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Adsorption of organochlorinated pesticides: Adsorption kinetic and adsorption isotherm study

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ABSTRACT

Adsorption of organochlorine pesticides (OCPs) on 4 contrasted activated carbons (ACs) and biochars (BCs) and 5 different basic substances of soil organic matter (SOM) in aqueous media was investigated using adsorption kinetic and isotherm study. This study was performed with emphasis on relationship between adsorption capabilities and physical-chemical properties of the OCPs and above-mentioned sequestration materials (SMs). A kinetic batch study revealed that adsorption efficiency of the SMs-OCPs is time- and dose dependent. Adsorption process between different OCPs and SMs showed diverse fitting to Freundlich isotherm model (R^2 ranked between 0.587 and 0.995). Interestingly, that Freundlich constants such as adsorption capacity and adsorption intensity of all SMs revealed a very similar uptake behavior for dichlorodiphenyltrichloroethane (DDT) metabolites ($P < 0.0001$). The principal component analysis (PCA) demonstrated that adsorption of porous SMs was driven by high carbon content and surface porosity, and adsorption of non-porous SOM-type samples was explained by richness of elemental composition and functional groups. In addition, DDT and metabolites, hexachlorocyclohexane isomers (HCHs) and chlordecone (CLD) showed a different degree of affinity and adsorption to the SMs indicating on an obvious molecular effect, which in case was explained by difference in molecular weight, stereochemistry and hydrophobicity. Generally, results of this study revealed the list of adsorbents which could be effectively applied in further investigations focused on sequestration of OCPs in environmental matrices.

1. Introduction

Organochlorine pesticides (OCPs) are highly toxic synthetic chemicals, most of which have been classified as persistent organic pollutants (POPs) [1]. These pesticides have been used due to their effectiveness against pests and insects on agricultural crops up to the 1970s [2–5] but have been withdrawn due to their toxic adverse effects on health such as cancer, but also different disorders of the reproductive, nervous and hormonal systems [6]; [7]; [8]. In addition, OCPs characterized by their high persistency in the environment, especially in soil, as this

media is a powerful reservoir of different contaminants. Indeed, the different elements of the soil organic matter (SOM) as humic acid and fulvic acid are playing a key role in adsorption of OCPs in soil [9] but the precise role of each SOM fraction in OCP adsorption may differ, even depending on the OCP. The OCP half-lives in soil varied from 60 days to 15 years [10]. In this context, soil is a huge storage reservoir for many POPs, and at the same time it's the key element in many food chains as well as its play an important role for water management systems. Therefore, soil could be the main vector for the transfer of POPs to agricultural animals through the oral soil ingestion (Collas et al., 2019;

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Healy, 1968; Jurjanz S. et al., 2012; Jurjanz, 2011), and, accordingly, to the food products they produce (meat, milk, eggs) [11–14]. This pathway is the highest exposure way of human to POPs because of their high persistence in soil and highest bioaccumulation ability, which would create a great health risk for people consuming contaminated food. Therefore, the presence of OCPs in the environment represents a global problem and its transfer appears to be a key physiological mechanism explaining the subsequent contamination of biota, food and, ultimately, humans [15].

A direct impact on this transfer could reduce contamination of the entire food chain. One possible strategy to reduce this transfer of organic contaminants is to sequester it in environmental carrier-matrix (soil or water) using activated carbon (AC) or biochar (BC). Application of carbon-rich mineral materials such as AC or BC has been efficiently used in sequestration of inorganic and organic pollutants in environmental matrices [15,16,18–20]. This technique is based on adsorption processes and therefore provides retention of the toxic substance rather than its depuration or removal [21]. The main effect of AC/BC based sequestration strategies is immobilization and reducing of pollutant bioavailability and therefore lowered risk of the transfer [21,22]. The main properties making these carbon-rich materials efficient and economically achievable for binding POPs are a highly porous structure, elevated carbon contents (up to 90%) on the one hand, and variety of raw materials, its availability and renewability on the other hand.

Therefore, the aim of the study was to investigate the adsorption behavior and physical-chemical properties of several sequestration materials (SMs) which could be a potential candidate to sequester OCPs and being applied as sequestrants in remediation of contaminated soil or water in perspective. The current study explored adsorption of OCPs with different hydrophobic nature, on 4 contrasted porous adsorbents (ACs and BCs) and 5 different basic substances of soil organic matter (SOM) in aqueous media using kinetics and isotherm batch studies with emphasis on relationship between adsorption capabilities and physico-chemical properties.

2. Materials and methods

Nine OCPs with different hydrophobic properties, α -HCH, β -HCH, γ -HCH, δ -HCH (log K_{ow} 3.8–4.1) chlordecone (log K_{ow} 4.5), 2,4-DDD, 4,4-DDE, 4,4-DDD, 4,4-DDT (6.5–6.9) were selected to investigate the adsorption behavior of nine adsorbents (AC DARCO, AC Shubarkol, BC oak tree, BC Japanese knotweed, peat, potassium humate, humic acid, fulvic acid and black coal Shoptkykol). Assessment of adsorption was based on 2 batch studies:

- 1) *Adsorption kinetic* study, which allows one to determine the time needed to reach equilibrium between OCPs and adsorbents.
- 2) *Adsorption isotherm* study, which allows determining OCPs adsorption behavior for different SM at equilibrium in constant time and temperature.

2.1. Chemical reagents and other consumables

Analytical standards of OCPs purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Sigma Aldrich (St Louis, USA) were used in the experiments. In addition, ^{13}C -labeled β -HCH analytical standard (Dr. Ehrenstorfer GmbH, Augsburg, Germany) was used as internal standard.

Organic solvents such as n-hexane, dichloromethane and acetone were GC grade (Sigma Aldrich, St Louis, USA). Magnesium sulfate used as a desiccant was >99% (Sigma Aldrich, St Louis, USA).

Laboratory glassware used throughout the experiment was rinsed with deionized water and calcined in a muffle furnace at 500 °C for 24 h.

2.2. Production and acquisition of sequestration materials

SMs involved two groups of adsorbents:

- 1) Porous adsorbents: AC DARCO®, AC Shubarkol, BC Japanese knotweed and BC oak tree.
- 2) Non-porous adsorbents: peat, humic acid, fulvic acid, potassium humate and lignite Shoptkykol.

Detailed information regarding production and acquisition of above mentioned sequestrants presented in supplementary materials.

2.3. Characterization of sequestration materials

Origin sources, acquisition, and production conditions, as well as adsorption characteristics (Brunauer-Emmet-Teller (BET) surface area, total pore volume, elemental composition, functional groups of studied SMs presented in tables S2, S3 and S4. The characteristics of AC DARCO and BC Oak tree were derived from available literature and indicated as footnotes in Table S2.

