared (FTIR) spectroscopy offers advantages such as immediate results, ease of use, and non-destructive measurements, enabling rapid on-site characterisation. Information obtained from IR spectroscopy has the potential to provide baseline data for environmental modelling. For example, when an oil spill or leak occurs on land, multiphase trapping and pH distribution in porous soil media depend on the hydraulic and physical properties of the soil as well as its hydration. The obtained data on these properties and measured TPH concentrations can be applied in mathematical models to assess potential risks of surface- and groundwater contamination downstream through migration and transport from contaminated sites.

Although under field conditions portable instrumental methods provide rapid results and better spatial coverage, which can meet the need for locating site hot spots P. Rosstron *et al.* (2014), and this is generally a trend in the application of in situ methods for characterisation of TPH-contaminated sites L. Wang *et al.* (2021), field measurements using methods that provide near-laboratory-quality data for rapid quantitative, definitive, and defensible sampling remain challenging. A. Fuente-Ballesteros *et al.* (2025) associate current directions for improving environmental efficiency with miniaturisation of analytical systems, reduction of solvent use, and implementation of field measurements. An increasing number of researchers report on this. New analytical procedures should comply with GAC principles, which is achieved both by modification of traditional methods and by the development of specialised sustainable methodologies. At the same time, it is often emphasised that classical laboratory approaches, even after optimisation, are frequently poorly suited for operational environmental monitoring, particularly under conditions of accidental releases or acute toxic impacts, which necessitates the use of fast-acting, compact, resource-efficient, and, where possible, portable analytical solutions.

In conclusion, it should be considered that analytical and monitoring systems are not a neutral reflection of the environment but the result of conscious construction of system boundaries of interest A. Knight *et al.* (2019). The choice of analytical methods determines which processes and risks become visible and which remain outside attention. Increasing the green index of analytical procedures in this study should be regarded as a conscious rethinking of system boundaries: from “ideal accuracy” to “sufficient environmental relevance” and from “universality” to “contextual adequacy”. This enables adaptation, simplification, and improvement of various analytical procedures to the specificity of the environment and research objectives while simultaneously enhancing their environmental efficiency. Overall, a conceptually sound and environmentally justified solution-though requiring appropriate scientific validation-is the application of such a rethinking concept to diagnostic and monitoring tasks, where the system of interest with defined boundaries can

be the landscape-hydrological continuum. Micro- and low-order catchments were selected as the focus of the study in the context of improving diagnostic and monitoring procedures for contamination, since such systems are considered the most sensitive to local anthropogenic impacts, as noted by J. Richardson (2019), and reflect the features of the hydrological continuum within the landscape. In addition, the scale of low-order catchments enables the effective application of models for identifying local pollution sources and accounting for fine-scale landscape features, which is important for the development of local water resource conservation measures, according to M. Myktysei *et al.* (2024).

Thus, the analysis of current approaches for the determination of petroleum hydrocarbons in environmental media demonstrates a wide range of analytical methods that differ significantly in sensitivity, selectivity, labour intensity, and environmental sustainability. Despite substantial advances in instrumental techniques, conventional approaches such as extraction-gravimetric and spectroscopic methods still form the basis of regulatory monitoring, while modern rapid and field-based techniques remain limited in practical implementation. A key issue is the lack of standardisation of results due to differences in extraction procedures, calibration strategies, and analytical standards. Current trends in analytical chemistry are increasingly focused on improving the environmental performance of methods, reducing solvent consumption, and shifting part of measurements to field conditions using portable instruments, particularly FTIR spectroscopy. In this context, the development of rapid, reproducible, and environmentally safe methodologies adapted to the local conditions of small catchments becomes especially important, as they can provide both sufficient analytical reliability and practical applicability for environmental monitoring purposes.

✓ Materials and Methods

Description of the research area

Demonstration experimental studies to test the methodological procedures were conducted between March and May 2025 within three micro-catchments identified as contamination hot spots (Fig. 1).

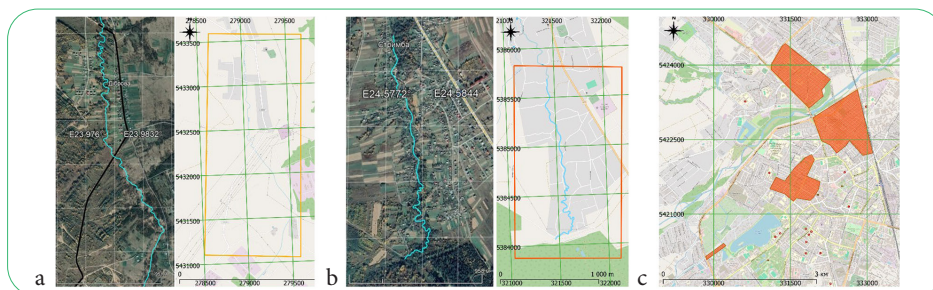


Figure 1. Study sites (micro-catchments) identified as “hot spots” with potential TPH contamination, selected to demonstrate the applicability of the proposed analytical procedure

Note: a – study site (micro-catchment of the Lushchava River (zone of oil extraction influence)); b – catchment of the mountain Strymba River within the area of an accidental oil spill (30.09.2023); c – urbanised micro-catchment within the catchment of the Bystrytsia Solotvynska River (Ivano-Frankivsk)

Source: created by the authors

Figure 1a – the technogenically loaded catchment area of the Lushchava River within the zone of influence of the activities of NGVU “Dolynanaftogaz”. This area represents a part of the catchment of the small Lushchava River within the settlements of Dibrova, Yavoriv, and Solukiv, Dolyna District, located in the zone of oil extraction and known for multiple environmentally hazardous emergency incidents (2017-2018). The watercourse, with a length of 15 km, originates in shrub-covered wetland areas 6 km south of the town of Dolyna and flows in a north-eastern direction. The channel is weakly sinuous, unbranched, with an average flow velocity of 0.2 m/s. The soil cover of the basin area consists of light loamy podzolic soils, locally alternating with alkaline podzolised soils. In its upper reaches, the river channel is hydraulically connected with anthropogenic elements of the flow drainage network, such as roadside ditches, gullies, and open drainage channels, which may act as primary water pathways and reservoirs for the transfer of petroleum hydrocarbons;

Figure 1b – the catchment area of the small mountain river Strymba, within a site known for an accidental rupture of an oil pipeline with a diameter of 150 mm on 30 September 2023, which resulted in an oil spill along the watercourse and a large-scale fire. According to data from the Dniester Basin Water Resources Administration, after the accident the concentration of petroleum products in the Strymba River exceeded hygienic standards for drinking and domestic water use by 10.6 times, and for fishery water bodies by 64 times. Subsequent consequences remained unknown and uninvestigated. The emergency situation demonstrated high environmental risks associated with the operation of oil pipelines in regions with a developed hydrographic network, as well as the necessity of implementing effective monitoring and response measures for such emergency situations. The micro-catchment area is predominantly covered by forest vegetation;

Figure 1c – the part of the Bystrytsia Solotvynska River catchment transformed by urbanisation, within the territory of the urban and suburban zones of the city of Ivano-Frankivsk. The micro-catchment covered the functioning system of an open-flow network of channels and small ditches used for runoff regulation, as well as the main open directed channel of an ancient small watercourse that crosses the western (in the past also the north-western) part of the city – the Stebnytska mlynivka (Mykytsei et al., 2024). In addition, through the system of stormwater sewer collectors of this territory, part of the storm and snowmelt wastewater of the settlement is discharged into the Bystrytsia Solotvynska River without treatment (collector outlets are located along V. Stefanyk Embankment Street).

In addition, through the system of stormwater sewer collectors of this territory, part of the storm and snowmelt wastewater of the settlement is discharged into the Bystrytsia Solotvynska River without treatment (collector outlets are located along V. Stefanyk Embankment Street). The main attribute of this micro-catchment is defined as surface sealing and artificial routing of stormwater runoff from the

city territory as pathways for interception and transport of pollutants to the point of discharge into the main watercourse. For all territories during March and April 2025, weather conditions in Ivano-Frankivsk were dynamic and diverse, which is typical for the transitional period from winter to spring. March began with moderately cool weather: daytime temperatures ranged from +3°C to +16°C, while nighttime temperatures ranged from -5°C to +7°C. In the middle of the month, gradual warming was observed, with daytime temperatures up to +16°C and nighttime temperatures around +7°C. April was characterised by a significant increase in temperature: during the first ten days, daytime temperatures ranged from +3...+9°C, and nighttime temperatures from -3 to +5°C. In the second half of the month, temperatures increased to +15...+21°C during the day and +6...+9°C at night.

