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Investigation of the sorption of 17α-ethynylestradiol (EE2) on soils formed under aerobic and anaerobic conditions

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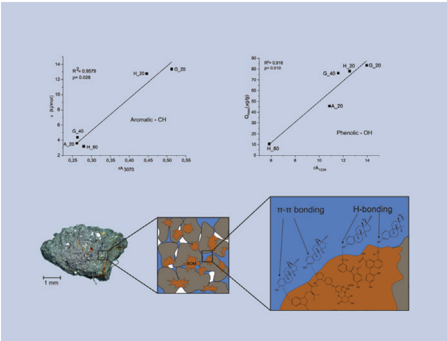
HIGHLIGHTS

- The adsorption of EE2 was connected with the redox potential of the soils.
- Aromatic and phenolic compounds were found to be abundant in anaerobic layers.
- Hydromorphic soils with organic matter accumulation had high adsorption capacity.
- π-π interaction and H-bonding were found the dominant sorption mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

A study was conducted on the sorption of 17α-ethynylestradiol (EE2) on five soils formed under different redox conditions: an Arenosol (A_20) with fully aerobic conditions, two Gleysol samples (G_20 and G_40) with suboxic and anoxic conditions and two Histosols (H_20 and H_80) with mostly anoxic conditions. The soils were characterized on the basis of total organic carbon (TOC), specific surface area (SSA) and the Fourier transform infrared spectra of the humic acid and humin fractions (the soil remaining after alkali extraction) of the soil. The maximum adsorption capacity of the soils (Q_{max}) ranged from 10.7 to 83.6 mg/g in the order G_20 > H_20 > G_40 > A_20 > H_80, which reflected the organic matter content of the soils. The sorption isotherms were found to be nonlinear for all the soil samples, with Freundlich n values of 0.45–0.68. The strong nonlinearity found in the adsorption of the H_80 samples could be attributed to their high hard carbon content, which was confirmed by the high aromaticity of the humin fraction. The maximum sorption capacity (Q_{max}) of the soils did not increase indefinitely as the organic carbon content of the soils rose. There could be two reasons for this: (i) the large amount of organic matter may reduce the number of binding sites on the surface, and (ii) the decrease in SSA with increasing soil OC content may limit the ability to adsorb EE2 molecules. In anaerobic soil samples, where organic matter accumulation is pronounced, the amount of aromatic and phenolic compounds was higher than in better aerated soil profiles. Strong correlations were found between the amount of aromatic and phenolic

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compounds in the organic matter and the adsorption of EE2 molecules, indicating that π-π interaction and H-bonding are the dominant sorption mechanisms.

1. Introduction

The fate and transport of endocrine-disrupting chemicals (EDCs), such as estrogens, in the soil-water system are a growing concern, because these bioactive compounds have been widely detected in wastewater, reclaimed water and rivers (Khanal et al., 2006; Citulski and Farahbakhsh, 2010; Song et al., 2018). In the study of Koplin et al. (2002), 139 streams were sampled in the United States and hormones were found in approximately 40% of them. In a study on Spanish groundwater samples (Jurado et al., 2019) for the emerging organic contaminants (EOCs), including several EDCs molecules, showed that the most of these substances are usually detected at low ng/L concentration range in the groundwater bodies. However, they are reported at concentrations >100 ng/L, consequently, it is required to set up threshold quality values, because groundwater is a valuable water resource worldwide. The animal manure applied to agricultural soils is considered to be a major source of estrogens in rural environments (Hanselman et al., 2003; Scherr et al., 2008; Adeel et al., 2017), while in urban areas, the wastewater effluents are the major source of hormones (Schlüsener and Bester, 2008). Moreover, the EDCs can interfere with the endocrine system in humans and aquatic life (Hanselman et al., 2003; Windsor et al., 2018). However, the current, three-step cleaning technologies are not able to fully eliminate these hormones from the wastewater (Kim et al., 2015).

Ethinyl estradiol (EE2) is a synthetic analogue of estradiol (E2), and is a highly potent estrogen receptor agonist (Laurenson et al., 2014). EE2 is a component in many frequently used contraceptives (Robles, 2010). The growing use of EE2 in human medicine and livestock farming has led to an increase in their occurrence in the environment, that is why EE2 was added to the European Watch List in 2018 (EC, 2018). Research has shown that EE2 is extremely resistant to the oxidation in the environment owing to the ethynyl-group in the 17-position due to the high energy of C≡C bonding (Li et al., 2013). Furthermore, EE2 showed the highest estrogenic potency in tests on fish, being 11–30 times more potent than E2 (Colman et al., 2009). Depending on the physical and chemical properties of the various soil phases, e.g. its pH, organic matter content and texture, EE2 can either be strongly bound to the soil and accumulate in the top soil layer or be moved down to deeper soil horizons and the groundwater (Tong et al., 2019).

A key process controlling the concentration, mobility, toxicity and fate of EDCs, including EE2, in the environment is their sorption on soils (Yamamoto et al., 2016). The organic matter (OM) of soils and sediments was found to be the principal factor controlling the sorption of organic compounds (Lambert, 1968). Moreover, researchers have found that the adsorption of organic compounds by soils or sediments is affected not only by the quantity of soil organic matter (SOM), but also by the chemical properties of the OM (Cornelissen et al., 2005; Jakab et al., 2018; Ping and Lou, 2019). The composition, quality and binding features of organic matter are, in turn, influenced by several environmental factors. For example, a change in the redox state of a soil can cause an alteration in microbial activity, leading to the leaching of dissolved organic carbon into surface water and causing a depletion of the labile organic carbon fraction, while more recalcitrant compounds are left behind (Kalbitz, 2001). Furthermore, in anaerobic conditions the decomposition of plant residues is slower and less complete than under aerobic conditions, leading to the accumulation of slowly decomposing organic compounds such as lipids in the residue (Sahrawat, 2003; Loffredo et al., 2016).

