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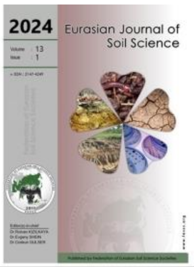

Investigating the possibility of using subcritical water for extracting polycyclic aromatic hydrocarbons from soils of the dry-steppe zone

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Abstract

In the course of the model experiment, extraction conditions of 16 priority PAHs in subcritical water medium were selected for soils of the chestnut-solonetz complex. For low molecular weight 2-ringed naphthalene and 3-ringed acenaphthene, acenaphthylene, anthracene, phenanthrene and fluorene, the optimal extraction conditions correspond to 10 minutes at a temperature of 200°C. For high molecular weight 4- and 5-ring benz(a)anthracene, fluoranthene, pyrene, chrysene, benz(b)fluoranthene, benz(k)fluoranthene, dibenz(a,h)anthracene, as well as the pollutant of the first hazard class - benz(a)pyrene, the optimal extraction time reached 20 minutes at a temperature of 250°C. For 6-ring benz(g,h,i)perylene and indeno(1,2,3-cd)pyrene, the optimum extraction time increased to 30 minutes and the temperature to 300°C. When comparing the methods of extraction of pollutants from soils, it is shown that the extraction methods can be placed in the following descending order by the value of the extraction coefficient of priority PAHs from the studied types of soils: ultrasonic extraction (1.05) > subcritical extraction (1.13) > saponification method (1.25). Using multivariate analysis of dispersion it is shown that the efficiency of subcritical aqueous extraction decreases with increasing number of benzene rings in the PAH molecule, as well as with increasing soil salinity in the following order: Gleyic Kastanozems < Endosalic Kastanozems < Kastanozems Sodic < Solonets.

Keywords: Priority PAHs, subcritical technologies, organic pollutants, Kastanozems, Solonets, PAH extraction method.

Introduction

Polycyclic aromatic hydrocarbons are a class of hazardous widespread organic compounds, many of which exhibit carcinogenic and teratogenic properties (ATSDR, 1995; IARC, 2020; Sushkova et al., 2021). The main sources of PAHs introduction into the environment include enterprises of extraction, processing and usage of liquid and solid fuels, motor and ship transportation, municipal wastes (Tsibart and Gennadiev, 2013). Despite the diversity of pathways and sources of pollutants, up to 90% of all emitted PAHs accumulate in the soil (Qu et al. 2020), which is a serious threat in areas with developed agricultural production. This is especially dangerous for vulnerable saline soils in the dry-steppe zone, which require special reclamation measures for stable high yields (Kalinitchenko et al., 2022).

To date, there is no unified concept for assessing the ecological status of PAH-contaminated soils. The International Agency for Research on Cancer publishes an annual list of substances and factors contributing to carcinogenesis. In this list, more than 30 PAHs are marked as substances likely to contribute to cancer formation (IARC, 2020). Nevertheless, only benz(a)pyrene is subject to control and regulation of its content in soils in Russia (GN 2.1.7.2041-06, 2006, 2017). In world practice, when assessing and forecasting the ecological state of soils, the content of 16 PAHs from the list of priority pollutants of the US EPA (US EPA, 2020) is often determined. The quality of assessment and forecasting is limited by a number of factors, including the relevance of generally accepted methods for determining the mass fraction of pollutants in soil. It is generally

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accepted that the most complete extraction of PAHs from soils takes place in the Soxhlet device (up to 99%) (Guerin, 1999; Castro-Guijarro et al., 2021; Silalahi et al., 2021). A significant disadvantage of the method is the 24 hours required for extraction, which significantly slows down the analysis and rapid assessment of the ecological status of soils. In general, organic solvent-based extraction methods are widely used in the analysis of PAH content from solid matrices (Wu et al., 2019; Mukhopadhyay et al., 2020). The simplest and most efficient methods of organic pollutants extraction include ultrasonic and microwave extraction of solid PAHs in solvent media (methanol, hexane, dichloromethane, acetone, etc.) (Zhang et al., 2020; Nowakowski et al., 2022). In Russia, the standard method in the study of environmental objects is the saponification method, in which the pre-interfering lipid fraction of soils, coastal and bottom sediments and plants is removed by boiling the sample in alkali followed by solvent ejection (IPA F 16.1:2.2:2.3:3.62-09, 2009). A common disadvantage of such methods is the high consumption of toxic volatile and semi-volatile reagents such as hexane, dichloromethane, methanol, acetone, acetonitrile etc. (Wu et al., 2019; Soursou et al., 2023). Extraction of pollutants from soils in subcritical water is an alternative to these extraction methods (Sushkova et al., 2014).

Subcritical water is water in the liquid state at a temperature above 100°C and pressure above saturated vapor (Figure 1). As we know, water at room temperature (23°C) and pressure of 1 atm. is a polar solvent with the density of 1000 kg m^{-3}, its dielectric permittivity is $\varepsilon = 79.73$ and its ionic product (Kw) = 10-14. As water temperature and pressure increase, water changes its properties from being a polar solvent to a non-polar solvent. The properties of water as a solvent change due to changes in its dielectric permittivity, ionic product, and hydrogen bond distribution. Changes in viscosity, heat capacity, diffusion coefficients and density affect the transport characteristics of aqueous solutions. At temperatures above 100°C but below 373°C, which is characteristic of the critical point of water, and pressures above 1 atm but below 218 atm (the region of the pre-critical state, respectively), water has an interface but changes its properties, becoming a highly efficient solvent. At constant temperature, the density of water changes continuously, within the existence of each of these phases, and only at the interface is there a density jump. At the critical point (373°C, 218 atm), the interface between the liquid and gaseous phases disappears, and the density of water becomes equal to 300 kg/m^3. However, near the critical point, water has unlimited compressibility, therefore, by varying (even in minor limits) the temperature and pressure in this area, it is possible to change the density of water in a wide range (Figure 1) (Touba and Mansoori, 1998; Islam et al., 2013). As a consequence, water in the subcritical state is a universal medium for chemical reactions.

