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Research article

Sample preparation method for IR analysis of petroleum-contaminated soil: An innovative technology for ecological remediation using *Miscanthus x giganteus*

Ruslana Huminilovych [a,*], Vitalii Stadnik [a], Martyn Sozanskyi [a], Pavlo Shapoval [a], Valentina Pidlisnyuk [c], Ihor Poliuzhyn [a], Viktoriia Kochubei [a], Yurii Hrynchuk [a], Bohdan Korchak [b]

[a] *Department of Physical, Analytical and General Chemistry, Lviv Polytechnic National University, 12 S. Bandery St., 79013, Lviv, Ukraine*
[b] *Department of Civil Safety, Lviv Polytechnic National University, 12 S. Bandery St., 79013, Lviv, Ukraine*
[c] *Department of Environmental Chemistry and Technology, Faculty of Environment, Jan Evangelista Purkyne University in Ústí nad Labem, 400 96, Ústí nad Labem, Czech Republic*

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ABSTRACT

Miscanthus x giganteus phytoremediation of soil contaminated with petroleum was assessed in this study. A method of soil sample preparation for determining the total content of petroleum products by infrared spectrophotometry has been developed. It is a one-stage extraction method with minimal use of carbon tetrachloride as an extractant. This soil sample preparation method was environmentally friendly and cost-effective, as it required a significantly lower amount of extractant (15–30 ml of tetrachloromethane) compared to the commonly used threefold extraction method, which uses up to 150 ml of extractant. The extraction degree of petroleum products (PP) was determined to be from 81.78 % to 94.22 % after two days of extraction using the additive method of determining PP. It was observed that the presence of different fertilizer additives in the soil samples led to a reduction in the determined PP content in the following series: "without fertilizer" – "Biochar" additive – "Biohumus" additive. These results were compared with reference samples that did not involve the use of *Miscanthus x giganteus*. Furthermore, the main thermolysis stages of petroleum products sorbed by the soil matrix and the thermal behavior of an artificial soil sample spiked with PP were examined. Detailed interpretation of thermograms of laboratory soil samples was conducted at various phytoremediation stages.

1. Introduction

The increased demand for petroleum products (PP) has driven growth in the oil industry, which causes environmental pollution with oil and its byproducts. These pollutants have harmful impacts on agricultural soils. Additionally, military activities significantly cause soil contamination with petroleum products. The impact of various pollutants on humans, wildlife, water resources, crops, and

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* Corresponding author.
E-mail addresses: ruslana.r.huminilovych@lpnu.ua (R. Huminilovych), vitalii.y.stadnik@lpnu.ua (V. Stadnik), martyn.a.sozanskyi@lpnu.ua (M. Sozanskyi), pavlo.y.shapoval@lpnu.ua (P. Shapoval), Valentyna.Pidlisniuk@ujep.cz (V. Pidlisnyuk), ihor.p.poliuzhyn@lpnu.ua (I. Poliuzhyn), viktoriia.v.kochubei@lpnu.ua (V. Kochubei), yurii.m.hrynchuk@lpnu.ua (Y. Hrynchuk), bohdan.o.korchak@lpnu.ua (B. Korchak).

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soils are given in Refs. [1–7].

This negative effect is primarily due to the toxicity of petroleum products to microorganisms involved in soil biological processes. Field studies of contaminated soils [8,9] have shown that higher PP content leads to reduced microbial population, reduced bacterial viability, inhibition of organic matter mineralization, reduced leaf decomposition rate, and reduced mycorrhizal root infection, among other effects. Furthermore, it has been established that organisms residing in contaminated environments for extended periods can accumulate petroleum products and heavy metals [1,5,7,10,11], thereby causing additional toxicological effects on health as contaminants enter more complex food chains [1,2].

Bioremediation methods using plants and microorganisms are widely applied for soil contamination with petroleum products and heavy metals since most pollutants are naturally converted into harmless compounds [8]. From a phytoremediation standpoint [12–14], perennial plant cultivation in contaminated areas is interesting, as their biomass can be utilized for valuable purposes.

However, the effectiveness of bio- and phytoremediation methods in soil purification largely depends on the nature and quantity of contaminants present in the soil. Such pollution can impede the vital activities of plants and microorganisms [8,9,15]. Therefore, it is crucial to preliminarily assess the level of soil contamination with petroleum products and heavy metals.

The process of soil purification through phytoremediation using perennial plants is long, but the soil depletion is much slower. This disadvantage is partially compensated by using biomass as biofuel. Among the most promising plants for phytoremediation is *Miscanthus x giganteus* (*M. x giganteus*) [15,16], a second-generation perennial energy crop. By the fourth year of cultivation, it reaches its peak biomass productivity, characterized by high cellulose content. This plant can be harvested for 25–30 years and utilized as a biofuel source [17,18]. The metabolism of organic compounds by plants plays a pivotal role in phytoremediation for waste management. For metabolism transformations to occur, the compounds must enter plant tissues. Therefore, the absorption of organic compounds is also a crucial aspect of phytoremediation with specific applications.

Research on plant metabolism of organic compounds began over 50 years ago, initially focusing on pesticide metabolism in crops due to potential contamination concerns. In recent years, the interest in plant metabolism of organic pollutants has expanded due to their relevance to phytoremediation. Scientists from various disciplines have shown interest in the metabolism of environmental pollutants that were previously overlooked. Researchers have gone beyond crops to determine the suitability of certain trees and wetland plants for phytoremediation.

The concept of plants detoxifying or storing organic compounds first emerged in 1977 based on the isolation of enzymes from plant cell cultures and the metabolism of non-polar compounds that were previously considered stable in plants, such as 1,1,1-trichloro-2,2-6-(4′-chlorophenyl)ethane (DDT) and benz(α)pyrene. This concept, referred to as the "green liver", draws parallels to the detoxification mechanisms found in mammalian livers [19].

The metabolism of xenobiotic chemicals in plants is largely similar to liver function. One similarity lies in the sequence of metabolic stages, which closely resemble the functions of the mammalian liver. Both plants and mammals eliminate and excrete xenobiotic contaminants from active organelles. In addition, a significant similarity lies in the broad range of substrates and enzymes involved in these processes. It has been demonstrated that the mechanisms of transformation and elimination are similar for a wide range of xenobiotic organic compounds [20].