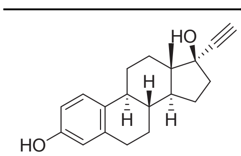
Although the sorption of EE2 has been widely studied in soils and sediments during the last decade (Bonin and Simpson, 2007; Sun et al., 2012; Mashtare et al., 2011; Li et al., 2013; Oliveira et al., 2019), the potential impact of this hormone on soils is still not fully understood, especially in environments where anaerobic conditions occur. Therefore, a series of experiments was conducted on soils having different oxidation stages with the following objectives: (i) to quantify the sorption of EE2 on the soils investigated, (ii) to reveal the intrinsic features of organic matter responsible for the differences in sorption by characterizing soil organic matter quality using FT-IR spectroscopy and (iii) to evaluate the parameters of isotherms used (Freundlich, Langmuir and Dubinin-Radushkevich) with respect to SOM quality.

2. Materials and methods

2.1. Chemicals

Standard (99%) 17α-ethynylestradiol (EE2) and fluorescence grade acetonitrile and methanol were purchased from Sigma-Aldrich. Table 1 summarizes the physico-chemical properties of EE2. The ultra-pure water was produced using ELGA labwater (resistance 18.2 Ω). The stock solutions were diluted in methanol and prepared in amber-stained borosilicate beakers. Aqueous solutions of EE2 were measured at different concentrations (ranging

Table 1
Physiochemical properties of EE2.

Chemical structure	Molecular weight (g/mol)	Water solubility (mg/l)	Octanol/Water partition coefficient ($\log k_{ow}$)	Dissociation constants (pK_a)
	296.41	9.20±0.09[a]	3.6–3.8[b]	10.4[c]

[a] Shareef et al. (2006).
[b] Zhang et al. (2010).
[c] Hurwitz and Liu(1977).

from 100 μg/L to 5000 μg/L) before instrumental analysis.

The sensitivity of a method is defined by the values of limit of detection (LOD) and limit of quantification (LOQ). The detection limit is the lowest concentration of drug in a sample which can be detected (LOD), while LOQ is the minimum quantifiable amount of analyte by the suggested method. The LOD and LOQ values were found to be 2.3 and 6.9 ng/L.

2.2. Soil sampling

Five soils were collected from different soil depths at three different locations in Ceglédbercel, Hungary (Fig. 1). The soil types of the samples were Eutric Arenosol (calcic, humic), Mollic Oxygleyic Calcic Gleysol (loamic, hyperhumic) and Eutric Calcic Histosol (haplic), respectively, according to the World Reference Base (WRB) soil classification (IUSS Working Group WRB, 2006). The soil samples were denoted as: A_20 (Arenosol sampled at 20 cm), G_20 (Gleysol sampled at 20 cm), G_40 (Gleysol sampled at 40 cm), H_20 (Histosol sampled at 20 cm) and H_80 (Histosol sampled at 80 cm). The redox potential measurements were performed using a combined Pt electrode with a reference. The electrodes were installed at depth of the soil samples by using a Pürckhauer hand auger. Eh, and pH values were recorded every 1 h for 9 months till the first frosts. Redox potential measurements were used to characterize the soils based on the duration of anoxic (Eh < 0 mV) conditions: A_20 (0% anoxic/year), G_20 (65% anoxic/year), G_40 (30% anoxic/year), H_20 (85% anoxic/year) and H_80 (100% anoxic/year).

2.3. Soil analysis

The samples were dried to constant weight at room temperature. To minimalize the effect of the particle size variation on the adsorption of EE2, the dried soil samples were passed through a 250 μm metal sieve.

The soil pH was measured in 1:2.5 soil:water and soil:1 M KCl suspensions 12 h after mixing (MSZ-08-0206/2, 1978). The organic carbon and nitrogen contents were determined using a CNS elemental analyzer (Thermo Scientific Flashsmart) (Matejovic, 1997). The $CaCO_3$ content was measured with a calcimeter using the Scheibler method (Loeppert and Suarez, 1996). The total iron content of the soils was determined by X-ray fluorescence spectroscopy (XRF) (Voglar and Lestan, 2013). The specific surface area (SSA) was calculated using the Brunaer–Emmett–Teller (BET) equation with multipoint adsorption isotherms of N_2 at 77 K (Petersen et al., 1996). These physicochemical properties are listed in Table 2.

2.4. Adsorption experiment and sorption models

The sorption of EE2 was measured at room temperature (22 ± 1 °C) using a batch equilibration method. The sorption experiment was carried out at a 1:12 soil:solution ratio for 2 h. The soil:solution ratio was set to obtain enough amount of supernatant for the filtration, because as shown in preliminary studies at least 10 mL of supernatant is needed to saturate the filter. According to the results of preliminary kinetic experiments, 2 h was sufficient to reach the equilibrium. Prior to measuring the EE2 concentration the suspensions were centrifuged at 5200 rpm for 10 min (MPW-352RH) and filtered through a 0.45 μm glass filter (Chromafil® GF/PET-45/25). Before every experiments the stock solution of EE2 was prepared in methanol with concentration of 10 mg/L. The EE2 concentrations applied were as follows: 100, 500, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500 and 5000 μg/L. To prevent the degradation of the EE2 during the batch experiment sodium-azid was added to each centrifuge tube. The measurements were done in dark under controlled temperature using 3 replicates. The 17α-ethynilestradiol concentrations were measured by HPLC (Shimadzu Prominance LC-20AR), using a fluorescence detector with an excitation wavelength of 280 nm and an emission wavelength of 310 nm. The mobile phase was a 50-50% mixture of ultra-pure water (acidified with 10 mM H_3PO_4) acetonitrile. The flow rate through the column (SunShell C18, 2.6 μm) was set at 0.5 mL/min at 40 °C. The injection volume of standards and samples was 10 μL. The amount of EE2 adsorbed on the soils was calculated using the following equation:

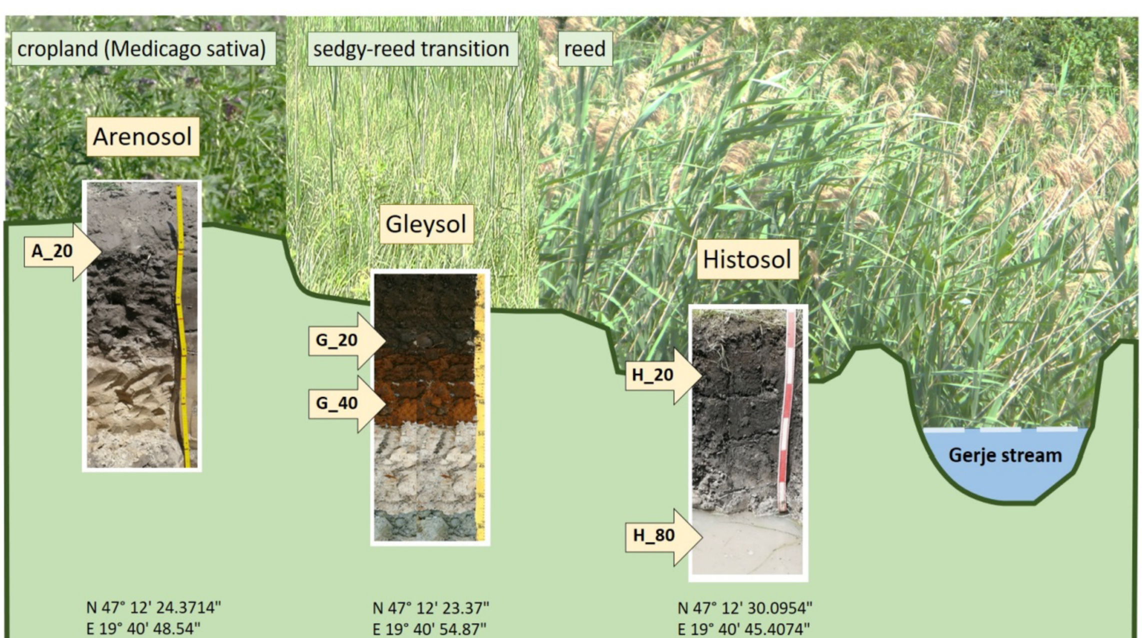


Fig. 1. The profiles and locations of the soil samples.

Table 2
Basic parameters of the soils.

Sorbent	pH (H_2O)	pH (KCl)	SOC (%)	C/N	$CaCO_3$ (%)	Fe (%)	SSA-N_2 (m^2/g)
G_40	7.5	7.3	2.9	10.3	7.2	37.2	93.6
H_80	8.4	8.1	0.25	nd	7.5	1.4	34.7
G_20	7.3	7.2	14.6	8.9	36.0	3.0	12.4
A_20	7.9	7.8	1.8	9.3	11.3	0.9	4.9
H_20	7.5	7.2	24.4	8.0	55.4	1.2	5.6

nd: not determined as the N content of the sample was below the detection limit.
G_40: Gleysol collected from 40 cm; G_20: Gleysol collected from 20 cm; H_80: Histosol collected from 80 cm; H_20: Histosol collected from 20 cm; A_20: Arenosol collected from 20 cm.

$$q = (C_0 - C_t)\frac{V}{m} \tag{1}$$

where q is the amount of EE2 adsorbed on the soil (mg/g), C_0 and C_t are the initial and final concentrations (mg/L), respectively, V is the volume of the initial solution (L), and m is the mass of the soil (g).

The Freundlich, Langmuir and Dubinin-Radushkevich models were used to describe the adsorption of EE2 on selected soils.

The Freundlich model:

$$q_e = K_F C_e^n \tag{2}$$

where qe is the amount of EE2 absorbed on the soil sample (μg/g), Kf is the Freundlich adsorption coefficient ((μg/g)/(μg/L)1/n), Ce is the equilibrium concentration of the aqueous phase (μg/L), and n is a dimensionless number which refers to the nonlinearity between the equilibrium concentration and the amount of EE2 adsorbed.

The Langmuir model:

$$q_e = Q_{max}\frac{K_L C_e}{1 + K_L C_e} \tag{3}$$

where Q_{max} is the maximum adsorption capacity (g/g) and K_L is the Langmuir fitting parameter (L/μg).

The Polanyi-based Dubinin-Raduskevich equation was applied to characterize the free energy of the adsorption:

$$q_e = q_m e^{(-\beta\varepsilon^2)} \tag{4}$$

where q_m is the theoretical saturation capacity (μg/g), β is the isotherm constant (mol^2kJ^{-2}) and ε is the Polanyi potential, which can be expressed by the formula below:

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \tag{5}$$

where R is the gas constant (8.314 kJ/mol) and T is the absolute temperature (K).

The adsorption energy (E) can be calculated from the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{6}$$

2.5. Preparation of humic acids

Humic acids (HA) were extracted from the soil samples with 0.1 M NaOH and purified using standard methods of the International Humic Substances Society (Swift, 1996). Briefly, 5 g of soil was shaken with 0.1 M HCl to remove the $CaCO_3$, followed by the extraction of humic substances with 0.1 M NaOH for 24 h, after which the solution was centrifuged, the supernatant was adjusted to a pH of 1 and 2, the solution was left to settle for a further 24 h. The precipitated HAs were then collected, washed and purified by dialysis. The remaining part of the soil sample (extracted with 0.1 M NaOH) was washed with water and dried at 60 °C; this sample contains the humin fraction (Hu) of the soil.