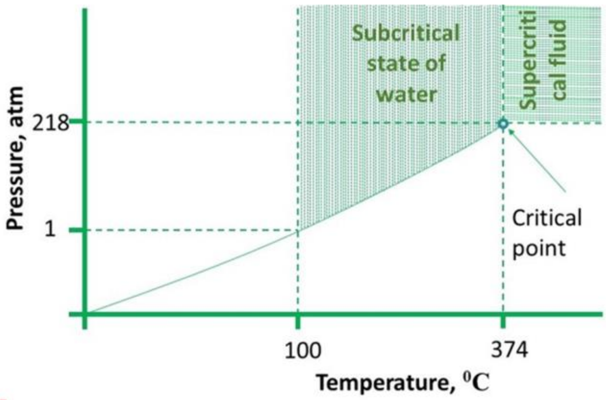

Figure 1. Phase state diagram of water at different pressure and temperature parameters

The efficiency of using water in sub- and supercritical state in the production of biologically active compounds has been repeatedly confirmed (Gbashi et al. 2017; Kim and Lim, 2020). In addition, along with almost complete elimination of toxic non-ionized solvents, the cost of extraction and time spent on this process are significantly reduced (Cheok et al., 2014). Subcritical aqueous method of processing chicken manure allowed to obtain a liquid extract containing organic acids, characterized by the presence of basic functional groups, high content of organic carbon and trace elements (Sushkova et al., 2021). Subcritical and supercritical states of water were used as extractants in the extraction of some individual PAH compounds (benz(a)pyrene, phenanthrene, fluoranthene, pyrene) from Calcic Chernozems, Andosols, sandy substrates and sewage sludge (Islam et al., 2013; Sushkova et al., 2013, 2014, 2015; Yabalak et al., 2024).

The development of pollutant extraction technology for qualitative assessment of ecosystem ecological state requires selecting conditions and testing the method of subcritical water extraction of the entire pool of priority PAHs for soils most vulnerable to pollution. In this regard, the aim of the study was to investigate the possibility of using subcritical water for extracting polycyclic aromatic hydrocarbons from soils of the dry-steppe zone.

Material and Methods

The object of the study were Gleyic Kastanozems, Endosalic Kastanozems, Kastanozems Sodic and Solonets sampled from the territory of the "Rostovsky" Natural Biosphere Reserve located in the dry-steppe zone of the Rostov region. Soil samples for the study were taken according to GOST 17.4.4.02-2017 (GOST 17.4.4.02-2017, 2019) at a depth of 0-20 cm. The studied soils are characterized as heavy loams, differing in the degree of salinization. Properties of soils are given in Table 1.

Table 1. Physical and chemical properties of soils in the dry steppe zone

Corg	Granulometric fractions		pH	$CaCO_3$	Solid residue	Exchange cations		
	<0.01 mm	<0.001 mm				Ca^{2+}	Mg^{2+}	Na^{+}
%				%		cmol (Eq) kg^{-1}		
Gleyic Kastanozems								
2,4±0,2	59,1±2,0	33,5±1,5	7,2±0,04	0,3±0,02	0,055±0,003	22,12±1,68	8,68±0,42	1,18±0,06
Endosalic Kastanozems								
2,8±0,1	54,2±0,9	30,4±1,4	7,8±0,04	0,6±0,02	0,040±0,001	16,49±1,13	6,86±0,52	1,13±0,18
Kastanozems Sodic								
2,1±0,1	57,4±2,3	31,2±1,1	7,8±0,03	0,7±0,03	0,030±0,002	17,75±1,24	5,33±0,47	1,20±0,11
Solonets								
1,5±0,2	59,2±2,0	32,9±1,5	8,5±0,04	0,7±0,05	0,221±0,001	17,17±1,16	5,89±0,33	4,11±0,26

Methods

Procedure for subcritical aqueous extraction of PAHs

The primary step of the PAH extraction procedure consisted of sample preparation by air-drying the soil, cleaning it of plant residue, and sieving it through a sieve with a 1 mm hole diameter. Extraction of PAHs from soil samples was carried out in a continuous pressurized water stream, which allows to extract more polyarenes than extractions in a closed loop cartridge using deionized water as solvent. The repetition of the experiment is 9-fold. After the extraction cell, the obtained extract was passed through a cooling system and then the cartridge was opened and the contents were filtered three times until the solution was clear. The obtained aqueous extract was mixed with 5 mL of n-hexane (99.9% w/w Aquatest, Russia) and placed on a shaker for 15 minutes. The layers were separated on a separating funnel in three successive steps with another portion of hexane (5 mL). The combined hexane extract was passed through a funnel with anhydrous sodium sulfate into a clean dry round bottom flask, evaporated on a rotary evaporator at a water bath temperature of 40-49°C to a dry residue. The resulting dry residue was dissolved in 1 mL acetonitrile (99.9%, b.w., Cryochrom, Russia) for further quantitative analysis.

The study tested different parameters of temperature (200°C, 250°C and 300°C) and extraction time (10, 20 and 30 minutes). The tested range of temperature and pressure is most commonly found as a recommendation for performing the extraction of organic compounds, including PAHs in subcritical water media (Sushkova et al., 2015, 2016; Taki et al., 2018; Yabalak et al., 2024; Zhu et al., 2024).