Considering the overall plant metabolism of organic compounds, it is important to note that the substance must first enter plant tissues, which can occur through various mechanisms: 1) groundwater movement via transpiration, 2) transfer from soil gases, and 3) absorption of gases or water from the atmosphere by extra-root tissues. Once transported to plant cells, the substance can be metabolized if it is a substrate for the available enzymes. It is also essential to consider enzymatic activity in specific plant tissues, as different tissues may have highly specific functions. Transpiration is the most common pathway for organic compounds to enter plant tissues. However, passive diffusion can also occur in wetlands and plant roots below the water table. While extra-root uptake has less significance in the phytoremediation of wastewater or contaminated soils and waters, foliar uptake has been proposed as the primary method for the uptake of anthropogenic air pollutants [21].

The influence of the soil matrix is manifested through competitive sorption, which limits the uptake of pollutants by plants and leads to the accumulation of organic compounds in the soil profile. Soil sorption does not affect the transpiration stream concentration factor (TSCF) sorbed compound but only reduces the water concentration on the roots' surface. Furthermore, compounds with an ionic charge undergo more regulated sorption compared to the passive sorption model described earlier for non-ionic organic compounds [22]. Active transport of ionized compounds has also been observed, and it has been demonstrated that the ion-trap effect is the dominant process in active transportation, particularly for weak electrolytes.

On the other hand, there are a lot of different methods, that could be used for organic contaminants determination such as [23].

- Chromatographic Methods (High-performance liquid chromatography (HPLC), Gas chromatography (GC), Capillary electrophoresis (CE));
- Mass Spectrometry Methods (Mass spectrometry (MS), Ambient ionization mass spectrometry (ambient MS));
- Electrochemical Methods (cyclic voltammetry (CV), differential pulse voltammetry (DPV), square wave voltammetry (SWV), Voltammetric methods in combination with electrochemical impedance spectroscopy (EIS));
- Field Effect Sensors;
- Colorimetric Methods;
- Plasmon Resonance Methods (Surface plasmonic resonance (SPR), Localized Surface Plasmonic Resonance (LSPR));
- Spectroscopy Methods (Infrared (IR) Spectroscopy, Fourier Transform Infrared (FT-IR) Spectroscopy);
- Surface-Enhanced Raman Spectroscopy (SERS);
- Fluorometric Methods etc.

Each one of the listed methods differs from the other in the sample preparation techniques, requires different and specified equipment, requires a skilled specialist, and has some differences based on the nature of the organic pollutant that should be determined by each method, especially the necessity of usage different extractants or their mixtures to determine different by nature and/or physical-chemical properties organic pollutants [24–26].

Based on the above, it is clear that absorption variations of different organic substances and differences in absorption between plant species are mainly related to variations in lipid content and the nature of sorbed substances. Enhancing the effectiveness of phytoremediation requires a reliable model for predicting the outcomes of this process. However, at the current research stage, a complete understanding of the influence of plant structure on the absorption characteristics of pollutants has not yet been achieved. Given this, this study aimed to examine the total content of petroleum products in soils and subsequently investigate the feasibility of growing *M. x giganteus* for phytoremediation purposes.

To achieve the goal, the following tasks must be solved.

- to develop a soil sampling method for determining PP content by IR-spectrophotometry (KN series analyzer), using single-stage extraction with an optimal duration of five days and a minimal amount of carbon tetrachloride as an extractant.
- implementation of the developed technique on artificially contaminated soils with PP and subsequent analysis of the obtained results.
- to investigate the thermal behavior of a model soil sample artificially contaminated with PP to identify the primary stages of thermolysis of PP sorbed by the soil matrix. To use results of the thermal behavior of a model soil sample to interpret thermograms of laboratory soil samples at various stages of the experiment.
- the study of the effect of the “Biochar” [27] and “Biohumus” fertilizers on the growth of *M. x giganteus* and the remediation of PP-contaminated soil.

2. Experimental

2.1. Materials

To extract petroleum products from soil samples during the method development to determine the total content of PP, spectroscopy-grade carbon tetrachloride (CCl_4) from Thermo ScientificTM was applied as the extractant. Euro-4 environmental standard diesel fuel was used for the artificial contamination of the soil samples with PP.

Alpha-phase aluminum oxide (Al_2O_3) with a purity of 99.99 % from Thermo ScientificTM was used as a reference substance for thermal analysis.

Biochar (Specifications: Organic matter $\geq$80 %, Phosphorus $\leq$3 %, Potassium $\leq$3 %, Nitrogen $\leq$3 %, Nutrient $\leq$6 %) fertilizers from Almiro company and Biohumus (Specifications: Enzymes, Plant Hormones, Humates, Amino Acids, Natural Antibiotics, Macro and Microelements, Spores of Beneficial Microorganisms, Humic and Fulvic Acids, Phosphorus - 2.1 %, Nitrogen - 1.8 %, Boron - 0.3 %, Copper - 0.26 %, Manganese - 1.04 %, Zinc - 0.362 %, Cobalt - 0.16 %, Magnesium - 0.12 %, Molybdenum - 0.141 %) from TRYVKOTM company were used in studies of the fertilizers’ effect on the *M. x giganteus* growth in artificially polluted soil.

2.2. Analysis

During the preparation of standard calibration solutions, the dosing of PP was conducted by a micro syringe MSH-10.

The determination of PP total content was carried out using a two-channel IR-photometer analyzer KN-2M from SIBEKOPRIBOR. This analyzer operates based on the principle of the difference in optical densities of petroleum product solutions in CCl_4 at two different wavelengths: the working region at $\lambda = (2930 \pm 70)\ cm^{-1}$, which corresponds to the absorption of $–CH$, $–CH_2$, and $–CH_3$ groups of hydrocarbons, and the comparison region at $\lambda = (3333 \pm 70)\ cm^{-1}$, where the radiation absorption by these groups is absent. To extract petroleum products from the soil, it was pre-dried to an air-dry condition, ground in a mortar, and sieved through a laboratory sieve SML-200 from the company PE “ALTAIR PLUS”, with a mesh diameter of 0.25 mm.

The mass losses of the extracts due to the evaporation of CCl_4 and the quality control of all intermediate stages of sample preparation were determined by weighing the samples on laboratory scales of the brand “Radwag AS 220.R2” from Radwag, with a measurement accuracy of $\Delta = \pm\ 0.0002$ g.

Thermal analysis was performed using a Q-1500D derivatograph from the Paulik-Paulik-Erdey system. A sample weighing 500 mg was used, and the temperature range was set from 20 to 1000 °C at a heating rate of 5 and 10 °C/min, with free access of air to the furnace.

2.3. Experiment design

Laboratory studies on the impact of soil contamination by PP were conducted in a 16-L vegetation vessel. The vessel contained predried soil sifted through a sieve with a mesh diameter of 3 mm. The required amount of soil was weighed on electronic scales “VTNE-30H1K-1” from ALS DOZAVTOMATY, with a measurement accuracy of $\Delta = \pm\ 10.0$ g. Each pot was filled with 1 kg of gravel and 1 kg of sand at the bottom, followed by 10 kg of soil and 1 kg of sand on the surface.