2.6. FTIR spectroscopy

The IR spectra of the HAs in the soils were obtained using a Bruker Vertex 70 with an ATR attachment containing a diamond crystal (Bruker Optics Ltd., Coventry, UK). The freeze-dried, powdered HA samples were measured with 64 scans and a resolution of 4 cm^{-1} between 4000 and 400 cm^{-1}. The IR spectra of the Hu (samples extracted with alkali) were measured with a Bruker Vertex 70 fitted with a diffuse reflectance attachment, again with 64 scans and a resolution of 4 cm^{-1} between 4000 and 400 cm^{-1}.

Relative absorbances (rA) were calculated by dividing the corrected peak height of a distinct peak by the sum of the heights of all peaks at 3070, 2920, 2850, 1730, 1630, 1510, 1450, 1370, 1270 and 1050 cm^{-1} and multiplying it by 100 (rA = % of the sum of all peak heights from 2920 to 1050 cm^{-1}).

The aromaticity index based on Chefetz et al. (1996) was calculated by dividing the intensity of absorption around 1620 cm^{-1} (I_{1620}) by the intensity of absorption at 2920 cm^{-1} (I_{2920}) for both HA (Ari_HA) and NaOH-treated humin samples (Ari_Hu).

2.7. Statistical analysis

Regression analysis was performed to quantify how the relative absorbance values (rA) of different samples influenced the parameters of the isotherms using Origin Pro 2018 software. To describe the relationship between two variables while controlling or adjusting the effect of one or more additional variables (e.g. SOM) a partial correlation analysis was made using SPSS 22.0 software.

3. Results and discussion

3.1. Characterization of soils and their organic fractions

The basic soil properties of the soils used in this experiment are shown in Table 2. The organic carbon content of the samples was in the order: H_20 > G_20 > G_40 > A_20 > H_80. The organic matter accumulation in the upper part of the H and G profiles is likely due to the anoxic conditions during most of the year (85 and 65%). Although the H_80 sample was formed under absolutely anoxic conditions, its organic matter content was very low (0.25%). This could be explained by the fact that this layer was formed under the root zone, thus excluding organic matter accumulation.

The specific surface area of the sorbents was in the order: G_40 > H_80 > G_20 > H_20 > A_20. Although SSA can be considered as one of the factors controlling the sorption of organic pollutants on soils (Kaiser et al., 1996; Nambu and Yonebayashi, 2000), the BET-N_2 SSA of soils is inversely related to their OC content (e.g. Kaiser et al., 1996; Rasmussen et al., 2018). Consequently, the soil sample with the highest OC content had one of the lowest SSA values (H_20: 5.6 m^2/g). It can be concluded from the Fe contents of the samples that substantial amounts of Fe-oxides may be formed in the lower part of the G profile, which may help to explain the very high SSA value of this sample (Heister, 2016).

FT-IR analysis was carried out on the HAs and Hu in adsorbent samples from different soil layers to characterize the organic matter in terms of the spectral data. The most characteristic bands in the IR spectra are presented in Table 3.

In general, the spectra of the HA samples were very similar and showed the same spectral patterns (Fig. 2). The evolution of the FTIR absorbance of humic substances was evaluated by establishing the ratios between the main absorbance peaks (Table 4).

As shown in Table 4, the band at around 3070 cm^{-1}, which could be assigned as aromatic C—H stretching vibration, differed greatly among the HA samples; those formed at lower depths, below the root zone, and under more anoxic conditions had lower relative absorbance values than those from the top soil. The bands at around 2920 cm^{-1} and 2850 cm^{-1} represent the aliphatic C—H vibrations of aliphatic methyl and methylene groups. In HA samples from H_80 and G_40, these peaks had lower intensity than in those from the upper part of the soils, probably because roots release a wide range of organic compounds, including aliphatic organic acids (Nardi et al., 2000). The 1720 cm^{-1} peak, which is characteristic of the aromatic carboxylic acids in HA samples, was low in samples with the highest OC content (G_20 and H_20) presumably due to the tendency for organic matter to retain water, leading to anaerobic conditions where oxidation is limited. A doublet in the spectrum at around 1650 cm^{-1} indicative of the aromatic C=C and carboxylate ions (Niemeyer et al., 1992) was slightly greater for the HA of aerobic samples than for hydromorphic ones, suggesting that aerated soils contain more carboxylic groups in HA molecules. This was especially true for the A_20 sample, which is under aerobic conditions throughout year.

There were no significant differences in the band at 1420 cm^{-1}, which is assigned to aromatic ring stretch COO^- of humic acids (Inbar et al., 1990; Dhillon et al., 2017). In samples G_20 and H_20 the relative absorbance of the band at around 1220 cm^{-1}, which can be assigned to phenolic-OH, was the highest, indicating organic matter accumulation. Substantial differences were found in the spectra of HA samples at around 1035 cm^{-1} (C—O vibrations of polysaccharides, carbohydrates). A significant difference was observed for the band at 1050 cm^{-1} between waterlogged and aerated samples; the HA fraction of the aerobic soil samples contained more O-alkyl structures than the hydromorphic HAs, which is in agreement with the findings of Artz et al. (2008) that the concentration of polysaccharides decreases with depths.