Comparison of PAH extraction results from soils by different methods

Comparison of extraction results of 16 prioritized PAHs from soils of dry-steppe zone with different degree of salinization (Gleyic Kastanozems, Endosalic Kastanozems, Kastanozems Sodic and Solonets) was carried out via subcritical water extraction with widely used methods: 1) ultrasonic extraction (US EPA, 2007), based on extracting pollutants with acetonitrile:dichloromethane (1:1) mixture (dichloromethane: h.p.a., ChemMed, Russia) under ultrasound; 2) saponification method (IPA F 16.1:2.2:2.2:2.3:3.62-09), which hydrolyzes the lipid fraction of the test sample with a 2% solution of KOH (99.8% p.o.a. Aquatest, Russia) in ethanol (99.8% p.o.a. Aquatest, Russia) followed by 3-fold extraction of hydrocarbons with n-hexane.

Assessment of PAH extraction completeness

In order to establish the completeness of extraction of priority PAHs (naphthalene, anthracene, acenaphthene, acenaphthylene, fluorene, phenanthrene, benz(a)anthracene, fluoranthene, pyrene, chrysene, benz(b)fluoranthene, benz(k)fluoranthene, benz(a)pyrene, dibenz(a, h)anthracene, benz(g,h,i)perylene, indeno(1,2,3-cd)pyrene) from soil by the methods under consideration, a blank experiment was additionally carried out with the application of solutions of a given concentration (10, 20, 40 and 80 ng g^{-1}) of each polyarene into soil (additive method). For this purpose, 16 priority PAH STANDARD was purchased. The additive was injected with an acetonitrile solution of each PAH into a 1 g soil sample placed in a rotary evaporator flask. After the evaporation of acetonitrile (at room temperature), the sample with the introduced additive was processed according to the proposed method of subcritical aqueous extraction. The experiment was repeated nine times.

The correction factor for PAH recovery in subcritical water was calculated according to the following formulas:

$$k = C1/C2 \tag{1}$$

$$C1 = Cst + Cs \tag{2}$$

where C1 is the total concentration of each PAH in the soil sample, μg kg^{-1}; C2 is the concentration of each PAH in the soil determined by the method used, ng g^{-1}; Cst is the concentration of each PAH in the soil due to the application of its standard solution, ng g^{-1}; Cs is the average concentration of each PAH in the soil sample, ng g^{-1}.

Quantitative analysis of PAHs in the extracts

Quantitative analysis of PAHs in the extracts was performed by high-performance liquid chromatography (HPLC) with an HPLC system equipped with UV and fluorescence detectors (Agilent Model 1260, USA, 2015). The limits of detection (LOD) and limits of quantification (LOQ) of PAHs are presented in Table 2.

Table 2. Limits of detection (LOD) and limits of quantification (LOQ) for 16 priority PAHs

No	PAHs	LOD	LOQ	Holding Time
1	Naphthalene	0.17	0.09	5.26
2	Acenaphthylene	0.08	0.12	6,58
3	Acenaphthene	0.05	0.10	7,11
4	Fluorene	0.08	0.26	8.05
5	Phenanthrene	0.09	0.17	8,90
6	Anthracene	0.01	0.05	9.20
7	Fluoranthene	0.08	0.20	10.30
8	Pyrene	0.10	0.28	11.92
9	Chrysene	0.03	0.15	13.75
10	Benz(a)anthracene	0.03	0.19	16.38
11	Benz(b)fluoranthene	0.03	0.07	22.82
12	Benz(l)fluoranthene	0.02	0.06	24.90
13	Benz(a)pyrene	0.01	0.06	26.80
14	Dibenz(a,h)anthracene	0.04	0.04	32.45
15	Benz(g,h,i)perylene	0.19	0.56	39.48
16	Indeno(1,2,3-cd)pyrene	0.11	0.31	44.51

Statistical treatment of the results obtained

The results were processed statistically using descriptive statistics, multivariate and single factor analysis of variance followed by Tukey's posterior criterion in STATISTICA 8. Visualization of the results is presented using Sigmaplot 12.5.

Results and Discussion

The methodology of extraction of 16 priority PAHs in subcritical water for soils of chestnut-solonetz complex was adapted. It was found that the yield of polyarenes in the extract depends on the temperature and extraction time, as well as on the type of PAHs and soil properties. For low molecular weight 2-ringed naphthalene and 3-ringed acenaphthene, acenaphthylene, anthracene, phenanthrene and fluorene, the optimal extraction conditions correspond to 10 minutes at a temperature of 200°C. For high molecular weight 4- and 5-ringed benz(a)anthracene, fluoranthene, pyrene, chrysene, benz(b)fluoranthene, benz(k)fluoranthene, dibenz(a,h)anthracene, as well as the pollutant of the first hazard class - benz(a)pyrene, the optimal extraction time reached 20 minutes at a temperature of 250°C. Similar results were demonstrated in the extraction of BaP from Calcic Chernozems (Sushkova et al., 2016) For 6-ring benz(g,h,i)perylene and indeno(1,2,3-cd)pyrene, the optimal extraction time increases up to 30 min and the temperature increases up to 300°C (Figure 2). At the same time, treatment of samples with water at 300°C for 30 minutes reduces the yield of less nuclear PAHs, especially their 2- and 3-ringed representatives, which is most likely due to the destruction of less stable pollutant molecules (Islam et al., 2012; Khanjari et al., 2016; Yabalak et al., 2023).

