Degradation of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils by Fenton's reagent: A multivariate evaluation of the importance of soil characteristics and PAH properties

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Abstract

In this study, we investigated how the chemical degradability of polycyclic aromatic hydrocarbons (PAHs) in aged soil samples from various contaminated sites is influenced by soil characteristics and by PAH physico-chemical properties. The results were evaluated using the multivariate statistical tool, partial least squares projections to latent structures (PLS). The PAH-contaminated soil samples were characterised (by pH, conductivity, organic matter content, oxide content, particle size, specific surface area, and the time elapsed since the contamination events, i.e. age), and subjected to relatively mild, slurry-phase Fenton's reaction conditions. In general, low molecular weight PAHs were degraded to a greater extent than large, highly hydrophobic variants. Anthracene, benzo(a)pyrene, and pyrene were more susceptible to degradation than other, structurally similar, PAHs; an effect attributed to the known susceptibility of these compounds to reactions with hydroxyl radicals. The presence of organic matter and the specific surface area of the soil were clearly negatively correlated with the degradation of bi- and tri-cyclic PAHs, whereas the amount of degraded organic matter correlated positively with the degradation of PAHs with five or six fused rings. This was explained by enhanced availability of the larger PAHs, which were released from the organic matter as it degraded. Our study shows that sorption of PAHs is influenced by a combination of soil characteristics and physico-chemical properties of individual PAHs. Multivariate statistical tools have great potential for assessing the relative importance of these parameters.
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1. Introduction

There is currently great concern regarding the occurrence and fate of polycyclic aromatic hydrocarbons (PAHs), which are among the most frequently detected environmental pollutants. Formed in anthropogenic processes, especially as by-products of incomplete combustion, PAHs are present in soils in concentrations and patterns that vary greatly depending on the source of contamination. Industrial sites formerly associated with gas production, petroleum refining, and wood preservation are often highly contaminated with PAHs, and the remediation of such sites poses a great challenge. However, not all PAHs are equally difficult to degrade. The physico-chemical properties of individual PAHs differ substantially. Low molecular weight (LMW) PAHs, with two or three fused aromatic rings, have a relatively high water solubility, while high molecular weight (HMW) PAHs, with four to six fused aromatic rings, are quite hydrophobic; as manifested in log octanol–water partitioning coefficients (log K_{ow}) above 5 [1]. The latter have, consequently, a higher affinity to particles.

When contaminants are released into the ground, they become sequestered in the soil matrix. Sorption strength

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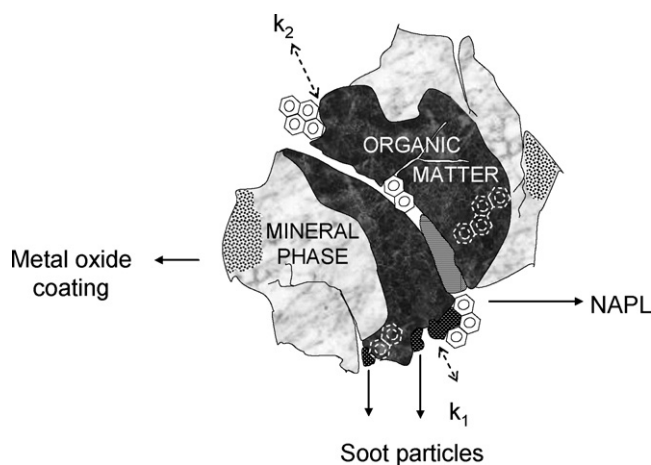*E-mail address:* sofia.jonsson@chem.umu.se (S. Jonsson).