Elemental composition of the SMs was tested using X-ray photoelectron spectrometry (XPS) analysis which was performed on a Kratos Axis Ultra (Kratos Analytical, U.K.). The spectrometer is equipped with a monochromatic Al K α source (1486.6 eV). All spectra were recorded at a 90° take-off angle, with an analyzed area of about 0.7 × 0.3 mm. Survey spectra were acquired with 1.0 eV step and 160 eV analyzer pass energy. The high-resolution regions were acquired with 0.1 eV step (0.05 eV for O 1s and C 1s) and 20 eV pass energy. A neutralizer was used to perform the recording to compensate charge effects. Curves were fitted using a Gaussian/Lorentzian (70/30) peak shape after Shirley's background subtraction and using CasaXPS software. The carbon C 1s is calibrated at 284.8 eV for C–C and C–H bonds.

Morphological characterization was studied by scanning electron microscope coupled with energy dispersive X-ray (SEM/EDX).

The measurements of **specific surface areas (SSA) and porosity** were performed based on nitrogen adsorption-desorption volumetry at 77 K. Nitrogen adsorption-desorption isotherms were recorded on a Belsorp max II (MicrotracBEL Corp.) which were equipped with a turbomolecular pumping unit which ensures a residual vacuum of 10⁻⁵ Pa. The device is equipped with 4 ports including 3 ports for samples and a reference port. Each sample port has 3 pressure sensors covering different ranges: 133 kPa (1000 Torr), 1.33 kPa (10 Torr), 0.0133 kPa (0.1 Torr). After outgassing the samples at 30 °C during 12 h under a residual vacuum of 10⁻⁵ Pa, nitrogen adsorption-desorption isotherms (i.e., volume of nitrogen adsorbed at 77 K vs relative pressure P/P₀, where P is the equilibrium pressure of the adsorbing gas and P₀ is the vapour saturation pressure) were performed using a step-by-step method in the interval of relative pressures, P/P₀, up to 0.98. All experiments were carried out with ultra-pure nitrogen (>99.9995%), supplied by Air Liquide).

The Brunauer-Emmet-Teller (BET) method was used to estimate the SSA, using a 16.3 Å cross-sectional area of nitrogen molecules (Brunauer et al., 1938).

The De Boer method (or t-plot [23]), was carried out to determine **microporous volume and external surface area**. Micropore filling happens at low and very low relative pressure values, and then includes the domain of the monolayer adsorption on the external surface. To be able to distinguish adsorption onto the external surface from adsorption into the micropores (pore size < Å), the experimental isotherm is compared to a reference curve obtained for a non-porous solid, with chemical features and energetic constant as close as possible to the studied matrix.

2.4. Adsorption of OCPs by sequestration materials

2.4.1. Batch adsorption kinetic and adsorption isotherm study

3.4.1.1. Kinetic adsorption study. Twenty mg of SM was distributed in six 250 mL flat bottom flasks. Each flask corresponded to a contact time after which collection of aliquots is performed. One hundred fifty mL of OCPs aqueous working solution (supplementary materials) was added to each flask and closed with a glass cap. The samples were mixed in a 3D orbital shaker (Isolab, Germany) at ambient temperature. Then, aliquot of 10 mL was collected after contact time of 1 min, 10 min, 30 min, 60 min, 120 min and 240 min using 10-mL disposable plastic syringe. The samples were filtered using 0.45 μm PFTE syringe filter and collected in 50 mL centrifuge tubes. The filter and syringe were rinsed by 2–3 mL of dichlormethane:hexane (1:1) and combined with the sample.

The control samples of this experiment (without addition of sequestration material) consisted of a working solution of 10 mL of OCP, which was transferred to a 50 mL centrifuge tube. All samples were performed in two replicates and then extracted and analyzed by GS-MS as described below.

3.4.1.2. Adsorption isotherm study. Sequestration material with masses of 1, 4, 20, 50, and 100 mg was transferred to five 125 mL amber bottles. Then 100 mL of OCPs working solution (supplementary materials) was added in each bottle. Samples were incubated for 48 h at room temperature by stirring (150 rpm) in an incubator with a laboratory shaker VS 150 OI (Lauda, France). Finally, an aliquot of 10 mL was sampled and filtered using 0.45 μm PFTE syringe filter and transferred in 50 mL centrifuge tubes for further extraction and GC analysis.

Control samples were incubated 48 h under the same conditions. All samples were prepared in 2 replicates and then extracted and analyzed by GS-MS as described below.

2.4.2. Liquid-liquid extraction (LLE)

The extraction procedure was in accordance with Fosu-Mensah et al. [24]. Samples were extracted by adding a 15 mL of dichlormethane:hexane (1:1) and vortexed 3 min. The samples were then centrifugated at 5000 rpm at 4 °C for 5 min. The supernatant was collected and passed through the paper filter with magnesium sulfate (0,5 g) directly to a 125 mL evaporation glass tube. The LLE procedure was repeated twice. The combined filtrate was evaporated at 60 °C under vacuum conditions of up to 1-1,5 mL (BUCHI MultivaporTM P-6 Parallel Evaporator).

Prior extraction of the samples, 50 μL of ^{13}C -labeled β -HCH (10 $\mu\text{g}/\text{mL}$) was added as internal standard for accurate quantification.

2.4.3. GC analysis

The determination of OCPs in the samples was carried out using a GC-MS (7890 B, Agilent Technologies) and GC-MS (5975C, Agilent Technologies) respectively for kinetic adsorption and equilibrium adsorption samples. Chromatographic conditions for determination of OCPs in the samples are detailed in Supplementary materials and in Table S1.

2.4.4. Data analysis

2.4.4.1. Quality control. Analysis of adsorption kinetic and equilibrium was performed in 2 replicates and included blank samples represented OCP aqueous solution without the presence of a SM. Calibration of GC-MS system was performed daily before analysis of samples using analytical standards of individually dissolved OCPs in n-hexane. Samples were quantified using internal standard (^{13}C -labeled β -HCH). In addition, n-hexane was used as equipment blank and was introduced between two samples on the analytical tray to avoid cross-contamination.

