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Nataliia Tereshchenko*

PhD in Chemical Sciences, Senior Researcher
Bogomolets National Medical University
01601, 13 T. Shevchenko Blvd., Kyiv, Ukraine
<https://orcid.org/0000-0003-0620-2888>

Olena Khyzhan

PhD in Chemical Sciences, Associate Professor
National University of Life and Environmental Sciences of Ukraine
03041, 15 Heroiv Oborony Str., Kyiv, Ukraine
<https://orcid.org/0000-0002-2986-3251>

Oleksandr Bobunov

Postgraduate Student
National University of Life and Environmental Sciences of Ukraine
03041, 15 Heroiv Oborony Str., Kyiv, Ukraine
<https://orcid.org/0000-0002-5754-9892>

Kateryna Nesterova

Postgraduate Student
National University of Life and Environmental Sciences of Ukraine
03041, 15 Heroiv Oborony Str., Kyiv, Ukraine
<https://orcid.org/0000-0003-4081-4570>

Methodology for determining the residual content of active ingredients of agrochemicals in surface waters

Abstract. Agricultural water bodies are multifunctional objects in the agricultural production cycle. Residual amounts of the active ingredients of pesticide agrochemicals can enter and contaminate a water body during some agro-technological tasks. The purpose of this study was to investigate the conditions for the extraction of residual amounts of xenobiotics from surface water containing suspended particles and to measure their content by chromatographic methods. To determine the optimal conditions for the extraction of target xenobiotics, the values of the lipophilicity parameters of their molecules were considered. The methodology for determining the content of lipophilic xenobiotics by chromatographic methods with mass-selective detection in surface water samples includes a step of separating suspended particles, the content of which in the samples under study was controlled by gravimetric analysis and varied within 135-1500 mg/m³. The target compounds were extracted using n-hexane and acetonitrile. The analytes in the acetonitrile concentrate were

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*Corresponding author



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determined according to high-performance liquid and gas chromatography with mass-selective detectors (HPLC/MS/MS and GC/MS). The achieved limit of detection of xenobiotics was $0.02 \mu\text{g}/\text{m}^3$, the limit of quantification of xenobiotics was $0.10 \mu\text{g}/\text{m}^3$. To substantiate the possibility of applying the proposed methodology, the following indicators were investigated: linearity of analytical signals with the amount of analytes in the solution, correctness, convergence, and accuracy of measurement results. The linear concentration range of the method for the determination of xenobiotics of diverse groups is $0.10\text{-}1.00 \mu\text{g}/\text{m}^3$, characterised by a regression coefficient of the linear dependence of the measurement of individual compounds (R^2) exceeding 0.99. The degree of analytes recovery (percentage of recovery r , %) was within 85-120%, which indicates the acceptability of the proposed xenobiotic extraction procedure. The error of the measurement results was calculated as the standard deviation (S_p , %), which did not exceed 6%. The findings of this study suggested that the developed methodology is suitable for monitoring the residual content of active ingredients of agrochemicals in surface waters and predicting the level of water pollution

Keywords: lipophilic xenobiotics; extraction; water bodies; surface water; suspended solids; chromatography

INTRODUCTION

The anthropogenic load of pesticides on the environment, specifically on water bodies located in close proximity to the area where plant protection products are used, is an undeniable fact. Crop cultivation technologies involve the use of plant protection products and require further control of their residual amounts in products and in the environment, including water.

It was proved (Kurbatova *et al.*, 2022) that xenobiotics of different chemical nature and mechanism of action, when released into natural water bodies with wastewater from industrial enterprises, municipal and agricultural facilities, adversely affect metabolic processes in the tissues of aquatic organisms. The impact of xenobiotic substances on aquatic organisms poses not only a constant threat but entails an urgent need to monitor the threats they pose and develop modern methods for restoring polluted ecosystems (Piwowska & Kiedrzyńska, 2022).

To assess xenobiotic contamination of a water body, the content of individual xenobiotics is measured and compared with their maximum permissible concentration (MPC) or assessed using multiplicative models using various parameters of anthropogenic load (DSanPiN 8.8.1.2.3.4.-000-2001, 2001; González-Gaya *et al.*, 2021). The results of monitoring the content of pesticides of different chemical groups in water correlate with the amount of precipitation that washes away and transfers xenobiotics directly with runoff to surface water bodies or