In March and April 2025, moderate precipitation was observed, typical for the spring period in the region. In March, the average precipitation amounted to approximately 55-66 mm, distributed over 11-13 days with precipitation. This indicates moderate humidity, with a predominance of rain and wet snow, especially at the beginning of the month. In April, precipitation slightly increased, reaching an average of 60-79 mm, with more frequent short-term rains and possible thunderstorms. Rapid and abrupt fluctuations in weather conditions against the background of changing climatic factors may significantly enhance the desorption of petroleum products that previously entered the environment from surface soil layers, road surfaces, and street dirt in urban systems, as well as under conditions of increased pollutant accumulation resulting from industrial activities or local emergency situations. Taken together, this often leads to intensive wash-off of petroleum products in stormwater runoff and an increased risk of secondary delayed or long-term persistent pollution of water bodies.

Experimental base, equipment, and tools

The basis for experimental tests and innovative developments within the framework of the memorandum of cooperation between the Ivano-Frankivsk National Technical University of Oil and Gas and the Dniester Basin Water Resources Administration was the Water Monitoring Laboratory of the Western Region. In 2023, within the framework of humanitarian and technical support to Ukraine, this laboratory in Ivano-Frankivsk received a modern Cary 630 FTIR infrared spectrometer (Agilent Technologies, USA), provided by the German Federal Agency for Technical Assistance. This instrument is generally intended for operational infrared analysis and provides the possibility of express determination of organic pollutants in water and soil matrices with minimal sample volume requirements. It was equipped with a TumbliIR sampling module with a fixed path length in the 100 µm analysis mode.

Additional analytical equipment included a conductometer pH meter (HORIBA, Japan), electronic laboratory scales with an accuracy of ±0.0001 g, and electronic labo-

ratory scales with an accuracy of ± 0.1 g. Auxiliary equipment included piston dispensers with adjustable dosing volume in the range of 0.5-5 ml and in the range of 100-1,000 μ l, and a drying oven. Extraction flasks were carefully cleaned, rinsed with distilled water, dried at 130°C, labelled, weighed, and packed for field sampling. Medical syringes with a nominal volume of 5 ml equipped with an irrigation tip (for liquid sampling) and 2 ml syringes with a cut connector for sampling individual solid material samples were used for sampling. Cyclohexane was used as the extraction solvent, replacing any carbon tetrachloride, freon, or fluorinated solvents. Cyclohexane is a less toxic and more environmentally safe solvent compared to traditional solvents such as freon-113, carbon tetrachloride, or toluene. An additional advantage is that its absorption spectrum in the IR region minimally interferes with the

detection of characteristic petroleum hydrocarbon bands during FTIR analysis, making it particularly suitable for express methods. An analytical standard of tetradecane from Sigma-Aldrich was used for instrument calibration.

Instrument calibration

A series of freshly prepared solutions from a certified standard sample of tetradecane and high-purity cyclohexane, with nominal concentrations of 0.5, 4, 6, 8, 25, 100 mg/ml, were measured under the same instrumental conditions in 5 repetitions. The instrument setup parameters for spectral data collection are presented in Table 1.

The collected spectral data in the MicroLab PC software were used in the process of creating a calibration model according to the Simple Beer's Law algorithm, which was implemented in the MicroLab Quant environment (Fig. 2).

Table 1. Instrument settings parameters of the Agilent Cary 630 FTIR infrared spectrometer for collecting spectral data of standard solutions of nominal concentrations

Parameters	Set parameter value
Spectral range (cm^{-1})	1,400-1,300
Background scan	32
Sample Scans	32
Resolution (cm^{-1})	4
Zero filling factor	4
Phase correction	Merz method of phase correction
Apodisation	Gamma-Genzel smoothing (apodisation) function
Sampling Technology	Transmission Cell: TumbIIR_100 μm

Source: created by the authors

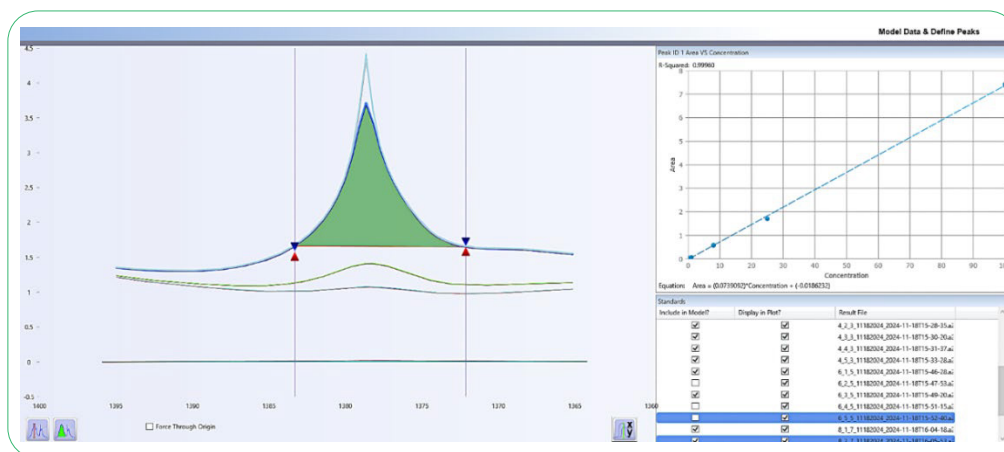


Figure 2. Calibration model for determining the mass concentration of TPH using Simple Beer's Law, implemented in the MicroLab Quant

Source: created by the authors

In the created quantitative model project, the nominal concentration values for each standard were entered, after which the Simple Beer's Law method was selected from the list of algorithms. This method is based on a direct linear relationship between optical absorbance and analyte concentration according to the Beer-Lambert law equation ($A = \epsilon bc$). The spectral feature used as the analytical signal for the model was the peak area, which was set interactively

in the spectral display window using the baseline and peak boundary positioning tools. The software automatically constructed the calibration line in the form of the equation $y = mx + b$, where y is the signal intensity, x is the concentration, m is the slope, and b is the intercept.

To assess the accuracy and reliability of the model, the Model Evaluation tools were applied, which included cross-validation (with stepwise exclusion of each standard

from the model) and verification on an independent sample set, for which concentration values were entered manually and predicted values were calculated automatically. During the evaluation, the model was assessed by key statistical indicators – the coefficient of determination (R^2), the overall standard error, and a plot comparing predicted and actual values. The coefficient of determination of the constructed calibration curve was 0.9996, indicating a very high approximation and acceptability of the model. After the modelling was completed and the parameter conformity was confirmed, the model was saved as a project file (.mpq), which included the defined component with all calibration parameters for further quantitative analysis in MicroLab PC.

Validation study

The intra-laboratory validation study was conducted in accordance with the requirements of the ISO/IEC 17025:2017 (2017) standard “General requirements for the competence of testing and calibration laboratories”, which establishes the fundamental criteria for ensuring the quality and reliability of laboratory measurements. The assessment of analytical uncertainty was carried out in accordance with the conceptual principles set out in the Guide to the Expression of Uncertainty in Measurement (GUM), published by the International Organization for Standardisation (ISO) in 1993, as well as in the adapted version of the American standard (US GUM) adopted by the American National Standards Institute (ANSI/NCSL Z540-2-1997, 1997). The practical implementation of uncertainty assessment was based on the algorithm of the Standard Operating Procedure (2003) of the Quality Assurance and Laboratory Accreditation Department of the Navy, which describes in detail the methodology for using a QC-based Nested Approach with the application of a Microsoft Excel spreadsheet for automated evaluation. The use of this approach allows effective distribution of uncertainty sources, their quantitative evaluation, calculation of expanded uncertainty with the possibility of correction for bias, as well as visual analysis through histogram plotting to identify significant components. This approach complies with the recommendations of ISO/IEC 17025:2017 (2017) and can be adapted using other methods that meet these requirements.

Field sampling procedure

The sampling volume and the type of equipment used were adapted according to the objectives of the analytical method. The instrument capabilities and the expected concentration range were taken into account, while the main emphasis was placed on achieving the environmentally required minimum to meet the procedure's objective, with a deliberate refusal of formal universality in order to potentially improve the green index. Operational sampling was carried out using carefully cleaned used glass vials from small-volume (20 cm³) paraphase extraction for GC-MS, with hermetic caps and Teflon septa. A small amount of

solid sample matrix (1.5-2 cm³ of soil or road dust) or approximately 10 ml of natural water was introduced by mechanical syringe sampling. This ensured rapid sampling while minimising the risk of cross-contamination. Acidification of the samples immediately after delivery to the laboratory to pH < 2 was carried out by adding 20-30 µl of formic acid instead of the known practices of acidification with hazardous HCl and H₂SO₄, which did not affect the quality of the results.