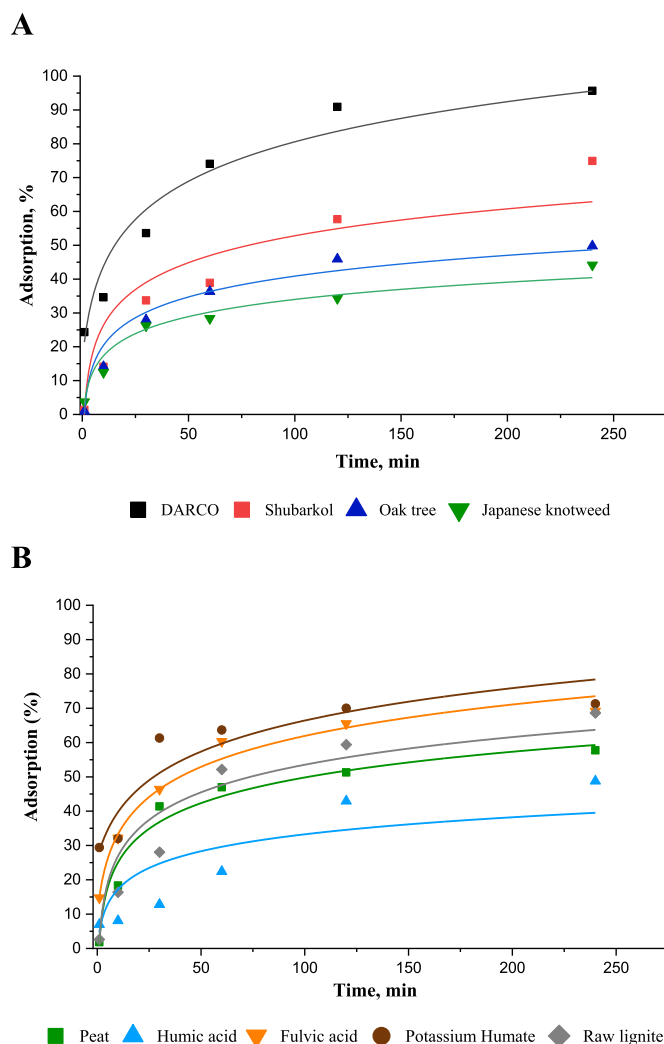


Fig. 1. Effect of contact time on 4,4-DDT adsorption on activated carbons and biochars (Fig. 1A) and on soil organic matter (Fig. 1B). Pesticide and sequestrant concentrations were 50 $\mu\text{g}/\text{L}$ and 0.13 g/L, respectively. Results based on 2 replicates.

2.4.4.2. Quantification. The concentrations of pesticides in the samples were calculated using internal calibration method and ^{13}C -labeled β -HCH as an internal standard (IS). Detailed of these calculations is presented in supplementary materials.

2.4.4.3. Statistical treatment. Kinetic adsorption data were presented as non-linear logarithmic regressions (Fig. 1 and Fig. S2). Equilibrium in kinetic study was defined when adsorption becomes stable in time and reaches a plateau. Adsorption efficiency of OCPs on SMs which revealed no observable growth after 2 h was set as criteria of achievement of the plateau.

Equilibrium adsorption data were fitted to the Freundlich isotherm model [25] to characterize the adsorption behavior of OCPs. This is an empirical adsorption isotherm model for heterogeneous adsorbent surfaces, which have been well validated for hydrophobic organic pollutants [26–30]. Linear form of the Freundlich model is represented by equation (3):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

where K_F [$(\mu\text{g}/\text{g}) (\text{g}/\text{L})$] and $1/n$ are Freundlich constants related to the adsorption capacity of the adsorbents and the surface heterogeneity,

Table 1
Comparison of adsorption kinetic parameters achieved in current study and in literature.

OCP name, concentration, µg/L	Adsorbent, concentration (g/L)	Total time and equilibrium time (h)	Adsorption (%)	Reference				
DDT and metabolites	50	AC DARCO	0.13	4	2	77	Current study	
		AC Shubarkol				4		71
		Shoptykol				4		75
		Potassium humate				4		67
		Peat				4		61
		Fulvic acid				4		66
DDT and metabolites	20	AC Palm date stone	5	2	>2	90–98	[35]	
4.4-DDT	20000	AC Nutshell	1	1.2	1	65	[17]	
4.4-DDT	5000	AC Coconut shell	1	24	6	75	[7]	
4.4-DDT and 4.4-DDE	2500	Clay	10	24	8	70	[39]	
HCH isomers	50	AC DARCO	0.13	4	4	76	Current study	
		AC Shubarkol				2		51
γ-HCH	20	AC pine bark	5	9	>3	80	[34]	
γ-HCH	100 000	AC date stone	1	24	4	98.6	[32]	
α-HCH	20	AC palm date stone	5	2	>1	93–98	[35]	
β-HCH		AC palm date stone		2	>1	93–98		
Chlordecone	50	AC DARCO	0.13	4	2	91	Current study	
		AC Shubarkol				4		93
		Shoptykol				4		70
		Potassium humate				4		58
		Peat				4		47
Chlordecone	2200	AC DARCO (FeOs Nps)	0.025	24	>24	95	[33]	
		AC DARCO						62
Chlordecone	2500	AC bagasse	0.06	200	50	–	[36]	

CA-T - Composite adsorbent with triolein. GAC-granular activated carbon.

Table 2
The adsorption capacity K_F ($\mu\text{g/g} (\mu\text{g/L})^{1/n}$) of studied couples of OCPs-SMs determined by the Freundlich equation.

SMs	α-HCH	β-HCH	γ-HCH	δ-HCH	2,4-DDD	4,4-DDD	4,4-DDE	CLD
AC1	0.000028	0.00001	5.80E-13	7.70E-06	2.10E-07	2.30E-15	1.30E-19	2.25
AC2	1.20E-06	0.12	0.52	3.33	12.8	13.48	62.24	0.02
BC1	1.10E-26	1.50E-06	4.50E-08	0.02	0.07	0.09	0.02	0.0002
BC2	4.40E-13	0.21	1.24	0.63	1.18	1.28	1.2	1.16
SOM1	2.70E-13	4.70E-06	1.49	0.00023	22.9	19.8	154.3	0.33
SOM2	3.20E-15	1.50E-08	7.00E-15	1.40E-04	2.70E-09	4.00E-12	2.60E-12	0.002
SOM3	6.30E-10	1.10E-07	0.39	4.70E-19	0.23	1.99	3.99	0.002
SOM4	4.70E-09	6.90E-33	2.40E-02	2.50E-67	0.0003	0.0007	0.0003	1.90E-36
SOM5	0.73	5.80E-11	2.00E-11	4.40E-06	1.50E-08	3.10E-11	3.80E-17	2.70E-14

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

Table 3
The absorption intensity N (dimensionless) of studied couples OCPs-SMs determined by the Freundlich equation.