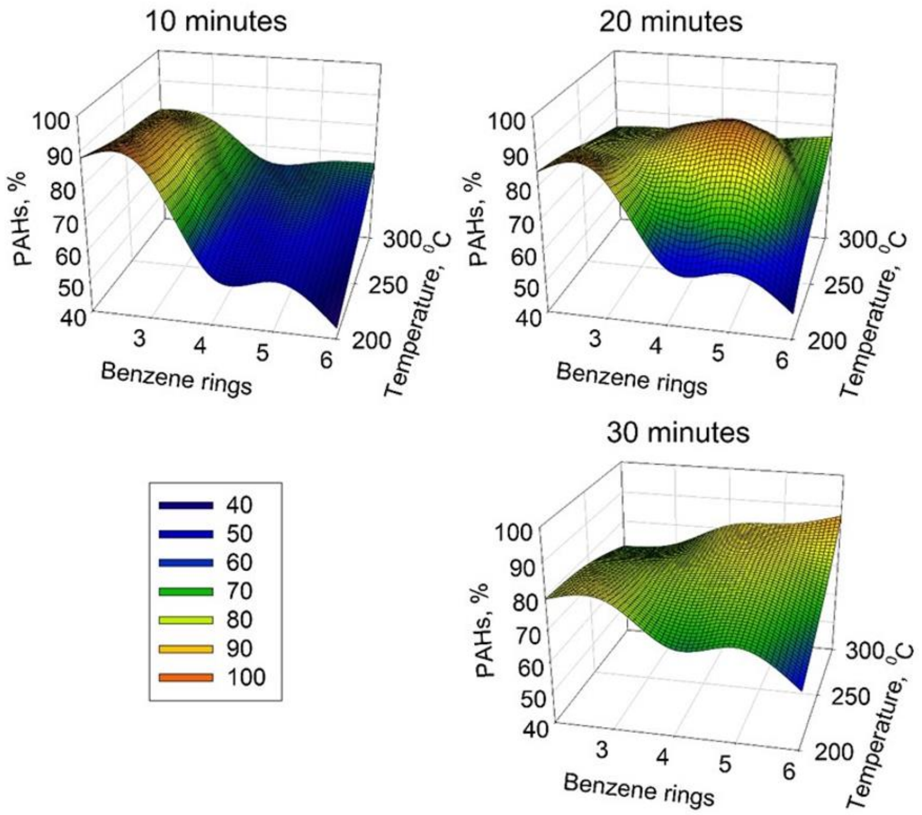

Figure 2. Content of 16 priority PAHs in soil depending on temperature and extraction time in subcritical water medium, ng g^{-1} (n=9)

In order to unify the method of PAH extraction in subcritical water, the conditions chosen as optimal were the 250°C temperature and 20 minute time, as the highest yield of a wide pool of the most toxic and widespread substances was recorded at these parameters (Chaplygin et al., 2022; Sushkova et al., 2020; Dudnikova et al., 2023a,b). The results of PAH content in soils of the dry-steppe zone obtained by extracting pollutants under optimal conditions of temperature and time are presented in Figure 3. It is shown that the studied soils of the natural territory of the dry-steppe zone are characterized by the predominance of low-molecular compounds, first of all, naphthalene and phenanthrene, the content of which exceeds 40 ng g^{-1} in almost all cases. Among high molecular weight compounds pyrene dominates, its amount in soils of the dry-steppe zone varies from 29 ng g^{-1} to 54 ng g^{-1} (Figure 3).

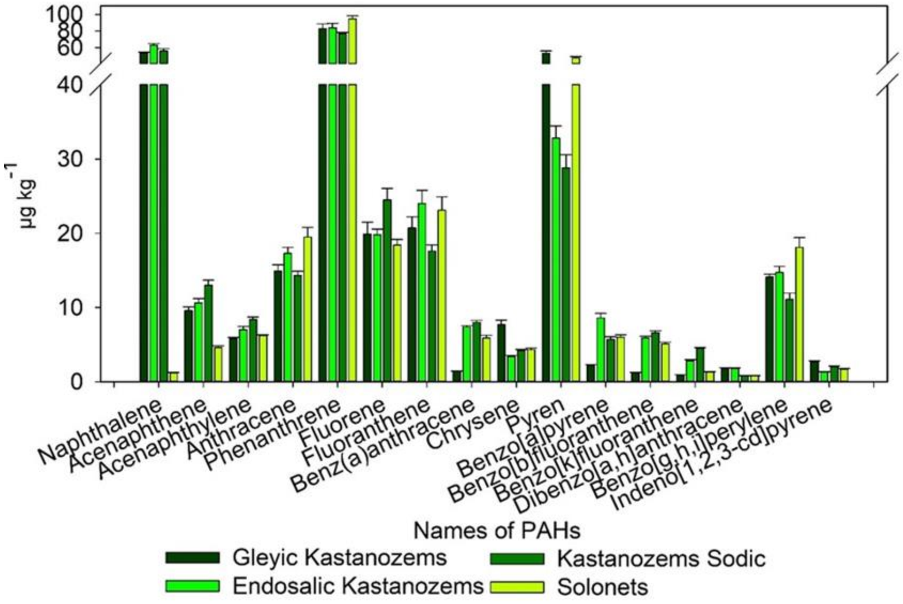

Figure 3. PAH content in soils of the dry-steppe zone based on the results of extraction with subcritical water at a temperature of 250°C for 20 minutes

According to the results of multivariate analysis of dispersion, it was found that the yield of PAHs in the extract depends on the type of PAH, type of extraction, and soil properties (Table 3). The coefficient value is actually an empirical value obtained during the development and approximation of PAH extraction methods. It is necessary for leveling the incompleteness of PAH extraction and it represents the number by which the obtained analytical data should be multiplied. In this regard, an increase in the value of the PAH extraction factor from soils indicates a decrease in the extraction efficiency of pollutants. According to the value of the extraction coefficient of priority PAHs from the studied soil types, the extraction methods can be arranged in the following descending order: ultrasonic extraction (1.05) > subcritical extraction (1.13) > saponification method (1.25). The differences between the methods are significant, which was confirmed using Tukey's posterior criterion at $p<0.05$ (Figure 4).