The influence of PP concentration in the soil on the growth and development of *M. x giganteus*, as well as the effect of fertilizers, was examined in three series with five rows of samples. Each series included different PP contents with four repetitions of each sample (three repetitions with *M. x giganteus* grown and one control sample without Miscanthus). The total number of laboratory samples was 60 units.

In this study, we also created a respective sample marking scheme to unify and simplify the results interpretation, as different parameters were planned to be studied simultaneously. This scheme is based on "number"-"letter"-"number" marking, where the first "number" or "number" before the "letter" represents the serial number: 1 - first, 2 - second or 3 - third experiment seria. Each seria is attributed to the respective studied parameter and detailed descriptions are listed below. The "letter" means artificially created in the soil PP content. The second "number" or "number" after "letter" describes the number of the repeats, for each PP concentration level four repetitions were made, including each fourth repeated without *M. x giganteus* rhizomes planting as the control sample.

In the first sample series, soil contamination with PP was conducted according to Table 1 by adding the appropriate volume of PP to a weighed portion of soil (10 kg) while mixing.

In the second sample series, contamination with PP was conducted similarly to the first series on the same amount of soil. Additionally, to the soil, while mixing was added “Biochar” fertilizer, which is made from wood waste in the amount of 5 wt %. (Table 2).

The third series of samples (Table 3) was made similarly to the first and second but in this case, the “Biohumus” fertilizers, which consisted of 25 % Biochar (made from wood waste), 50 % Biohumus (a product derived from processing organic agricultural waste by earthworms), and 25 % other fillers, was used in the same amount, as the “Biochar” fertilizer in the second sample series.

The humus content in the arable layer of the soil, used for samples preparation, was assessed following DSTU 4289:2004 “Soil quality. Method of determination of organic matter”, and according to the methods [28], it was determined to be 2.63 wt%.

To determine the total PP content in laboratory soil samples, a single-stage extraction was performed using CCl_4 as the extractant. CCl_4, regardless of the brand, was purified by re-distillation in a water bath to enhance the sensitivity of PP determination. The soil samples were tightly sealed in vessels with ground corks and extracted for 120 h.

Standard solutions were prepared to cover the linear range of IR radiation absorption corresponding to the PP concentration in the extract up to 300 mg/dm^3 CCl_4. This range was chosen to avoid the need for further dilution of the solutions.

By analyzing the nature of weight loss and thermal effects, we obtained data on the processes occurring during the heating of soil samples. This allowed us to determine the presence of clay and organic components, as well as the nature of bound water and dehydration processes [29].

To minimize the amount of extractant used in the single-stage extraction and account for the content of incompletely chlorinated components in CCl_4 (which was (35 ± 5) mg/dm^3 after distillation), the mass of soil samples (m_{sample}) with an approximate known PP content was calculated based on the linearity of the dependence $C(PP)$ - $f(C)$ (Fig. 1).

Since it is not possible to completely purify CCl_4 before analysis, it is important to ensure that the concentration of extracted PP in the extractant is equal to or greater than the concentration of incompletely chlorinated components. This will increase the absorption of infrared radiation by two times and allow for reliable determination of the PP content in soil samples with the lowest concentration ($C(PP) = 250$ mg/kg). Based on the device’s specifications, the determination of the PP content in the extract (Eq. (1)) requires consideration of the ratio of the CCl_4 volume to the soil mass ($R(V/m_{sample})$):

$$R\left(V \ / \ m_{sample}\right) = \frac{V_0(CCl_4)}{m_{sample}} \geq 1.5 \tag{1}$$

Based on the considerations mentioned above, the ratio between the weight of the soil sample and the volume of the extractant can be determined as follows (Eq. (2)):

$$250 \cdot m_{sample} \geq (35 \pm 5) \cdot V_0(CCl_4) \tag{2}$$

According to equation (Eq. (2)), the mass of the soil sample (g) should be approximately 6.25–8.33 times smaller than the volume of CCl_4 (ml). However, considering the uneven distribution of PP in the soil and the possibility of incomplete extraction, a value of 3 for the parameter $R(V/m_{sample})$ was chosen to prepare soil extracts with a lower approximate PP content, as stated in equation (Eq. (1)). On the other hand, for a solution with the maximum PP content ($C(PP) = 5000$ mg/kg) and accounting for the presence of incompletely chlorinated components in CCl_4, the expression to determine the ratio between the weight of the soil sample and the volume of the extractant will be (Eq. (3)):

$$5000 \cdot m_{sample} \leq (265 \pm 5) \cdot V_0(CCl_4) \tag{3}$$

Table 1
The first experiment series scheme.

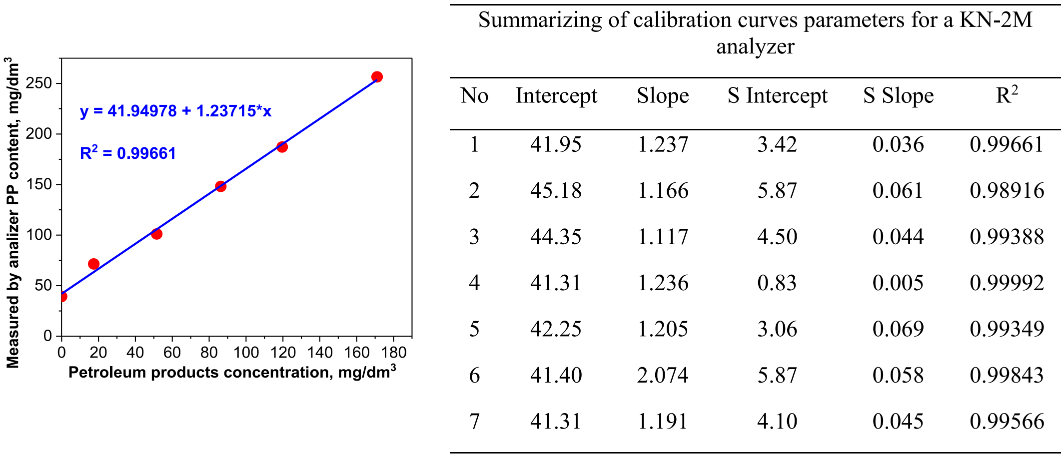
	With Miscanthus			Without Miscanthus
PP concentration, [mg/kg]				
Sample marking	Repeating			
	1	**2**	**3**	**4**
1A	0.0			0.0
1B	250.0			250.0
1C	1000.0			1000.0
1D	3000.0			3000.0
1E	5000.0			5000.0

Table 2
The second experiment series scheme.