SMs	α-HCH	β-HCH	γ-HCH	δ-HCH	2,4-DDD	4,4-DDD	4,4-DDE	CLD
AC1	0.24	0.22	0.11	0.2	0.15	0.09	0.06	0.48
AC2	0.18	0.46	0.7	0.92	0.97	0.92	0.35	0.4
BC1	0.06	0.2	0.19	0.5	0.39	0.37	0.24	0.28
BC2	0.1	0.48	0.78	1.22	2.19	2.33	3.37	0.66
SOM1	0.09	0.21	0.99	0.27	0.95	1	0.9	0.5
SOM2	0.1	0.15	0.1	0.26	0.11	0.09	0.07	0.28
SOM3	0.14	0.17	0.8	0.08	0.46	0.66	0.43	0.32
SOM4	0.16	0.05	0.07	0.02	0.2	0.22	0.14	0.04
SOM5	0.93	0.12	0.13	0.2	0.11	0.09	0.05	0.1

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

respectively. To determine the Freundlich constants, $\log q_e$ plotted against $\log C_e$, and data have been analyzed by linear regression. Intercept equals to $\log K_F$ and K_F is antilogarithm of intercept. Slope is equal to $1/n$.

Linear (isotherms) and non-linear (kinetics) logarithmic regression analysis and ANOVA test was performed by using OriginPro 2018 (ver. b9.5.1.195, OriginLab Corporation, Northampton, MA, USA). The Pearson correlation tests (XLSTAT, 2022, Addinsoft, New York, USA) were performed for adsorption capacities (Table 2) or adsorption intensities (Table 3) between OCP couples.

For better understanding adsorption behavior of studied OCPs on SMs, two principal component analysis (PCA) were carried out to explore relationship between physico-chemical characteristics and adsorption capacities resulted by Freundlich isotherm model (Table 2).

First PCA (not shown) was built to define the main SMs properties which would significantly impact on the adsorption process between OCPs-SMs couples. Thus, adsorption capacities (K_F) of OCPs-SMs couples were explained by BET SSA and porosity (Table S2), mineral elements (Table S3) and functional groups (Table S4). Results of the PCA were presented as squared cosines to show correlation between K_F of

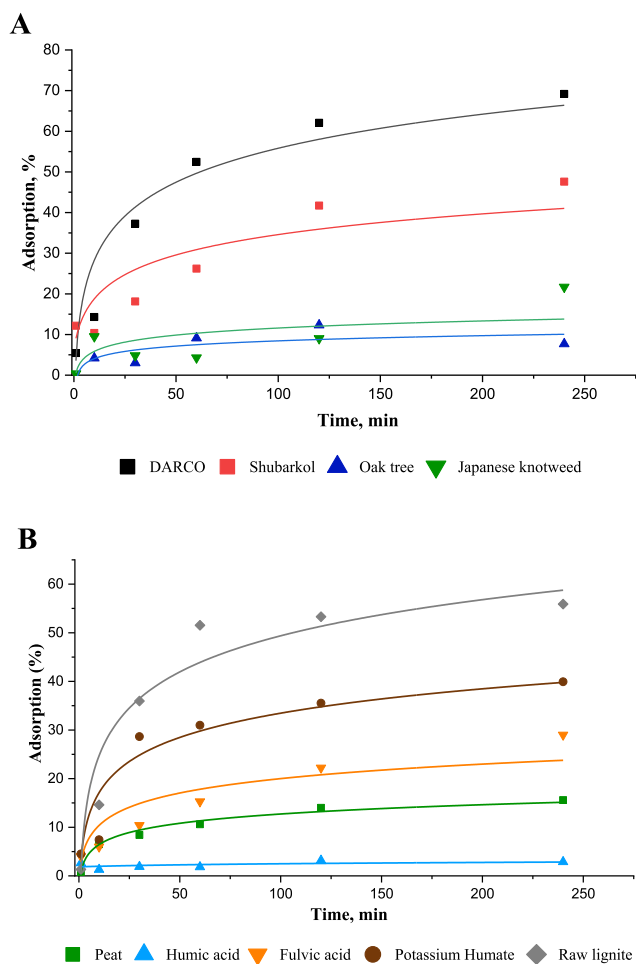


Fig. 2. Effect of contact time on α -HCH adsorption on activated carbons and biochars (Fig. 2A) and on soil organic matter (Fig. 2B). Pesticide and sequestrant concentrations were 50 $\mu\text{g/L}$ and 0.13 g/L, respectively. Results based on 2 replicates.

OCPs-SMs couples, porosity, mineral elements and functional groups of SMs (Table S9).

Afterwards, agglomerative hierarchical clustering (AHC) was carried out in regard to mineral elements (Fig. 5) and functional groups of SMs (Fig. 6) to simplify the global view. Results of the SMs classification were integrated into second PCA (Fig. 7). This PCA represented a dispersion composed of 2 plots with quantitative variables (i.e., K_F of OCPs-SMs couples and porosity) and qualitative variables (i.e., SM classes depending on mineral elements and functional groups). Missing values in PCA were set as zero.

3. Results and discussion

3.1. Characterization of SMs

Generally, the studied SMs have been divided in porous (AC/BCs) and non-porous (peat, potassium humate, humic acid, fulvic acid and raw lignite Shoptkyol) sequestration materials. Porous carbonaceous matrices demonstrated by a set of different textural characteristics as shown by the specific surface areas (SSA) ranging from 144 to 794 m^2/g (Table S2). Activated carbons (AC1, AC2) displayed the highest SSAs (between 723 and 794 m^2/g) and biochars (BC1 and BC2) clearly lower (144 and 196 m^2/g , respectively). The higher SSAs could be associated with the use of high temperatures during productions of the studied AC/BCs.

Results of element composition presented in Table S3 showed that ACs (AC1, AC2) and BCs (BC1, BC2) are mainly composed of carbon (C) and oxygen (O). The carbon concentrations in these matrices are generally higher compared to the other non-porous organic materials. This can be explained by application of the high temperature's treatment during the production of studied AC/BCs. The highest concentrations of C with more than 90% were found in AC1 and BC1. However, AC2 (72%) and BC2 (85%) with a less carbon content showed a presence of minerals such as potassium (K), calcium (Ca) and chlorine (Cl).

Non-porous organic matrices differed by their richer element composition (including K, Ca and Cl) compared to the studied AC/BCs. Among the richest by mineral composition was fulvic acid (SOM3) which was composed of Cl, K, Fe, Al, N, Cr and Ca (Table S3).

The oxygen to carbon ratio (O/C) indicated the typical polarity, i.e., abundance of polar oxygen functional groups on the AC/BC surface. Results showed that O/C ratio of studied SMs varied between 0.04 and 0.65. The most polar surface had SOM5 and the most non-polar AC1 (Table S3).