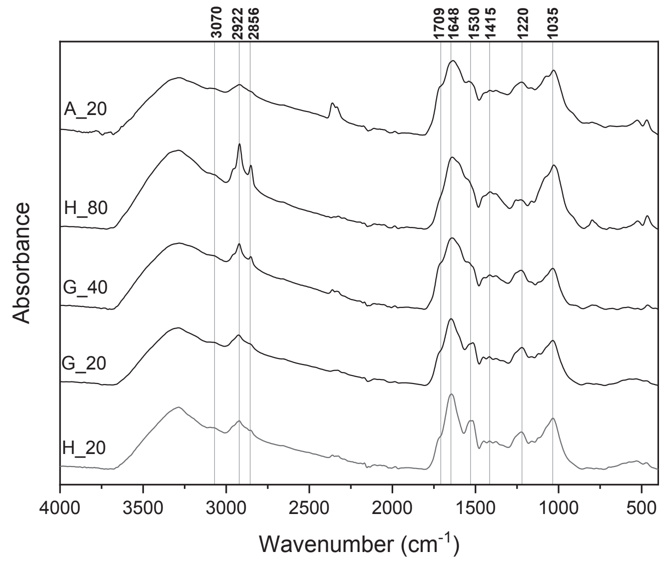


Fig. 2. FT-IR spectra of HA samples.

The aromaticity index (I_{1620}/I_{2920}, Ari), calculated from the FTIR data ranged from 5.2 to 11.3 for the extracted humic acids, while there was enormous variability for the humin fraction (Table 4). Dick et al. (2006) found a strong relationship between the aromaticity index obtained from FTIR and the ratio of aryl and alkyl C calculated from the NMR data, so Ari could be a useful tool for characterizing organic matter. Based on this evaluation it can be stated that the A_20 sample had the most aromatic HA. In the case of H_80 and A_20, the aromaticity of the humin fraction was found to be extremely high, this value was very low for G_40 and G_20. This confirmed findings suggesting that the organic carbon associated with mineral surfaces in aquifers has high aromatic carbon (Murphy et al., 1990; Fu et al., 2018).

3.2. Adsorption of EE2 on soils

Batch adsorption experiments were conducted with EE2 on soil samples with organic matter in different stages of decomposition. The adsorption isotherms for EE2 on soils collected from field sites, shown in Fig. 3, were found to be nonlinear for all the soil samples, which is consistent with other reports on the adsorption of EE2 (Bonin and Simpson, 2007; Sun et al., 2012). The sorption of EE2 increased in the order H_80 < A_20 < G_40 < H_20 < G_20.

The Freundlich, Langmuir and Dubinin-Radushkevich equations were used to fit the isotherm data (Table 5). Although the Langmuir model fitted the data best (Table 5), the Freundlich and DR parameters were also calculated for sake of comparison.

Table 3
Assignment of the principal IR absorption bands.

Absorption band (cm^{-1})	Assignment	Reference
~3070[a] (3030)	Aromatic C—H stretching	Niemeyer et al. (1992)
~2922 (2920)	Aliphatic asymmetric C—H stretching	Haberhauer et al. (1998)
~2856 (2840)	Aliphatic symmetric C—H stretching	Niemeyer et al. (1992)
~1709 (1720)	—C=O stretching in —COOH	Niemeyer et al. (1992)
~1648 (1632)	Aromatic C—C vibrations and C=O vibrations of carboxylic acid anions	Tivet et al. (2013)
~1530 (1510)	Aromatic C=C stretching	Haberhauer et al. (1998)
~1415 (1420)	O—H deformation and C—O stretching of phenolic OH	Wu et al. (2016)
~1220 (1215)	-C-O, phenolic	Niemeyer et al. (1992)
~1035 (1050)	Combination of C—O stretching and O—H deformation	Grube et al. (2006)

[a] Values measured in this study, band values found in the given reference are in parenthesis.

Table 4
Relative absorbance (%) of the sum of all selected peak heights in the FTIR spectra.

Sample	1035	1220	1415	1540	1648	1709	2858	2922	3070	Ari_HA	Ari_Hu
G_40	21.9	11.6	5.6	12.7	25.1	15.6	2.5	4.8	0.26	5.2	1.1
H_80	23.3	5.8	5.9	13.6	26.7	16.7	2.7	5.1	0.28	5.2	84.1
G_20	26.0	13.9	6.4	12.7	27,9	11.4	1.7	3.4	0.51	7.2	1.9
A_20	30.0	10.9	4.4	11.4	29,1	15.9	1.0	2.1	0.26	11.3	161.2
H_20	27.6	12.5	5.5	14.5	27,1	9.7	1.4	2.9	0.45	8.7	2.6

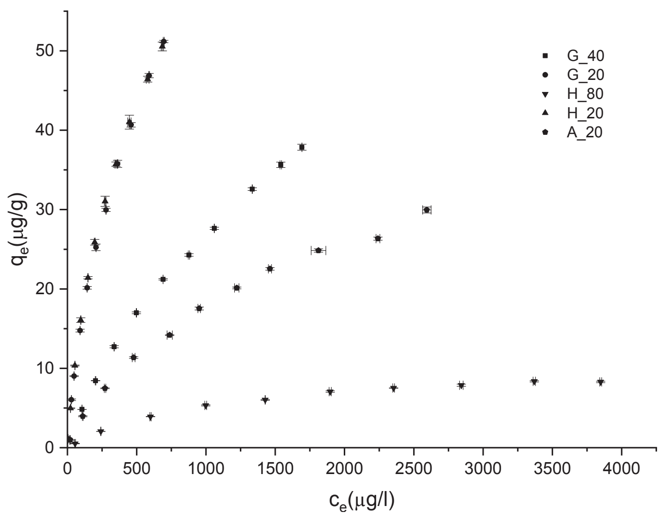


Fig. 3. Adsorption isotherms of EE2 on soils. G_40: Gleysol collected from 40 cm; G_20: Gleysol collected from 20 cm; H_80: Histosol collected from 80 cm; H_20: Histosol collected from 20 cm; A_20: Arenosol collected from 20 cm.

In the Langmuir equation Q_{max} shows the maximum adsorption capacity for EE2, while in the Freundlich model the constant K_F is an approximate indicator of the relative adsorption capacity (Dada et al., 2012). The samples showed considerable variability for Q_{max} (Table 5).