Extraction and concentration procedure

Extraction of samples with a fixed single volume of cyclohexane was carried out directly in the sampling vials by mechanical shaking. All vials of one analytical series (up to 50 units) were placed in a rigid transport container with internal partitions that provided stable fixation of the vials and prevented their mutual movement. Mechanical shaking was performed manually by intensive movements of the container for 5 minutes, ensuring equal duration and intensity of mechanical action for all samples. After extraction, 10 ml of deionised water with pH $\approx 5.6 \pm 0.2$ was added to the extraction vials containing soil samples to transfer the extract from the solid sample to the solution surface and ensure its further accurate sampling. From each vial, the entire possible volume of extract was taken, avoiding the inclusion of the aqueous layer, after which it was passed through a small layer of Florisil into cleaned chromatographic vials. At the first stage, TPH concentrations in the extract were determined before further concentration, using the separately filtered extract residue. If the measurement result was below the instrument's limit of detection, the extract preparation was continued. For this, 2 ml of the purified extract of the same sample was evaporated in a drying chamber equipped with an exhaust system and a fan at a temperature of 35-40°C. The dry residue was resuspended in a small volume of solvent (50 µl) using a piston dispenser with a disposable tip, repeatedly initiating the jet within the vial environment to achieve complete dissolution and uniform mixing. After that, 40 µl was quickly introduced into the instrument to avoid losses associated with evaporation.

Results and Discussion

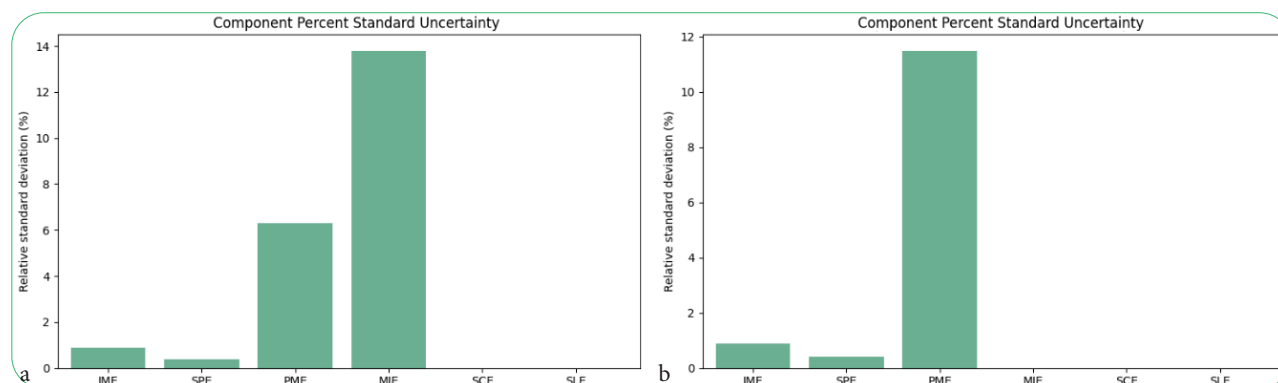
Method validation and comparative evaluation of analytical procedures

The methodology for assessing analytical measurement uncertainty using an Excel-based QC nested approach (Nested Approach) (Fig. 3) was applied to determine the contributions of various factors to the overall uncertainty of test results (Fig. 4a; Fig. 4b) obtained using this method, as well as to evaluate systematic procedural error.

Calibration standard of tetradecane in cyclohexane with a nominal concentration of 8 mg/mL, and the calibration verification standard with a nominal concentration of 5 mg/mL were analysed in 10 parallel replicates in order to account for internal instrumental measurement effects and the effects of preparing the standard spike.

QC-based Nested Approach for Estimating Analytical Measurement Uncertainty						QC-based Nested Approach	
Page 1						Total Petroleum Hydrocarbons (TPH) in soil percolate Page 2	
What are the analyte, matrix, and technology? Enter 10 replicate results for the following quality control samples as relative deviation (%): ICS - Instrument calibration standard ICV - Second source calibration verification standard LCS - Laboratory control sample MIS - Matrix interference sample (matrix spike, organic surrogate, radiochemical tracer) FDS - Field-split duplicate sample CLS - Co-located duplicate sample						Components of Analytical Uncertainty IME - Intrinsic instrumental measurement effects SPE - Spike preparation effects PME - Preparation method effects MIE - Matrix interference effects SCE - Sample collection effects SLE - Sample location effects	
ICS	ICV	LCS	MIS	FDS	CLS	Component Percent Standard Uncertainty	Component Percent Recovery
5.36	7.58	4.96	-33.06	-28.23	0	IME ~ 0.9 % relative standard deviation	IME ~ 105
4.33	6.28	16.18	6.46	-42.84	0	SPE ~ 0.4 % relative standard deviation	IME ~ 5 percent
5.74	6.80	18.17	-7.86	-51.84	0	PME ~ 6.3 % relative standard deviation	SPE ~ 103
5.65	7.94	16.11	-8.50	-47.96	0	MIE ~ 13.8 % relative standard deviation	PME ~ 102
3.49	8.10	17.35	3.46	-51.02	0	SCE ~ 0.0 % relative standard deviation	MIE ~ 85
6.73	7.36	11.68	-1.25	-36.41	0	SLE ~ 0.0 % relative standard deviation	
4.48	7.24	3.37	-0.92	-45.56	0		
4.60	8.94	8.53	3.85	-52.70	0		
4.90	9.62	3.40	9.11	-55.56	0		
5.29	8.36	2.41	-33.09	-58.04	0		
Std. Dev.	0.90	0.97	6.4	15.3	9.1	What is the Confidence Level (CL)? Enter ONLY one of these percentages: 80, 90, 95, 99 Your specified t-value is 2.093 for a Two-Tailed Normal Distribution Confidence Interval	
Bias	5.1	7.8	10.2	-6.2	-47.0	Relative Analytical Measurement Uncertainty for routine field samples (Only the IME, PME, and MIE are combined for the analytical measurement uncertainty) 31.9 % relative uncertainty	
Recovery	105.1	107.8	110.2	93.8	53.0	Relative Systematic Error associated with the measurement of routine field samples (Only the IME, PME, and MIE biases are combined for the analytical measurement systematic error) -8.6 % relative systematic error	

Figure 3. Example of implementing the methodology for assessing analytical measurement uncertainty in Excel using a QC-based nested approach (Nested Approach)
 Source: created by the authors based on W. Ingersoll (2003)



To determine the contribution of the sample preparation procedure, model samples were prepared in 10 replicates (Table 2) and analysed to reproduce the extraction process from liquid and solid matrices. Instead of a water matrix, 10 ml of deionised water were placed into clean 20 ml glass flasks. To model extraction from a solid matrix, 1.5 g of clean calcined sand were pre-weighed into the flasks and moistened with 0.45 ml of deionised water. A volume

of 50 µl of tetradecane solution in cyclohexane with a concentration of 250 mg/mL was added to each flask to reach the nominal concentration in the extract of 5 mg/mL. After the standard was added, the flasks were shaken vigorously. Acidification to pH < 2 was performed by adding 20-30 µl of formic acid. For extraction, 2.5 ml of pure cyclohexane was added to each sample, and intensive mechanical shaking was carried out for 5-7 minutes.

Table 2. Results of laboratory measurements for the main components of analytical variation

No.	Standard solutions			Laboratory samples				Matrix samples			
	Tetradecane 8 mg/mL	CCS 5 mg/mL	Grude oil 8 mg/mL	Deionised water		Calcined sand		Soil percolate		Soil	
				nominal concentration of tetradecane in the extract 5 mg/mL							
				C_{is} mg/mL	C_{exs} mg/mL	C_{is} mg/mL	C_{exs} mg/mL	C_{is} mg/mL	C_{exs} mg/mL	C_{is} mg/mL	C_{exs} mg/mL
1	8.429	5.379	7.789	44.616	5.249	51.745	6.088	28.449	3.347	36.915	4.343
2	8.346	5.314	7.861	49.376	5.809	49.824	5.862	45.252	5.324	40.706	4.789
3	8.459	5.34	7.75	50.223	5.909	37.86	4.454	39.161	4.607	39.736	4.675
4	8.452	5.397	7.939	49.348	5.806	46.956	5.524	38.889	4.575	42.688	5.022

Table 2. Continued

No.	Standard solutions			Laboratory samples				Matrix samples			
	Tetradecane 8 mg/mL	CCS 5 mg/mL	Crude oil 8 mg/mL	Deionised water		Calcined sand		Soil percolate		Soil	
				nominal concentration of tetradecane in the extract 5 mg/mL							
				C_i , mg/mL	C_{ex} , mg/mL	C_i , mg/mL	C_{ex} , mg/mL	C_i , mg/mL	C_{ex} , mg/mL	C_i , mg/mL	C_{ex} , mg/mL
5	8.279	5.405	7.578	49.873	5.867	49.425	5.815	43.97	5.173	31.477	3.703
6	8.538	5.368	7.627	47.466	5.584	43.371	5.102	41.968	4.937	35.173	4.138
7	8.358	5.362	8.118	43.934	5.169	50.206	5.907	42.109	4.954	41.468	4.879
8	8.368	5.447	7.94	46.126	5.427	50.847	5.982	44.135	5.192	30.699	3.612
9	8.392	5.476	8.119	43.943	5.170	55.385	6.516	46.372	5.456	36.84	4.334
10	8.423	5.418	8.254	43.524	5.120	50.5	5.941	28.436	3.345	40.601	4.777

Note: CCS – calibration verification standard; C_i – concentration measured by the instrument; C_{ex} – concentration recalculated to the initial volume of the extractant

Source: created by the authors

In the soil sample preparation models, an additional 10 ml of deionised water was added along the walls of the flask to bring the organic layer (extract) to the surface. After phase separation, the maximum possible volume of extract was withdrawn from each flask, avoiding the aqueous layer, and 2 ml was passed through a small layer of florisil (0.2 g) into clean flasks. Concentration of the extracts was performed in a drying chamber equipped with an exhaust system and a fan at a temperature of 35-40°C. To determine matrix effects, 10 parallel samples of real soil samples and fresh soil percolate samples, previously spiked with tetradecane to a nominal extract concentration of 5 mg/mL, were processed. For this purpose, 10 ml of fresh soil wash with a mass concentration of suspended solids of 230 mg/dm³ was added to 20 ml flasks. For the soil matrix, 2 g of dry homogenised topsoil were weighed into flasks and moistened by adding 0.45 ml of deionised water. After spiking with the standard solution, all the above-described steps of the procedure were repeated before analysis.