Fig. 1. Conceptual model of a soil particle.

increases over time, which often reduces the susceptibility of the contaminants to remediation processes [2–8]. Processes known to influence the sequestration and degradability of organic pollutants have been discussed in detail in a number of review articles [9–13], and an understanding of the underlying mechanisms of contaminant sequestration is essential if effective and cost efficient remediation methods are to be developed. The notional soil particle in Fig. 1 illustrates the processes involved when the contaminants are released into soil. PAHs are efficiently adsorbed onto the surface of the soil organic matter (SOM) [14–18] and slowly start to penetrate into cavities and/or diffuse into the organic soil fraction. However, SOM is not homogenous; it consists of varying proportions of combustion residues, non-aqueous phase liquids (NAPLs), and natural organic matter (NOM), all of which vary in their affinity for contaminants. For example, PAHs are strongly adsorbed to soot carbon [19], but may also partition into humic matter [12,20], and this will affect the success of any remediation process. However, even in soils with low organic content, the availability of PAHs may be low due to entrapment in pores and voids [7,8]. The importance of the soil particle size distribution on contaminant sequestration was demonstrated by Hwang and Cutright [21], who reported that clay minerals have greater adsorption capacities than SOM. Inorganic surfaces, which consist of minerals, oxides, and metals, may also have an impact on PAH availability [2,7,14,20,22–28]. Finally, the concentration of contaminants and their physico-chemical properties have also been shown to affect the sequestration process [4,21,28–31].

From the discussions above it is clear that PAH sorption strength can only be reliably assessed using aged soils with a history of contamination. However, the disadvantage of using such soils is that soil parameters cannot easily be altered in a controlled manner. So the alternative approach used in the present study was to use several soils with different intrinsic properties, sources of pollution, and PAH composition patterns, and investigate how these affect the PAH removal efficiency in a chemical oxidation process. To fully exploit the pollutant–matrix interactions, a relatively mild Fenton treatment was adopted; which is also more relevant for future in situ applications. Most importantly, the relatively mild conditions

evade direct oxidation of contaminants adsorbed to particle surfaces [25,32], since stronger oxidation methods have shown to be less dependent on the desorption of contaminants prior to oxidation [33,34].

Fenton treatments are frequently used to oxidise contaminants in soil, sludge, and wastewaters. It utilises hydrogen peroxide as oxidant, which is decomposed to hydroxyl radicals, in the presence of ferrous sulphate:

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^- + Fe^{3+}$$

In natural systems like soils, for instance, iron and other metals are also present in the soils and may assist in generating hydroxyl radicals. Fenton-like reactions are known to occur without the addition of iron salts, thus, in our system it is reasonable to expect that both added ferrous iron and various metal ions from the test soils will take part in the hydroxyl radical generation process. This complicated the situation, which, however, could be resolved using a multivariate statistical analysis tool, partial least squares projections to latent structures (PLS). The PLS analysis also revealed correlations between soil properties, PAH sorption strength and chemical degradability and, thus, generated valuable information that may be used to guide future remediation efforts.

2. Material and methods

2.1. Soil sampling

Five Swedish industrial sites were carefully selected in order to obtain soil samples that were expected to contain multiple PAHs at varying compositions and concentrations. These consisted of a former gas works, three former wood impregnation sites, and a working coke plant (see Table 1). Ten soil samples, each 5–10 kg in weight, were transported back to the laboratory in new, solvent-washed steel containers, where they were air-dried at room temperature, passed through a 2 mm sieve, and kept at constant temperature (4 °C) prior to analysis.

2.2. Chemicals

All solvents used were of analytical or glass-distilled grade. Glassware was machine-washed with alkaline detergent and rinsed with solvent prior to usage. Hydrogen peroxide (30%) was purchased from J.T Baker (Deventer, Holland). $FeSO_4 \times 7H_2O$ (p.a.), sulphuric acid (p.a.), silica gel 60 (0.063–0.20 mm), and sodium sulphate (p.a.) were from Merck (Darmstadt, Germany). The silica gel was activated at 130 °C for 24 h and sodium sulphate at 550 °C for 48 h. Silica gel was deactivated with 10% water (w/w) prior to use. Filter papers were purchased from Munktell (Grycksbo, Sweden), and the internal (IS) and recovery (RS) standards were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). The IS consisted of $^2[H_8]$naphthalene, $^2[H_8]$acenaphthylene, $^2[H_{10}]$acenaphthene, $^2[H_{10}]$fluorene, $^2[H_{10}]$anthracene, $^2[H_{10}]$pyrene, $^2[H_{12}]$benz[a]anthracene, $^2[H_{12}]$benzo[k]fluoanthene, $^2[H_{12}]$benzo[g,h,i]perylene (31.5–41.3 ng/μl in toluene), and the RS of $^2[H_{10}]$fluoranthene