Results of morphological characterization via SEM of studied SMs (Fig. S1) was described in Supplementary materials.

3.2. Effect of contact time

Adsorption of organochlorine pesticides (chlordecone, α -HCH, β -HCH, δ -HCH, 2,4'-DDD, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT) from aqueous solution (50 $\mu\text{g/L}$) onto 20 mg of studied ACs/BCs/SOMs were measured after different contact time (1 min, 10 min, 30 min, 60 min, 120 min and 240 min).

Results of kinetic adsorption study were based as non-linear logarithmic regressions and represented dependences of contact time between OCPs-SMs (min) and adsorption (%). This kinetics presented for 4,4-DDT (Fig. 1) and for α -HCH (Fig. 2) as an example in the text below and in supplementary materials for all other studied OCPs. In addition, correlation coefficients (R^2) indicated that most of the of studied OCPs-SMs were significantly fitted to the kinetic logarithmic model ($P < 0.01$) ranking between 0.633 and 0.986 with exception to adsorption of α -HCH on BC Japanese knotweed and humic acid ($p > 0.01$) (Table S5). Perhaps, these SMs are required to have more than 4 h of contact time for their removal from aqueous media (discussed further below).

As expected, the adsorption efficiency of the sequestrants-OCPs was time-dependent i.e., the longer the contact time the higher the adsorption (Figs. 1 and 2 and Fig. S2). Generally, results showed that most of the SMs achieved an equilibrium after 2 h for all OCPs. Achieving an equilibrium means that the adsorbent matrix (or in case of AC/BCs on pore space) was fully saturated by the tested OCP and thus the adsorption becomes stable after reaching a plateau. Indeed, kinetic data showed that ACs (DARCO and Shubarkol) achieving a time-stable adsorption values remained higher than 50% after 2 h of contact time. Commercial AC DARCO revealed the highest adsorption of studied OCPs ranging between 75 and 80% after 2 h of contact (Figs. 1 and 2 and Fig. S2).

Interestingly, SOMs such as peat (SOM1), fulvic acid (SOM3) and potassium humate (SOM4) showed the similar adsorption efficiency (up to 50%) preferable for DDT and its metabolites as well as CLD. These results could be explained by higher hydrophobic nature of DDT and its metabolites (K_{ow} between 6.6 and 6.9) and CLD ($K_{ow} = 4.5$) compared to HCH isomers (K_{ow} between 3.7 and 3.8). Indeed, according to elsewhere [9,31], POPs with medium to high hydrophobic properties ($K_{ow} > 4.5$) tend to remove from aqueous media more efficiently and bind to SOM.

However, there were also SMs, which did not achieve equilibrium such as BC1, BC2 and SOM2. Adsorption of OCPs for these SMs was continuing to increase during the 4 h of the kinetic study (Figs. 1 and 2 and Fig. S2). These data indicated that contact time of more than 4 h would be needed to achieve an equilibrium for above-mentioned adsorbents.

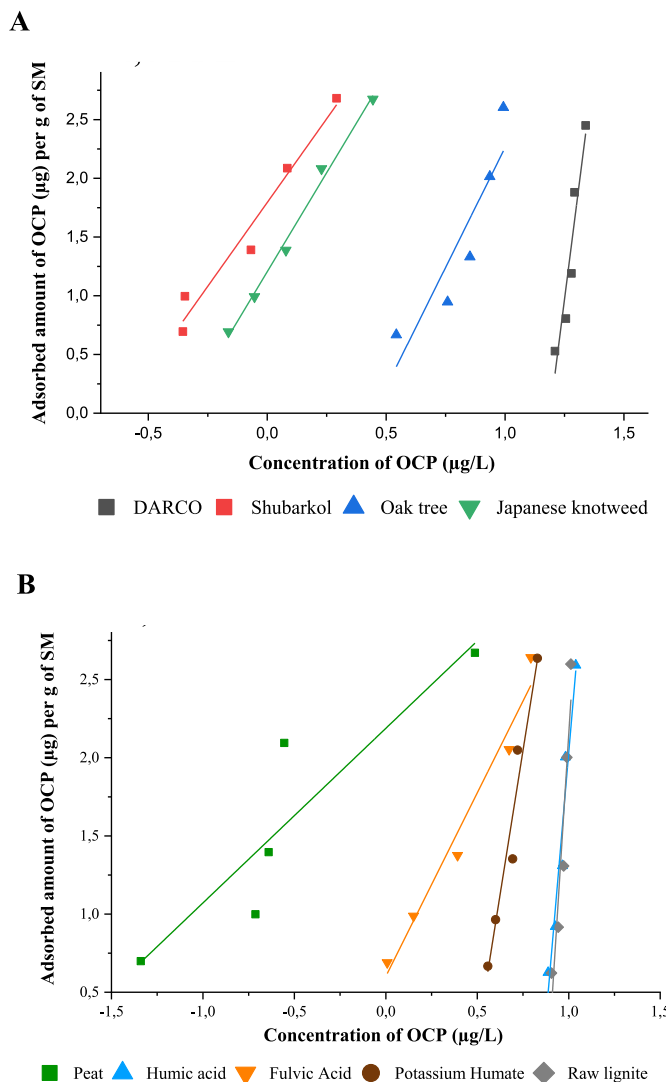


Fig. 3. Freundlich adsorption isotherms of 4,4-DDE and studied activated carbons and biochars (Fig. 3A) and soil organic matters (Fig. 3B). Working conditions: Contact time 48 h, temperature 25 °C, agitation 150 rpm, initial OCP concentration 50 µg/L, SM concentrations: 0.1. 0.4. 2.0. 5.0. 10 g/L.

Equilibrium time of OCPs in this study was generally in agreement with literature data indicated in Table 1. However, for completed saturation on the adsorbent (especially to organic matter) a longer time was needed as adsorption of the pesticides in our study was lower than elsewhere [32–35]. In addition to this, low adsorption of OCPs (<50%) could also be explained by two points: i) competition process occurred between the different studied pesticides for active adsorption sites and ii) the adsorbent concentration of 0.13 g/L was 10–100 times lower than in similar studies (Table 1). Perhaps, increasing adsorption dose to several times would increase adsorption degree and decrease the time to reach equilibrium for studied OCPs. Therefore 48 h as the contact time was set in subsequent adsorption isotherm studies to guarantee achieving of adsorption equilibrium. Effect of different adsorbent concentrations was also investigated to describe the adsorption efficiency for studied OCPs-adsorbents after 48 h.