Soil organic matter is believed to be the most important component in the adsorption of hydrophobic organic pollutants (Chiou et al., 1979; Bielská et al., 2018), which explain why in this experiment the Q_{max} values ranged from 10.7 to 83.6 mg/g in the order G_20 > H_20 > G_40 > A_20 > H_80, reflecting the organic matter content of the soils. The calculated K_F values showed the same pattern as Q_{max}, indicating that the soils exhibited different sorption capacity for EE2, probably due to the different redox states, which resulted in different SOM quantity and quality. For example, the H_20 sample had the highest K_F value of 1.09, while the H_80 had the lowest, with a value of 0.22. Apart from the two soils with very high organic matter content, K_F values were comparable to those reported in the literature. Hildebrand et al. (2006) found K_F values ranging from 0.028 to 0.121, Sun et al. (2012) values of 0.064–0.144, while in the study of Ma et al. (2016) the K_F values are ranging from 0.181 to 0.316. The high K_F, and consequently the high adsorption capacity, of H_20 and G_20 was probably caused by the higher organic matter content compared to that in the studies mentioned above.

In order to compare samples with different organic matter content, it was proposed to normalize solid-water distribution coefficients to the organic carbon content of the sorbents (Chiou et al., 1979; Karickhoff, 1980). The Freundlich K_F and Langmuir Q_{max} values were organic carbon-normalised to cancel the effect of the abundance of OM (K_{OC} and Q_{OC}; Table 5). The higher the value of these normalised parameters, the higher the contribution of minerals to the adsorption of EE2 on the soils. Q_{OC} ranged from 320 to 4280 mg/g, in the order H_80 > G_40 > A_20 > G_20 > H_20, and a similar pattern was found in the case of K_{OC} (Table 5). This can be attributed to the large contribution of the mineral phase to the sorption of EE2 on H_80, G_40 and A_20. It could be expected that these samples would have greater SSA, but in fact the A_20 sample had the lowest SSA value (Table 2). This may indicate that QOC only has limited applicability for complex systems such as soils, which contain minerals and organic matter with varying quality.

The sorption isotherms were observed to be nonlinear for all the soil samples with, Freundlich n values ranging from 0.45 to 0.68 (Table 5). Sorption isotherm nonlinearity has also been reported for estrogen compounds by other researchers (Yu et al., 2004; Lai et al., 2000; Sun et al., 2012; Ma et al., 2016). For example, Sun et al. (2012) reported n values in the range of 0.73–0.90 for EE2. In the present study, the lowest n value was recorded for the H_80 sample, indicating the lowest energy of adsorption for EE2, while the n value of the G_40 sample was much closer to unity, suggesting that the sorption of EE2 by the soil increased more linearly when increasing concentrations of EE2 were added to the soil. It also showed that the adsorption of EE2 molecules on G_40 was much stronger. This was confirmed by the Langmuir K_L values and the adsorption energy calculated from the Dubinin-Radushkevich model (Table 5). Based on the dual-mode model (Pignatello, 1998), in which SOM is classified into two domains, namely, the hard and soft carbon domains, another interpretation of the Freundlich n parameter is possible. The nonlinearity of EE2 sorption on soils was attributed to the specific sorption between the functional sorbate group and the specific sorption sites of hard carbon (Li et al., 2013), because the degree of curvature of the isotherm

Table 5
Parameters of the isotherms.

Sample	Freundlich				Langmuir				Dubinin-Radushkevich	
	K_F ((μg/g)/(μg/L)1/n)	K_{OC}[a]	n	R^2	Q_{max} (g/g)	Q_{OC}[b]	K_L (10^{-3}) (L/μg)	R^2	E (kJ/mol)	R^2
A_20	0.31	17.2	0.58	0.994	45.9	2550	0.65	0.996	3.6	0.883
G_20	0.94	6.4	0.61	0.998	83.6	573	2.14	0.996	13.4	0.842
H_20	1.09	4.5	0.59	0.996	78.2	320	2.52	0.998	12.8	0.820
G_40	0.23	7.9	0.68	0.999	76.3	2631	0.56	0.998	4.4	0.891
H_80	0.22	88.0	0.45	0.969	10.7	4280	0.97	0.998	3.2	0.906

[a] K_{OC} organic carbon-normalised K_F.
[b] Q_{OC} organic carbon-normalised Q_{max}.

expressed by the value of n represents the contribution of the hard carbon domain: the smaller the n value, the greater the hard carbon contribution (Pignatello, 1998). In the present study, the smaller n value of the H_80 sample can be explained by the extremely high aromaticity of the humin fraction (Table 4), which may be correspond to the amount of the hard carbon phase.

3.3. Control of EE2 sorption mechanisms by the organic matter quality

The organic matter content was found to be the most important property of the soils with regard to the capacity and strength of sorption. However, since soils consist of many inorganic and organic compounds with various structures and properties, several mechanisms can be assumed to function during the sorption process.

The Q_{max} of the soils in this study did not always reflect the increasing organic carbon content of the soils (Fig. 4). The accessibility of binding sites in the soils to organic pollutants may be influenced by the OM of the sorbents (Chen et al., 2005; Ren et al., 2018). For example, several studies have demonstrated that the removal of soil lipid resulted in an increase in organic compound sorption, suggesting that soil lipid components may block high affinity sorption sites (Kohl and Rice, 1999; Ahangar et al., 2009). It was also reported by Mitchell and Simpson (2012) that the O-alkyl components (carbohydrates and peptides) of the organic matter block high affinity sorption sites in soil OM and decrease the sorption of organic contaminants.