Table 1
Location of sample sites, industry characteristics and soil types

Site #	Location	Coordinates	Industry	Period of operation	Sampling depth (cm)	Soil	Observations
1	Holmsund	63°42′N, 20°21′E	Wood preservation	1943–1983	20–30	Sandy till	Black aggregated soil, strong smell of tar
2	Holmsund	63°42′N, 20°21′E	Wood preservation	1943–1983	10–20	Sandy till	Black aggregated soil, strong smell of tar
3	Holmsund	63°42′N, 20°21′E	Wood preservation	1943–1983	10–20	Sandy till	Smell of tar
4	Luleå	65°35′N, 22°09′E	Coke production	[a]	Top soil	Sediment	Black waterlogged sediment, oily film on water surface
5	Forsmo	63°16′N, 17°12′E	Wood preservation	1933–1950	2–18	Fine sand	Black aggregated well sorted sandy soil
6	Forsmo	63°16′N, 17°12′E	Wood preservation	1933–1950	0–10	Fine sand	Black aggregated well sorted sandy soil
7	Hässleholm	56°09′N, 13°46′E	Wood preservation	1946–1965	40	Coarse sand	Smell of tar
8	Hässleholm	56°09′N, 13°46′E	Wood preservation	1946–1965	40–60	Coarse sand	Smell of tar
9	Husarviken	59°21′N, 18°06′E	Gas work	1893–1972	[b]	Sand	Smell of tar
10	Husarviken	59°21′N, 18°06′E	Gas work	1893–1972	[b]	Sand	Smell of tar

[a] Facility still in operation, start unknown.
[b] Not known.

(26.6 ng/μl in toluene). The compounds were quantified using the certified 24-PAH reference standard mixture SRM 2260 (National Institute of Standards & Technology, Gaithersburg, MD, USA), containing the PAHs compiled in Table 2.

2.3. Soil characterisation

The soils were characterised according to "age", pH, conductivity, loss-on-ignition (LOI), oxide content, particle size, and specific surface area (calculated from the particle size distribution). The "age" was defined as the mid-point of the time elapsed since the contamination took place; date of start and end of activity, respectively. Conductivity was measured using soil/water slurries, and pH using slurries consisting of soil mixed with both distilled water and calcium chloride solution. To determine the LOI, which is a measure of the organic matter content in soils, 1 g samples were dried overnight at 105 °C, weighed, then baked in an oven for 6 h at 550 °C and reweighed. Total concentrations of iron, aluminium, and manganese oxides in the samples were determined following extraction with sodium citrate and sodium dithionite. Amorphous oxides were extracted with oxalate. The oxide analyses were performed using an ICP/AES instrument (Plasma 200, Perkin Elmer, Norwalk, CT, USA). Particle sizes were determined by mechanical sieving and sedimentation analyses were performed for particles smaller than 0.074 mm.

2.4. Physico-chemical properties

Data on the physico-chemical properties were obtained from articles in the international literature [1,35,36]. All physico-chemical properties are summarised in Table 3 and the values of the properties are presented in Table 4.