3.3. Adsorption isotherms

An adsorption isotherm is the relationship between the studied compound (here OCPs) in the liquid phase and the compound adsorbed on the surface of the adsorbent at equilibrium at constant temperature.

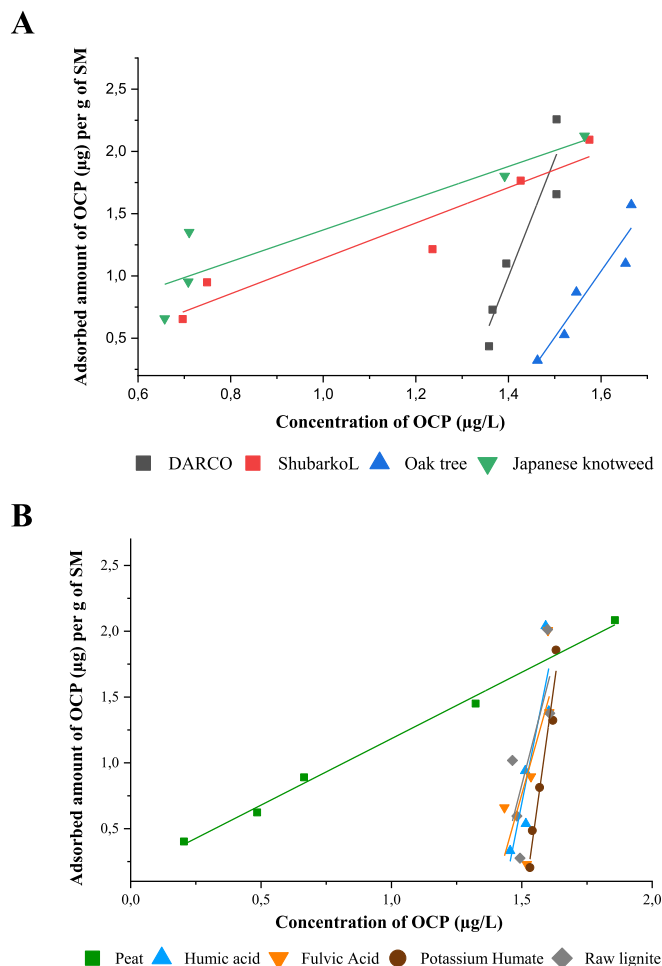


Fig. 4. Freundlich adsorption isotherms of γ -HCH and studied activated carbons and biochars (Fig. 4A) and soil organic matters (Fig. 4B). Working conditions: Contact time 48 h, temperature 25 °C, agitation 150 rpm, initial OCP concentration 50 µg/L, SM concentrations: 0.1. 0.4. 2.0. 5.0. 10 g/L.

Adsorption isotherms represented an experimental dataset based on the aqueous solution of the pesticide mixture with a concentration of 50 µg/L, which interacted with different adsorbent doses (0.1, 0.4, 2.0, 5.0, 10 g/L) during 48 h.

Experimental data were applied to Freundlich isotherm model and shown as logarithmic plots which were based on concentration of OCPs (C_e) versus adsorbed amount of OCPs (q_e) per gram of SM at equilibrium. These plots presented for 4,4-DDE and lindane (γ -HCH) as example in text below (Fig. 3 and Fig. 4, respectively) and for other OCPs in supplementary materials (Fig. S3).

Analysis of variance (ANOVA) performed for initial parameters (C_e and q_e) and used to build Freundlich isotherms revealed three levels of relationships: very significant ($P \leq 0.01$), significant ($P \leq 0.05$ but >0.01) and non-significant ($P > 0.05$) fitted to the Freundlich isotherm model and showed as correlation coefficients (Table S6). The correlation coefficients (R^2) were derived from linear regression plots and were based on correlations between concentration of OCPs (µg/L) (X-axis) and adsorbed amounts of OCPs (µg) per gram of SM (Y-axis) at equilibrium (Fig. 2). Resulted R^2 values ranked between 0.587 and 0.995 for all studied couples OCP-SMs (Table S6).

The parameters of the Freundlich isotherm model such as adsorption capacity (K_F) and adsorption intensity (N) for different OCPs-adsorbents were presented in summary Tables 2 and 3, respectively. A very high variation of K_F and N values between OCP profile and studied SMs were observed. Therefore, Pearson correlation test was performed for

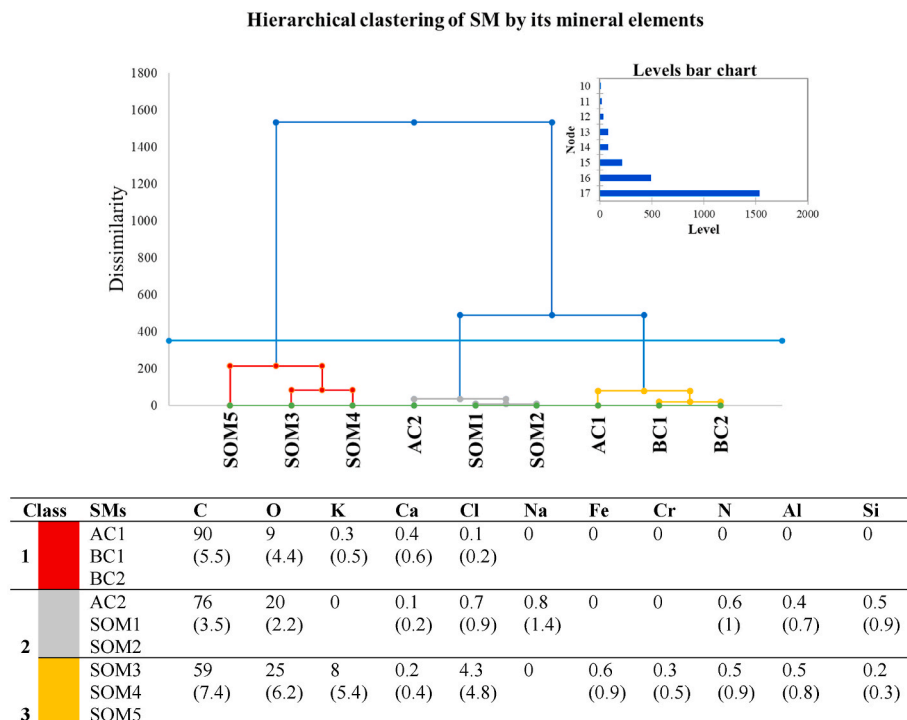


Fig. 5. Hierarchical classification of SM by mean values of mineral elements (percent). Values in parentheses are standard deviations. AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

adsorption capacities (Table S7) as well as adsorption intensities (Table S8) between OCP couples.