Besides the blocking effect of molecules in the soil organic matter, numerous investigations have revealed that the removal of organic matter increases the external specific surface area of the soils (Burford et al., 1964; Kaiser and Guggenberger, 2003; Rabot et al., 2017). Correspondingly, organic coatings reduce the surface of the soil particles and mineral surfaces (Kaiser and Zech, 1998; Rabot et al., 2017). Thus, there may be two reasons for relative decrease in sorption capacity in the two samples with high organic matter content: (i) the large amount of organic matter may reduce EE2 binding on the surface by blocking high affinity sites, and (ii)

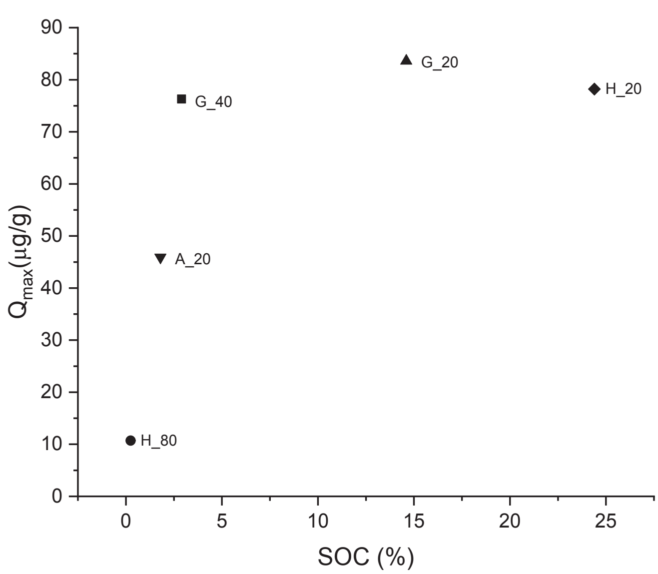


Fig. 4. Relationship between the organic carbon content of the soil (SOC) and the maximum adsorption capacity (Q_{max}). G_40: Gleysol collected from 40 cm; G_20: Gleysol collected from 20 cm; H_80: Histosol collected from 80 cm; H_20: Histosol collected from 20 cm; A_20: Arenosol collected from 20 cm.

the decrease in SSA with increasing OC content may lower the ability to adsorb EE2 molecules. In the present study, the relative content of O-alkyl compounds assessed by FTIR spectra at 1035 cm^{-1} was high for G_20 and H_20 (26.0 and 27.6, respectively), so the hypothesis of Mitchell and Simpson (2012) was confirmed.

Our own hypothesis in this research was that the binding of hydrophobic molecules such as ethinyl estradiol could be significantly affected by not only by the amount of organic matter in different degradation stages but also by its quality. Several mechanisms may be responsible for the binding of such molecules: hydrophobic interaction, π-π interaction and H-bonding. In simple system of sediments the hydrophobic interaction was found to be the main adsorption mechanism (Sun and Zhou, 2015), but in the study of Yamamoto et al. (2003) the hydrophobic interaction did not prove to be the predominant sorption mechanism. In the present study, no significant relationship was found between the quantity of alkyl compounds and any of the adsorption parameters (e.g. E, Q, K_F) suggesting that the hydrophobic interaction was not the dominant mechanism in the system investigated.

According to a previous study (Grathwohl, 1990) the sorption of EE2 will decrease with an increase in the degree of weathering of the organic matter. As the O-alkyl-C abundance can serve as a sensitive indicator of the decomposition and oxidation organic matter (Tfaily et al., 2014), the relative absorbance of humic acids at 1035 cm^{-1} (Table 3) as a proxy for the decomposition and oxidation of the soil organic matter. The data showed that the upper part of the soils had high relative amounts of O-alkyl compounds due to the enhanced microbial activity. These results contradicted Grathwohl's hypothesis, since the decomposition and oxidation of the soil organic matter increased the adsorption of EE2, especially for A_20, which had very high adsorption capacity for organic matter.

The aromatic structures of the organic matter in soils and sediments are believed to be important binding sites (Lima et al., 2012) by creating π-π bonds between the aromatic moieties of organic matter and the EE2 molecule. In the upper and well aerated region the organic matter was found to have higher aromaticity, expressed by the aromaticity index and the relative absorbance at 3070 cm^{-1} (Table 4), likely due to the abundance of plant residues with high lignin content in these profiles. The interaction between the aromatic compounds of the organic matter and EE2 molecules was demonstrated by the strong relationship between rA_{3070} and the adsorption energy of EE2 (Fig. 5). A partial correlation analysis was made to check the effect of the organic matter content of the samples, and significant correlation ($r = 0.927$) was detected. It can thus be concluded that a strong relationship exists between rA_{3070} and E.

As shown in Fig. 6, Q_{max} correlated with the amount of phenolic groups in SOM for EE2. The highest Q_{max} values were found for the G_20, H_20 and G_40 samples. This high affinity may be the result of interactions between the abundant phenolic groups in the organic matter of these soils and the phenolic group in the steroid EE2. Phenolic hydroxyl moieties are known to be active proton donors, and these can bond to EE2 molecules via intermolecular hydrogen bonds (Han et al., 2012). The strong relationship between adsorption capacity and the relative amount of phenolic groups confirms the findings of Yamamoto et al. (2003), who reported that the sorption of estrogen compounds on dissolved organic matter correlated well with the amount of phenolic groups.