ensures their movement to different depths up to groundwater layers. The presence of long-term effects and remote occurrence of some pollutants from diverse groups of pesticides in water bodies is associated with the physicochemical properties of their molecules, the specific features of the processes of degradation, migration and biotransformation of molecules in the soil (Baran *et al.*, 2021). The duration of migration in soil layers ranges from one year to decades, especially for organochlorine pesticides. Atrazine, the active ingredient of herbicides, has an MPC in water of reservoirs of $0.001 \text{ mg}/\text{m}^3$ (DSanPiN 8.8.1.2.3.4.-000-2001, 2001). Residual amounts of atrazine are found in water bodies almost after several months of the last application in agricultural areas close to water (Prukjareonchook *et al.*, 2023). Scientists use different methods to determine atrazine in water bodies (Hassan *et al.*, 2023, Huang *et al.*, 2023). Since 2004, according to the Stockholm Convention on Persistent Organic Pollutants, nearly 170 countries have banned the use of DDT insecticides for agricultural purposes. The MPC for this persistent pollutant in water is $0.002 \text{ mg}/\text{m}^3$. It is in the focus of modern monitoring studies of water resources around the world (Sackaria & Elango, 2020; Linlin *et al.*, 2020).

Considering the nature of the samples and detection methods, researchers managed to detect even small concentrations of xenobiotics in water bodies, their accumulation processes and dispersed-phase distribution (Štefanac *et al.*,

2021; Milyukin & Gorban, 2021). Atrazine and DDT are lipophilic xenobiotics that are absorbed by aquatic organisms in aquatic ecosystems and adsorbed to suspended particles of sand, clay, silt, plankton, and plant decomposition products. The component composition of not only the extracts obtained from water, but the sediment removed during the preparation of a laboratory water sample is also under investigation (Tereshchenko *et al.*, 2020).

The purpose of this study was to investigate the conditions of extraction from surface water and to measure the content of residual amounts of active ingredients of agrochemicals by chromatographic methods.

MATERIALS AND METHODS

The solvents and reagents used in the study corresponded to the qualification “for chromatography” and “purity for analysis”: acetonitrile, isopropanol, acetone, deionised water, n-hexane, sodium chloride, sodium citrate, magnesium sulphate. Water samples from non-flowing water bodies and from adjacent rivers were collected per (DSTU ISO 5667-4:2003, 2003; DSTU ISO 5667-6:2009, 2012), and a series of laboratory samples were prepared. These samples contained suspended compounds. Model systems (based on deionised water and on laboratory samples of surface water) were created to find optimal conditions for sample preparation for extraction of xenobiotics. The model systems contained lipophilic and hydrophilic xenobiotics introduced by dissolving the respective analytical standards produced by Sigma-Aldrich. Reference data on the physical and chemical properties of these xenobiotic molecules were collected from the ChemDraw library. Suspended solids were extracted from water samples according to the vacuum filtration method developed and tested in our previous studies using nylon membrane filters (Tereshchenko *et al.*, 2020). The gravimetric analysis was performed using a KERN analytical balance of the first accuracy class (division value of 0.0001 g). The dry residue (D_r) was quantified by mass concentration, calculated according to the following formula:

$$D_r = m/V, \quad (1)$$

where D_r is the mass concentration of suspended solids in the water sample, mg/m³; m is the mass of suspended solids removed from the water

sample on the filter, mg; V is the volume of the water sample, m³.

The dry residue was quantitatively transferred to an extractor and extracted in two steps with n-hexane and acetonitrile. The aqueous filtrate was divided into two parallel laboratory samples and subjected to extraction with n-hexane, buffering of the solution, followed by extraction with acetonitrile. The obtained extract was evaporated in portions of 10 cm³ and dried to dryness in a flask of a rotary evaporator RV05 basic 2-B IKA, the concentration ratio was 30:1. The content of chemical compounds in the obtained concentrate was investigated according to chromatographic methods. The xenobiotics content was measured by high-performance liquid and gas chromatography with mass-selective detectors (HPLC/MS/MS and GC/MS) using HPLC UltiMate 3000-MSD 3200 Q TRAP and Agilent Technologies 7890-MSD 5975C instruments. Statistical processing of the experimental data was performed using the Microsoft Excel software package, the measurement error was calculated as the standard deviation (S_r , %), and the degree of xenobiotic extraction from artificially enriched laboratory samples was estimated as a percentage (r , %). The proper functioning of the measuring equipment was checked using test mixtures, and the test results were recorded and analysed using Schuchart's control cards (DSTU ISO 7870-2:2016, 2016).

RESULTS AND DISCUSSION

To perform laboratory control of the content of residual amounts of pesticide formulations in surface water, standardised or proprietary methods that have passed the validation procedure are used. However, the variability of the component composition of agrochemicals, the complexity and high cost of xenobiotic determination studies prompts researchers to further search for optimal conditions for the extraction and determination of pollutants in surface waters. The methodology proposed in this paper differs from the existing ones (Lopez *et al.*, 2015; Milyukin & Gorban, 2021) by using organic solvents unified for chromatographic analysis and extraction of target substances, a lower temperature regime at the stage of evaporation of the extractant, and a new concentration interval that allows working with water samples contaminated with

pesticides of different chemical groups. Validation studies of the developed model of the methodology for investigating safety indicators allow applying the methodology for monitoring surface waters of Ukraine. The search for a methodology for effective monitoring and detection of the effects of mixing surface water with various sources of pollution is described in the studies of other authors (Linlin *et al.*, 2020; Pinasseau *et al.*, 2023), which do not consider the content of suspended particles and their ability to absorb pesticides, but assume the presence of xenobiotics of various chemical groups in water.

