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Profile distribution of polycyclic aromatic hydrocarbons in coastal soils of the Lower Don and Taganrog Bay, Russia

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Abstract

The main regularities of pollutant distribution through the soil profile were established based on the analysis of the content of 15 priority PAHs in 29 soil sections of different soil types located in the coastal zone of the Lower Don and Taganrog Bay with different anthropogenic loads. It was shown that the total content of PAHs in the 0-20 cm layer of soils of coastal territories varies from 172 μg kg^{-1} to 16006 μg kg^{-1}. In addition, according to the total pollution indicator, (Zc) determines the level of soil pollution, which varies from "not polluted" to "extremely polluted". The influence of pollution sources falls on the 0-20 cm layer of soils of different types and is especially pronounced for subordinate landscapes. With increasing sampling depth, the total PAH content decreases with the redistribution of individual compounds of the PAH group towards the dominance of low molecular weight and 4-ring compounds in the composition of the sum of 15 PAHs and depends largely on the content of organic matter and soil pH. Based on the cluster analysis results, the main factor determining the profile distribution of PAHs is the type of pollutant origin source and its intensity.

Keywords: Landscape, Fluvisols, pollution, migration of pollutants, priority PAHs, organic carbon, coastal zone, transformation of pollutants.

Introduction

Regular flooding of soils of superaqual landscapes, the proximity of groundwater, the inflow of chemical elements with river runoff and from adjacent catchments, and intensive biological cycling have caused high activity and intensity of geochemical processes in floodplains. Such frequency of flooding creates special conditions for the formation of terrestrial landscapes of coastal territories, migration and concentration of chemical substances in them. The hierarchical ordering of the landscape organisation of coastal territories implies the accumulation of chemical substances in soils of subordinate positions of coastal territories landscape influenced by the unidirectional downward water current (Avessalomova et al., 2016). Natural-anthropogenic transsuperaqual and superaqual landscapes of coastal territories often experience a complex anthropogenic impact under conditions of urbanisation, developed agriculture, industry and transport infrastructure while performing the most important regulatory, resource-ecological and socio-ecological

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functions. In this regard, the impact of industry, road and water transport, cities and agriculture leads to the accumulation of hazardous ecotoxicants in the soils of coastal territories.

Polycyclic aromatic hydrocarbons (PAHs) are among the most ecologically significant pollutants that enter the soil of coastal waters of various seas. This is a group of carcinogenic substances, the spread of which in the environment is primarily associated with fuel combustion and spills, as well as fires. 16 PAHs are listed as priority pollutants by the US Environmental Protection Agency (US Environmental Protection Agency, 2020), of which five compounds are highly likely to be carcinogenic, and benz(a)pyrene is a Class 1 carcinogen and mutagen (IARC, 2020). PAHs are not easily soluble in water, are stable in environmental objects, and can accumulate in soils and living organisms, causing various teratogenic and mutagenic effects (Chaplygin et al., 2022; Sun et al., 2021).

Contaminated soils of coastal territories are not subject to remediation. Methods of phytoremediation of such soils are ineffective due to the lack of information on PAH hyperaccumulator plants capable of vegetation under overwatering conditions, and common macrophytes growing near water bodies serve as indicators of environmental stress without significantly changing the concentration of PAHs in soils and sediments (Minkina et al., 2021; Chaplygin et al., 2022).

At the same time, coastal soils contaminated with PAHs can act as a secondary source of pollution by transporting PAH carrier soil particles with water mass (Zhao et al., 2021). Meanwhile, about 19% of the total annual PAH release enters water sources through soil erosion (Qiu et al., 2019). The intensification of coastal zone utilisation for economic purposes is increasing every year (Clark, 2008; Khan et al., 2015). The contradictions associated with the increased intensity of coastal use inevitably lead to acute conflicts between the desire to utilise coastal resources and the need to ensure their long-term reserve. Forecasting the transformation of coastal ecosystems is an urgent problem due to the general intensification of economic activity. Such a forecast requires knowledge of the regularities of coastal ecosystem development, including both general conditions and individual natural and anthropogenic factors.

Currently, an approach called Marine spatial planning is being actively developed, which involves making informed and coordinated decisions on the long-term, sustainable use of marine resources, including those adjacent to the coastal zone (Santos et al., 2019; Boretti and Rosa, 2019). A crucial tool for sustainable coastal management is modelling pollutant mass transfer processes in coastal soils, which is impossible without understanding the main patterns of migration and profile distribution of PAHs. A number of general regularities of pollutant behaviour in coastal soils and peculiarities of their lateral migration are described in the works of Dudnikova et al. (2023a,b), Dai et al. (2022), Shi et al. (2021) and Yang et al. (2015). It has been shown that the type and intensity of the source of PAH input, as well as soil properties, are key factors that determine the quantitative and qualitative content of pollutants in the soils of coastal areas. Peculiarities of the water regime of soils in coastal areas, including water level pulsation, upwelling, and recurrent flooding of soils, may contribute to PAHs leaching deep into the soil profile. In this regard, this study aimed to determine the main patterns of PAH profile distribution in soils of natural and natural-anthropogenic landscapes of the coastal zone.

Material and Methods

General characterisation of the study area

Under the influence of anthropogenic factors, the unstable balance of natural processes is rapidly disrupted, and the conditions for the formation of floodplain landscapes are significantly altered. The Lower Don Valley is characterised by a wide floodplain with an abundance of emergent and meadow vegetation. The Don Delta is represented by several sandy islands densely indented by shallow depressions of dried-up old river channels, arms and canals. The northern shore of the Taganrog Bay coastline is characterised by the predominance of abrasion and erosion processes, while the southern part is characterised by relatively more intensive accumulative processes. Floodplain and coastal landscapes of the Lower Don and Taganrog Bay are represented by alternating water bodies, willow thickets, floodplain meadows, sand dunes, beaches and spits, parks, gardens, and other tree plantations, some of which are shown in Figure 1.

The Lower Don River and the Taganrog Bay are key sections on the route of long-distance multi-tonnage tankers from the Sea of Azov and the Black Sea inland to the Gulf of Finland. Every day, dozens of water transport units pass through the Don Delta in the Volga-Don shipping channel (Kuzmichev et al., 2020), which forms a threat of accumulation of carcinogenic substances of the PAH group in soils and coastal sediments. In addition, the concentration of industrial, residential, agricultural, recreational and natural objects within the coastal zone of Taganrog Bay reflects the general trends of the intensity of the coastal territories' involvement for various human needs, a common feature of the entire southern coast of Russia.

(A) (B) (C)

Figure 1. General view of coastal-water communities of the Don delta (A), floodplain meadows (B), sandy loam-meadow community (C)

Soil cover characterisation and soil sampling

For the study, 29 full-profile transects were laid out in elluvial, trans-elluvial, and superaqual positions of the coastal zone landscape to assess the influence of topographic position on PAH accumulation in the soil. The trans-elluvial and superaqual positions contain predominantly Salic Fluvisols, Tidalic Fluvisols, Calcaric Fluvisols, Histic Fluvisols and Gleyic Solonchaks (Nachtergaele et al., 2023). Eluvial positions of landscapes are dominated by Calcic Chernozems, the most common soils occupied mainly for agricultural purposes (Kalinitchenko et al., 2022), but Rendzic Leptosols and Mollic Leptosols also occur (Figure 2) (World Reference Base for Soil Resources). In full-profile transects, soil sampling was conducted by soil horizon (Table 1). Often, when investigating the profile distribution of PAHs in soils, sampling is done layer by layer in 5, 10 or 20 cm increments. For the current study, a genetic approach was chosen in which the sampling depth corresponds to soil horizon boundaries. It was assumed that similar processes occur within the same horizon, with pollutants occurring regardless of the depth of the horizon. For horizon thicknesses above 40 cm, at least two samples were taken from different depths. The mass of the combined sample was 1 kg. To determine the level of soil contamination and to compare the content of PAHs in soils of the study area with background areas, a 0-20 cm soil layer was taken according to GOST 17.4.3.01-2017 (GOST 17.4.3.01-2017, 2018).