	With Miscanthus			Without Miscanthus
PP concentration, [mg/kg]; ω("Biochar") = 5 wt%				
Sample marking	Repeating			
	1	**2**	**3**	**4**
2A	0.0			0.0
2B	250.0			250.0
2C	1000.0			1000.0
2D	3000.0			3000.0
2E	5000.0			5000.0

Table 3
The third experiment series scheme.

	With Miscanthus			Without Miscanthus
PP concentration, [mg/kg]; ω("Biohumus") = 5 wt%				
Sample marking	Repeating			
	1	**2**	**3**	**4**
3A	0.0			0.0
3B	250.0			250.0
3C	1000.0			1000.0
3D	3000.0			3000.0
3E	5000.0			5000.0



Summarizing of calibration curves parameters for a KN-2M analyzer

No	Intercept	Slope	S Intercept	S Slope	R^2
1	41.95	1.237	3.42	0.036	0.99661
2	45.18	1.166	5.87	0.061	0.98916
3	44.35	1.117	4.50	0.044	0.99388
4	41.31	1.236	0.83	0.005	0.99992
5	42.25	1.205	3.06	0.069	0.99349
6	41.40	2.074	5.87	0.058	0.99843
7	41.31	1.191	4.10	0.045	0.99566

Fig. 1. Example of calibration curves for a KN-2M analyzer.

According to equation (Eq. (3)), the volume of CCl_4 (ml) should be approximately 19.23 to 18.52 times greater than the weight of the soil sample (g). However, to ensure that the calibration dependence is not exceeded (as shown in Fig. 1), a value of 30 was chosen for the parameter $R(V/m_{sample})$ (Eq. (1)) for soils with a high approximate PP content.

The developed method of soil sample preparation is more cost-effective in terms of the amount of extractant required, using only 15–30 ml according to Table 4. This is significantly less than the three-fold extraction method that uses 90 ml, as proposed in

Table 4
Scheme of sample preparation for PP extraction.

C(PP), [mg/kg]	m_{sample}, [g]	$V(CCl_4)$, [ml]	$P = m_{sample}/V(CCl_4)$
0–250	10.0	30.0	3
250–1000	2.5	15.0	6
1000–3000	1.0		15
3000–5000	0.5		30

regulatory documentation such as EPA Method 418.1 Petroleum Hydrocarbons (Spectrophotometric, Infrared) [30]. Soxhlet extraction normally requires large volumes (up to 150 ml) of often chlorinated solvent to be refluxed through the solid sample for between 6 and 24 h. While several experimental set-ups can be assembled and operated at the same time, it is both labor-intensive and time-consuming (at least at the start and end of the process). Shake-flask extraction, on the other hand, requires minimal glassware, and smaller volumes of organic solvent and is relatively fast (10–30 min). However, it is unlikely to have produced a quantitative extract [31]. As supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) or pressurized liquid extraction (PLE) [32] often could not be used, our proposed method which is in between Soxhlet and Shake-flask extraction, where we decrease the extractant amount (up to five-time decrease) and use cheap and accessible equipment for this purpose, but increase extraction duration to obtain a quantitative extract can be promising for this purpose.

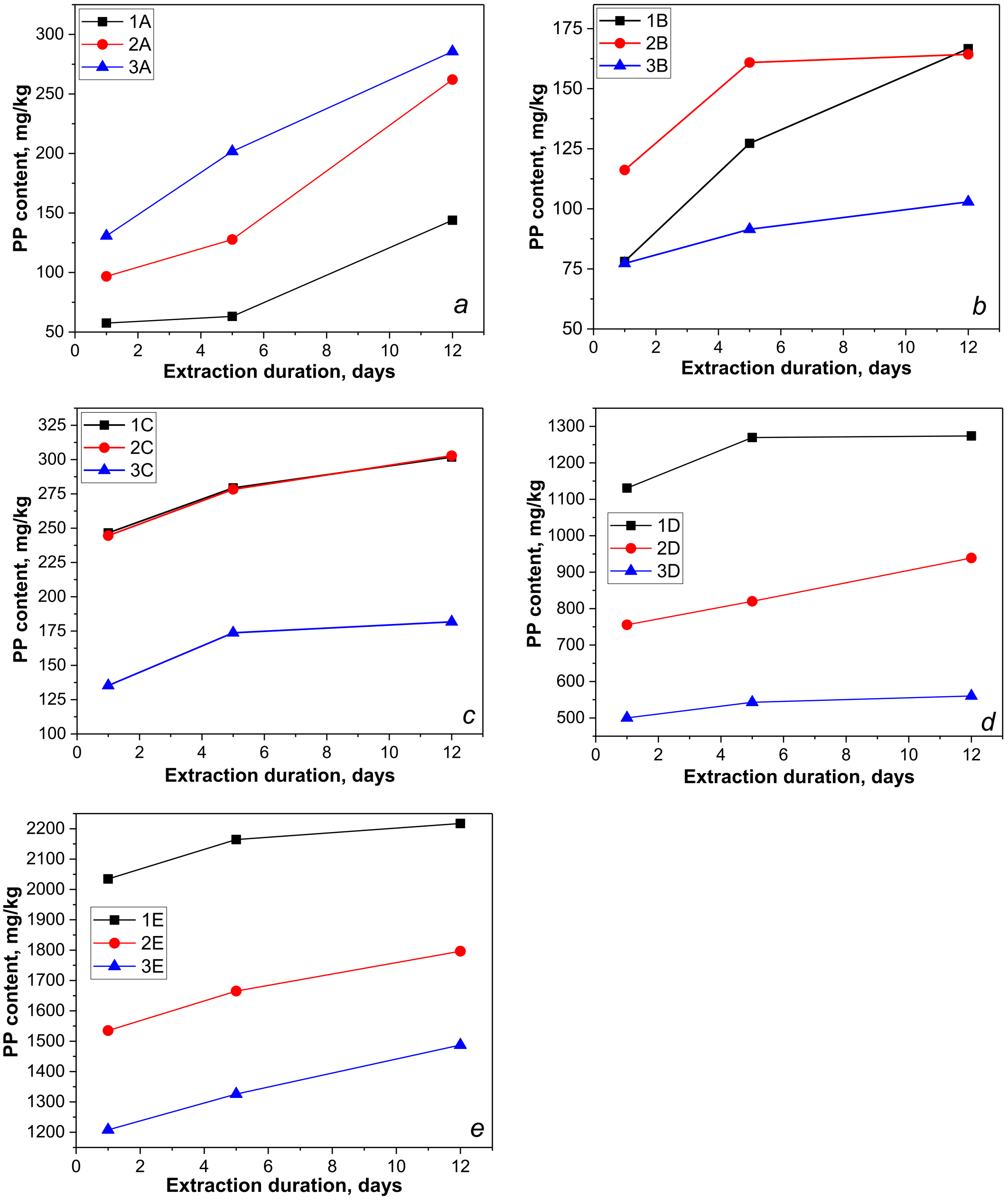


Fig. 2. Dependence of the determined PP content in the soil samples of A, B, C, D, and E series (according to Table 1, Table 2 or Table 3) on the extraction duration.