Table 3. Results of one-factor analysis of dispersion. Variation of PAH extraction coefficient depending on extraction method, soil type, and pollutant type

Factor	SS	MS	F	p
PAH	0.162	0.011	6.7	<0.000001
Extraction	5.137	2.568	1602.8	<0.000001
Soil type	0.049	0.016	10.1	0.000002
PAH*Extraction	0.416	0.014	8.7	<0.000001
PAH*Soil type	0.057	0.001	0.8	0.836616
Extraction*Soil type	0.160	0.027	16.6	<0.000001
PAH*Extraction*Soil type	0.134	0.001	0.9	0.654836

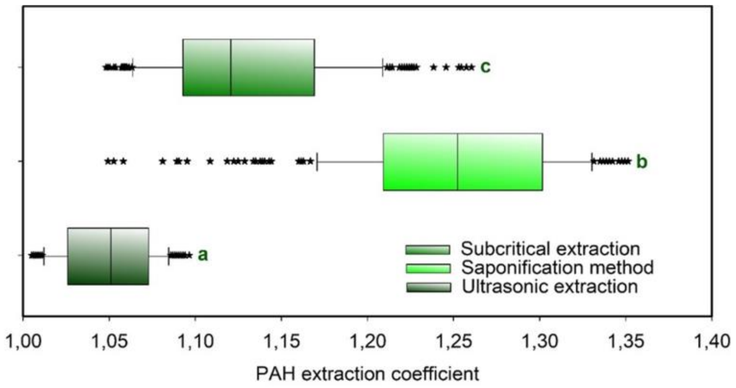

Figure 4. PAH extraction coefficient from soils of the dry-steppe zone depending on the extraction method. Letters indicate differences in PAH extraction coefficient for different extraction methods calculated using Tukey's apposterior criterion at $p<0.05$.

Using multivariate analysis of dispersion it is shown that at PAH extraction by methods based on the use of organic solvents (ultrasonic extraction and saponification method), soil properties do not significantly affect the degree of extraction of pollutants. On the contrary, at subcritical aqueous extraction there is a tendency towards an increase in the degree of PAHs extraction depending on the level of soil salinity in the series: Gleyic Kastanozem > Endosalic Kastanozem > Kastanozem Sodic > Solonets. At the same time, the PAH extraction coefficient from Solonets is significantly higher than from less saline soils (Figure 5), which is due to a decrease in dialectic permittivity of water under the influence of sodium salts (Patel et al. 2021).

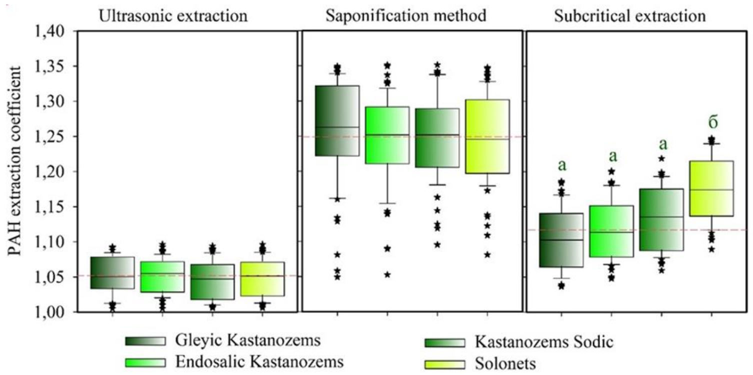

Figure 5. PAH extraction coefficient from dry-steppe zone soils depending on extraction method. Letters indicate differences in PAH extraction coefficient from soils of different types calculated using Tukey's apposterior criterion at $p<0.05$.

Differences between the extraction rates of individual compounds were not established when the pollutants were extracted with solvents in ultrasonic or saponification methods. For subcritical water extraction, the extraction ratio of 4- and 5-ringed compounds is significantly lower than that of low molecular weight and 6-ringed compounds (Figure 6). This because as the number of benzene rings in the PAH molecule increases, their molecular weight, lipophilicity and binding affinity to soil increases, the energy cost of desorption of pollutant from soil particles increases (Liang et al. 2016).