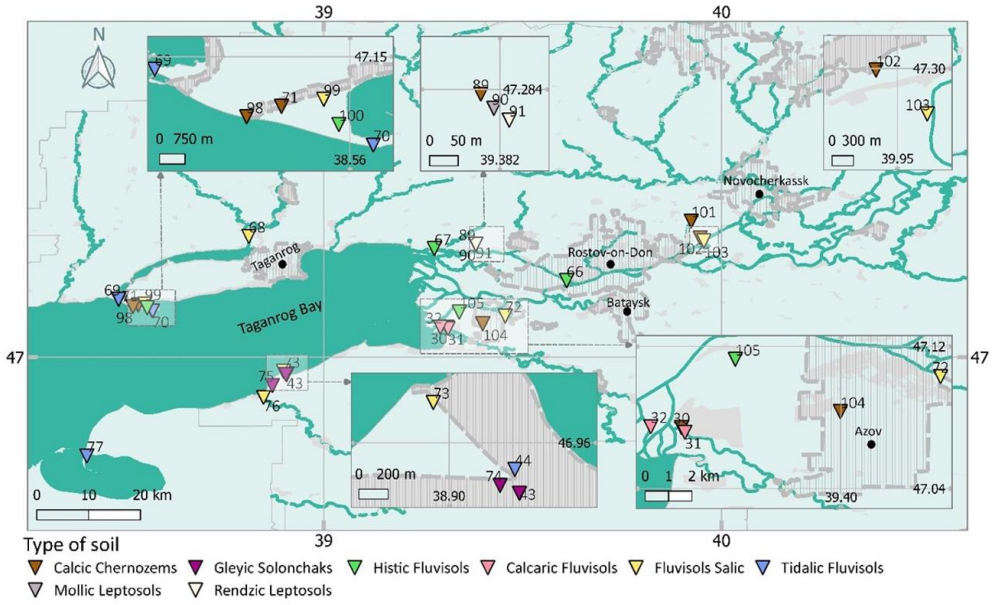

Figure 2. Location map of monitoring sites with soil type names indicated

Table 1. Correlation of PAH content with soil properties obtained by calculation of Spearman correlation coefficient

	Soil properties			Soil properties	
PAHs	Organic carbon	pH	PAHs	Organic carbon	pH
Naphthalene	0.40	-0.19	Chrysene	0.50	-0.22
Fluorene	0.58	-0.44	Benzo[a]anthracene	0.55	-0.23
Phenanthrene	0.55	-0.35	Benzo[b]fluoranthene	0.44	-0.12
Anthracene	0.36	-0.44	Benzo[k]fluoranthene	0.50	-0.25
Acenaphthene	0.52	-0.35	Benzo[a]pyrene	0.59	-0.36
Acenaphthylene	0.46	-0.20	Dibenzo[a,h]anthracene	0.39	-0.13
Fluoranthene	0.48	-0.15	Benzo[g,h,i]perylene	0.46	-0.15
Pyrene	0.54	-0.23			

Methods

Determining physical and chemical soil properties

The main physicochemical properties of soil samples were determined: organic carbon content – by bichromate oxidation method with titrimetry; content of granulometric fractions of physical clay (<0.01mm) and silt (<0.001mm) – by sedimentation method using Kachinsky pipette with pyrophosphate preparation (Korchagina and Vadyunina, 1986); pH of soil samples was determined by potentiometric method in the suspension of soil: water 1:2.5.

Identification and quantitative analysis of PAH content in soil samples

To determine the PAHs, 1 g of soil sample was weighed each. To remove the interfering lipid fraction, the soil sample was saponified by boiling for 3 h in 30 ml of 2% potassium hydroxide solution in a water bath with a reflux condenser. PAH extraction was carried out with 98% purity n-hexane (ISO 13877-2005, 2020). For this purpose, 15 ml of hexane was poured into the sample and placed on a shaker. After 10 min, the hexane supernatant was carefully poured into a separating funnel. The operation was repeated three times. After that, the hexane layers were separated from the residual fraction of the alcoholic alkali solution in the separating funnel. The extract was filtered through a paper filter with anhydrous sodium sulphate for mechanical purification and removal of residual liquid. The hexane extract was then evaporated at a rotary evaporator. After evaporation, the precipitate was dissolved in 1 mL of 99.9% acetonitrile.

Samples were analysed for the presence of PAHs using an Agilent 1260 Infinity high-performance liquid chromatography (HPLC) (Agilent Technologies, Santa Clara, CA, USA) equipped with fluorescence and UV detectors, in accordance with the requirements of ISO 13877-2005 (ISO 13877-2005). The HPLC system was equipped with a Hypersil BDS C18 reversed-phase column (Agilent Technologies) (125 × 4.6 mm, 5 µm). A mixture of 99.9% acetonitrile (Cryochrome, Moscow, Russia) (75%): bidistilled water (25%) at a flow rate of 0.5 ml min-1 was used as the mobile phase. The volume of extract injected was 20 µl. The present study determined the content of 15 priority PAHs from the US EPA priority pollutants list (US Environmental Protection Agency, 2020). Of these, the following are low molecular weight: 2-ringed (naphthalene) and 3-ringed (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene), and high molecular weight: 4-ringed (fluoranthene, pyrene, benzo(a)anthracene, chrysene), 5-ringed (benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene) and 6-ringed benz(g,h,i)perylene.

The extraction efficiency of target PAHs from soils was determined using the matrix method by constructing calibration curves. A fresh soil sample as well as an air-dry soil sample (1 g) were placed in a round bottom flask, and a standard solution of PAHs in acetonitrile was added to target PAH concentrations of 2, 4, 6, 8, 16 or 32 µg kg^{-1}. After evaporating the solvent for 30 min under a fume hood, the PAH-added soil samples were incubated for 24 h at 4 °C. The samples were then analysed by the saponification method described above, followed by HPLC analysis.

Quality control of each detection by HPLC was performed according to Agilent Application Solution (Certificate 27-08). Individual standard solutions were purchased from Sigma-Aldrich (Merch) (Burlington, MA, USA). A calibration standard of the PAH mixture was injected after every six samples to correct for retention time drift during the analysis. After plotting the calibration curve, a detection coefficient was calculated for each detected PAH:

The PAH content in the tested samples was determined using the external standard method. The PAH content in soil was calculated using the equation (1):

$$Cs = k\,Si \times Cst \times V/(Sst \times m) \quad (1)$$

where Cs is the PAH content in the soil sample (µg kg^{-1}); Sst and Si are the areas of PAH peaks for standard solution and sample, respectively; Sst is the concentration of PAH standard solution (µg kg^{-1}); k is the PAH extraction factor from the sample; V is the volume of acetonitrile extract (ml); m is the mass of the sample (g).

Certified reference materials and calibration curves were used to calculate the limits of detection and limits of quantification, which were 2-200 µg kg^{-1}. For the developed methods for the isolation of target PAHs in soil, the random component of the measurement error was estimated, which was 3.5-14 % for the concentration range of 2-200 µg kg^{-1}.

Solvents and reagents were of HPLC purity and included ethanol (96%, p.a.) (Aquatest, Rostov-on-Don, Russia), n-hexane (99%, p.a.) (Aquatest, Rostov-on-Don, Russia), potassium hydrate (98%, p.a.) (Aquatest), acetonitrile (99.9%, p.a.) (Kriochrome, St. Petersburg, Russia), NaOH (97%, p.a.) (Kriochrome, St. Petersburg, Russia). (Aquatest), acetonitrile (99.9%, b.w.a.) (Cryochrom, St. Petersburg, Russia), NaOH (97%, b.w.a.)

(Aquatest) and anhydrous Na2SO4 (Aquatest, Rostov-on-Don, Russia). A total of 15 priority PAH standards in acetonitrile with a concentration of 200 μg/cm³ manufactured by Merch Burlington, MA, USA (NIST® SRM® 1647f Priority PAH Contaminants (in acetonitrile)) were used to prepare standard solutions of total PAHs for HPLC analysis. Analytical standards were purchased from Sigma-Aldrich (Merch) and used as an internal analytical standard.

Determining the level of surface layer pollution and migration of PAHs along the profile

The degree of soil contamination was assessed using the total contamination index (Zc) according to the formula (2) (MU 2.1.7.7330-99, 1999; Kasimov and Vlasov, 2012; Fedorets et al., 2015):

$$Z_C = \sum Kc_i - (n-1) \quad (2)$$

where KCi is the concentration factor of individual compounds, n is the number of considered elements and compounds with KCi >1.

The concentration factor is calculated relative to background values (3):

$$Kc_i = Kb/K \quad (3)$$

Only soils with a profile depth of more than 40 cm were included in the calculation. Where Kb is the content of individual compounds in the background soil, K is the content of individual compounds in the studied soil. The background values determined in a study conducted earlier (Dudnikova et al., 2023a) were used for calculation.

The ratio of PAH content in the upper horizon to the lower horizon was calculated to study the migration capacity of PAHs in soils.

Statistical analysis and data visualisation

Statistical analysis of the obtained data and visualisation of the analysis results were performed using SigmaPlot 12.5, Origin 2018, STATISTICA 8 and QGIS 3.2 software. The relationship between the content of low and high molecular weight PAHs and depth was determined using regression analysis based on the exponential equation. Cluster analysis was performed using Ward's method with Euclidean distance as a proximity measure.

Results and Discussion

Profile characterisation of physical and chemical soil properties

The result of the analysis of the profile distribution of organic carbon showed that the thickness of organogenic horizons varies greatly. The highest thickness is Calcic Chernozems 41-52 cm, and the lowest is for alluvial meadow carbonate 10-11 cm. Organic carbon accumulation in soil profiles corresponds to the accumulative type, except for alluvial meadow-saturated layered soils of monitoring sites No. 68-70, 77. Redistribution of organic carbon in the soil profile is characteristic of the eluvial-illuvial type with maximum accumulation in the upper horizon (Figure 3).