3. Results and discussion

The results of minimizing the amount of extractant for a single-stage extraction are presented in Table 4, showing the variations based on the mass of soil samples and their approximate PP content.

To determine the optimal duration of single-stage extraction, soil samples from series A, B, C, D, and E were subjected to extraction for 1, 5, and 12 days, considering the losses of CCl_4 determined by weight (as shown in Fig. 2, *a–e*). Based on the results obtained (as depicted in Fig. 2, *b–e*), a five-day extraction duration was selected as the working time, as it ensures maximum extraction of PP while establishing equilibrium between phases in a single extraction.

However, in the case of series A, due to significant heterogeneity in the distribution of PP and considering its lowest content, this equilibrium was not achieved. According to the experimental series preparation scheme outlined in Table 1, Tables 2, and Table 3, the soil in series C was contaminated with 1000 mg/kg of PP. However, the laboratory-analyzed samples exhibited variations in PP content ranging from 170 to 280 mg/kg (as shown in Table 5). These deviations in PP determination results were attributed to the influence of fertilizers in series 2C and 3C compared to the soil in series 1C. The substantial difference between the technically calculated and laboratory-determined PP values (which were five times lower) is evidently due to the specific adsorption characteristics of petroleum products, rock-forming soil minerals, and the fertilizers introduced into the samples as additives [33–37].

Polar organic compounds in soil can interact with the surface of clay minerals through various forces such as hydrogen and coordination bonds, ion-dipole interactions, acid-base interactions, and van der Waals forces [38]. Neutral organic ligands can form intercalation complexes with interlayer cations of clay minerals. Ionic organic compounds can undergo ion exchange with mobile mineral cations, resulting in the formation of organo-mineral compounds. The active centers on the basal surfaces of clay minerals in the soil can catalyze the decomposition and polycondensation processes of the organic component, leading to its conversion into sediments [39]. Components of PP and their transformation products that are strongly bound to the mineral matrix cannot be easily extracted from soil samples. In such cases, the additional presence of a substance, that can adsorb organic contaminants, will positively influence the growth and development of the *M. x giganteus*, and the remediation respectively as the pollutants in the soil provide some stress influence on the plant. A decrease in the amount of the stress factor will cause an increase in the plant growth and development rate, which also will positively affect the remediation process in the future. Another interesting observed feature was the presence of organic compounds in the samples of A-series, as according to the experiment design section there were no additional PP added to the soil samples in this series. However, after extraction, a small amount of PP was found, which could be explained that soil can contain some organic matter that can be extracted by CCl_4, and that is why we did not get a zero PP content. Another thing, that can influence the result was the quality of CCl_4, because before the extraction it was necessary to further distilled it to receive it in a better quality. Any other analysis of the initial soil samples was not performed in order to approve such an assumption.

The uncertainty in the measurement results is also partly attributed to the inhomogeneous distribution of PP during the technological preparation of the studied soils and the sampling of laboratory samples due to the specific sample preparation procedures. Therefore, the extraction degree of PP during single-stage extraction and the duration of PP contact with soil for two days was determined using the developed method. For the soil in series C, the extraction degree ranged from 81.78 % to 94.22 % (as shown in Table 5 and Fig. 3).

To obtain a more accurate understanding of the reproducibility of the results obtained using the “liquid extraction-IR” technique and to account for the heterogeneity of PP distribution in soil samples, six soil samples were collected from each variant of the A, B, C, D, and E series (as shown in Table 6). These samples were then analyzed under the established extraction conditions specific to each variant.

Based on the reproducibility test results, the standard deviation ranged from 45 to 300, indicating the heterogeneity of petroleum product distribution in the soil sample. Such a deviation in the analysis results can be explained by the nature of the investigated matrix and the way of soil pollution by PP. As described in the manuscript, we use 10 kg for the soil sample preparation and add PP from 0.0 to 0.5 wt % of dry soil is a small amount compared to the matrix. In such a situation, it is very difficult to achieve a homogeneous PP distribution even with soil mixing, not taking into account the natural ways of soil contamination by PPs. In our experiment to get more or less adequate results, authors collected six soil samples from each vegetation pot for the extraction in the amount total of 3–60 g of soil according to the decrease of PP contamination. Other extraction conditions were taken as a constant, so mainly an inhomogeneity of PP distribution can explain a such deviation of PP content in the samples with a low amount of PP artificially added to the soil at the beginning of the experiment. In the second turn, the presence of organic matter in the soil, which can be extracted with the use of CCl_4 and what was established during the experiment, also provides a small deviation from the results of PP determination.

As a result, the measurement data obtained through the applied method, which involves small soil samples and low extractant costs, can only be considered as estimates. To enhance the reliability of the method’s results, one can increase the number of parallel

Table 5
The results of the “added-confirmed” experiment.

Sample marking	Initial PP content, [mg/kg]	Additive of PP, [mg/kg]	Theoretical PP content in soils with additive, [mg/kg]	Practically defined PP content with an additive, [mg/kg]	Confirmed PP additive amount [mg/kg]	The additive removal degree, [%]
1C	279.40	637.10	916.5	800.43	521.03	81.78
2C	278.27	639.23	917.5	834.20	555.93	86.97
3C	173.70	550.25	723.95	692.14	518.44	94.22

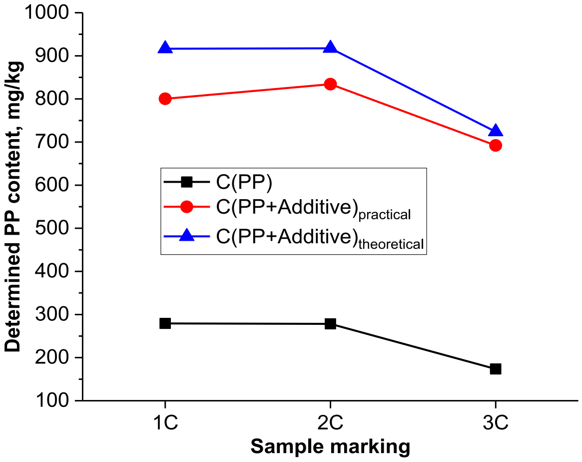


Fig. 3. The results of the PP content determination in the C series soil samples by the "added-found" method.