To determine the systematic bias caused by the sampling procedure for liquid matrices and by the mixing (homogenisation) process of the composite sample of solid matrices obtained from different sampling points within the study area, and to enable correct recalculation of the

measured concentration to the actual average content within the test site, a separate series of experiments was conducted (Table 3). For soil samples, two clean containers were weighed twice with 0.5 kg of previously dried, stone-free soil. Two grams of crude oil dissolved in cyclohexane were added to one portion, thoroughly mixed to achieve maximum homogenisation, moistened to 25% with deionised water, mixed again, and left for 24 hours. The second uncontaminated portion was moistened to 25% moisture and kept under the same conditions, after which both portions were mixed thoroughly. Ten replicate samples (~2 cm³) were collected by mechanical pressing using a cut-off syringe and placed into pre-weighed extraction flasks. For the aqueous matrix, a soil filtrate (percolate) was prepared by passing distilled water through a layer of uncontaminated soil (10-15 cm). To 1,000 ml of the filtrate, 0.5 g of crude oil was added, followed by vigorous mixing. Composite samples were formed in 10 parallel extraction vials (10 ml each) using a syringe irrigation tip, so that each sample consisted of separate aliquots of the filtrate collected during sample mixing. The samples were reweighed on an analytical balance in closed vials. Subsequent sample preparation and analysis were performed as described above.

Table 3. Results of laboratory measurements of variations caused by the sampling procedure

No.	Soil percolate (nominal concentration of crude oil 500 mg/L)			Soil, w = 25% (nominal concentration of crude oil 1,000 mg/kg d.w.)			Soil, w = 45% (nominal concentration of crude oil 1,000 mg/kg d.w.)		
	V (mL)	C_i , mg/mL	C_s , mg/L	m(dry), g	C_i , mg/mL	C_s , mg/L	m(dry), g	C_i , mg/mL	C_s , mg/L
1	11.2278	13.699	358.852	2.4239	4.539	550.760	1.1550	1.876	477.718
2	11.5503	11.223	285.783	3.2837	5.77	516.809	0.8464	2.064	717.229
3	11.8595	9.71	240.810	2.7162	4.937	534.592	1.0931	2.144	576.867
4	11.262	9.963	260.193	2.7546	5.075	541.874	0.8113	2.115	766.739
5	10.6591	8.876	244.916	4.2302	6.841	475.639	1.1353	2.306	597.430
6	10.7534	11.624	317.930	2.8856	5.625	573.344	0.9282	1.851	586.502
7	11.2683	10.428	272.185	2.4910	7.241	854.969	1.1329	2.208	573.235
8	11.2284	9.028	236.480	2.5034	4.802	564.168	1.1080	2.029	538.608
9	12.011	9.075	222.223	3.5561	6.178	510.966	1.0189	2.216	639.656
10	11.3103	8.068	209.804	3.3017	5.893	524.960	0.9731	1.654	499.939

Note: V – volume of the composite sample; C_i – concentration measured by the instrument; C_s – concentration recalculated to the initial volume/mass of the sample; m(dry) – mass of the dry soil sample

Source: created by the authors

In addition, to verify the intensity of the crude oil signal in comparison with the calibration standard, a solution of crude oil in cyclohexane (5 mg/mL) was analysed in 10 replicates. The solution was prepared in a Class A volumetric flask (10 ml) by accurately weighing 50 mg of crude oil. All validation results were tested for normality of distribution using the Shapiro-Wilk test. The test statistic (W) values for all data sets exceeded the critical value of 0.781 (at a significance level of 0.01 and a sample size of $n = 10$), confirming normal distribution. Instrumental and matrix-specific characteristics were established (Table 4),

demonstrating both the analytical suitability of the method and the influence of complex effects prior to the extraction stage in practical application. However, all results and their interpretation should primarily be considered in the context of the method's intended purpose, hardware configuration, and application concept. The instrumental limits of detection ($LOD_{inst} = 0.15$ mg/mL) and quantification ($LOQ_{inst} = 0.5$ mg/mL) for the configuration with the Tumbler 100 μ m sampling module of the Agilent Cary 630 FTIR correspond to the expected parameters for rapid analysis while maintaining a classical instrumental-laboratory approach.

Table 4. Summary of operational characteristics of the analytical procedure

Type of sample (environmental matrix)	Operating characteristics of the analytical procedure							
	LOD_{inst}	LOQ_{inst} (MRL)	S_r , %	Bias, %	R, %	SE, %	U (k = 2.0)	SCE
								Bias, % R, %
Soil at natural moisture, w = 25% (n = 10)	0.15 mg/mL	0.5 mg/mL	11.07	-11.5	88.5	-13.7	± 24.0	-43.5 56.5
Overwatered soil, w = 45% (n = 10)								-40.3 59.7
Surface water, drainage water, soil leachates, percolate (n = 10)			16.26	-6.2	93.8	-8.6	± 31.9	-47.0 53.0

Note: LOD_{inst} – instrument limit of detection; LOQ_{inst} – instrument limit of quantification (for Transmission Cell: Tumbler 100 μ m); MRL – minimum laboratory reporting level (the concentration level for which the analytical procedure performance criteria have been verified); S_r – relative standard deviation of repeatability; SE – relative systematic error (bias); U – procedural relative expanded uncertainty ($p = 0.95$); SCE – sample collection effects (field-homogenised composite sample)

Source: created by the authors

However, this sensitivity can be easily increased by changing the optical path length to 1,000 μ m through replacing the sampling module, as provided by P. Scardina *et al.* (2014) in the FTIR method based on ASTM D7678 (2022) using DialPath 1,000 μ m. For wet soils and bottom sediments, the analysis demonstrates good internal consistency ($RSD \approx 11\%$, $n = 10$) and a small systematic bias (bias -11.5%), indicating sufficient precision for quantitative determination of petroleum hydrocarbons in complex matrices with natural moisture content. Compared to chromatographic GC-FID methods, which showed poorer repeatability and reproducibility when working with dried soils (S_r 6.3%, S_R 9.9%), as reported by M. Şenilä *et al.* (2015), the proposed approach demonstrates comparable performance without multistage extraction or sample drying. Similar relative standard deviation values (3.8-12.5%) were also reported for ultrasound-assisted centrifugal extraction with IR detection by H. Qin & H. Huang (2021). Despite some underestimation of the results (bias), the obtained values remain within the range typical of laboratory methods for petroleum hydrocarbon determination in soils with natural moisture content, according to M. Şenilä *et al.* (2015) and H. Qin & H. Huang (2021).

The obtained results indicate a high efficiency of the proposed approach for the extraction of petroleum hydrocarbons from soil matrices. In particular, the recovery of petroleum hydrocarbons during mechanical extraction reached 88.5%, which is comparable to or higher than the values reported in recent studies for the extraction of PAHs and petroleum hydrocarbons. Thus, H. Guo *et al.* (2025) demonstrated that mechanical shaking using

dichloromethane provided an average recovery of polycyclic aromatic hydrocarbons of approximately 85%, whereas conventional Soxhlet extraction without sample pretreatment achieved only about 53% recovery. After solvent pretreatment of the samples, the efficiency of Soxhlet extraction increased to approximately 94%, while mechanical shaking exceeded 100% recovery for certain compounds, which the authors attributed to matrix heterogeneity and the sorption behaviour of analytes on fine-dispersed particles. The study also emphasised that mechanical shaking ensures efficient contact between the solvent and particles of wet fine-grained matrices, thereby promoting enhanced desorption of petroleum hydrocarbons. The recovery value of 88.5% obtained in the present study confirms the effectiveness of the applied approach and is consistent with current findings regarding the performance of mechanical extraction methods for the determination of petroleum hydrocarbons in complex natural matrices. At the same time, the obtained expanded measurement uncertainty values for soils ($\pm 24\%$) and water samples ($\pm 31.9\%$) correspond to typical ranges reported for environmental analyses of naturally heterogeneous objects and do not exceed the levels described in methodological guidelines and contemporary analytical studies for similar matrices.