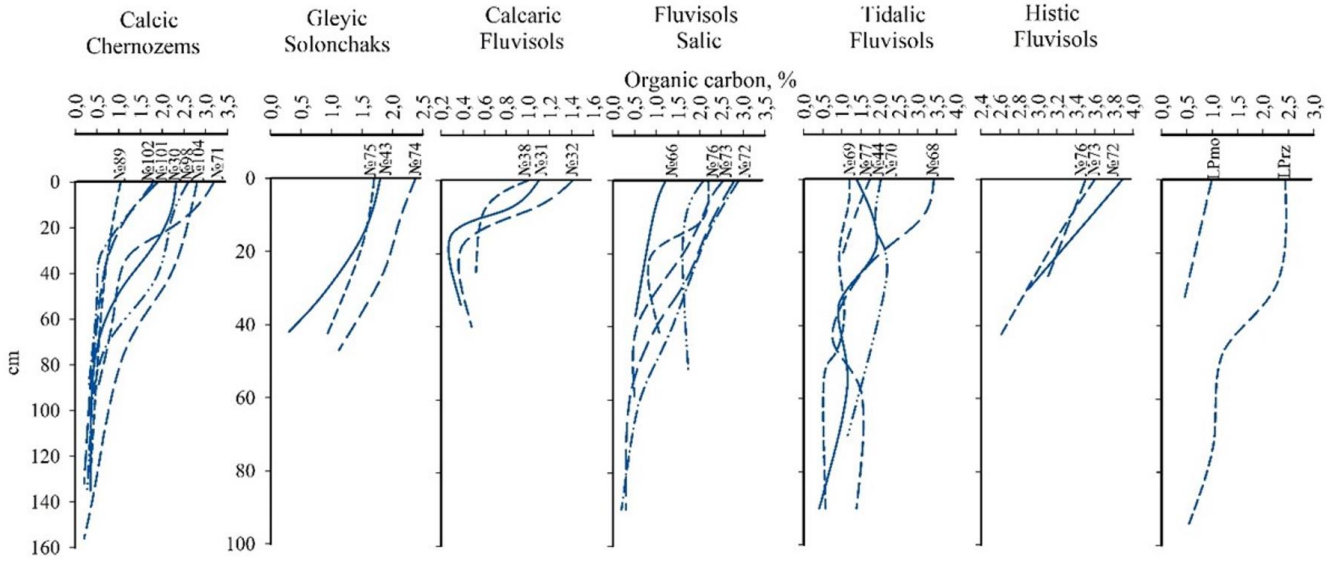

Figure 3. Profile distribution of organic carbon in soils of different types of the coastal zone of the Lower Don and Taganrog Bay (Note: LPmo - Mollic Leptosols, LPrz - Rendzic Leptosols)

The change of pH in soil profiles varies from neutral to slightly alkaline. Neutral reaction of the medium is typical for the upper horizons of Calcic Chernozems of monitoring site No. 71 and alluvial meadow carbonate soils of monitoring sites No. 31 and No. 32. In most of the soil profiles under consideration, the carbonate content increases with depth, which is caused by their occurrence in loess-like loams, alluvial, marine and alluvial-marine sediments. No significant changes in pH values were observed in the profile of the considered soils (Figure 4).

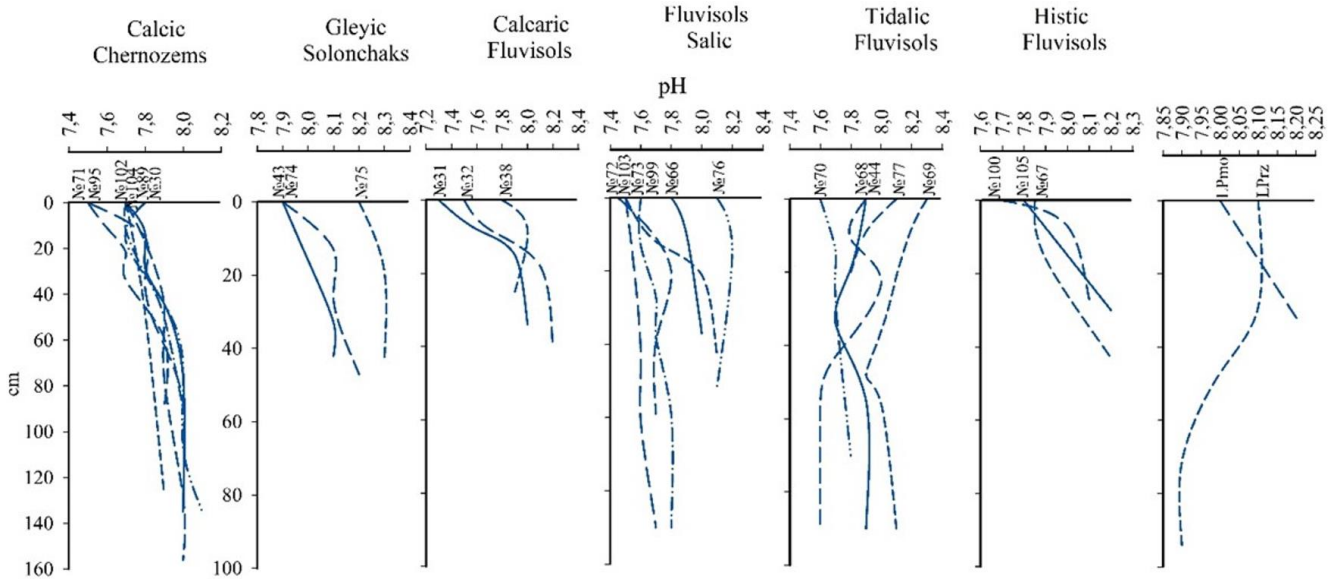

Figure 4. Profile distribution of pH in different types of soils of the coastal zone of the Lower Don and Taganrog Bay (Note: LPmo - Mollic Leptosols, LPrz - Rendzic Leptosols)

Profiles are predominantly undifferentiated in terms of the distribution of silt and physical clay fractions. In the presence of the gley process in the lower part of the profile, the content of fine-dispersed fraction of soils increases with depth, which is especially characteristic of Gleyic Solonchak and Calcaric Fluvisols. In alluvial sod carbonate, on the contrary, the content of physical clay and silt decreases with depth (Figure 5).

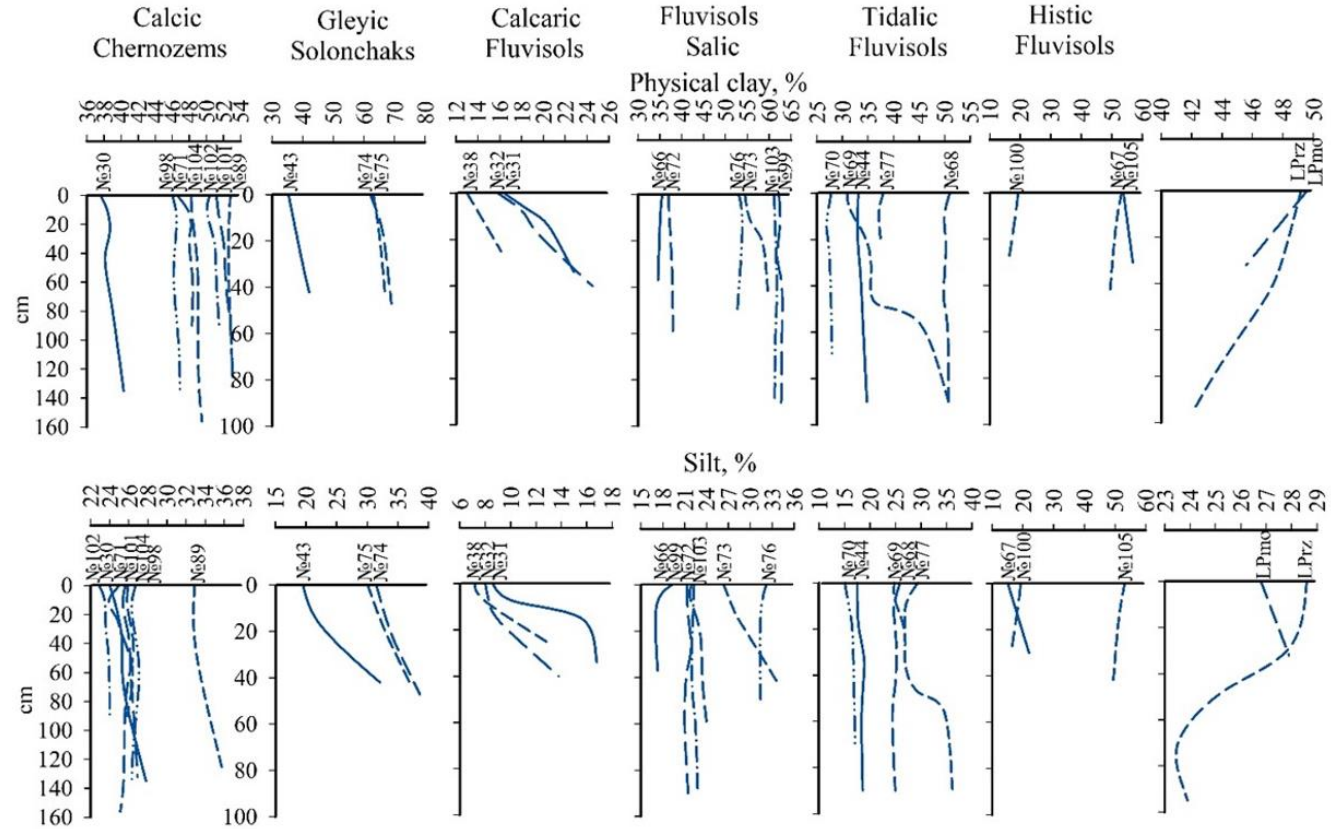

Figure 5. Profile distribution of physical clay and silt in different types of soils of the coastal zone of the Lower Don and Taganrog Bay (Note: LPmo - Mollic Leptosols, LPrz - Rendzic Leptosols)