Pearson correlation tests applied on adsorption capacity K_F values showed that DDT metabolites (2,4-DDD, 4,4-DDD and 4,4-DDE) have the most significant correlation ($P \leq 0.0001$) within all SMs (Table S7). In addition, γ -HCH also showed a significant correlation ($P < 0.05$) to DDT and its metabolites. This means that these OCPs demonstrated a very similar uptake behavior during interaction with SMs. Comparison of the remained pesticide pairs within all sets of SMs for K_F was not significant.

Regarding adsorption intensity data (N values), Pearson correlation indicated that DDT metabolites had the strongest correlation ($P \leq 0.0001$) (Table S8) for all SMs. In addition, both β -HCH and CLD also showed a significant correlation to all studied DDT metabolites with $P < 0.05$. These relations mean that these OCPs revealed similar distribution during adsorption to SMs and therefore competition process may occur between them for heterogeneous active sites on the SMs matrix [36].

All SMs demonstrated a variable degree of non-linearity ($N \neq 1$) which corresponds to N-values (Table 3). Non-linear sorption confirms the dominance of pesticide adsorption onto the studied SM rather than absorption. Results showed that N-values of all SMs (with exception BC2 for some of the studied OCPs) were generally less than 1 and represented a favorable isotherm. This could indicate on high SM loading at low OCP concentrations [37]. Contrary to this, adsorption intensities (N) of DDT and metabolites as well as δ -HCH for BC2 (oak) were between 1.22 and 3.37 indicating on unfavorable isotherms [37,38].

The isotherm adsorption of all studied OCP-SMs follows a C-type profile for linear curves according to Giles et al. [39]. The C-type is characterized by two main observations: i) target OCPs have a higher affinity for SMs than for solvent and therefore ii) studied OCPs have a better penetration power due to molecular geometry into SM matrix. In this case, the linearity of the data obtained can be interpreted as the constant presence of active sites on the surface of the SM. i.e. the more pesticide molecules are adsorbed, the more active sites are created.

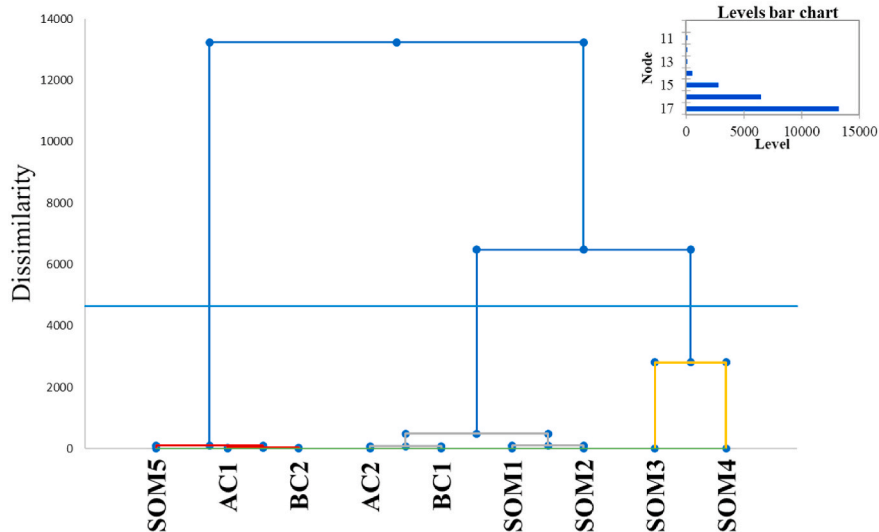
3.4. Relationship between adsorption capabilities and characteristics of OCP-SMs

To better understand relationship of studied physico-chemical properties of SM and adsorption of OCPs, PCA with all variables (K_F , porosity via BET SSA, micro-, and macroporous volume, as well as mineral elements and functional groups) was performed (not shown). Squared cosines were derived from this PCA analysis to demonstrate correlation between the studied variables and factors (Table S9). The analysis showed a modest impact of porosity on the obtained results (Table S9). This could be partly explained by the nature of SOM-type samples, which are non-porous and represent more than half of the studied matrices. The SOM samples adsorption behavior could be explained only by mineral composition and functional groups presented on their surfaces. In addition, studied SMs have a very diverse elemental composition and surface functional groups (Table S3 and Table S4, respectively) containing a lot of zero values complicating the overall view. Therefore, AHC was done separately for mineral elements (Fig. 5) and functional groups (Fig. 6) of SMs and revealed 3 classes of SMs.

Classification of studied SMs by mineral elements was mainly dependent on carbon content: 1st class (AC1, BC1 and BC2) or carbon content $90 \pm 5.5\%$. 2^d class (AC2, SOM1 and SOM2) or carbon content $76 \pm 3.5\%$. 3^d class (SOM3, SOM4, SOM5) or carbon content $59 \pm 7.4\%$ (Fig. 5). The SMs classification by functional groups revealed a very similar distribution with exception for BC1 and SOM5 (Fig. 6). Thus, results of the cluster analysis were integrated into further PCA analysis to explain an adsorption processes between OCPs and SMs (Fig. 7).

The PCA analysis showed three major distinctions of the investigated OCP-SM couples showing obvious molecular effect (Fig. 7). Thus, each group of pesticides DDT metabolites (2,4-DDD, 4,4-DDD and 4,4-DDE), HCH-isomers and CLD showed a different degree of affinity and adsorption to the studied SM and the two main axis (axis F1 and F2) of the PCA explained 68% of the total variation. The exception in this distribution was α -HCH, which unlike other HCH isomers showed the highest affinity for SOM-type SMs (Fig. 7). Different hypothesis could explain this different adsorption behavior: 1) Even if α -HCH has similar

Hierarchical clustering of SM by its functional groups



Class	SMs	C _{Sp2}	C-C/ C-H	C=C	C-O	C=O	O-C=O
1	AC1	69	17	0	6.7	1.9	4.9
	BC2	(5.1)	(2.9)		(2.1)	(3.3)	(4.8)
	SOM5						
2	AC2						
	BC1	0	22	58	12	1.7	4.9
	SOM1		(5.5)	(12)	(6.1)	(3.3)	(2.1)
3	SOM3	0	49	0	12	29	9.4
	SOM4		(33.5)		(4.9)	(40.7)	(0.07)

Fig. 6. Hierarchical classification of SM by mean values of functional groups. Values in parentheses are standard deviations. AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