At the preparatory stage of creating a new laboratory control methodology, it is necessary to assess the possibility of extracting target analytes from the sample (Tereshchenko *et al.*, 2020), and, considering potential sources of contamination and the results of literature research, to create an expanded list of contaminants (Lopez *et al.*, 2015; Pinasseau *et al.*, 2023). The study of lipophilic xenobiotics in natural water samples is complicated by the presence of suspended particles that can be adsorbed by analytes (Milyukin & Gorban, 2021). Sample preparation for testing should include the extraction of xenobiotics from the dispersed medium

(water) and their desorption from the dispersed phase (suspended particles). The main parameters that allow predicting the course of the extraction process of each xenobiotic are the value of the dipole moment of its molecule, the analyte distribution constant in the octanol-water system (C_{ow}) and the logarithm of the distribution coefficient in the octanol-water system ($\log D$) (Sangster, 1997). These parameters are widely used in numerous theoretical and experimental models and studies of the distribution of differently functional chemical compounds in a system of two immiscible solvents (Ferrari *et al.*, 2018; Milyukin & Gorban, 2021). Given the changes in the component composition of agrochemicals, the persistence of xenobiotics in the environment and the prevalence of the use of a certain list of pesticides (Pinasseau *et al.*, 2023), the search for optimal conditions for the methodology of extraction of target xenobiotics began with the consideration of the values of lipophilicity parameters ($\log D$) of the molecules of active ingredients of various pesticide formulations (Table 1), which are allowed for use in Ukraine and are subject to laboratory control in products and environmental objects (DSanPiN 8.8.1.2.3.4.-000-2001, 2001).

Table 1. $\log D$ parameter and pesticidal effect of xenobiotic molecules

Pesticide	$\log D$	Pesticidal effect
Atrazine	2.58	Herbicide
Acetochlorine	4.14	
Bifenox	4.37	
Glyphosate	-3.12	
Dicamba	-1.88	
Paraquat	-4.50	
Acephate	-0.85	
DDT	6.86	Insecticide
Deltamethrin	6.21	
Imidocloprid	1.19	
Oxadixyl	1.38	
Propamocarb	0.84	Fungicide
Ciproconazole	3.09	
Fosetyl	-0.70	
Ethephone	-1.89	Growth regulator

Source: compiled by the authors of this study

Table 1 shows that the following pesticides cannot be extracted with octanol in the model laboratory methodology for the study of the list

of pesticides: acephate, glyphosate, dicamba, paraquat, fosetyl, ethephon, since they are lipophobic (hydrophilic) compounds. Therewith,

atrazine, acetochlor, biphenox, DDT, deltamethrin, imidacloprid, oxadixyl, propamocarb, and ciproconazole are lipophilic and are subject to redistribution to the organic layer. To extract xenobiotics from the samples considered in Table 1, the extraction conditions proposed in this study were applied, which differ from the extraction conditions proposed by other authors, specifically, at the first stage by gravimetric

accounting of suspended particles and subsequent extraction of xenobiotics (Sackaria & Elango, 2020; Milyukin & Gorban, 2021; Milyukin & Gorban, 2022).

In general, the scheme of sample preparation according to the proposed methodology is presented in Figure 1, aimed at the extraction of target xenobiotics molecules characterised by a wide range of lipophilicity parameters (Table 1).