PAH content in the upper 0-20 cm soil layer

In the surface horizon of soils (0-20 cm), the total PAH content varies widely from 172 μg kg^{-1} to 16006 μg kg^{-1} with a median value of 269 μg kg^{-1} (Figure 6). In the soils of subordinate landscapes, the median PAH content, as well as the variability of data, increases relative to eluvial landscapes. At the same time, the increase in the median value in the Autonomous (227 μg kg^{-1}) > Downslope (301 μg kg^{-1}) > Superaquatic (319 μg kg^{-1}) row indicates the migration of pollutants under gravitational and hydrological forces (Glazovskaya, 1998; Avessalomova et al., 2016). Increased variability of PAH values in a similar series may indicate greater vulnerability of superaquatic landscape soils to pollutants (Xu et al., 2021).

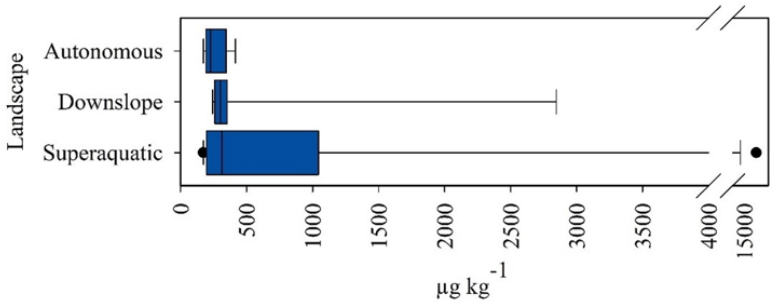

Figure 6. Total PAH content in 0-20 cm layer of soils of different landscapes of the Lower Don and Taganrog Bay

At low PAH content in soils relative to the global average, an increased number of individual compounds is observed compared to the regional background (Dudnikova et al., 2023a). The composition of individual PAHs by median values is dominated by pyrogenic-coal association of pollutants (Yunker et al., 2015; Tsibart et al., 2016; Sushkova et al., 2020; Dudnikova et al., 2023b), represented by phenanthrene, fluoranthene, pyrene, chrysene and benz(g,h,i)perylene, as well as benz(b)fluoranthene, the accumulation of which is characteristic of the soils of coastal areas influenced by liquid fuel spills (Figure 7).

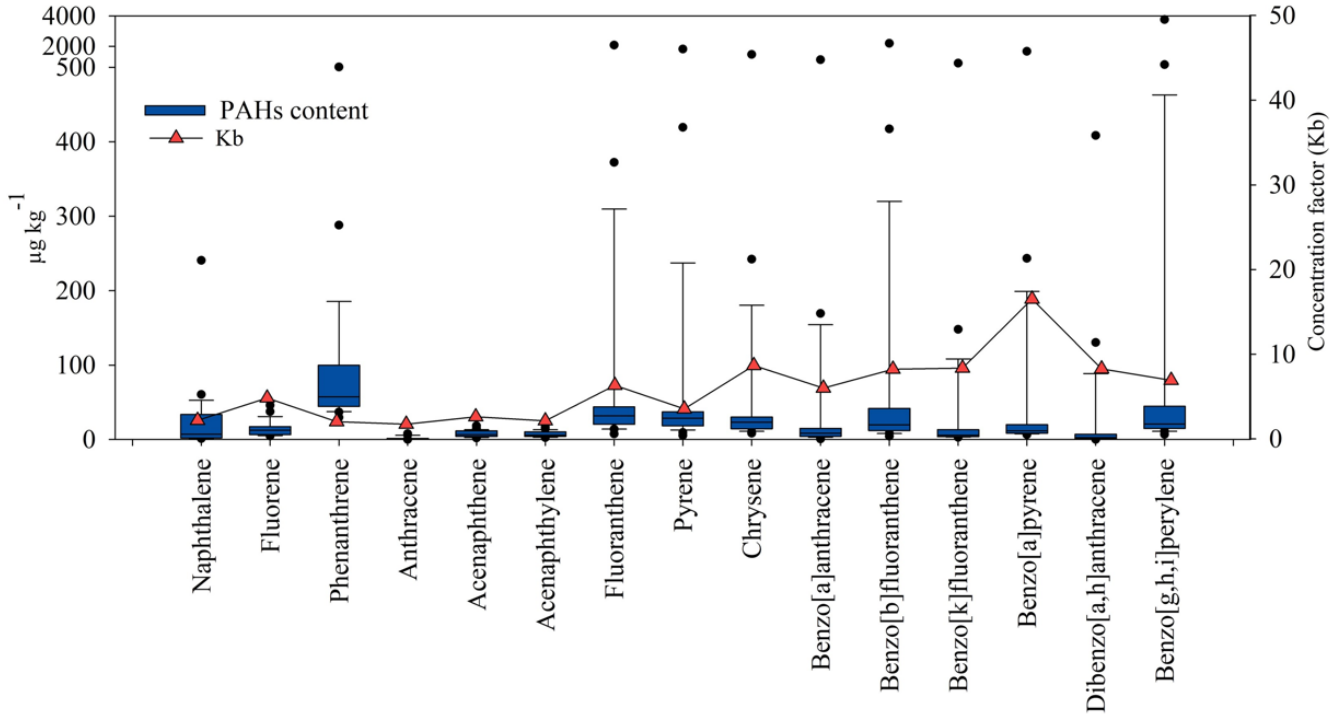

Figure 7. Content and median value of the concentration coefficient (Kb) of individual PAH compounds in the 0-20 cm layer of the Lower Don and Taganrog Bay soils

The results of the Kb calculation showed that with an increasing number of benzene rings in the PAH molecule, their accumulation in soil increases. High content of phenanthrene compared to other studied PAHs is noted both for soils of background areas and impact zones (Sushkova et al., 2020; Chaplygin et al., 2022; Dudnikova et al., 2023a,b). At the same time, its median Kb value is lower than the lowest phenanthrene concentration. Accordingly, about 50% of soils of the study area are characterised by pollutant dispersion. In this case, dispersion means not only its faster biodegradation compared to high molecular weight PAHs, but also more intensive mass transfer of phenanthrene in association with organic matter of coastal soils (Zhang and Fan, 2016; Benhabib et al., 2017).

Assessment of PAH contamination of the upper 0-20 cm soil layer

It has been established that the level of total PAH pollution in the soils of the monitoring sites varies from non-hazardous to extremely hazardous. The heterogeneity of pollutant sources causes wide limits of the variability of soil pollution in the study area, their proximity to monitoring sites and intensity, as well as soil properties (Dudnikova et al., 2023a). The higher degree of pollution is characteristic of the soils of the monitoring sites confined to the northern coast of Taganrog Bay, the territory of Beglitskaya Spit and the mouth of the Mius River. For the soils of the Don Delta, the highest degree of pollution is confined to the northern and southern parts of Taganrog Bay. Soils of the territories of periodically waterlogged gully No. 89- 91, located remotely from the Don River and Taganrog Bay, are characterised by low PAH content (Figure 8). It should be noted that the soils of the study area are contaminated with heavy metals to different degrees (Minkina et al., 2021). The presence of metal cations in clay minerals leads to an increase in pore size, causing aggregation and greater hydrophobicity of clay (Saeedi et al., 2018). Heavy metal ions can also accumulate on the clay surface, providing sites for π-bonding of the cation to PAHs (Saeedi et al., 2018; Duan et al., 2022).