For aqueous matrices, the analytical characteristics of the procedure remain stable: recovery is higher than in soils, close to 94%, systematic deviation is small, and precision is at a borderline but acceptable level. The increased total uncertainty and significant SCE in this case reflect real processes of losses and redistribution of petroleum hydrocarbons in the aquatic environment before analysis. In the

proposed method, cyclohexane extraction (which does not contain methyl groups and therefore does not cause interference in the $1,380\text{ cm}^{-1}$ region), combined with extract purification through florisil and operation at high concentrations (LOQ 0.5 mg/mL) ensured the absence of significant instrumental matrix effects. However, for application at low concentrations (especially when using $1,000\text{ }\mu\text{m}$ DialPath) additional research on potential influence is required, considering that review data on the use of FTIR spectroscopy for qualitative and quantitative analysis of organic components and TPH in soils often indicate that soil matrix spectra are largely determined by their mineral and organic composition, which requires corrections and mathematical data processing to interpret organic contaminant signals against the matrix background.

Model experiments to evaluate the contributions of Sample Collection Effects (SCE) were conducted separately for water matrices (soil percolate) and soil matrices (dermo-podzolic soil) and showed significant bias: -47% (for soil percolate), -43.5% for soil ($w = 45\%$) and -40.3% for overwatered soil ($w = 45\%$). Recoveries at $50\text{--}60\%$ indicate

substantial heterogeneity of TPH concentration in the overall sample volume even after mixing, i.e., already before the extraction stage, which occurs due to complex interphase interactions, sorption processes, sample heterogeneity, and transformations during sampling and homogenisation. The obtained results for SCE generally confirm the importance of ensuring a sufficient number of analytical replicates and sample size if the research strategy involves assessing the average level of contamination within the study area.

In addition, a comparative assessment of several well-known analytical procedures for TPH determination in water and soil was performed using the AGREE and AGREEprep tools F. Pena-Pereira *et al.* (2020) (Table 5). Evaluation was performed using 12 AGREE criteria for the overall method and 10 AGREEprep criteria for the sample preparation stage, according to the workflow protocol. The obtained values of the integral AGREE index (Fig. 5) for the classical well-known normative methods were predictably very low: 0.20 for the gravimetric method, 0.26 for the infrared spectrophotometry method according to MVI, and 0.33 for the ASTM D7678-17 (2022) standard.

Table 5. List of TPH determination methods evaluated using AGREE/AGREEprep

No.	Name and code of the analytical procedure
I	MVI No. 081/12-0645-09 (2010). WASTEWATER, SURFACE, GROUNDWATER. Method for measuring the mass concentration of petroleum products using the gravimetric method
II	MVI No. 081/12-0877-13 (2014). WASTEWATER, SURFACE, GROUNDWATER. Method for measuring the mass concentration of petroleum products using infrared spectrophotometry
III	ASTM D7678 – 17 (2022). Standard test method for determination of total oil and grease (TOG) and TPH in water and wastewater by solvent extraction using mid-infrared laser spectroscopy
IV, V	Developed author's procedure for TPH analysis based on Cary 630 FTIR, Agilent Technologies. (IV – calculation of the procedural index for TPH analysis in water; V – the same in soils and bottom sediments)

Source: created by the authors

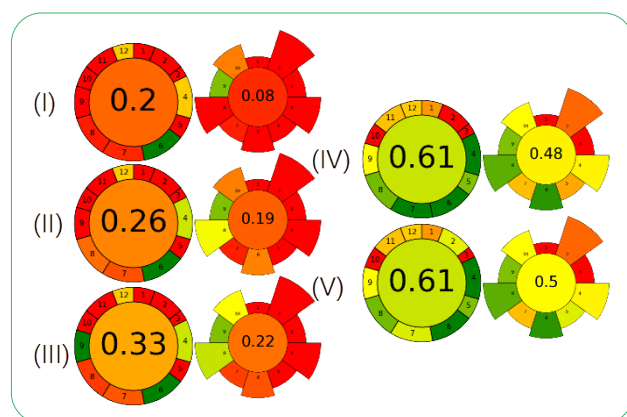


Figure 5. Results of the calculation of green indices for several well-known procedures for TPH analysis using the GREENness analytical calculator, and the additional AGREEprep tool

Note: numbering corresponds to Table 5

Source: created by the authors based on F. Pena-Pereira *et al.* (2020)

Such values are associated with large sample volumes, multi-stage sample preparation (5-6 operations), the use of toxic organic solvents, aggressive precursor acids, and

increased energy consumption. For the developed procedure, the AGREE index value was 0.61 for both water and soil matrices. This is due to smaller sample volumes, a reduced number of sample preparation stages, the transition to automation of certain operations, and a significant reduction in extractant consumption. The separate assessment of the sample preparation stage using AGREEprep showed index values in the range of $0.08\text{--}0.22$ for the normative methods and $0.48\text{--}0.50$ for the developed procedure. It should be noted that the assessments for the developed procedures were obtained for the configuration with a $100\text{ }\mu\text{m}$ optical path, which requires an extractant evaporation stage. When using an attachment with a larger optical path ($1,000\text{ }\mu\text{m}$), the sample preparation procedure can be shortened by eliminating this stage, which will increase the index value and corresponds to the conclusions of B. Abdykarimov *et al.* (2025). The obtained results reflect relative differences between procedures according to the criteria of GAC within the applied assessment methodology. Thus, although the method cannot be classified as fully GAC due to the use of cyclohexane as an extractant, the AGREE/AGREEprep assessment demonstrates its noticeably better procedural safety and environmental friendliness compared to classical laboratory methods.

Field study results and analysis of TPH contamination in urban, suburban, and industrial zones

Sampling from the three demonstration territories (Fig. 6) was carried out using disposable piston medical syringes, from which the connector tip was previously removed to enable the collection of solid samples by mechanical pressing. Samples were placed in clean, pre-weighed

amber glass vials for headspace extraction (20 ml) with screw caps and PTFE septa. For sampling liquid matrices, medical syringes with an attached irrigation tip were used, which was immersed under the water surface. During the collection of composite water samples, equal aliquots were transferred into a vial to a total volume of approximately 10 ml.



Figure 6. Sampling of soil and water in potential TPH contamination hot spots

Note: a – study area (micro-watershed of the Lushchava River within the oil production impact zone); b – watershed of the mountainous Strymba River within the area of the oil spill accident (30.09.2023); c – urbanised micro-watershed within the Bystrytsia Solotvynska River basin (suburbs of Ivano-Frankivsk)

Source: created by the authors

To assess the average level of TPH contamination for each selected area within the urban and suburban zones of Ivano-Frankivsk, composite samples were formed from road soil and street dust samples. All samples were

delivered to the laboratory (Fig. 7) for analysis. For composite samples, after mixing the entire volume, the analytical aliquot was taken in three replicates from each container, corresponding to a separate averaging area.



Figure 7. Method validation tests and analysis of field samples based on the Water Monitoring Laboratory of the Western Region of the Dniester Basin Water Resources Management, Ivano-Frankivsk

Source: created by the authors

The results of the analysis indicate that the analytical procedure is capable of correctly handling matrices of different origin – from perennial flowing waters to temporary storm runoff collected directly from puddles and watercourses along roads. In the water of

the Lushchava River downstream of the potential anthropogenic impact zone, the TPH content was below the detection limit ($<LOD_{inst} = 0.15 \text{ mg/mL}$) (Table 6), whereas the soil sample from the shoreline exhibited a TPH mass concentration of 211.14 mg/kg (moderate/

low contamination), indicating contact of the riverbank with oil film patches moving on the water surface and

being trapped in the coastal soils downstream from the extraction area.

Table 6. Results of field sample testing of soil and water for TPH within the Lushchava River catchment area (in the operational zone of the “Dolynanaftogaz” Oil and Gas Production Department)

No.	Sample type	Sample name	Mass concentration	% of mass	U ³ , % (k = 2; p = 0.95)
1	Water samples	Lushchava River (downstream of oil production influence zone)	< LOD _{inst} ¹	-	±31.9
2		Roadside and verge water flows during rainfall	3.77 mg/dm ³	< LOQ _{inst} ²	
3		Puddles and ruts filled with rainwater within 10-15 m of operating pump jack No. 1	257.93 mg/dm ³	0.026	
4		Puddles and ruts filled with rainwater within 3-5 m of operating pump jack No. 1	7.35 mg/dm ³	< LOQ _{inst}	
5		Shoreline of swampy water bodies adjacent to a paved road	< LOD _{inst}	-	
6	Soil samples	Bottom of a natural ditch along a paved road	727.00 mg/dm ³	0.073	±24.0
7		Left bank of the Lushchava River (exposed eroded terraces, riverbank line)	211.14 mg/kg	0.021	
8		Within 10-12 m of a decommissioned well	189.97 mg/kg	0.019	
9		Within 10-12 m of operating pump jack No. 1	35,853.90 mg/kg	3.585	
10		Within 2-3 m of operating pump jack No. 1	167.92 mg/kg	0.017	
11		Within 10-12 m of operating pump jack No. 2	338.40 mg/kg	0.034	
12		Within 2-3 m of operating pump jack No. 2	16,186.58 mg/kg	1.619	
13		Inactive unpaved (field) road overgrown with reeds	25.41 mg/kg	< LOQ _{inst}	
14		Within 10-15 m of an operating well	37,265.37 mg/kg	3.727	
15		Lesya Ukrainka Street, roadside verge	691.28 mg/kg	0.07	