Table 6
The results of the reproducibility study of determining the PP content in all series of soil samples.

Sample marking	PP content [mg/kg] observed values for parallel measuring the sample items with numbers						Average value	Sample standard deviation
	1	2	3	4	5	6		
1A	143.90	57.55	63.18	234.28	58.60	41.93	99.91	75
2A	262.08	96.78	127.76	262.28	124.32	138.24	168.58	74
3A	285.63	130.80	201.73	177.22	59.05	69.18	153.94	86
1B	166.67	78.13	127.26	184.03	82.11	91.92	121.69	45
2B	164.30	116.15	160.90	294.32	216.42	184.30	189.40	61
3B	102.92	77.27	91.49	228.31	71.88	81.64	108.92	60
1C	301.79	246.54	279.40	656.19	350.70	283.74	353.06	152
2C	302.80	244.53	278.27	335.82	398.48	311.58	311.91	53
3C	181.71	135.25	173.70	245.90	165.01	171.45	178.84	37
1D	1273.86	1130.84	1269.46	1509.46	949.44	827.79	1160.14	246
2D	939.02	755.72	820.07	1244.97	546.67	734.02	840.08	236
3D	560.21	500.11	542.92	435.21	477.59	624.83	523.48	67
1E	2217.47	2034.76	2164.44	2008.52	1619.12	1484.82	1921.52	300
2E	1796.46	1535.11	1665.15	1859.67	1473.87	1325.16	1609.24	203
3E	1487.29	1207.78	1325.90	1283.12	1344.52	1781.72	1405.06	206

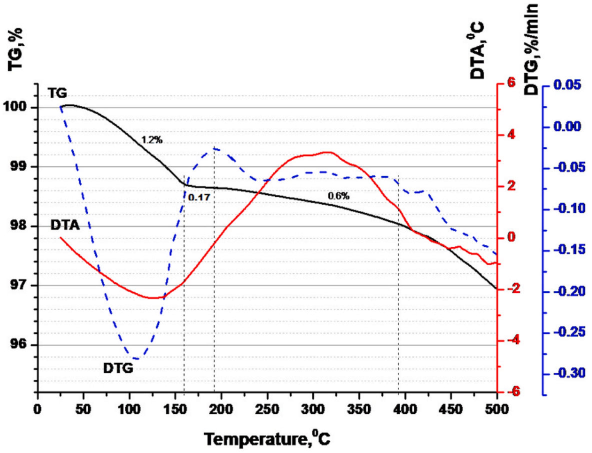


Fig. 4. Thermogravimetry analysis of pre-calcined soil sample spiked by PP.

measurements or switch to methods involving larger soil samples and triple extraction, as recommended in the regulations. It should be noted that there is a tendency to reduce the variance in parallel measurements of PP in soil samples of series C, D, and E, indicating better reproducibility at higher PP content, even with a significant effect of heterogeneity in PP distribution within the soil sample.

The determination of the additives removal degree was confirmed through thermal analysis. For this purpose, the soil sample was pre-calcined at 350 °C for 2 h, removing effectively physically adsorbed water, chemically bound water, and natural organic matter. The macro composition of the soil sample matched the composition of the studied soil samples. To create a PP content of 0.85 % in the soil, 5 μl of PP was added to 0.5 g of pre-calcined soil using a micro syringe (MSH-10), and the mixture was left for two days in a dark glass vessel with a tightly ground cork to ensure homogenization of its distribution.

The thermogravimetry results of the pre-calcined soil sample with the PP additive are presented in Fig. 4. Four main thermolysis stages based on the thermal analysis of the model soil sample (Fig. 4) were identified. The first stage, occurring between 50 and 155 °C, involves the residual water release, with the possibility of partial evaporation of low-boiling PP components within the same temperature range. This process is accompanied by the appearance of an endothermic effect on the DTA curve, and the weight loss at this stage is 1.2 %.

In the second stage of thermolysis, which occurs between 155 and 195 °C low-boiling PP components evaporate ($\Delta m = 0.17$ %). The third stage, ranging from 195 to 395 °C, involves the thermooxidative destruction of high-boiling sorbed PP components ($\Delta m = 0.60$ %). This process is accompanied by the appearance of an exothermic effect on the DTA curve. In the temperature range of 400–500 °C, the fourth stage is observed, which corresponds to the destruction of the minerals' structure within the soil and the release of volatile decomposition products. Additionally, clay minerals lose their constitutional water [40]. The total weight loss in stages II and III is greater than 0.77 %. Considering the small amount of PP that partially evaporates in the first stage of the experiment, the thermal analysis data are reasonably consistent with the theoretically calculated PP content of 0.85 %, which was derived from the previously introduced amount of PP into the soil.

The thermal analysis results and data give an idea of the effect of PP interaction duration on the likely binding nature of PP with the inorganic matrix of minerals. The values obtained for the PP extraction degree demonstrate the applicability of the developed method for soil sample preparation in determining PP content.

In the case of soil samples from the C, D, and E series, a trend was observed in the determination of PP content, where soils with different fertilizer additives showed a decrease in the determined PP content in the following order: "without fertilizer" – "Biochar" additive – "Biohumus" additive (Fig. 5).

This trend can be attributed to the higher sorption capacity of soils with fertilizers, which contributes to the nearly irreversible sorption of PP. This property of soils with fertilizers can be advantageous in reducing stress on plants caused by high initial PP content during the initial stage of phytoremediation.

Satisfactory correlations were obtained between the average and control dependencies of the determined PP content in the soil before *M. x giganteus* planting (Fig. 6, *a*–*c*). These correlations confirm the effect of fertilizer additives on the results of PP content determination, as evidenced by the close correlation with control samples, with slight differences observed for soil samples without added fertilizer and significant differences for samples with fertilizers. The maximum determined PP content in the reference soil samples with fertilizers is approximately half of that for soil without fertilizers, which can be attributed solely to the sorption capacity of the fertilizers. This observation aligns with the findings presented in Fig. 5.