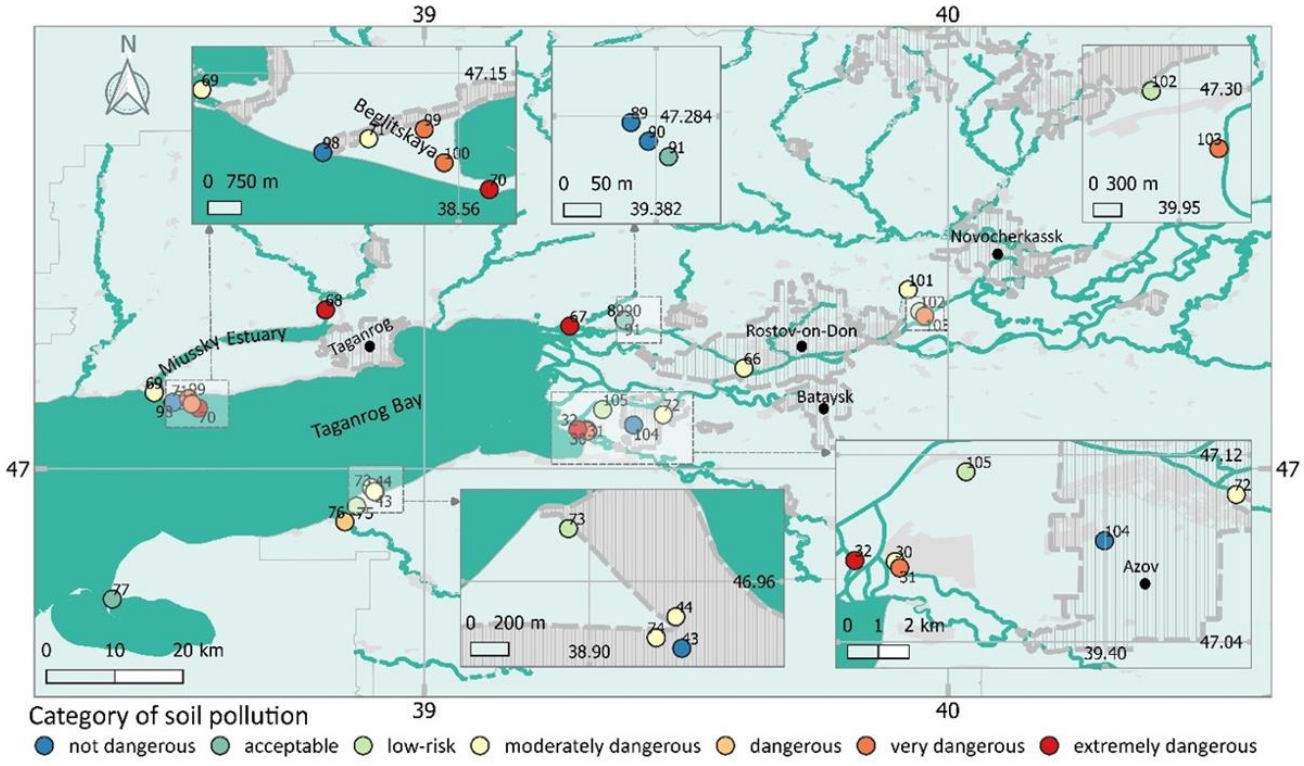

Figure 8. Soil pollution categories of the Lower Don and Taganrog Bay by total pollution indicator (Zc)

PAH distribution in the soil profile

The distribution analysis of the sum of 15 priority PAHs showed that the highest accumulation in the soils of the study area is in the upper horizons of 0-20 cm, in rare cases in the underlying horizons of 0-40 cm, which is more typical for Gleyic Solonchak and is caused by the distribution of organic matter in the soil profile (Figure 3, 9). The character of pollutant distribution corresponds to the accumulative type, which is consistent with studies of solonchaks in Portugal (Martins et al., 2008), the Niger Delta soils (Abbas and Brack, 2006), brown soils near Beijing (Cai et al., 2019), Albic Podzols of Siberia (Dymov and Gabov, 2015). The exception was Histic Fluvisoils type soils, for which the PAH distribution profile is either not differentiated or a slight increase in total PAH content with depth is present (Figure 9). In soils with standing water and reduction conditions, an increased PAH content compared to the upper horizon can be observed at depths below 70 cm (Atanassova and Brümmer, 2004), which is consistent with the results of studies of marsh soils of the Pearl River estuary (Xiao et al., 2014) and is due to the transformation of soil organic matter under the influence of reduction conditions (Thiele and Brummer, 2002). In this case, pedogenic PAHs are firmly bound to the highly aromatic soil organic matter (Aemig et al., 2016). In this regard, PAHs in the lower soil horizons become less labile, making them inaccessible to microbial degraders (Delegan et al., 2022; Ren et al., 2018). In addition, the activity of PAH-degrading microorganisms is predominantly observed in the most aerated 0-20 cm layer, which also does not favour the biodegradation of pollutants deep in the soil profile (Mazarji et al., 2022; Ren et al., 2018). Consequently, this group of pollutants is poorly degraded in the depth of the soil profile (Bu et al., 2009).

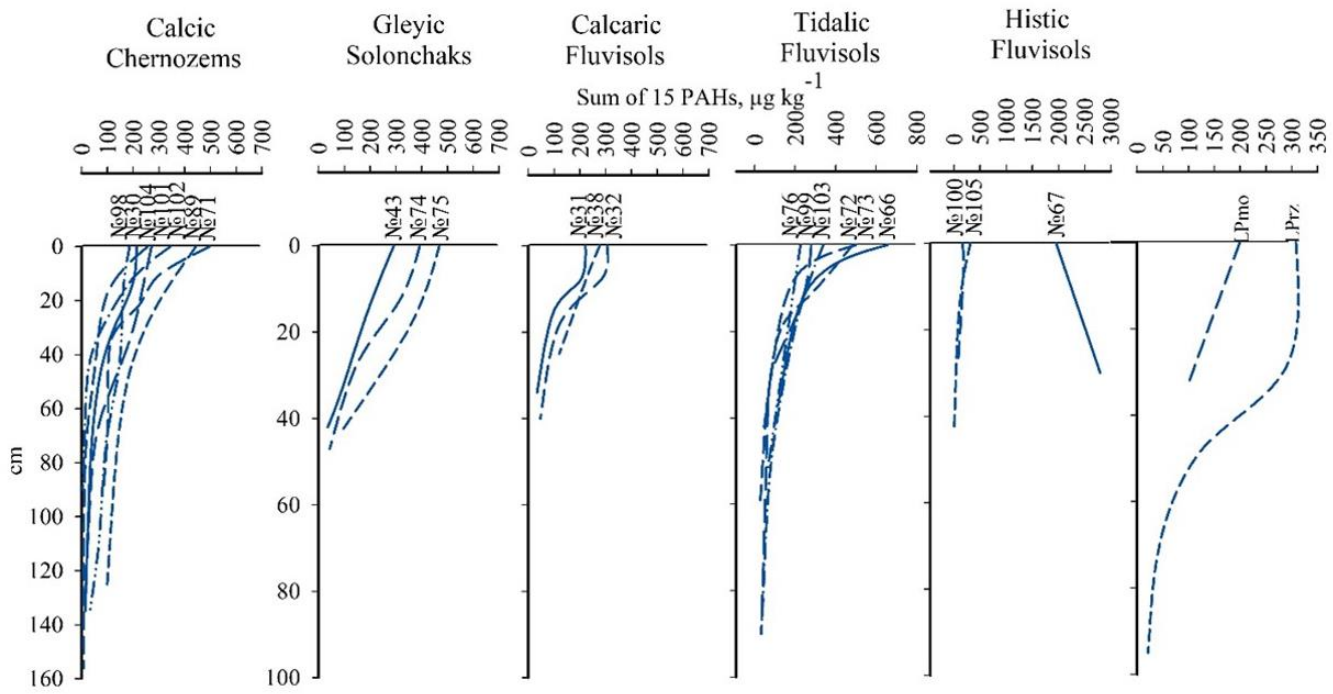

Figure 9. Profile distribution of the total content of 15 PAHs in different soil types of the Lower Don and Taganrog Bay soils

As the pollutant concentration decreases with depth, changes in the PAH composition are observed. For almost all soil types, there is an increase in low molecular weight compounds, especially phenanthrene, and 4-ring fluoranthene and pyrene (Figure 10). In general, low molecular-weight compounds are more capable of migration than high molecular-weight compounds (Cai et al., 2019). As noted by Ping et al. (2007), phenanthrene, due to its higher solubility, occurs in quantities of 50% of its content in the upper horizon, indicating its ability to migrate with groundwater as true solutes (Krauss et al., 2005). However, due to leaching, PAHs can be transported down the profile in concentrations that exceed their solubility (Benhabib et al., 2017). The accumulation and distribution of pollutants along the profile also depend on the degree of exposure to input sources (Mayer et al., 2019). The higher the PAH content in the surface horizon, the lower the percentage of migration across the profile (Cai et al., 2019).