Note: ¹ – LOD_{inst} = 0.15 mg/mL; ² – LOQ_{inst} = 0.5 mg/mL (according to Table 3); ³ – expanded procedural uncertainty (according to Table 3)

Source: created by the authors

In samples of surface stormwater collected on roads and roadside areas, significantly higher concentrations were recorded (3.77 mg/dm³ in water streams during rainfall; 257.93 mg/dm³ in puddles and ruts within a radius of 10-15 m from the operating oil pumping unit No. 1; 7.35 mg/dm³ in puddles and ruts within a radius of 3-5 m from the operating oil pumping unit No. 1). The highest values were obtained for water from a natural ditch along a paved road (727.00 mg/dm³), confirming the role of linear elements of the drainage network as effective pathways for accumulation and transport of petroleum hydrocarbons. The obtained distribution of concentrations in water samples reflects high spatial variability caused by surface runoff formation conditions, the nature of underlying surfaces, and the influence of weather factors during the spring period. Dynamic temperature regimes and moderate precipitation contribute to the mobilisation of petroleum hydrocarbons from surface soil layers, road pavement, and anthropogenic elements, resulting in their short-term but intense input into water bodies. In this context, the obtained results demonstrate that the developed procedure provides quantitative determination of TPH in water matrices under conditions of pulse loads and abrupt concentration changes.

These observations are consistent with international data on spatial heterogeneity and migration of TPH in the environment. For example, Y. Wu *et al.* (2024) indicated that TPH concentrations in soils and water largely depend on local hydrogeological conditions, with TPH

often accumulating in surface soil layers and showing limited vertical migration to groundwater due to adsorption and diffusion, which confirms the high spatial variability of contamination similar to that observed in this study. Similarly, W. Sim *et al.* (2024) showed that in industrially polluted regions, concentrations of petroleum-derived components in surface waters and bottom sediments significantly exceeded natural background levels, while the distribution patterns of TPH depended on the intensity of anthropogenic runoff and seasonal precipitation fluctuations, reinforcing the role of surface runoff as a pathway for pollutant transport.

Analysis of soil samples revealed a wide range of TPH concentrations, from 189.97 mg/kg to 37,265.37 mg/kg. In percentage terms, this corresponds to 0.019-3.73% of the sample mass. The highest TPH values were recorded in areas influenced by active oil pumping units and wells, reflecting the localised input and accumulation of petroleum components in near-surface horizons. At the same time, within the catchment area of the Lushchava River under the influence of the “Dolynanaftogaz” oil and gas production department (NGVU “Dolynanaftogaz”), significant variability in values was recorded even at comparable distances from potential sources (e.g., 189.97-35,853.90 mg/kg within a radius of 10-12 m), indicating a complex influence of microrelief, surface runoff directions, and previous anthropogenic events on the spatial distribution of pollutants. Maximum concentrations do not always

correspond to the minimum distance to the source, which emphasises the heterogeneity of contamination and the limitations of using spatial criteria alone for interpreting field measurement results. The obtained data are considered as a demonstration of the analytical capabilities of the method when working with heterogeneous soil matrices, rather than a basis for final assessment of the environmental status of the area.

Results of the analysis of water samples from the Strymba River indicate a clearly expressed longitudinal gradient of TPH concentrations downstream (Table 7, Fig. 8). The highest values were recorded in water near the accident epicentre: 18.85 mg/dm³ in the shoreline zone with mechanically disturbed bottom sediment and visible oil films. At distances of 100-700 m downstream, concentrations decreased to 12.17 and 2.65 mg/dm³, respectively, reflecting dilution, sedimentation, and redistribution processes of petroleum hydrocarbons in the channel system. From distances of 1.5-2 km downstream, petroleum hydrocarbon concentrations in water samples were minimal or not detected ($<LOD_{inst}$), indicating the limited range of their stable presence in the water phase under the given hydrodynamic regime.

Analysis of soils and bottom sediments revealed a much more complex and heterogeneous spatial distribution of petroleum hydrocarbons. In disturbed bottom sediment near the accident epicentre (319.79 mg/kg) and on eroded bank protrusions, significant differences in concentrations were recorded: 60.22 mg/kg on the right protrusion and 4,826.92 mg/kg on the left, indicating an asymmetric nature of deposition and accumulation of petroleum products. Much higher values in soils on the left bank protrusion compared to the right may be due to local flow features, channel morphology, and directions of petroleum fraction movement at the time of the accident discharge. Bottom sediments are characterised by a mosaic distribution of TPH concentrations along the flow, as noted by U. Umueni *et al.* (2025). Elevated values were found both in close proximity to the pollution source (2,063.75 mg/kg at 100 m downstream) and at certain locations more than 1 km downstream (1,476.60 mg/kg at 1.5 km and 873.23 mg/kg at 2 km). Such a distribution indicates a significant role of mechanical transport of fine silt-clay fractions, repeated resuspension of bottom sediments and their local redeposition, which is consistent with the conclusions of U. Umueni *et al.* (2025).

Table 7. Results of field sample testing of soil and water for TPH within the area of the pipeline rupture accident on 30.09.2023 on the Strymba River

No.	Sample type	Sample name	Mass concentration	% of mass	U, % (k = 2; p = 0.95)
1	Water samples	Near the accident epicentre (≈ 20 m), riverbank zone, disturbed bottom sediment of the Strymba River (oil films visible on the water surface)	18.85 mg/dm ³	0.002	± 31.9
2		100 m downstream, water from the mechanically disturbed bottom sediment zone, depth 7-10 cm	12.17 mg/dm ³	$< LOQ_{inst}$	
3		700 m downstream, water from the mechanically disturbed bottom sediment zone, depth 7-10 cm	2.65 mg/dm ³	$< LOQ_{inst}$	
4		1.5 km downstream, water from the mechanically disturbed bottom sediment zone, depth 7-10 cm	$< LOD_{inst}$	-	
5		2 km downstream, water from the mechanically disturbed bottom sediment zone, depth 7-10 cm	$< LOD_{inst}$	-	
6	Soil samples	Near the accident epicentre (≈ 20 m), disturbed bottom sediment (oil films visible on the water surface)	319.79 mg/kg	0.032	± 24.0
7		Right eroded riverbank protrusion, ≈ 20 m from the accident epicentre	60.22 mg/kg	0.006	
8		Left eroded riverbank protrusion, ≈ 20 m from the accident epicentre	4,826.92 mg/kg	0.483	
9	Bottom sediments (fine-dispersed fluvial bottom sediments of silt-clay composition)	100 m downstream, bottom sediment, depth 7-10 cm	2,063.75 mg/kg	0.206	± 24.0
10		200 m downstream, bottom sediment, depth 7-10 cm	523.50 mg/kg	0.052	
11		300 m downstream, bottom sediment, depth 7-10 cm	$< LOD_{inst}$	-	
12		600 m downstream, bottom sediment, depth 7-10 cm	$< LOD_{inst}$	-	
13		850 m downstream, bottom sediment, depth 7-10 cm	540.23 mg/kg	0.054	
14		1 km downstream, bottom sediment, depth 7-10 cm	$< LOD_{inst}$	-	
15		1.3 km downstream, bottom sediment, depth 7-10 cm	157.98 mg/kg	0.016	
16		1.5 km downstream, bottom sediment, depth 7-10 cm	1,476.60 mg/kg	0.148	
17		2 km downstream, bottom sediment, depth 7-10 cm	873.23 mg/kg	0.087	

Source: created by the authors

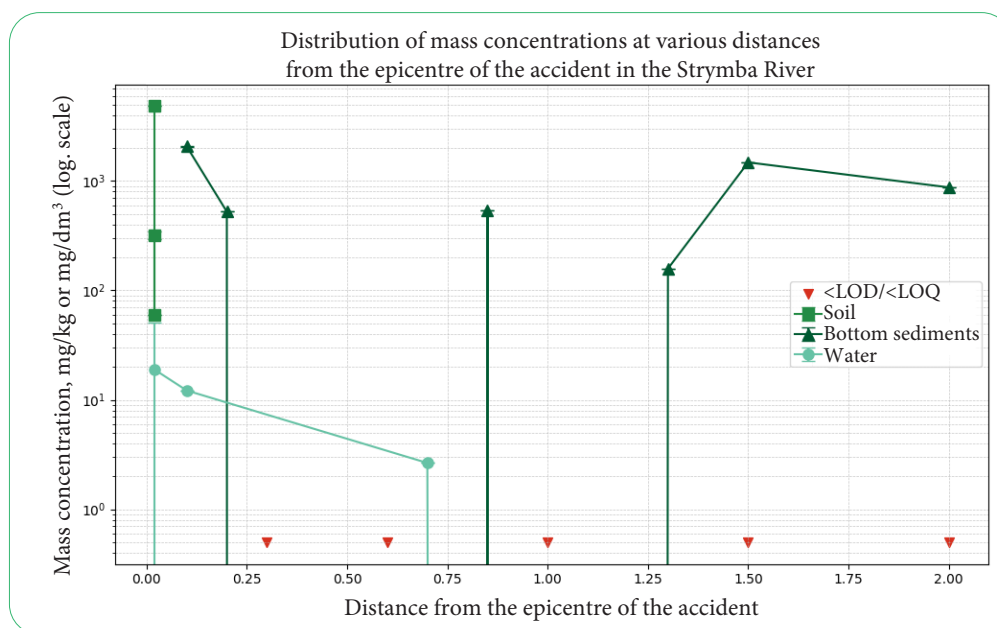


Figure 8. Integrated longitudinal concentration profile of TPH based on the analysis of different types of environmental matrices: water, soil, and bottom sediments