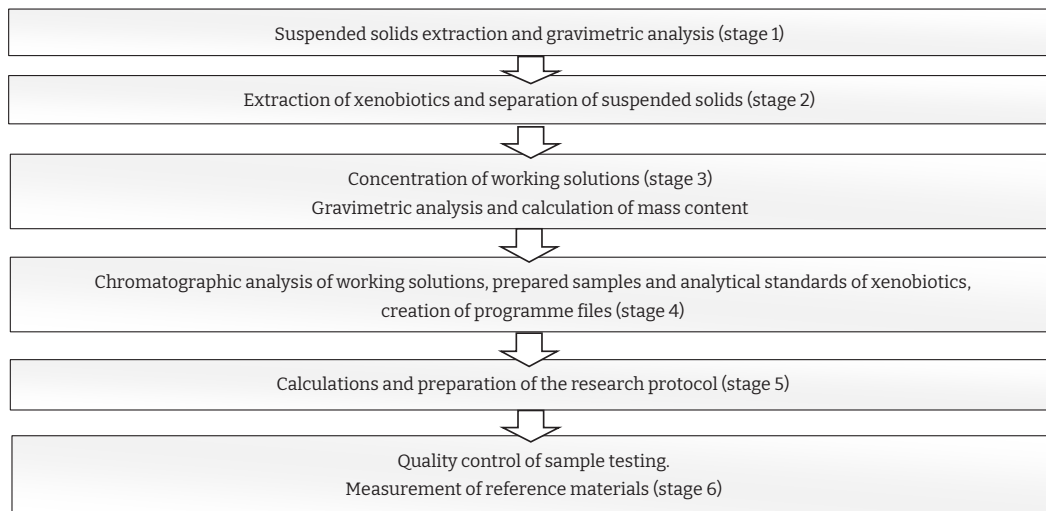


Figure 1. Schematic of the methodology for laboratory control of xenobiotics in water samples with suspended solids

Source: compiled by the authors of this study

The proposed methodology is interesting because different molecules with appropriate $\log D$ parameters (Table 1) can be studied in the extract, and the methodology is not overloaded with the extraction and measurement of pesticide degradation products, specifically atrazine, which was investigated by other authors (Lopez *et al.*, 2015) in surface water extracts.

Since mass spectrometric methods of research allow identifying chemical compounds according to their individual characteristics, namely: retention time on the chromatographic column (t , min), the ratio of the ion mass to its charge (m/z). The results are used to obtain calibration dependencies (Fig. 2) and further quantitative analysis.

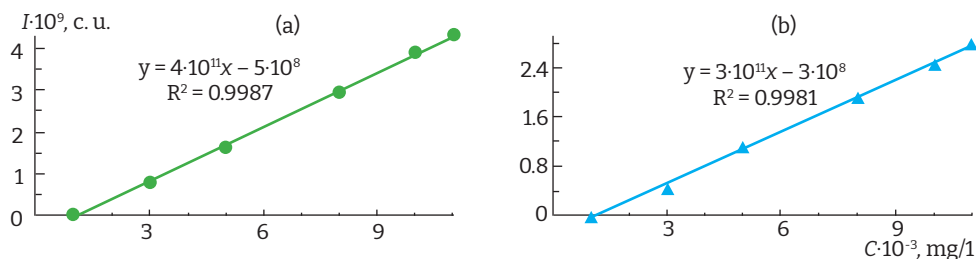


Figure 2. Scaling dependence of the intensity of the analytical signal of DDT (a) and imidacloprid (b) on their content in the calibration solution: study by GC/MS (a) and HPLC/MS/MS (b)

Source: compiled by the authors of this study

To establish the specificity of the methodology and the efficiency of the extraction of target components, mixtures of xenobiotics characterised by different $\log D$ values were used in the study (Table 1). Due to their physicochemical properties, hydrophilic xenobiotics are not extracted by organic extractants and do not interfere with the chromatographic control of target substances. The difference in $\log D$ values of lipophilic analytes is noteworthy. Based on the analysis of $\log D$ values, it can be expected that DDT will be extracted into the organic layer most rapidly and in larger quantities, while imidocloprid will be extracted most slowly and with concentration losses. The efficiency of lipophilic xenobiotics extraction into the organic layer can be amplified by buffering the aqueous layer with salt mixtures (Hrybova et al., 2019), the ions of which inhibit the ionisation of functional groups of xenobiotic molecules and shift the equilibrium towards the formation of target organic molecules, which ensures reproducibility of the results of the study of model solutions and is a more affordable way to extract pesticides compared to the method of their solid-phase extraction from water and water-containing objects (Harshit et al., 2017). Quantitative control of the analytes content was performed using the methods of chromatographic separation and mass spectrometric measurement described above in the experimental procedure.

Fixing the noise value and calculating the ratio of the noise value on the chromatogram to the analytical signal value of each individual xenobiotic allowed determining the limit of identification (qualitative detection) and the limit of quantification of the lipophilic substances mentioned in the study. The limit of quantification of a xenobiotic is set as the concentration of a substance that produces an analytical signal (peak) on a chromatogram, the intensity of which is 10 times higher than the intensity of system noise (signal: noise ratio ≥ 10). Considering the preliminary concentration (30 times), the limit of