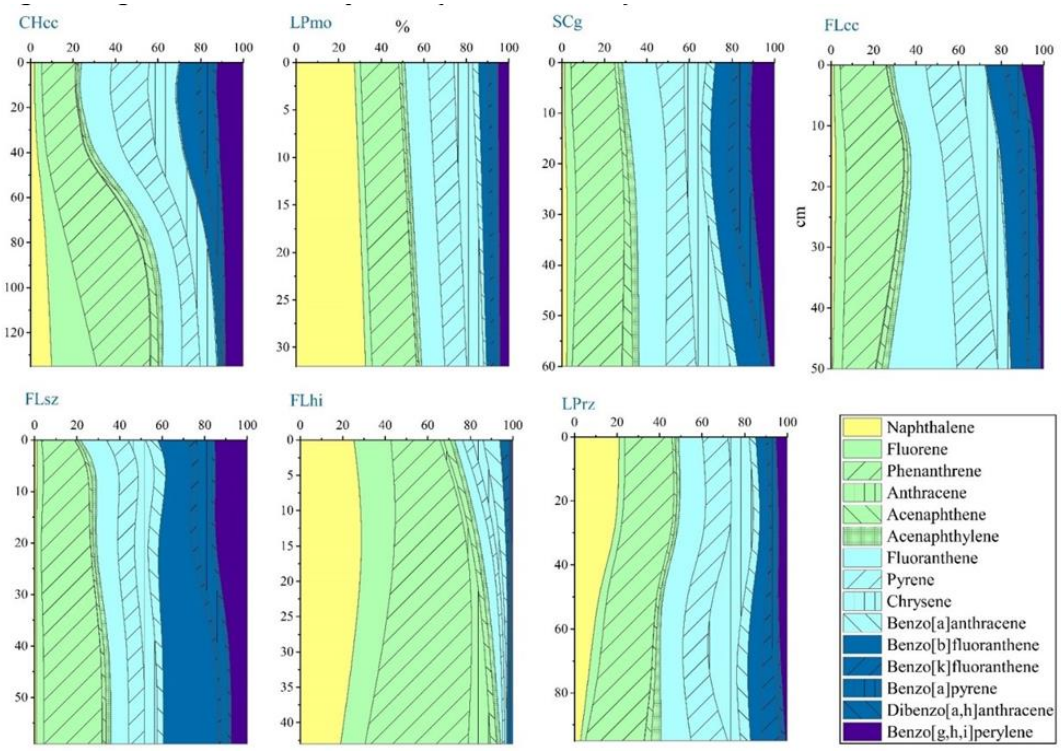

Figure 10. Profile distribution of individual compounds of 15 PAHs as a percentage of their total content in the soils of the Lower Don and Taganrog Bay soils

A distinctive feature of the profile distribution of PAHs in Tidalic Fluvisols is the presence of the second accumulation maximum in the middle of the profile. This effect is typical for less polluted soils of monitoring sites No. 69 and 77, where the total PAH content of upper horizons does not exceed 500 μg kg^{-1}. In case of higher pollution of the surface layer, the accumulation of pollutants in the middle of the profile is not pronounced.

When analysing individual PAH compounds, their differentiation along the soil profile is clearly traceable regardless of the pollution level (Figure 11). In general, changes in individual PAH compounds correspond to the distribution of organic carbon and pH in the profile of Tidalic Fluvisols (Figure 3, 4). This effect is due to the fact that the amount of low molecular weight compounds is almost unchanged across the soil profile, while the content of high molecular weight compounds decreases across the soil profile. Tidalic Fluvisol horizons with increased organic matter content prevent the movement of high molecular weight PAHs, primarily 4-ring compounds, acting as a natural "filter" on the way of pollutants migration from the soil profile surface deep into the parent rock. The most dangerous 5- and 6-ring compounds accumulate at a depth of up to 10 cm (Figure 11).

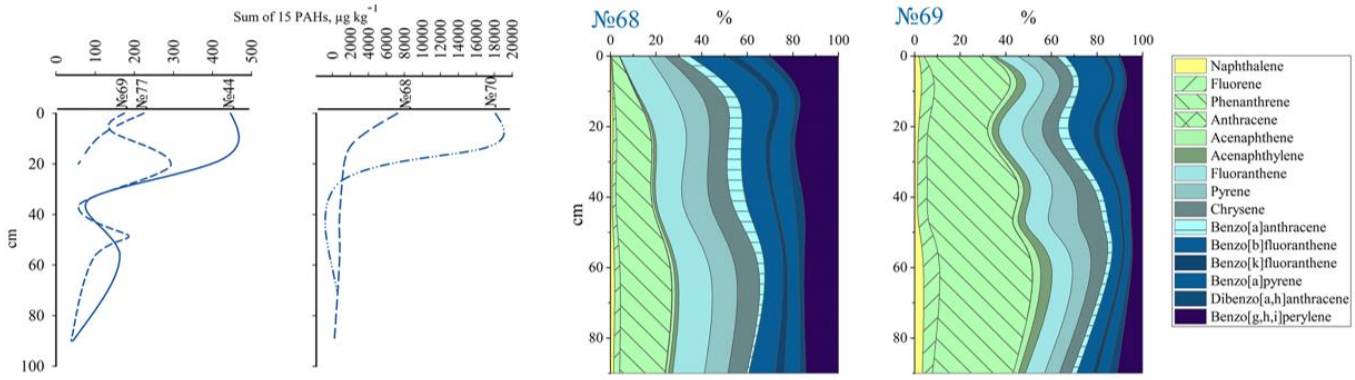

Figure 11. Profile distribution of total PAHs and individual compounds as a percentage of the total content in Tidalic Fluvisols of the Lower Don and Taganrog Bay

Transformation of PAH composition along the soil profile

It was found that with increasing molecular weight and size of the PAH molecule, the degree of PAH reduction with depth increases, as evidenced by the increase in the ratio of PAH content in the upper horizon to its content in the lower horizon (Figure 12).

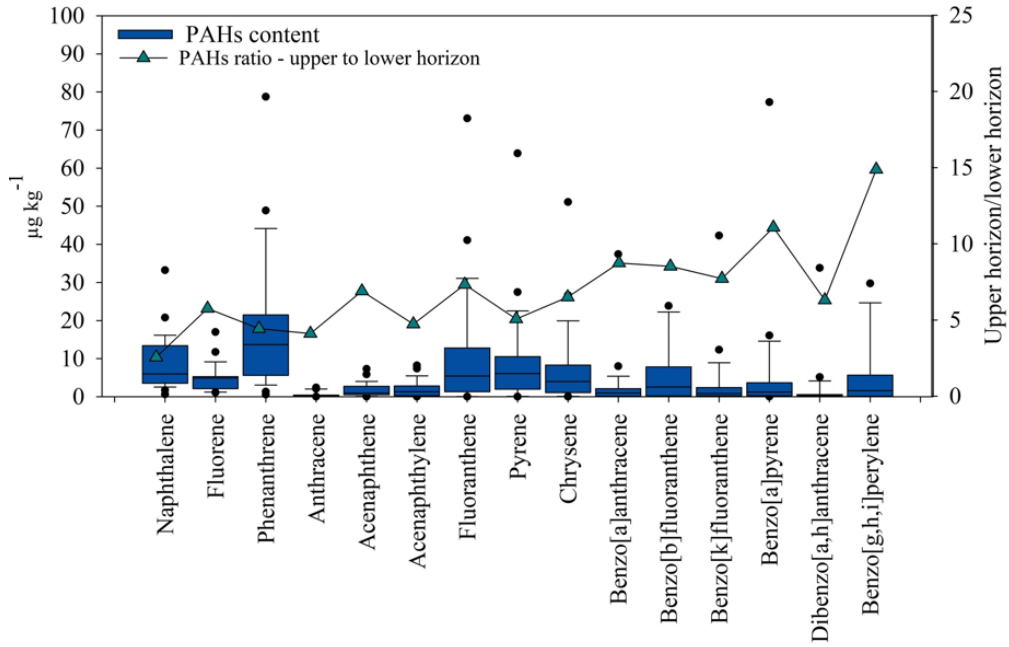

Figure 12. Content of individual PAH compounds in the lower soil horizons (below 40 cm), as well as the ratio of pollutant content in the upper (up to 20 cm) to lower (below 40 cm) soil horizons of the Lower Don and Taganrog Bay soils

The results were confirmed by regression analysis. The decrease in PAH content was approximated by an exponential equation, where the coefficient of determination R^2 =0,41 for low molecular weight compounds and R^2=0,50 for high molecular weight compounds (Figure 13). It was found that with increasing molecular

weight and size of the PAH molecule, the degree of PAH reduction with depth increases, as evidenced by the increase in the ratio of PAH content in the upper horizon to its content in the lower horizon (Figure 12). The results were confirmed by regression analysis. The decrease in PAH content was approximated by an exponential equation, where the coefficient of determination R^2 =0.41 for low molecular weight compounds and R^2=0.50 for high molecular weight compounds (Figure 13). Among all investigated compounds, phenanthrene and naphthalene clearly dominate due to their high migration ability in comparison with other PAHs and the increased content of relatively low molecular weight compounds. A noticeable contribution to the content of pollutants of the underlying soil horizons is made by 4-ring compounds, which are the dominant PAHs of the upper horizon and are the most soluble from the pool of pyrogenic-coal association (Figure 12).