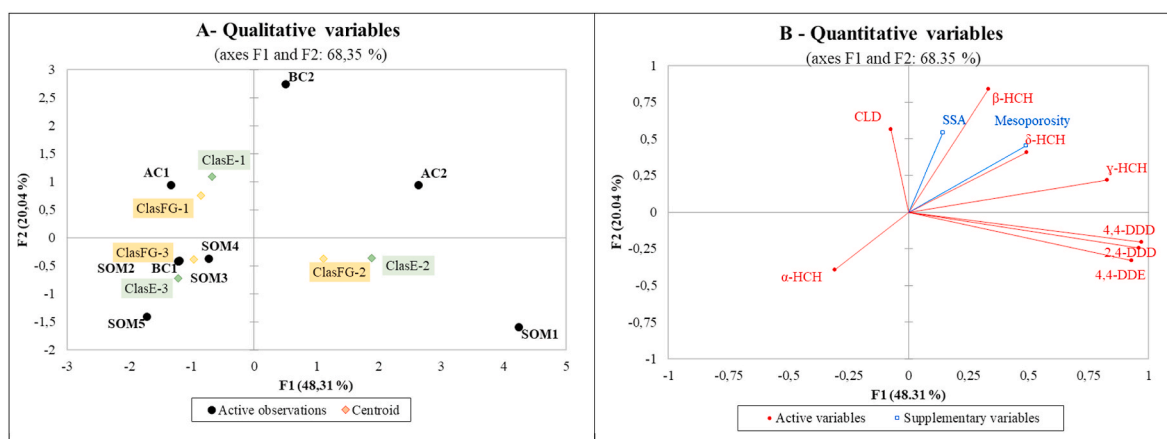


Fig. 7. Dispersion of A-qualitative and B-quantitative variables describing sequestration materials (A) and adsorption capacities of OCPs-SMs couples (B). A-the qualitative descriptors used to qualify the SMs depending on the class of functional group (yellow. ClasFG) and class of elemental composition (green. ClasE). The different SMs (AC/BC/SOM) were arranged as illustrative data presented in bold black. Indication of SMs: AC1 – DARCO, AC2 – Shubarkol, SOM5 – Shoptykol, BC1 - Oak tree, BC2 - Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate. B- the quantitative descriptors of the materials are composed of adsorption capacities (K_p) indicated as OCPs (red color) and porosity properties (blue color). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

hydrophilicity ($K_{ow} = 3.7$) than the other HCH isomers (3.8). the position of the chlorine atoms and by consequence metabolic stability differs. Moreover, its mole fraction in water is much lower (Henry's constant $K_H > 6.8 \times 10^{-6}$) than in other HCH isomers $K_H \leq 3.5 \times 10^{-6}$),

2) SOM-type SMs have a very polar surface containing oxygen containing functional groups (Table S4) and therefore are very soluble in water (compare to AC/BCs).

Adsorption behavior of studied DDT metabolites explaining 48% of

variations (F1 axis) showed the highest adsorption potential for SOM1 (raw peat) and AC2 which is characterized by the highest mesoporosity.

The second PCA-axis (F2, 20%) indicated that HCH isomers (except α -HCH) and CLD showed the preferential adsorption to AC1, AC2 and BC2 but with different adsorption degree. Adsorption capacities of these OCPs-SMs couples is not alike which could be also due to the molecular properties of HCHs and CLD. Indeed, ketone groups of CLD may easily interact with other functional groups (i.e., hydrogen) of SMs due to the presence of an oxygen atom in the structure even despite on the larger molecular weight (491 amu) and moderate hydrophobicity (K_{ow} 4.5) compared to HCHs (291 amu and K_{ow} 3.7–4.1) and DDTs (318–320 amu and K_{ow} 6.0–6.5). Adsorption of HCHs to these highly porous SMs could be associated with lowest molecular weight and as consequence indicate on a higher speed of adsorption during the competition with other molecules.

In general, PCA supported the previous observations and confirmed that the adsorption of OCPs on studied SMs was driven by various physico-chemical properties. Therefore, it is difficult to select one key property to explain the efficiency of OCPs adsorption and affinity between OCPs and SMs is the result of a combination of several factors within lipophilicity, presence of functional groups and carbon content seem to be key parameters. It seems likely that parameters describing the surface charges, the degree of competition between different compounds in soil for adsorption on SMs (OCPs but also other soil compounds) and strong variations in porosity of SMs would also make vary the effective adsorption of OCPs by different SMs.

4. Conclusions

Adsorption kinetic and adsorption isotherm studies have been shown to be an efficient tool to investigate adsorption behavior of OCPs to different contrasted SMs. The classification of SMs in ACs, BCs and SOMs allows a better understanding of adsorption mechanisms. Indeed, a very high proportion of carbon in ACs and BCs allowed them a high adsorption degree, especially on hydrophobic OCPs even if other physico-chemical characteristics as the presence of functional groups make vary the degree of adsorption. The most effective SMs which could effectively adsorb all studied compounds were mainly ACs: DARCO and Shubarkol, BCs: Oak tree and Japanese knotweed, SOMs: peat and humic acid. This study demonstrated that SMs parameters, which favorably affected on adsorption of OCPs were porosity, i.e SSA and mesoporosity (porous SMs), mineral elements (especially carbon) and functional groups (SOM type samples). Other factors as competition between different OCPs present in soil or between OCPs and soil compounds should be included to improve the prediction of adsorption. Finally, the proportion of amended SM on soil and by consequence the amount of available adsorption surface should be pathways to reduce the OCP availability in contaminated soils.

The data presented allow to conclude that above mentioned SMs could be effectively used in sequestration strategy studies as amendment which could immobilize OCPs in contaminated soil and water.

Author contributions statement

Farida Amutova: Investigation (lead), Conceptualization (equal), Visualization (lead), Methodology (equal), Writing - original draft (lead), Writing-review & editing (equal). Formal analysis. **Stefan Jurjanz:** Conceptualization (equal), Data curation (equal), Writing-review & editing (equal), Validation (equal), Supervision (equal). **Nurlan Akhmetsadykov:** Project administration (equal), Funding acquisition, Review (supporting). **Maira Kazankapova:** Resources (equal), Review (supporting). **Angelina Razafitianamaharavo:** Investigation (equal), Review (supporting). **Aurélien Renard:** Investigation (equal), Review (supporting). **Moldir Nurseitova:** Project administration (equal), Funding acquisition, Review (supporting). **Gaukhar Konuspayeva:** Writing-review & editing (equal), Formal analysis (equal).

Mathieu Delannoy: Conceptualization (lead), Data curation (equal), Resources (equal), Methodology (equal), Project administration (equal), Writing-review & editing (equal), Funding acquisition (equal), Validation (equal), Supervision (equal).

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rineng.2022.100823>.

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