detection of xenobiotics is $0.02 \mu\text{g}/\text{m}^3$, the limit of quantification of xenobiotics is $0.10 \mu\text{g}/\text{m}^3$. The linearity of the analytes' signals on the chromatograms with their content in the samples is within $0.10 \mu\text{g}/\text{m}^3$ to $1.00 \mu\text{g}/\text{m}^3$. The analysis of the experimental observations and the obtained equations of calibration dependencies, together with the approximation values, indicate the high sensitivity of the mass spectrometric detectors used in this study (Fig. 2). The water samples, with a content of 135 ± 20 to $1,500 \pm 100 \text{ mg}/\text{m}^3$ of suspended solids, required a stepwise extraction of the dispersion medium and dispersed phase analytes. The resulting acetonitrile extracts were combined for chromatographic control. For the metrological certification of the multi-stage methodology for measuring the xenobiotic content, a study was conducted to determine the convergence, accuracy, and reproducibility of the measurement results. Given that the amount of data required for statistical analysis can vary, four parallel water samples were prepared in each series of studies. One sample from the created parallel of samples was studied as a blank sample of surface water (without xenobiotics), which helped control matrix signals and identify non-target co-extractive substances. Three samples were studied in parallel after artificial introduction of xenobiotics in the amount of: 0.10 , 0.50 , and $1.00 \mu\text{g}/\text{m}^3$. The measurements of each sample were repeated ten times, which helped obtain a sample of data for estimating the standard deviation (S_r , %). The results of the chromatographic control of artificially contaminated samples were compared with the expected xenobiotic content. The parameter that characterised the accuracy of the measurement results was the degree of xenobiotic extraction after artificial contamination, or the percentage of return (r , %) of the xenobiotic added to the sample. Quantitative parameters for assessing the convergence and accuracy of measurements are presented in Table 2.

Table 2. Results of the evaluation of xenobiotics measurement in surface water samples under convergence conditions ($n=10$, $P=0.95$)

Xenobiotic	Added to the sample	Defined	r	S_r
	$\mu\text{g}/\text{m}^3$			%
Atrazine	0.10	0.12	120.0	5.5
	0.50	0.49	98.0	2.9
	1.00	1.00	100.0	3.1

Table 2. Continued

Xenobiotic	Added to the sample	Defined	r	S_r
	$\mu\text{g}/\text{m}^3$			%
Acetochlorine	0.10	0.10	100.0	4.1
	0.50	0.51	102.0	2.9
	1.00	1.00	100.0	2.7
Bifenox	0.10	0.11	110.0	5.4
	0.50	0.48	96.0	5.1
	1.00	1.00	100.0	3.1
DDT	0.10	0.11	110.0	2.7
	0.50	0.50	100.0	1.9
	1.00	1.00	100.0	1.5
Deltamethrin	0.10	0.10	100.0	4.8
	0.50	0.50	100.0	3.5
	1.00	1.00	100.0	1.9
Imidocloprid	0.10	0.12	120.0	5.1
	0.50	0.50	100.0	4.1
	1.00	1.00	100.0	2.9
Oxadixyl	0.10	0.11	110.0	4.7
	0.50	0.48	96.0	4.5
	1.00	1.00	100.0	2.9
Propamocarb	0.10	0.11	110.0	5.9
	0.50	0.45	90.0	3.9
	1.00	1.00	100.0	5.4
Ciproconazole	0.10	0.10	100.0	4.9
	0.50	0.50	100.0	2.5
	1.00	1.00	100.0	1.7

Source: compiled by the authors of this study

Comparison of the amounts of xenobiotics introduced into the sample with the determined amounts showed that under the optimal conditions of the proposed method, both a decrease (loss) of analyte content and an increase in analyte content occurred. As the amount of analyte added to the sample increases, the recovery rate of this substance approaches 100%. The lowest concentrations of administered xenobiotics are characterised by results that exceed the corresponding expected value. By examining the degree of extraction of substances that were added to the sample in an amount according to the values of the middle of the linear range, one can see a decrease in the parameter (90-100%). This is conditioned upon the integration of analytical signals on the chromatogram with random noise, which has the greatest impact on the signals generated by the lowest concentrations of analytes. Analysing the obtained values and considering the methodological recommendations for acceptance of measurement results

(Document SANCO/12571/2013, 2013), the results obtained can be considered satisfactory, as they do not exceed the permissible deviation of the expected content (80-120%) and indicate the suitability of the methodology for measurement. In turn, the value of the standard deviation (S_r , %) can be used to assess the convergence of measurement results, as it is obtained as a result of experimental work carried out under the same conditions using the same equipment, by the same researcher, in a short period of time, i.e., under convergence conditions. The obtained standard deviation value does not exceed 6.0%, which shows the proximity of the results obtained, the result being within a fairly narrow range within the method error.

To verify the possibility of performing measurements according to the optimal conditions of the methodology by independent performers using different batches of reagents and at different times of measurement, the conditions were created, and the metrological parameters

of intra-laboratory accuracy were calculated. Four parallel water samples were prepared: a blank sample and three samples with artificially

added xenobiotics, $\mu\text{g}/\text{m}^3$: 0.20, 0.40, 0.60. The quantitative parameters of the definition are presented in Table 3.