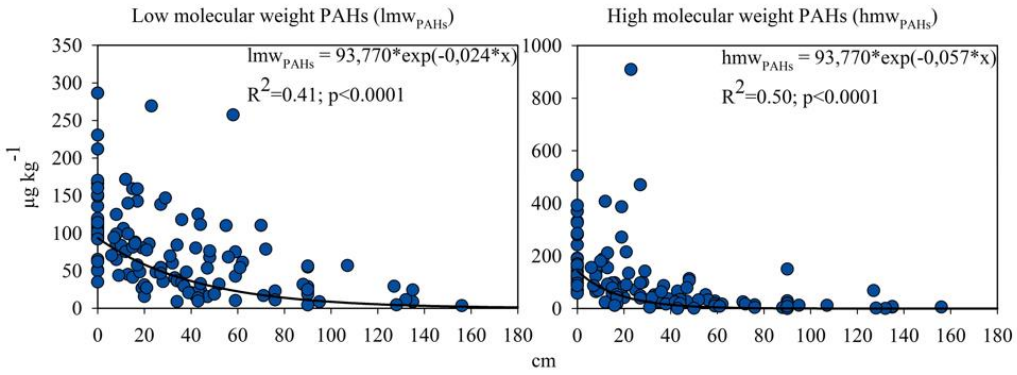

Figure 13. Correlation between the content of low-molecular and high-molecular PAHs and soil profile depth, obtained by regression analysis using the exponential equation

The results of the correlation analysis revealed the correlation between PAH content and soil properties. A significant positive correlation is observed between organic carbon and the total pool of PAHs considered, consistent with Fengpeng et al.'s studies (Fengpeng et al., 2009). The degree of correlation between soil organic matter and PAHs may vary depending on the type of land use (Xiao et al., 2014) and is due to the heterogeneity of soil organic matter and its amount (Ukalska-Jaruga et al., 2019). At the same time, less aromatic fractions of soil organic matter, such as fulvic acids, play a major role in the migration of PAHs through the soil profile (Dong et al., 2017). PH values mainly affect the redistribution of low molecular weight compounds in the soil profile (Table 1).

The clustering of PAHs in the upper (0-20 cm) layer of soils showed that pollutants constitute two distinct groups. The first one is represented by pyrogenic-coal association-benz(g,h,i)perylene, chrysene, pyrene, fluoranthene and phenanthrene, as well as benz(b)fluoranthene. These substances dominate the PAHs in the upper soil layer and are presumably introduced by the combustion of hydrocarbon materials from point and linear emission sources such as factories and motor vehicles, as well as from spills of hydrocarbon materials. Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene benz(g,h,i)perylene constitute the second group of the PAHs less abundant in surface soil horizons (Figure 14). In the lower soil horizons, pollutants are grouped similarly to the upper 0-20 cm layer (Figure 14). This indicates the migration of PAHs through the soil profile. The composition of pollutants in the lower horizons depends primarily on the type of emission source and its intensity.

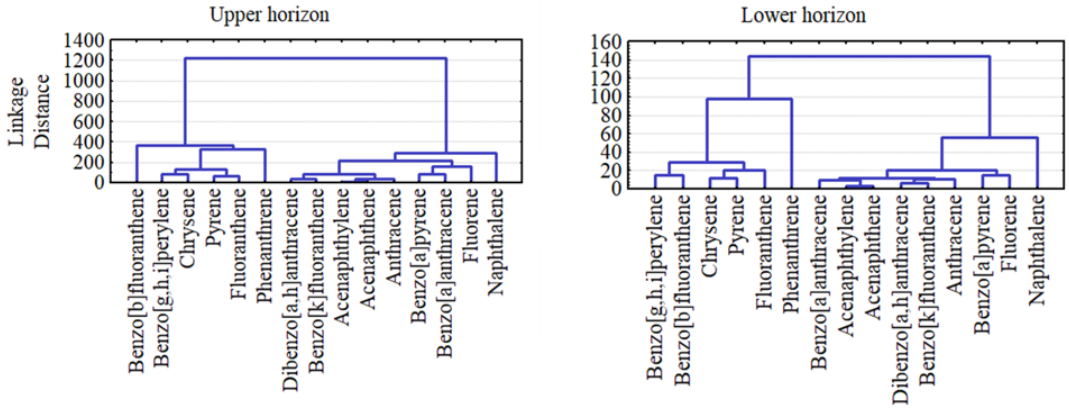

Figure 14. Grouping of individual PAH compounds in the upper and lower horizons according to the results of cluster analysis

Conclusion

In conclusion, it was found that the total PAH content in the 0-20 cm layer of the soils of the coastal territories of the Lower Don and Taganrog Bay varies from 172 μg kg^{-1} to 16006 μg kg^{-1}. The soils of subordinate landscapes are more susceptible to technogenic influence. The median value of the total PAH content increases in the Autonomous (227 μg kg^{-1}) > Downslope (301 μg kg^{-1}) > Superaquatic (319 μg kg^{-1}) row. The level of soil pollution varies from non-hazardous to extremely hazardous. It depends mainly on the content in the surface layer of pyrogenic coal association PAHs (phenanthrene, fluoranthene, pyrene, chrysene, benz(g,h,i)perylene) or benz(b)fluoranthene, the accumulation of which is associated with fuel spills. The distribution of PAHs in the soil profile of the studied soil types corresponds to the accumulative type, where the main influence of pollution sources falls on the 0-20 cm layer. The total PAH content decreases with increasing sampling depth. The decrease intensifies with increasing size and molecular weight of pollutant molecules, which leads to the redistribution of individual compounds of the PAH group in lower soil horizons. At the same time, 4-ringed PAHs and phenanthrene dominate in the lower soil horizons. Their migration depends on the organic matter content and pH in the soil profile. Using cluster analysis, it is shown that the main factor determining the profile distribution of PAHs is the type of pollutant origin source and its intensity.

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References

Abbas, A.O., Brack, W., 2006. Polycyclic aromatic hydrocarbons in Niger Delta soil: contamination sources and profiles. *International Journal of Environmental Science and Technology* 2: 343–352.

Aemig, Q., Chéron, C., Delgenès, N., Jimenez, J., Houot, S., Steyer, J.P., Patureau, D., 2016. Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in sludge organic matter pools as a driving force of their fate during anaerobic digestion. *Waste Management* 48: 389–396.

Atanassova, I.D., Brümmer, G.W., 2004. Polycyclic aromatic hydrocarbons of anthropogenic and biopedogenic origin in a colluviated hydromorphic soil of Western Europe. *Geoderma* 120(1-2): 27–34.

Avessalomova I.A., Khoroshev A.V., Savenko A.V., 2016. Barrier function of floodplain and riparian landscapes in river runoff formation. In: Riparian zones. Characteristics, management practices, and ecological impacts, Pokrovsky, O.S., (Ed.). Nova Science Publishers, pp. 181-210.

Benhabib, K., Simonnot, M.O., Faure, P., Sardin, M., 2017. Evidence of colloidal transport of PAHs during column experiments run with contaminated soil samples. *Environmental Science and Pollution Research* 24: 9220–9228.

Boretti, A., Rosa, L., 2019. Reassessing the projections of the world water development report. *NPJ Clean Water* 2: 15.

Brümmer, G.W., Sören, T.B., 2002. Bioformation of polycyclic aromatic hydrocarbons in soil under oxygen deficit conditions. *Soil Biology and Biochemistry* 34(5): 733-735.

Bu, Q.W., Zhang, Z.H., Lu, S., He, F.P., 2009. Vertical distribution and environmental significance of PAHs in soil profiles in Beijing, China. *Environmental Geochemistry and Health* 31: 119-131.

Cai, T., Ding, Y., Zhang, Z., Wang, X., Wang, T., Ren, Y., Dong, Y., 2019. Effects of total organic carbon content and leaching water volume on migration behavior of polycyclic aromatic hydrocarbons in soils by column leaching tests. *Environmental Pollution* 254: 112981.

Certificate 27-08. Procedure of Measurements Benz(a)pyrene Content in Soils, Sediments and Sludges by Highly Effective Liquid Chromatography Method. State Register no. FR.1.31.2005.01725. 2008; 27p. Available at [Access date: 01.04.2008]: https://files.stroyinf.ru/Data2/1/4293809/4 293809324.htm?ysclid=ljg45vs6ub561614960

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.

Clark, J.R., 2008. Coastal Zone Management Handbook. First edition. CRC Press, Boca Raton, FL, USA.

Dai, C., Han, Y., Duan, Y., Lai, X., Fu, R., Liu, S., Leon, K.H., Tu, Y., Zhou, L., 2022. Review on the contamination and remediation of polycyclic aromatic hydrocarbons (PAHs) in coastal soil and sediments. *Environmental Research* 205: 112423.

Delegan, Y., Sushkova, S., Minkina, T., Filonov, A., Kocharovskaya, Y., Demin, K., Gorovtsov, A., Rajput, V.D., Zamulina, I., Grigoryeva, T., Dudnikova, T., Barbashev, A., Maksimov, A., 2022. Diversity and metabolic potential of a PAH-degrading bacterial consortium in technogenically contaminated haplic chernozem, Southern Russia. Processes 10: 2555.