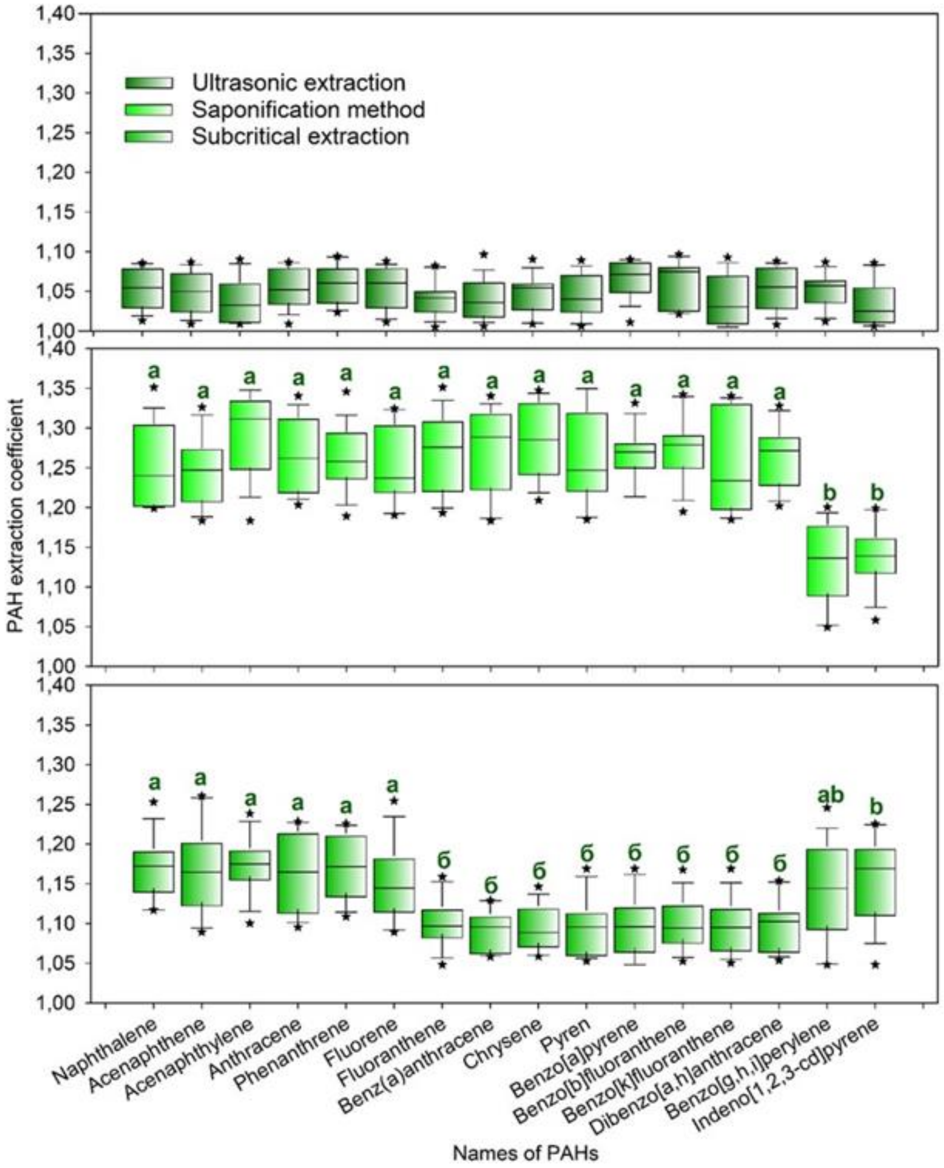

Figure 6. PAH extraction coefficient from soils of the dry-steppe zone depending on the extraction method. Letters indicate differences in the extraction coefficient of individual PAHs at different methods of their extraction from soils, calculated using Tukey's apposterior criterion at $p<0.05$.

Based on the results of a model experiment using soils of the dry-steppe zone, the optimal conditions for extraction of 16 priority PAHs in subcritical water were determined. It is shown that PAH extraction in subcritical water allows to significantly reduce the time spent on analysis, as well as almost completely exclude the use of toxic organic solvents. At the same time, the adapted method is more effective than the saponification method and is comparable to ultrasonic extraction for the most common and hazardous high-molecular-weight 4- and 5-ringed PAHs (Table 4).

Table 4. Comparison of methods for extraction of PAHs from natural objects

Comparison parameters		Subcritical extraction	Saponification method	Ultrasonic extraction
Time, min			240	30
Solvent, mL	Hexane	15	60	45
	Acetonitrile	1	1	2
	Dichloromethane	-	-	45
Average extraction coefficient			1.25	1.05

Conclusion

The optimal conditions of extraction of priority PAHs in subcritical water medium from soils of chestnut-solonetz complex of dry-steppe zone were determined using Gleyic Kastanozems, Endosalic Kastanozems, Kastanozems Sodic, and Solonets as examples. It was shown that for low molecular weight compounds of 2- and 3-ringed PAHs, the optimal extraction conditions correspond to 10 minutes at a temperature of 200°C, for high molecular weight 4- and 5-ringed PAHs - 20 minutes at a temperature of 250°C, for 6-ringed PAHs - 30 minutes at a temperature of 300°C. In order to unify the method of extraction of pollutants in subcritical water medium, the conditions corresponding to the temperature of 250°C for 20 minutes were chosen as optimal, since at these parameters the highest yield of a wide pool of the most toxic and widespread PAHs was recorded. Using the proposed parameters it was established that naphthalene, phenanthrene and pyrene dominate in the studied soils of the dry-steppe zone.

The efficiency of PAH extraction by widely used methods based on the use of organic solvents and subcritical extraction was compared. By means of multifactor dispersion analysis performed based on the results of calculating the PAH extraction coefficient, it was found that the peculiarities of soil properties and the type of pollutant significantly affect the degree of extraction of pollutants from soils during subcritical extraction in optimal parameters of temperature and time. The efficiency of subcritical water extraction decreases with increasing number of benzene rings in the PAH molecule, as well as with increasing soil salinity in the series: Gleyic Kastanozems < Endosalic Kastanozems < Kastanozems Sodic < Solonets. According to the extraction coefficient value of priority PAHs from the studied soil types, the extraction methods can be placed in the following descending row: ultrasonic extraction (1.05) > subcritical extraction (1.13) > saponification method (1.25). Despite the more complete extraction of PAHs from soils by ultrasonic extraction, subcritical extraction significantly reduces the time and the amount of toxic organic solvents spent on analysis.

Acknowledgments

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References

ATSDR, 1995. Toxicological profile for polycyclic aromatic hydrocarbons. Washington, DC, U.S. Department of Health and Human Services. Agency for Toxic Substances and Disease Registry. Available at [Access date: 02.09.2023]: https://wwwn.cdc.gov/tsp/ToxProfiles/ToxProfiles.aspx?id=122&tid=25

Castro-Guijarro, P.A., Álvarez-Vázquez, E.R., Fernández-Espinosa, A.J., 2021. A rapid Soxhlet and mini-SPE method for analysis of polycyclic aromatic hydrocarbons in atmospheric particles. *Analytical and Bioanalytical Chemistry* 413: 2195-2206.