Table 3. Results of evaluation of xenobiotics determination in surface water samples under precision conditions ($n=10$, $P=0.95$)

Xenobiotic	Added to the sample	Defined	r	S_r
	$\mu\text{g}/\text{m}^3$		%	
Atrazine	0.20	0.18	90.0	3.7
	0.40	0.39	97.5	4.3
	0.60	0.59	98.3	2.7
Acetochlorine	0.20	0.20	100.0	3.5
	0.40	0.38	95.0	2.9
	0.60	0.62	103.3	2.7
Bifenox	0.20	0.19	95.0	4.9
	0.40	0.37	92.5	4.7
	0.60	0.57	95.0	4.4
DDT	0.20	0.20	100.0	2.5
	0.40	0.39	97.5	1.9
	0.60	0.61	101.7	1.6
Deltamethrin	0.20	0.20	100.0	2.3
	0.40	0.39	97.5	3.4
	0.60	0.58	96.7	2.8
Imidocloprid	0.20	0.18	90.0	4.1
	0.40	0.41	102.5	4.0
	0.60	0.60	100.0	3.9
Oxadixyl	0.20	0.18	90.0	4.5
	0.40	0.42	105.0	4.1
	0.60	0.58	96.7	3.8
Propamocarb	0.20	0.17	85.0	5.7
	0.40	0.36	90.0	4.9
	0.60	0.61	101.7	5.0
Ciproconazole	0.20	0.20	100.0	2.5
	0.40	0.39	97.5	2.3
	0.60	0.62	103.3	2.7

Source: compiled by the authors of this study

As a result of the studies, it was found that the standard deviation of the results of determining the content of xenobiotics in water samples obtained under conditions of intra-laboratory precision ranges from 1.6 to 5.7%, which indicates the absence of systematic errors in the implementation of laboratory control according to the conditions of the proposed methodology.

CONCLUSIONS

Thus, the laboratory control of xenobiotics in surface waters with suspended solids content from 135 ± 20 to 1500 ± 100 mg/m^3 has several

features. The proposed method for determining the content of lipophilic xenobiotics in surface water samples includes several stages: separation of suspended particles from water samples by vacuum filtration using membrane filters; extraction of target compounds from the dry residue using *n*-hexane and acetonitrile.

The treatment of the aqueous filtrate between the *n*-hexane and acetonitrile extractions includes a stage of buffering the solution with salt mixtures to enhance the efficiency of xenobiotic extraction into the organic layer. Hydrophilic xenobiotics are not extracted with an

organic extractant and do not interfere with the chromatographic control of target substances. The resulting extracts are concentrated thirty times in a rotary evaporator at 40°C to a volume of 1 ml. Laboratory control of xenobiotics is conducted according to high-performance liquid and gas chromatography with mass-selective detectors (HPLC/MS/MS and GC/MS).

The linearity of the analytical signal on the chromatograms was recorded in the study of xenobiotics of diverse groups in the concentration range of 0.10-1.00 µg/m³, the regression equations are characterised by correlation coefficients (R²) greater than 0.99. The limit of detection for xenobiotics is 0.02 µg/m³, and the limit of quantification is 0.10 µg/m³. The degree of analytes extraction ranges from 85 to 120%, which indicates the acceptability of the proposed xenobiotic extraction procedure.

The results of measuring the content of xenobiotics in surface water analysed in this study, obtained under conditions of convergence and intra-laboratory reproducibility, give grounds to assert that the developed method is suitable for use in other laboratories equipped pursuant to the requirements of the method. The proposed methodology will allow monitoring the content of xenobiotics in the surface waters of Ukraine. Further research in the context of this issue may expand the list of xenobiotics that can be identified by the developed methodology in surface waters.

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None.

CONFLICT OF INTEREST

The authors of this study declare no conflict of interest.