Dong, W., Wan, J., Tokunaga, T.K., Gilbert, B., Williams, K.H., 2017. Transport and humification of dissolved organic matter within a semi-arid floodplain. *Journal of Environmental Sciences* 57: 24–32.

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.

Dymov, A.A., Gabov, D.N., 2015. Pyrogenic alterations of Podzols at the North-east European part of Russia: Morphology, carbon pools, PAH content. *Geoderma* 241-242: 230-237.

Fedorets, N.G., Bakhmet, O.N., Medvedeva, M.V., Akhmetova, G.V., Novikov, S.G., Tkachenko, Y.N., Solodovnikov, A.N., 2015. Heavy metals in the soils of Karelia. Akhmetova, G.V., (Ed.). Karelian Research Centre of the RAS, Petrozavodsk, Russia.

Fengpeng, H., Zhang, Z., Yunyang, W., Song, L., Liang, W., Qingwei, B., 2009. Polycyclic aromatic hydrocarbons in soils of Beijing and Tianjin region: Vertical distribution, correlation with TOC and transport mechanism. *Journal of Environmental Sciences* 21(5): 675–685.

Glazovskaya, M.A., 1998. Geochemistry of natural and technogenic landscapes of the USSR. High School, Moscow, Russia.

GOST 17.4.3.01-2017. Nature protection. Soils. General requirement for sampling. Standartinform, Moscow, Russia, 2018; p5. [in Russian]

Guidelines MU 2.1.7.730-99. Hygienic Evaluation of Soil in Residential Areas; Rospotrebnadzor: Moscow, Russia, 1999. [in Russian]

IARC, 2020. List of classifications, volumes 1-123.IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. WHO International Agency for Research on Cancer. Lyon, France. Available at [Access date: 25.07.2020]: https://monographs.iarc.fr/list-of-classifications-volumes/

ISO 13877-2005. Soil Quality-Determination of Polynuclear Aromatic Hydrocarbons—Method Using High-performance Liquid Chromatography. ISO: Geneva, Switzerland.

Kalinitchenko, V.P., Glinushkin, A.P., Minkina, T.M., Mandzhieva, S.S., Sushkova, S.N., Sukovatov, V.A., Il'ina, L.P., Makarenov, 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: 1355-1376.

Kasimov, N.S., Vlasov, D.V., 2015. Technophilicity of chemical elements at the beginning of the XXI century. Moscow University Geology Bulletin 5: 15–22.

Khan, M.M.H., Bryceson, I., Kolivras, K.N., Faruque, F., Rahman, M.M., Haque, U., 2015. Natural disasters and land-use/land-cover change in the southwest coastal areas of Bangladesh. *Regional Environmental Change* 15: 241–250.

Korchagina, Z.A., Vadyunina, A.F., 1986. Methods of investigation of physical properties of soils. Third edition. Agropromizdat, Moscow, Russia. [in Russian]

Krauss, M., Wilcke, W., Martius, C., Bandeira, A.G., Garcia, M.V., Amelung, W., 2005. Atmospheric versus biological sources of polycyclic aromatic hydrocarbons (PAHs) in a tropical rain forest environment. *Environmental Pollution* 135(1): 143–154.

Kuzmichev, I.K., Kolotukhina, E.L., Kostrov, V.N., 2020. Technological and economic aspects of increasing the capacity of the shipping channel. In: Proceedings of the Great Rivers-2020. 27–29 May 2020. Nizhniy Novgorod, Russia.

Martins, M., Ferreira, A.M., Vale, C., 2008. The influence of Sarcocornia fruticosa on retention of PAHs in salt marsh sediments (Sado estuary, Portugal). *Chemosphere* 71: 1599–1606.

Mayer, S., Kölbl, A., Völkel, J., Kögel-Knabner, I., 2019. Organic matter in temperate cultivated floodplain soils: Light fractions highly contribute to subsoil organic carbon. *Geoderma* 337: 679–690.

Mazarji, M., Minkina, T., Sushkova, S., Mandzhieva, S., Barakhov, A., Barbashev, A., Dudnikova, T., Lobzenko, I., Giannakis, S., 2022. Decrypting the synergistic action of the Fenton process and biochar addition for sustainable remediation of real technogenic soil from PAHs and heavy metals. *Environmental Pollution* 303: 119096.

Minkina, T., Fedorenko, G., Nevidomskaya, D., Konstantinovna, E., Pol'shina, T., Fedorenko, A., Chaplygin, V., Mandzhieva, S., Dudnikova, T., Hassan, T., 2021. The Morphological and functional organization of cattails Typha laxmannii Lepech. and Typha australis Schum. and Thonn. under soil pollution by potentially toxic elements. *Water* 13: 227.

Nachtergaele, F., van Velthuizen, H., Verelst, L., Wiberg, D., Henry, M., Chiozza, F., Yigini, Y., 2023. Harmonized World Soil Database version 2.0. Food and Agriculture Organization of the United Nations and International Institute for Applied Systems Analysis, Rome, Laxenburg. 62p.

Ping, L.F., Luo, Y.M., Zhang, H.B., Li, Q.B., Wu, L.H., 2007. Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, east China. *Environmental Pollution* 147(2): 358–365.

Qiu, Y.Y., Gong, Y.X., Ni, H.G., 2019. Contribution of soil erosion to PAHs in surface water in China. *Science of the Total Environment* 686: 497–504.

Ren, X., Zeng, G., Tang, L., Wang, J., Wan, J., Liu, Y., Yu, J., Yi, H., Ye, S., Deng, R., 2018. Sorption, transport and biodegradation–an insight into bioavailability of persistent organic pollutants in soil. *Science of the Total Environment* 610-611: 1154–1163.

Saeedi, M., Li, L.Y., Grace, J.R., 2018. Effect of organic matter and selected heavy metals on sorption of acenaphthene, fluorene and fluoranthene onto various clays and clay minerals. *Environmental Earth Sciences* 77: 305.

Santos, S.F., Ehler, C.N., Agardy, T., Andrade, F., Orbach, M.K., Crowder, L.B., 2019. Marine spatial planning. In: World Seas: an environmental evaluation. Sheppard, C., (Ed.). Vol. 3, Academic Press, London, UK, pp. 571–592.

Shi, R., Li, X., Yang, Y., Fan, Y., Zhao, Z., 2023. Contamination and human health risks of polycyclic aromatic hydrocarbons in surface soils from Tianjin coastal new region, China. *Environmental Pollution* 268: 115938.

Sun, K., Song, Y., He, F., Jing, M., Tang, J., Liu, R., 2021. A review of human and animals exposure to polycyclic aromatic hydrocarbons: Health risk and adverse effects, photo-induced toxicity and regulating effect of microplastics. *Science of the Total Environments* 773: 145403.

Sushkova, S., Minkina, T., Tarigholizadeh, S., Antonenko, E., Konstantinova, E., Gülser, C., Dudnikova, T., Barbashev, A., Kizilkaya, 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.

Tsibart, A.S., Gennadiev, A.N., Koshovskii, T.S., Gamova, N.S., 2016 Polycyclic aromatic hydrocarbons in pyrogenic soils of swampy landscapes of the Meshchera lowland. *Eurasian Soil Science* 49: 285–293.

Ukalska-Jaruga, A., Smreczak, B., Klimkowicz-Pawlas, A., 2019. Soil organic matter composition as a factor affecting the accumulation of polycyclic aromatic hydrocarbons. *Journal of Soils and Sediments* 19: 1890-1900.

US Environmental Protection Agency, 2020. Integrated Risk Information System (IRIS). Office of Research and Development, Washington DC, USA. Available at [Access date: 13.06.2023]: https://cfpub.epa.gov/ncea/iris_drafts/AtoZ.cfm

Xu, Y., Shi, H., Fei, Y., Wang, C., Mo, L., Shu, M., 2021. Identification of soil heavy metal sources in a large-scale area affected by industry. *Sustainability* 13(2): 511.

Yang, W., Lang, Y.-H., Bai, J., Li, Z.-Y., 2015. Quantitative evaluation of carcinogenic and non-carcinogenic potential for PAHs in coastal wetland soils of China. *Ecological Engineering* 74: 117-124.

Yunker, M.B., Macdonald, R.W., Ross, P.S., Johannessen, S.C., Dangerfield, N., 2015. Alkane and PAH provenance and potential bioavailability in coastal marine sediments subject to a gradient of anthropogenic sources in British Columbia, Canada. *Organic Geochemistry* 89-90: 80–116.

Zhang, J., Fan, S.K., 2016. Influence of PAH speciation in soils on vegetative uptake of PAHs using successive extraction. *Journal of Hazardous Materials* 320: 114–122.

Zhao, Y., Li, J., Qi, Y., Guan, X., Zhao, C., Wang, H., Zhu, S., Fu, G., Zhu, J., He, J., 2021. Distribution, sources, and ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the tidal creek water of coastal tidal flats in the Yellow River Delta, China. *Marine Pollution Bulletin* 173: 113110.