Source: created by the authors

The absence of a uniform decrease in concentrations with distance from the accident epicentre highlights the complexity of petroleum hydrocarbon migration processes in fluvial systems. Thus, the obtained results demonstrate that the aqueous phase responds to the accidental input of petroleum hydrocarbons mainly in a short-term and spatially limited manner, whereas shoreline soils and bottom sediments act as more inert components capable of accumulating contaminants and forming extended zones. In this context, the applied analytical procedure demonstrated stable performance for different types of environmental matrices formed both in the zone of direct accident impact and at considerable distances from the source.

Soil and street dust samples (roadside/curb mud) within the urban and suburban zones of Ivano-Frankivsk city (the urbanised part of the Bystrytsia Solotvynska micro-catchment) showed significantly higher concentrations of TPH (Table 8) compared to samples from the mountain basin of the Strymba River. In most samples, mean mass concentrations ranged within $1.6\text{--}2.8 \times 10^3$ mg/kg, indicating a persistent impact of road operation, technical leaks, and accumulation of petroleum product fractions in dust and soil deposits along transportation routes M. Bayramoğlu Karşı (2025), and stormwater collectors, where these contaminations pose particular risks to aquatic ecosystems, as reported by E. Amurri *et al.* (2025) and D. Frau *et al.* (2026).

Table 8. Results of field sample tests of soil and street dust (roadside dust) for TPH within the city of Ivano-Frankivsk

No.	Sample type	Sample name	Mass concentration	% of mass	No.	U, % (k = 2; p = 0.95)
1	Soil/ road dust (composite sample, combined)	Drahomyrchany village, open drainage along H9 road and Nadrichna Street: roadside soils, road dust and particulate matter, bed soils and embankment soils of roadside drainage ditches along an 850 m section	1,437.27 mg/kg	2,068.98 mg/kg	0.207	±24.0
			3,451.50 mg/kg			
			1,318.17 mg/kg			
2		Ivano-Frankivsk city, Khimikiv Street – Celevycha Street: roadside soils, dust and debris accumulations in the curb zone near stormwater inlets along a 1.5 km section	2,306.07 mg/kg	1,945.03 mg/kg	0.195	
			1,863.05 mg/kg			
			1,665.98 mg/kg			
3		Ivano-Frankivsk city, Nadrichna Street – Promyslova Street – Makohona Street – O. Kobylianska Street: roadside soils, dust and debris accumulations in the curb zone near stormwater inlets along a 1.8 km section	2,837.90 mg/kg	2,419.30 mg/kg	0.242	
			1,908.92 mg/kg			
			2,511.08 mg/kg			

Table 8. Continued

No.	Sample type	Sample name	Mass concentration	% of mass	No.	U, % (k=2; p=0.95)
4	Soil / road dust (composite sample, combined)	Ivano-Frankivsk city, P. Orlyk Street – Belvederska Street – Pivnichnyi Boulevard – Korolya Danyla Street: roadside soils, dust and debris accumulations in the curb zone near stormwater inlets along a 2 km section	2,655.02 mg/kg	2,795.43 mg/kg	0.280	±24.0
			2,455.18 mg/kg			
			3,276.09 mg/kg			
5	Soil / road dust (composite sample, combined)	Krykhyivtsi village, Priozerna Street, near the water intake structures of the city lake on the mlynivka Stebnytska River: roadside soils, dust and debris accumulations along the channel edges in puddle formation zones	573,037.18 mg/kg	467,532.99 mg/kg	46.753	
			650,435.55 mg/kg			
			179,126.25 mg/kg			
6	Water samples	Krykhyivtsi village, Priozerna Street, near the water intake structures of the city lake on the mlynivka Stebnytska River: puddles at the edge of the water distribution structure	433.82 mg/dm ³		0.043	±31.9

Source: created by the authors

The highest values were recorded in roadside deposits along the sections of Nadrychna St. – Promyslova St. – Makohona St. – O. Kobylanska St. (point 3) and P. Orlyk St. – Belvederska St. – Northern Boulevard – King Danylo St. (point 4), which is consistent with traffic intensity. A distinct case is the sample from Krykhyivtsi village, where mass concentrations reached $4.7\text{--}6.5 \times 10^5$ mg/kg (mean 4.7×10^5 mg/kg), which is an order of magnitude higher than at other sampling points. Such elevated values in direct contact with the water intake structures of the city lake on the mlynivka Stebnytska river channel are a consequence of vehicular traffic along a road constructed with environmental violations along the protective riparian strip. The presence of puddles with fuel films and the accumulation of dust/debris with high petroleum hydrocarbon content in the riparian zones create high local threats and risks to the urban aquatic ecosystem. Rainwater puddles at this location also contained a very high measurable amount of petroleum hydrocarbons (433.82 mg/dm³), confirming the potential for pollutant migration from surface accumulations into water bodies under conditions of standing water and limited self-purification in the urban hydrological network.

Therefore, the results of field investigations within the urban microcatchment of the Bystrytsia Solotvynska river confirm that the main mechanisms of petroleum hydrocarbon transport and accumulation are surface sealing, artificial runoff routing, accumulation of dust and debris in curb zones, and the untreated discharge of stormwater into the water body. Thus, for each of the three studied territories, a pronounced spatial-typological heterogeneity of TPH distribution was observed, manifested as local zones of elevated concentrations in close proximity to potential pollution sources (oil and gas infrastructure, accidental spills, urban runoff) and varying degrees of pollutant migration through aquatic and terrestrial media.

It should be noted that at the scale of microcatchments and small-order catchments, the effects of pulse loadings formed during precipitation, snowmelt, or accidental events are also significant and more traceable. The identification, quantitative assessment, and control of the first flush (FF)

are considered critically important in urban stormwater management Z. Gao *et al.* (2023). This well-known “first flush” concept describes how pollutants accumulated on soil surfaces, road pavements, drainage channels, and other anthropogenic landscape elements can be rapidly mobilised and transported into the watercourse as a short-term but highly concentrated runoff M. Maniquiz-Redillas *et al.* (2022). Such a mechanism is typical and may have critical consequences for small catchments, where the ratio of catchment area to pollutant source area is small and hydrological processes are highly dependent on local conditions (precipitation intensity, surface condition, imperviousness, presence of drainage channels). Consequently, risks may arise not from average background pollution levels in water, but from short-term concentration peaks that have substantial ecological impacts, especially when such peaks recur or coincide with additional stressors (low flow, high temperatures, reduced dissolved oxygen).

The results of field investigations conducted across three distinct types of environments—an oil-production micro-catchment (Lushava), an accident-affected mountainous stream (Strymba), and an urban basin (Ivano-Frankivsk, Bystrytsia Solotvynska River) – indicate a common fundamental mechanism governing the spatiotemporal dynamics of TPH. In all cases, the observed behaviour is consistent with the FF concept and the pulse-driven nature of hydrological contaminant mobilisation. As demonstrated in recent studies by Z. Gao *et al.* (2023), the first flush effect is characteristic of small- and medium-sized catchments, where short-term peak discharges during rainfall or snowmelt events lead to the rapid wash-off of surface-accumulated pollutants. Moreover, M. Maniquiz-Redillas *et al.* (2022) emphasise that the key controlling factor is not the mean contamination level but rather short-term peak concentrations generated by intensive wash-off from anthropogenic and natural surfaces.

This behaviour is most pronounced in the urban environment of Ivano-Frankivsk. Elevated TPH concentrations in roadside soils and in accumulated road dust and debris (approximately $1.6\text{--}2.8 \times 10^3$ mg/kg at most sampling points

and up to 4.7×10^5 mg/kg at local hotspots) indicate a substantial surface reservoir of contaminants. Under conditions of a high proportion of impervious surfaces, a well-developed system of curbs and stormwater inlets, and engineered surface runoff pathways, an environment is formed that strongly facilitates the first flush mechanism. Measured TPH concentrations in rainwater puddles (433.82 mg/dm³) and roadside drainage channels confirm that the initial phase of precipitation rapidly mobilises accumulated petroleum fractions, generating short-term but highly elevated peak loads to the drainage network. Thus, urban conditions combine both substantial contaminant accumulation and highly efficient pulse-driven transport into the aquatic system, which is consistent with the classical manifestation of FF as the dominant process in urban runoff.