REFERENCES

- [1] Baran, N., Surdyk, N., & Auterives, C. (2021). Pesticides in groundwater at a national scale (France): Impact of regulations, molecular properties, uses, hydrogeology and climatic conditions. *Science of the Total Environment*, 791, article number 148137. doi: 10.1016/j.scitotenv.2021.148137.
- [2] Document SANCO/12571/2013. (2013). Retrieved from https://www.eurl-pesticides.eu/library/docs/allcrl/AqcGuidance_Sanco_2013_12571.pdf
- [3] DSANPiN 8.8.1.2.3.4.-000-2001. (2001). Retrieved from <https://zakon.rada.gov.ua/rada/show/v0137588-01#Text>
- [4] DSTU ISO 5667-4:2003. (2003). *Water Quality. Sample selection. Part 4. Regulations regarding sampling from natural and artificial lakes*. Kyiv: UkrNDNC.
- [5] DSTU ISO 5667-6:2009. (2012). *Water Quality. Sampling of samples. Part 6. Guidelines for taking samples from rivers and streams*. Kyiv: UkrNDNC.
- [6] DSTU ISO 7870-2:2016. (2016). *Statistical Control. Control cards. Part 2. Shukhart's maps*. Kyiv: UkrNDNC.
- [7] Ferrari, T., Lombardo, A., & Benfenati, E. (2018). QSARpy: A new flexible algorithm to generate QSAR models based on dissimilarities. The log Kow case study. *Science of the Total Environment*, 637, 1158-1165. doi: 10.1016/j.scitotenv.2018.05.072.
- [8] González-Gaya, B., Lopez-Herguedas, N., Santamaria, A., Mijangos, F., Etxebarria, N., Olivares, M., Prieto, A., & Zuloaga, O. (2021). Suspect screening workflow comparison for the analysis of organic xenobiotics in environmental water samples. *Chemosphere*, 274, article number 129964. doi: 10.1016/j.chemosphere.2021.129964.
- [9] Harshit, D., Charmy, K., & Nrupesh, P. (2017). Organophosphorus pesticides determination by novel HPLC and spectrophotometric method. *Food Chemistry*, 230, 448-453. doi: 10.1016/j.foodchem.2017.03.083.
- [10] Hassan, H.E., Gumus, Z.P., & Soylak, M. (2023). Determination of atrazine in food, water, and synthetic urine by activated carbon cloth (ACC) micro-solid-phase extraction (µSPE) with high-performance liquid chromatography – diode array detection (HPLC-DAD). *Analytical Letters*, 1-13. doi: 10.1080/00032719.2023.2221754.
- [11] Hrybova, N.Y., Khyzhan, O.I., Maksin, V.I., Kavshun, L.O., & Tankha, O.L. (2019). Determination of xenobiotic imidacloprid content in surface waters. *Journal of Water Chemistry and Technology*, 41, 313-317. doi: 10.3103/S1063455X19050072.

- [12] Huang, S., Yu, J., Li, J., Tang, X., Wu, Y., & Wang, C. (2023). Determination of the pesticides ethoprophos and atrazine in water by T-shaped atmospheric pressure chemical ionization (APCI) mass spectrometry (MS). *Analytical Letters*, 1-12. doi: [10.1080/00032719.2023.2213361](https://doi.org/10.1080/00032719.2023.2213361).
- [13] Kurbatova, I.M., Zakharenko, M.O., Chepil, L.V., & Tupytska, O.M. (2022). Metabolic processes peculiarities in fish under the influence of xenobiotics. *Biological Safety*, 4(43), 27-31. doi: [10.32846/2306-9716/2022.eco.4-43.5](https://doi.org/10.32846/2306-9716/2022.eco.4-43.5).
- [14] Linlin, L., Yizhang, Z., Jun, W., Shaoyong, L., Yingjie, C., Changyuan, T., Zhenguang, Y., & Lei, Z. (2020). History traces of HCHs and DDTs by groundwater dating and their behaviours and ecological risk in northeast China. *Chemosphere*, 257, article number 127212. doi: [10.1016/j.chemosphere.2020.127212](https://doi.org/10.1016/j.chemosphere.2020.127212).
- [15] Lopez, B., Ollivier, P., & Togola, A. (2015). Screening of French groundwater for regulated and emerging contaminants. *Science of the Total Environment*, 518, 562-573. doi: [10.1016/j.scitotenv.2015.01.110](https://doi.org/10.1016/j.scitotenv.2015.01.110).
- [16] Milyukin, M.V., & Gorban, M.V. (2021). Concentrations and regularities of disperse-phase distribution of organochlorine pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in natural water. *Mediterranean Journal of Chemistry*, 11(1), 32-42. doi: [10.13171/mjc10902011211519mvm](https://doi.org/10.13171/mjc10902011211519mvm).
- [17] Milyukin, M.V., & Gorban, M.V. (2022). Patterns of the disperse-phase distribution of organic ecotoxicants in the water of the world river systems. *Methods and Objects of Chemical Analysis*, 17(3), 133-140. doi: [10.17721/moca.2022.133-140](https://doi.org/10.17721/moca.2022.133-140).
- [18] Pinasseau, L., Mermillod-Blondin, F., Fildier, A., Fourel, F., Vallier, F., Guillard, L., Wiest, L., & Volatier, L. (2023). Determination of groundwater origins and vulnerability based on multi-tracer investigations: New contributions from passive sampling and suspect screening approach. *Science of The Total Environment*, 876, article number 162750. doi: [10.1016/j.scitotenv.2023.162750](https://doi.org/10.1016/j.scitotenv.2023.162750).
- [19] Piwowska, D., & Kiedrzyńska, E. (2022). Xenobiotics as a contemporary threat to surface waters. *Ecohydrology & Hydrobiology*, 22(2), 337-354. doi: [10.1016/j.ecohyd.2021.09.003](https://doi.org/10.1016/j.ecohyd.2021.09.003).
- [20] Prukjareonchook, A., Alahmad, W., Kraiya, C., Kulsing, C., Chaisuwan, T., & Dubas, L. (2023). A selective and sensitive colorimetric method for semi-automated solid-phase extraction of atrazine in environmental water samples. *Microchemical Journal*, 186, article number 108326. doi: [10.1016/j.microc.2022.108326](https://doi.org/10.1016/j.microc.2022.108326).
- [21] Sackaria, M., & Elango, L. (2020). Organic micropollutants in groundwater of India: A review. *Water Environment Research*, 92(4), 504-523. doi: [10.1002/wer.1243](https://doi.org/10.1002/wer.1243).
- [22] Sangster, J.M. (1997). *Octanol-water partition coefficients: Fundamentals and physical chemistry*. Hoboken: John Wiley & Sons.
- [23] Štefanac, T., Grgas, D., & Landeka, T. (2021). Xenobiotics-division and methods of detection: A review. *Journal of Xenobiotics*, 11(4), 130-141. doi: [10.3390/jox11040009](https://doi.org/10.3390/jox11040009).
- [24] Tereshchenko, N.Y., Khyzhan, O.I., Maksin, V.I., & Kovshun, L.O. (2020). Quantitation of polycyclic aromatic hydrocarbons and organochlorine pesticides in surface waters. *Journal of Water Chemistry and Technology*, 42, 281-286. doi: [10.3103/S1063455X20040153](https://doi.org/10.3103/S1063455X20040153).