In Fig. 7, a strong correlation was evident between the rA_{1709} values, which show the amount of carboxylic groups, and the energy of adsorption for EE2. Most carboxylic groups are negatively charged at the pH of the soils investigated here, and can thus significantly contribute to the sorption of cations. However, the selected endocrine disruptors with pK_as above 10 (Table 1) are

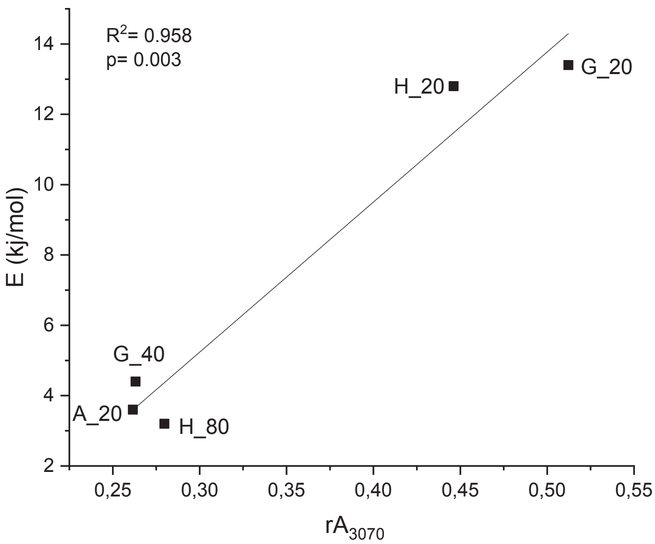


Fig. 5. Relationship between the relative absorbance of the humic acids in the samples at 3070 cm^{-1} (rA_{3070}) and the adsorption energy (E). G_40: Gleysol collected from 40 cm; G_20: Gleysol collected from 20 cm; H_80: Histosol collected from 80 cm; H_20: Histosol collected from 20 cm; A_20: Arenosol collected from 20 cm.

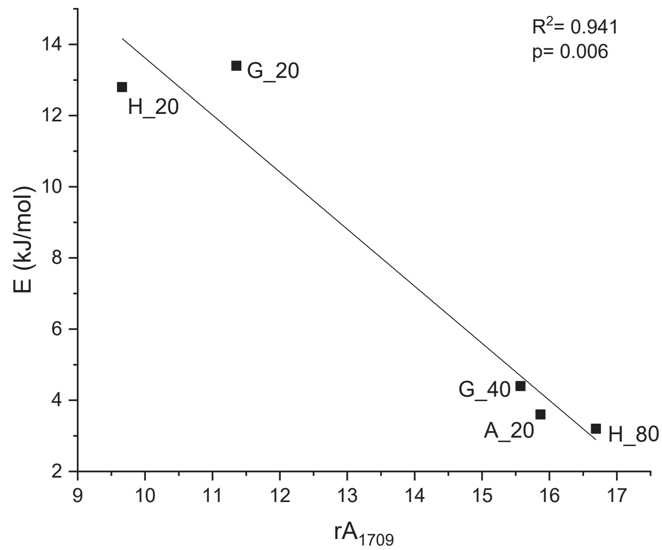


Fig. 7. Relationship between the relative absorbance of the humic acids of the samples at 1709 cm^{-1} (rA_{1709}) and the energy of adsorption (E). G_40: Gleysol collected from 40 cm; G_20: Gleysol collected from 20 cm; H_80: Histosol collected from 80 cm; H_20: Histosol collected from 20 cm; A_20: Arenosol collected from 20 cm.

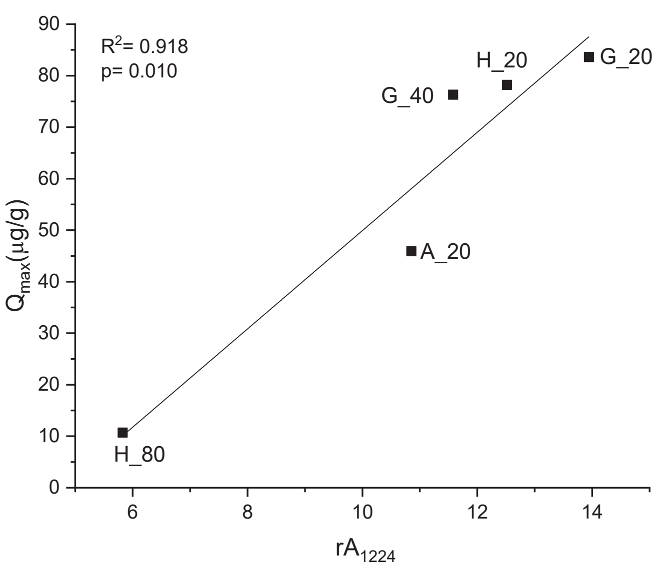


Fig. 6. Relationship between the relative absorbance of the humic acids of the samples at 1224 cm^{-1} (rA_{1224}) and maximum adsorption capacity (Q_{max}). G_40: Gleysol collected from 40 cm; G_20: Gleysol collected from 20 cm; H_80: Histosol collected from 80 cm; H_20: Histosol collected from 20 cm; A_20: Arenosol collected from 20 cm.

predominantly non-ionic at these pH values, and their charge contributions to overall sorption are small. The lowest carboxylic group concentration was found in the G_20 and H_20 samples probably due to their very high organic matter content, which has a substantial ability to retain water.

4. Conclusions

This study investigated the adsorption of EE2 on soils with organic matter in different decomposition stages and with different quality based on redox status. The oxidation state of the soils, which may influence the decomposition of organic matter, was found to be the reason for differences in the organic matter quality of the soils, which can be expressed in terms of decomposition rate and litter quality. More aromatic and phenolic compounds were found in reduced, anaerobic layers where substantial organic matter accumulation occurred. These two types of compounds resulted from the limited decomposition of lignin-rich plant residues due to the limited oxygen supply to the microbes and were found to be sites with the highest affinity for the adsorption of EE2. As a result, hydromorphic soils, in which organic matter accumulation occurred, were found to have high adsorption capacity for EE2, not only due to their high organic matter content, but also as a consequence of the chemical structures of the OM. These sorption data could be useful for predicting the ecological risks of EE2 through an understanding of its fate in soils forming under different oxidation conditions, and for application in transport and risk assessment models.

Conflicts of interest

There is no conflict of interest between any of the authors.

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