A similar mechanism is observed in the Lushava catchment, although with a different spatial organisation of processes. Despite relatively low concentrations in the water phase (up to 727 mg/dm³ in drainage elements), soils in the vicinity of anthropogenic impact sources exhibit very high TPH levels (up to 37,265 mg/kg). This indicates the formation of local contamination depots that do not continuously interact with the aquatic phase and are activated only under specific hydro-meteorological conditions. In this context, the first flush effect manifests as an episodic mobilisation mechanism, whereby precipitation or surface runoff events trigger the short-term release of petroleum hydrocarbons from soil reservoirs into watercourses. A characteristic feature is the pronounced variability of concentrations in the water phase, including values below detection limits, confirming the pulsed nature of contaminant inputs. In the case of an accidental oil pipeline rupture above the Strymba River channel, a spatially extended variant of the first flush effect is observed. At the impact zone, a sharp peak in water concentration is recorded (18.85 mg/dm³), followed by a rapid downstream decrease. At the same time, a highly heterogeneous and mosaic pattern of TPH accumulation develops in bottom sediments and soils, including secondary maxima located more than 1 km downstream (873–1,476 mg/kg).

A key process is that a portion of petroleum hydrocarbons, after initial deposition, is not removed from the system but becomes buried within bottom sediments through mechanical coverage by sediment layers. These buried fractions remain potentially mobile and can be re-released into the water column during hydrodynamic disturbances of the riverbed, such as floods, intense rainfall events, erosional processes, or mechanical disruption of sediments (e.g., by riparian root systems). This leads to a phenomenon of secondary pulsed remobilisation, which can be interpreted as a “buried first flush” (buried FF), i.e., a reactivation of contaminant release from sedimentary reservoirs. In this context, the first flush process in mountainous streams acquires a multi-phase character, comprising an initial hydrological impulse in the water phase and a delayed but reactivated sediment-associated impulse linked to periodic remobilisation of contaminated bottom deposits. Overall,

the results demonstrate that the first flush is a universal mechanism governing TPH mobilisation across different catchment types. However, its manifestation strongly depends on landscape structure, contaminant source characteristics, and hydrological regime. In all cases, risk is governed not by mean concentrations but by the magnitude and recurrence of pulse loadings, which is consistent with modern interpretations of the FF concept.

In this context, the developed and tested analytical procedure for quantitative determination of TPH provides a consistent quantitative basis across different matrices (various water matrices, soil, bottom sediments, road dust/debris), which is a necessary condition for the correct construction of risk matrices and pollutant transport scenarios and for integrated risk assessment. These assessments involve analysis of several components: (I) characterisation of sources and their potential activity, (II) evaluation of transport pathways (surface runoff, drainage networks, groundwater flow, transport to bottom sediments), (III) quantitative evaluation of concentrations in different matrices reflecting both current pollution and accumulation, and (IV) determination of the frequency and intensity of pulse events generating peak loads. Such approaches allow the construction of risk matrices that reflect not only mean pollution levels but also the probability of hazardous pulse states. Consequently, integrated risk assessment in micro-catchments can be used to identify priority monitoring zones, develop emergency response scenarios, evaluate the effectiveness of measures to limit pollutant transport, and support management decisions aimed at minimising short-term peak impacts and long-term pollution accumulation.

✓ Conclusions

Although FTIR methods are widely used for the determination of petroleum and hydrophobic organic contaminants in environmental matrices due to their speed and relative simplicity, they are generally considered to have inherent limitations in selectivity and sensitivity compared to other analytical techniques, such as gas chromatography coupled with mass spectrometric detection (GC-MS) or GC-FID methods for TPH in water/soil. At the same time, studies evaluating the optimisation and validation of FTIR methods using similar approaches (e.g., the use of alternative solvents or other conceptual modifications) demonstrate that the FTIR analytical approach can, conversely, be significantly faster and more efficient for diagnostic and monitoring purposes, owing to the capabilities of modern FTIR spectrometer designs, which allow sample preparation to be modified and adapted more effectively.

Field testing of environmental samples in selected areas showed that the proposed method enables rapid and reliable quantification of TPH mass concentrations in various matrices (water, soil, sediments, road dust/deposits) with acceptable procedural uncertainty, as confirmed by validation. The obtained quantitative data demonstrated a wide range of contamination levels depending on the type of matrix and proximity to anthropogenic sources. In soils,

TPH concentrations varied from 189.97 to 37,265.37 mg/kg, with local maxima exceeding 16,000-35,000 mg/kg in areas influenced by oil extraction infrastructure. In urban roadside deposits, mean concentrations were typically within $1.6\text{--}2.8 \times 10^3$ mg/kg, while extreme values reached $4.7\text{--}6.5 \times 10^5$ mg/kg in zones of direct technogenic impact. In water samples, concentrations ranged from below the detection limit (<0.15 mg/dm³) in river water to 3.77-727.0 mg/dm³ in surface runoff and drainage elements, indicating strong pulse-driven variability of contamination. The described sampling procedure is aligned with the analytical method and is focused on assessing primary pollutant transport pathways (rills, drainage channels) and extends the “first flush” concept for further application of the obtained data in spatial contamination dispersion models and environmental risk assessment. This approach is an important step in studying contaminant migration, as these hydrocarbons may be the most mobile under flowing water conditions and thus contribute to the further spread of pollution in ecosystems. The procedure facilitates adaptation of sampling to the needs of rapid environmental assessment of urban and industrial areas within the framework of comprehensive and integrated environmental analysis and risk assessment in low-order catchments.

Further research should be directed toward applying the validated analytical procedure for quantitative

determination of petroleum hydrocarbons within integrated risk assessments of micro-catchments, involving modelling of hydrological regimes and transport processes (surface runoff, drainage networks, sediments), as well as quantitative consideration of both impulsive and chronic cyclical loadings. Such an approach allows obtaining quantitative parameters necessary for constructing risk matrices and scenarios, assessing the resilience of aquatic ecosystems, and making management decisions to minimise both short-term peak impacts and long-term accumulation of petroleum pollutants.

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✓ Conflict of Interest

None.

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Нафтові вуглеводні в ґрунтових та водних матрицях: випробування нової процедури експрес-екстракції та FTIR-спектроскопії для інтегрованої оцінки ризиків на мікро- та низькопорядкових водозборах

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✓ **Анотація.** Метою дослідження було розробити швидкий і ефективний підхід, чим забезпечити можливість подальшої інтегрованої оцінки ризиків у мікро- та низькопорядкових водозборах. Процедура передбачала альтернативний підхід до відбору зразків, швидку одноетапну екстракцію циклогексаном, очищення екстракту через флорисил, концентрування та аналіз на FTIR-спектрометрі Agilent Cary 630 із пробовідбірним модулем TumbIR 100 з можливою адаптацією під 1 000 мкм, або інші комерційно доступні системи, для досягнення нижчих концентрацій. Результати валідаційних випробувань показали, що для ґрунтових матриць (вологий ґрунт, донні осади) метод забезпечує добру внутрішню узгодженість відносно стандартного відхил $\approx 11\%$ ($n = 10$) та систематичне зміщення $\approx -11,5\%$ за відновлення $88,5\%$. Розширена невизначеність вимірювань становить $\pm 24\%$ для ґрунту та $\pm 31,9\%$ для води, що відповідає типовим рівням для цих екологічних матриць. Для водних матриць (поверхневі та дренажні води, ґрунтові змиви, перколяти) відновлення перевищує 94% , систематичне зміщення є невеликим, а прецизійність знаходиться на прийнятному рівні. Водночас модельні експерименти для оцінки ефектів стратегії відбору зразків показали значні систематичні зсуви: -47% для ґрунтового перколяту, $-43,5\%$ для ґрунту ($w = 45\%$) та $-40,3\%$ для перезволоженого ґрунту, що свідчить про неоднорідність розподілу TPH у пробах до етапу екстракції. Оцінка за індексами зеленої аналітичної хімії з використанням інструментів AGREE та AGREErper показала переваги розробленої методики над класичними нормативними процедурами: інтегральний індекс AGREE для розробленого методу становить $0,61$ (у порівнянні з $0,20$ - $0,33$ для гравіметричного методу, ІЧ-методики за MBV та ASTM D7678-17. Було встановлено, що в межах Івано-Франківська концентрації в складі дорожнього пилу та придорожніх ґрунтах становили $1,6$ - $2,8 \times 10^3$ мг/кг, а локально – до $4,7$ - $6,5 \times 10^5$ мг/кг, що обумовлює високі ризики, пов'язані з імпульсним навантаженням під час опадів, зливом забруднювачів у дощові колектори з подальшим потраплянням у річку Бистрицю Солотвинську

✓ **Ключові слова:** пробопідготовка; валідація методу; невизначеність вимірювань; матричні ефекти; забруднення водозборів