Наталія Юрївна Терещенко

Кандидат хїмічних наук, старший дослідник
Національний медичний університет імені О.О. Богомольця
01601, бульвар Т. Шевченка, 13, м. Київ, Україна
<https://orcid.org/0000-0003-0620-2888>

Олена Ісаївна Хижан

Кандидат хїмічних наук, доцент
Національний університет біоресурсів та природокористування України
03041, вул. Героїв Оборони, 15, м. Київ, Україна
<https://orcid.org/0000-0002-2986-3251>

Олександр Юрїйович Бобунов

Аспірант
Національний університет біоресурсів і природокористування України
03041, вул. Героїв Оборони, 15, м. Київ, Україна
<https://orcid.org/0000-0002-5754-9892>

Катерина Андрїївна Нестерова

Аспірант
Національний університет біоресурсів та природокористування України
03041, вул. Героїв Оборони, 15, м. Київ, Україна
<https://orcid.org/0000-0003-4081-4570>

Методика визначення залишкового вмісту активних інгредієнтів агрохімічних препаратів у поверхневих водах

Анотація. Водойми сільськогосподарського призначення є багатофункціональними об'єктами у циклі виробництва сільськогосподарської продукції. Залишкові кількості активних інгредієнтів агрохімікатів групи пестицидів можуть потрапляти і забруднювати водоймище під час виконання низки агротехнологічних завдань. Метою даної роботи стало вивчення умов вилучення з поверхневої води, що містила завислі частинки, залишкових кількостей ксенобіотиків та вимірювання їх вмісту хроматографічними методами. Для визначення оптимальних умов екстракції цільових ксенобіотиків розглянуто величини параметрів ліпофільності їх молекул. Методика визначення вмісту ліпофільних ксенобіотиків хроматографічними методами з мас-селективним детектуванням у зразках поверхневої води містить етап відокремлення завислих частинок, вміст котрих в досліджених зразках контролювався гравіметричним аналізом та варіювався в діапазоні 135-1500 мг/м³. Екстракцію цільових сполук здійснено за допомогою н-гексану та ацетонїтрилу. В ацетонїтрильному концентраті визначали аналіти безпосередньо методами високоефективної рідинної та газової хроматографії з мас-селективними детекторами (ВЕРХ/МС/МС та ГХ/МС). Досягнута межа виявлення ксенобіотиків становила 0,02 мкг/м³, межа кількісного визначення ксенобіотиків становить 0,10 мкг/м³. Для обґрунтування можливості застосування запропонованої методики проведено дослідження показників: лінійності величин аналітичних сигналів від кількості аналітів в розчині, правильності, збіжності, прецизійності результатів вимірювань. Лінійний діапазон концентрацій застосування методики для визначення ксенобіотиків різних груп становить 0,10-1,00 мкг/м³, характеризується величиною коефіцієнта регресії лінійної залежності вимірювання індивідуальних сполук (R^2), що перевищує 0,99. Ступінь вилучення аналітів (відсоток повернення r , %) знаходиться в межах 85-120 %, що вказує на прийнятність

запропонованої процедури екстракції ксенобіотиків. Похибка результатів вимірювання розраховано через середньоквадратичне відхилення (S_r , %), не перевищувала 6 %. Результати дослідження показують, що розроблена методика є придатною для моніторингових досліджень залишкового вмісту активних інгредієнтів агрохімічних препаратів у поверхневих водах та прогнозування рівня забруднення водойм

Ключові слова: ліпофільні ксенобіотики; екстракція; водні об'єкти; поверхнева вода; завислі частинки; хроматографія