Chaplygin, V., Dudnikova, T., Chernikova, N., Fedorenko, A., Mandzhieva, S., Fedorenko, G., Sushkova, S., Nevidomskaya, D., Minkina, T., Sathishkumar, P., Rajput, V.D., 2022. Phragmites australis cav. As a bioindicator of hydromorphic soils pollution with heavy metals and polyaromatic hydrocarbons. *Chemosphere* 308: 136409.

Cheok, C.Y., Salman, H.A.K., Sulaiman, R., 2014. Extraction and quantification of saponins: A review. *Food Research International* 59: 16-40.

Dudnikova, T., Minkina, T., Sushkova, S., Barbashev, A., Antonenko, E., Konstantinova, E., Shuvaev, E., Nevidomskaya, D., Ivantsov, A., Bakoeva, G., Gorbunova, M., 2023. Background content of polycyclic aromatic hydrocarbons during monitoring of natural and anthropogenically transformed landscapes in the coastal area soils. *Water* 15(13): 2424.

Dudnikova, T., Sushkova, S., Minkina, T., Barbashev, A., Ferreira, C.S.S., Antonenko, E., Shuvaev, E., Bakoeva, G., 2023. Main factors in polycyclic aromatic hydrocarbons accumulations in the long-term technogenic contaminated soil. *Eurasian Journal of Soil Science* 12(3): 282-289.

Gbashi, S., Adebo, O.A., Piater, L., Madala, N.E., Njobeh, P.B., 2017. Subcritical water extraction of biological materials. *Separation & Purification Reviews* 46 (1): 21-34.

GN 2.1.7.2041-06, 2006; 2017. Resolution of the Chief State Sanitary Doctor of the Russian Federation dated 01/23/2006 No. 1 (ed. dated 06/26/2017) "On the introduction of hygienic standards GN 2.1.7.2041-06" (together with "GN 2.1.7.2041-06. 2.1.7. Soil, cleaning of populated areas, waste of production and consumption, sanitary protection of soil. Maximum permissible concentrations (MPC) of chemicals in the soil. Hygienic standards", approved by Chief State Sanitary Doctor of the Russian Federation on 19.01.2006) (Registered with the Ministry of Justice of the Russian Federation on 07.02.2006 N7470).

GOST 17.4.4.02-2017, 2019. Protection of Nature. Soils. Methods of sampling and preparation of samples for chemical, bacteriological, helminthological analysis. Moscow. Standartinform, Russia. 12p.

Guerin, T.F., 1999. The extraction of aged polycyclic aromatic hydrocarbon (PAH) residues from a clay soil using sonication and a Soxhlet procedure: a comparative study. *Journal of Environmental Monitoring* 1 (1): 63-67.

IARC, 2020. List of classifications, volumes 1-123. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Lyon: International Agency for Research on Cancer. Available at [Access date: 02.09.2023]: https://monographs.iarc.fr/list-of-classifications-volumes/

IPA F 16.1:2.2:2.3:3.62-09, 2009. Quantitative chemical analysis of soils. Methodology for measuring the mass fractions of polycyclic aromatic hydrocarbons in soils, bottom sediments, sewage sludge and production and consumption waste by high–performance liquid chromatography. Standartiform, Moscow, Russia, 11p.

Islam, M.N., Jo, Y.T., Jung, S.K., Park, J.H., 2013. Thermodynamic and kinetic study for subcritical water extraction of PAHs. *Journal of Industrial and Engineering Chemistry* 19 (1): 129-136.

Islam, M.N., Jo, Y.T., Park, J.H., 2012. Remediation of PAHs contaminated soil by extraction using subcritical water. *Journal of Industrial and Engineering Chemistry* 18(5): 1689-1693.

Kalinitchenko, V.P., Glinushkin, A.P., Minkina, T.M., Mandzhieva, S.S., Sushkova, S.N., Sukovatov, V.A., Il'ina, L.P., Makarenkov, D.A., Zavalin, A.A., Dudnikova, T.S., Barbashev, A.I., Bren, D.V., Rajput, P., Batukaev, A.A., 2022. Intra-soil waste recycling provides safety of environment. *Environmental Geochemistry and Health* 44 (4): 1355-1376.

Khanjari, Y., Eikani, M.H., Rowshanzamir, S., 2016. Remediation of polycyclic aromatic hydrocarbons from soil using superheated water extraction. *The Journal of Supercritical Fluids* 111: 129-134.

Kim, D.S., Lim, S.B., 2020. Kinetic study of subcritical water extraction of flavonoids from citrus unshiu peel. *Separation and Purification Technology* 250: 117259.

Liang, X., Zhu, L., Zhuang, S., 2016. Sorption of polycyclic aromatic hydrocarbons to soils enhanced by heavy metals: perspective of molecular interactions. *Journal of Soils and Sediments* 16: 1509-1518.

Mukhopadhyay, S., Dutta, R., Das, P., 2020. A critical review on plant biomonitors for determination of polycyclic aromatic hydrocarbons (PAHs) in air through solvent extraction techniques. *Chemosphere* 251: 126441.

Nowakowski, M., Rykowska, I., Wolski, R., Andrzejewski, P., 2022. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (O-PAHs, N-PAHs, OH-PAHs): Determination in suspended particulate matter (SPM)–A review. *Environmental Processes* 9:2.

Patel, L.A., Yoon, T.J., Currier, R.P., Maerzke, K.A., 2021. NaCl aggregation in water at elevated temperatures and pressures: Comparison of classical force fields. *The Journal of Chemical Physics* 154 (6): 064503.