When comparing the ratios (Fig. 6, *d*–*f*) of the PP content in the soil after five months of *M. x giganteus* growth, a second-order polynomial dependence of the determined PP content is observed. In the case of soil without fertilizers (Fig. 6, *d*), for PP content up to 3000 mg/kg, there is a slight decrease in PP content ($1(\mathrm{A}-\mathrm{E})^{\text{average}}_{(1-3)}$ dependence) relative to the reference series ($1(\mathrm{A}-\mathrm{E})^{\text{control}}_{(4)}$ dependence), likely due to PP sorption by plant roots. When the PP content exceeds 3000 mg/kg, the dependencies overlap (especially on Fig. 6, *e* and *f*), which can be explained by the reduction in plant growth effect due to the excessive stress factor of pollutants,

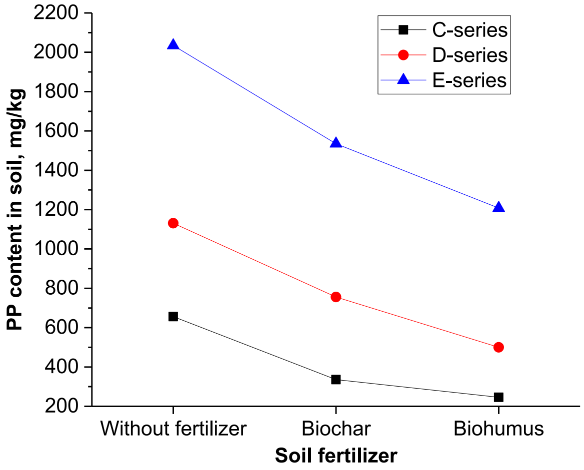


Fig. 5. The results of PP content determination in the soil samples depending on the fertilizer type.

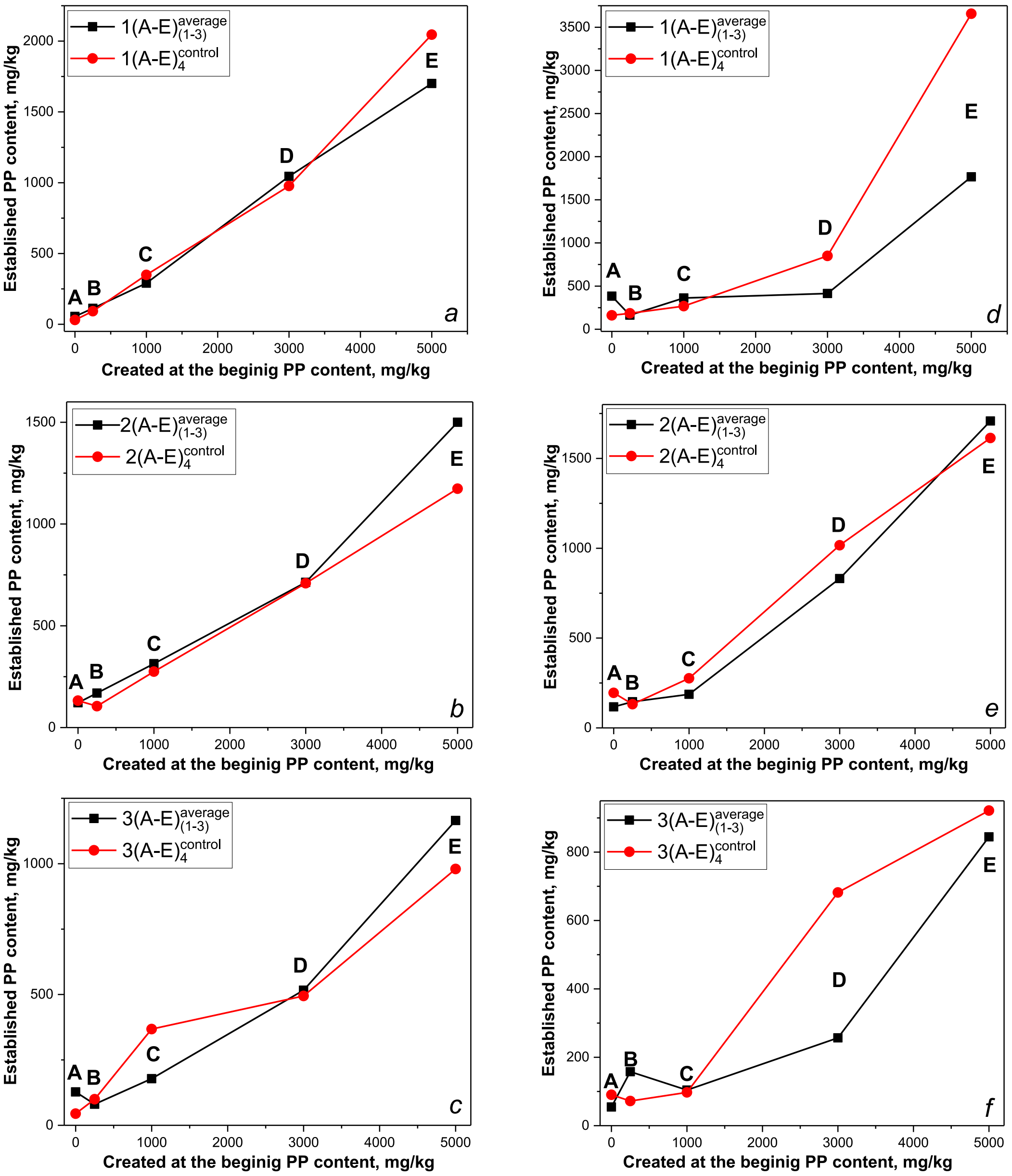


Fig. 6. The PP content in the soil before *M. x giganteus* rhizomes planting (graphs *a* - *c*) and after five months of their growth (graphs *d* - *f*).

resulting in growth inhibition and developmental issues.

For soil with the addition of the “Biochar” (Fig. 6, *b–e*) fertilizer, the effect of the plant on the PP content (Fig. 6, *e*) is observed for PP content up to 700 mg/kg, leading to a slight decrease in PP content ($2(A-E)^{average}_{(1-3)}$) relative to the straight line ($2(A-E)^{control}_{(4)}$). This decrease can be attributed to the sorption of PP by plant roots, as observed in soil without fertilizers, in addition to additional sorption by the fertilizer itself. In soil samples with the “Biohumus” fertilizer addition (Fig. 6, *c–f*), after five months of *M. x giganteus* growth (Fig. 6, *f*), a significant decrease in PP content is observed compared to its initial content in the soil (Fig. 6, *c*) for all tested samples, indicating more favorable conditions for plant growth and development in the presence of this fertilizer.

To study the effect of fertilizers on the phytoremediation processes of petroleum products under the influence of *M. x giganteus* perennial plants, thermal studies were conducted on samples 1E1, 2E2, and 3E3, with a theoretical PP concentration of 5000 mg/kg. Sample 2E2 contains 5 wt % “Biochar” fertilizer in addition to PP contamination, while sample 3E3 contains 5 wt % “Biohumus” fertilizer.