Qu, Y., Gong, Y., Ma, J., Wei, H., Liu, Q., Liu, L., Wu, H., Yang, S., Chen, Y., 2020. Potential sources, influencing factors, and health risks of polycyclic aromatic hydrocarbons (PAHs) in the surface soil of urban parks in Beijing, China. *Environmental Pollution* 260: 114016.

Silalahi, E.T.M.E., Anita,S., Teruna, H.Y., 2021. Comparison of extraction techniques for the determination of polycyclic aromatic hydrocarbons (PAHs) in soil. *Journal of Physics: Conference Series* 1819: 012061.

Soursou, V., Campo, J., Picó, Y., 2023. Revisiting the analytical determination of PAHs in environmental samples: An update on recent advances. *Trends in Environmental Analytical Chemistry* 37: e00195.

Sushkova, S., Minkina, T., Chaplygin, V., Nevidomskaya, D., Rajput, V., Bauer, T., Mazarji, M., Bren, A.B., Popov, I., Mazanko, M., 2021. Subcritical water extraction of organic acids from chicken manure. *Journal of the Science of Food and Agriculture* 101(4): 1523-1529.

Sushkova, S., Minkina, T., Mandzhieva, S., Tjurina, I., Bolotova, O., Vasilyeva, G., Orlović-Leko, P., Varduni, T., Kizilkaya, R., Akca, I., 2015. Solubility of benzo[a]pyrene and organic matter of soil in subcritical water. *Croatica Chemica Acta* 88(3): 247-253.

Sushkova, S., Minkina, T., Tarigholizadeh, S., Antonenko, E., Konstantinova, E., Gülser, C., Dudnikova, T., Barbashev, A., Kızılkaya, R., 2020. PAHs accumulation in soil-plant system of Phragmites australis Cav. in soil under long-term chemical contamination. *Eurasian Journal of Soil Science* 9 (3): 242-253.

Sushkova, S., Minkina, T., Tarigholizadeh, S., Rajput, V., Fedorenko, A., Antonenko, E., Dudnikova, T., Chernikova, N., Yadav, B.K., Batukaev, A., 2021. Soil PAHs contamination effect on the cellular and subcellular organelle changes of *Phragmites australis* Cav. *Environmental Geochemistry and Health* 43: 2407-2421.

Sushkova, S.N., Minkina, T.M., Mandzhieva, S.S., Tjurina, I.G., 2013. Elaboration and approbation of methods for benzo[a]pyrene extraction from soils for monitoring of the ecological state in technogenic landscapes. *World Applied Sciences Journal* 25(10): 1432-1437.

Sushkova, S.N., Minkina, T.M., Mandzhieva, S.S., Vasilyeva, G.K., Borisenko, N.I., Turina, I.G., Kızılkaya, R., Bolotova, O.V., Varduni, T.V., 2016. New alternative method of benzo[a]pyrene extractionfrom soils and its approbation in soil under technogenic pressure. *Journal of Soils and Sediments* 16: 1323-1329.

Sushkova, S.N., Vasilyeva, G.K., Minkina, T.M., Mandzhieva, S.S., Tjurina, I.G., Kolesnikov, S.I., Kizilkaya, R., Askin, T., 2014. New method for benzo[a]pyrene analysis in plant material using subcritical water extraction. *Journal of Geochemical Exploration* 144: 267-272.

Taki, G., Islam, M.N., Park, S.J., Park, J.H. 2018. Optimization of operating parameters to remove and recover crude oil from contaminated soil using subcritical water extraction process. *Environmental Engineering Research* 23(2): 175-180.

Touba, H., Mansoori, G.A., 1998. Structure and property prediction of sub-and supercritical water. *Fluid phase equilibria* 150-151: 459-468.

Tsibart, A.S., Gennadiev, A.N., 2013. Polycyclic aromatic hydrocarbons in soils: sources, behavior, and indication significance (a review*). Eurasian Soil Science* 46(7): 728-741.

US EPA, 2007. SW-846 Test Method 3550C: Ultrasonic Extraction. US Environmental Protection Agency, Washington DC, USA. Available at [Access date: 02.09.2023]: https://www.epa.gov/hw-sw846/sw-846-test-method-3550c-ultrasonic-extraction

US EPA, 2020. IRIS Assessments. Integrated Risk Information System (IRIS). US Environmental Protection Agency, Washington DC, USA. Available at [Access date: 02.09.2023]: https://cfpub.epa.gov/ncea/iris_drafts/AtoZ.cfm

Wu, L., Sun, R., Li, Y., Sun, C., 2019. Sample preparation and analytical methods for polycyclic aromatic hydrocarbons in sediment. *Trends in Environmental Analytical Chemistry* 24: e00074.

Yabalak, E., Akay, S., Kayan, B., Gizir, A.M., Yang, Y., 2023. Solubility and decomposition of organic compounds in subcritical water. *Molecules* 28 (3): 1000.

Yabalak, E., Aminzai, M.T., Gizir, A.M., Yang, Y., 2024. A Review: Subcritical water extraction of organic pollutants from environmental matrices. *Molecules* 29 (1): 258.

Zhang, Q., Liu, P., Li, S., Zhang, X., Chen, M., 2020. Progress in the analytical research methods of polycyclic aromatic hydrocarbons (PAHs). *Journal of Liquid Chromatography and Related Technologies* 43 (13-14): 425-444.

Zhu, M.H., Yin-Dong, L., Wang, L.T., Huang, Z.B., Yuan, P.Q. 2024. Selective extraction of aromatics from residual oil with subcritical water. *Chemical Engineering Research and Design* 202: 444-454.