During the first stage of thermolysis, in the temperature range of 20–232 °C, the mass loss of the samples corresponds to the release of water adsorbed by the soil. In the same temperature range, there is a loss of interlayer water present in the structure of clay minerals that are part of the soil [41]. In samples 1E1, 2E2, and 3E3, the most volatile components, including a portion of the PP, can evaporate during this stage. This process is accompanied by an endothermic effect on the DTA curves. Mass loss in the temperature range of 210–472 °C, during the second stage of thermolysis, corresponds to the thermo-oxidative destruction and combustion of the organic matter sorbed by the soil, including components from the soil and fertilizers. This process is accompanied by the release of volatile combustion products and the appearance of an exothermic effect on the DTA curve. In the same temperature range, oxidation of iron atoms, which are present in the mineral component of soil samples, is also possible [42].

It should be noted that samples 2A2 and 3A3 from the A series have a higher content of bound organic matter compared to the natural soil sample 1A1. The weight loss of sample 1A1 in the second stage of thermolysis is 2.68 %, while for sample 2A2, it is 3.36 % and for sample 3A3, it is 2.80 %. The E-series samples, which contain PP, have a higher content of bound organic matter than the A-series samples, as evidenced by more pronounced mass loss during the second stage of thermolysis. Among the E-series samples, sample 3E3 has the lowest content of bound organic matter.

In the second stage of thermolysis, it exhibits the lowest weight loss (3.36 %). This result can be explained by the presence of “Biohumus” fertilizer in sample 3E3, which creates favorable conditions for the growth and development of the *M. x giganteus* perennial plant and facilitates the phytoremediation processes of soil contaminants. The thermal analysis data for sample 3E3 are in good agreement with the results obtained from the extraction-based determination of PP content (Table 6).

Sample 2E2, on the other hand, has the highest content of bound organic matter. This result can be attributed to the presence of Biochar fertilizer in the sample, which actively binds organic compounds through adsorption.

During the third stage of thermolysis, in the temperature range of 452–773 °C, the structure of minerals present in the soil is destroyed, resulting in the release of volatile decomposition products. Clay soil minerals in this temperature range lose the constitutional water presented in the form of -OH groups [40]. This process is accompanied by an endothermic effect on the DTA curves.

In the temperature range of 733–1000 °C, during the fourth stage of thermolysis, the combustion of the carbonized residue formed as a result of thermal oxidation and combustion of organic matter in the sample takes place. This process leads to a slight loss of sample mass and deviation of the DTA curve in the region of exothermic effects.

It should be noted that among the A series samples, sample 2A2 has the highest content of carbonized residue (0.06 %). Among the E series samples, sample 2E2 has the highest content of carbonized residue (0.10 %).

Thermal studies of soil samples with different content of PP were carried out to study the ability of soil components to bind PP. Similar to the pre-calcined soil sample spiked with PP (Fig. 4), the first stage of thermolysis corresponds to the release of adsorbed and interlayer water bound by soil minerals. In the same temperature range, the evaporation of low-boiling components of PP occurs, which explains the increase in mass loss of the samples with higher PP content as described in Refs. [43–47].

Based on thermal analysis of the soils, the weight loss of sample 2E2, which has the highest PP content, during the first stage of thermolysis was 3.72 %. The weight losses of samples 2D2, 2C2, and 2B2, in which the PP content gradually decreased, were 3.25 %, 3.49 %, and 3.06 %, respectively. The more significant mass loss of sample 2C2 compared to sample 2D2 can be explained by the higher moisture content in sample 2C2, which is supported by a slight shift in the temperature of the maximum endothermic effect of this sample to lower temperatures.

During the second stage of thermolysis, in the temperature range of 208–475 °C, oxidative destruction and combustion of the organic matter in the soil samples occur, resulting in the release of volatile combustion products. Samples with higher PP content exhibit more pronounced weight loss during this stage. Thus, the weight loss of sample 2E2 during the second stage of thermolysis is 4.14 %, while for sample 2D2, it is 4.02 %, for sample 2C2, it is 3.80 %, and for sample 2B2, it is 3.80 %. Samples 2C2 and 2B2 have similar organic component contents.

During the fourth stage of thermolysis, in the temperature range of 699–1000 °C, the carbonized residue of the samples is burned. Sample 2E2 is characterized by the highest content of pyrolytic residue (0.12 %).

4. Conclusions

A method for preparing soil samples for PP content determination by IR-spectrophotometry has been developed. This method has a single-stage extraction with an optimal duration of five days and a minimum amount of carbon tetrachloride as the extractant. This environmentally friendly method requires a significantly lower amount of extractant, with a range of 15–30 ml, compared to the commonly used three-fold extraction method that consumes up to 90 ml of extractant.

The developed technique was tested on artificially contaminated soils containing PP at different stages of phytoremediation. The extraction efficiency of PP was determined to be in the range of 81.78–94.22 % for a two-day extraction period. The results were compared with reference samples where *M. x giganteus* was not grown. The experiment, which lasted five months, confirmed the potential of using this plant species to slightly reduce PP content in the soil through sorption by the plant’s root system.

The addition of fertilizers, specifically “Biochar” and “Biohumus”, resulted in a significant decrease in PP content relative to the initial levels in the soil samples. The observed reduction followed the series: “without fertilizer” – “Biochar” – “Biohumus”. This effect can be explained by the influence of fertilizers on PP sorption. The presence of fertilizers in the soil can help alleviate the stress that PP initially causes during phytoremediation, thereby improving the survival of plants at this stage.

The thermal behavior of a model soil sample artificially contaminated with PP was investigated to identify the main stages of thermolysis associated with PP sorbed by the soil matrix. Based on the findings from the thermal behavior analysis of the model soil sample, interpretations were made for the thermograms obtained from laboratory soil samples at different stages of the experiment.

CRediT authorship contribution statement

Ruslana Huminilovych: Writing – original draft, Supervision, Project administration, Methodology, Conceptualization. **Vitalii Stadnik:** Writing – review & editing, Supervision, Project administration. **Martyn Sozanskyi:** Writing – review & editing, Validation, Methodology, Formal analysis, Data curation. **Pavlo Shapoval:** Writing – review & editing, Formal analysis, Data curation. **Valentina Pidlisnyuk:** Supervision, Project administration, Methodology, Conceptualization. **Ihor Poliuzhyn:** Software, Investigation, Formal analysis, Data curation. **Viktoriia Kochubei:** Investigation, Formal analysis, Data curation. **Yurii Hrynchuk:** Supervision, Methodology, Conceptualization. **Bohdan Korchak:** Formal analysis, Data curation.

Data availability statement

Data will be available upon request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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