2.5. Soil treatment

A few pilot studies were conducted using soil number 9, which contains relatively high amounts of iron. The PAH removal when no iron salt was added was approximately 50% compared to the removal achieved with the addition of iron. It was then decided that additional iron was needed. However, in order to emphasise the influence of soil properties on the removal efficiency the soils were subjected to oxidation with Fenton's reagent under relatively mild reaction conditions. Oxidations were performed in triplicate for all samples in 250 ml glass bottles with Teflon-lined screw caps. Mixtures of 20 g of soil and 30 ml of deionised water were incubated for 1 h at 25 °C with agitation in a water bath, after which the pH was adjusted to pH 3 with 5% sulphuric acid, and the reactants added. Oxidation was initiated by adding 10 ml of 10 mM iron sulphate and 20 ml of 15% hydrogen peroxide, reaching a final peroxide concentration of 5%, and a soil to liquid (S/L) ratio of 1:3. The

Table 2
Polycyclic aromatic hydrocarbon species analyzed in this study

Two rings	Three rings	Four rings	Five rings	Six rings
Naphthalene	Biphenylene	Fluoranthene	Benzo(*b*)fluoranthene[a]	Benzo(*g,h,i*)perylene
2-Methylnaphthalene	Acenaphthylene	Pyrene	Benzo(*k*)fluoranthene[a]	Indeno(*c,d*)pyrene[a]
1-Methylnaphthalene	Acenaphthene	Chrysene[a]	Benzo(*e*)pyrene	
2,6-Dimethylnaphthalene	Fluorene	Benz(*a*)anthracene[a]	Benzo(*a*)pyrene[a]	
2,3,5-Trimethylnaphthalene	Anthracene		Perylene	
	Phenanthrene		Dibenz(*a,c*)anthracene	
	1-Methylphenanthrene			

[a] Carcinogenic PAH according to the Swedish EPA.

Table 3
Physico-chemical parameters used in PLS calculations

Descriptor	Abbreviation	Units	Calculation method	Reference
Number of rings	NOR		–	–
Number of aromatic rings	NOAR		–	–
Number of five-membered rings	5 ring		–	–
Melting point	MP	°C	–	[35]
Boiling point	BP	°C	–	[35]
Heat of vaporization	H_{vap}	kcal/mol	–	[35]
Ionisation potential (HOMO energy)	Ip	eV	AM1	[35]
Electron affinity (LUMO energy)	Ea	eV	AM1	[35]
Length/breadth ratio	L/B		–	[35]
F-number	F		–	[35]
Water solubility	$\log S_w$	mmol/l	–	[35]
Molecular volume	m.vol	cm^3/mol	–	[35]
Total surface area	TSA	$Å^2$	–	[1]
Octanol/water partition coefficient	$\log K_{ow}$	atm m^3/mol	–	[35,1]
Octanol/carbon partition coefficient	$\log K_{oc}$		–	[35,36]
Solvent accessible area	Area	$Å^2$	QSAR	[35]
Solvent accessible volume	Vol	$Å^3$	QSAR	[35]
Refractivity	Ref		QSAR	[35]
Polarisability	Pol		QSAR	[35]
Molecular weight	Mw	g/mol	QSAR	[35]

slurries were agitated in a water bath for 24 h, after which the reaction was terminated by adding five drops of concentrated H_2SO_4 (pH < 1), as this has shown to markedly lower the reaction rate of Fenton's reagent due to minimal decomposition of H_2O_2 at pH < 2. [37].

2.6. Extraction and sample clean up

Extraction and clean up of PAHs were performed simultaneously, using a modification of a previously described in-cell clean up method [38] based on pressurised liquid extraction (PLE) with adsorbent packed extraction cells. The extraction was performed using a Dionex ASE 200 (Sunnyvale, CA, USA), equipped with 11 ml stainless steel extraction cells. All extractions were performed at 14 MPa and 150 °C, with 7 min of dynamic extraction, two static cycles of 5 min each, one cell volume for rinsing, and a purge time of 60 s.

The PLE extraction cells were packed as follows: a cellulose filter to prevent clogging of the metal frit at the outlet of the cell, 4 g of silica gel (deactivated with 10% water, w/w), a second cellulose filter placed on top of the silica, to which 50 μl internal standard (IS) was added, followed by 1 g of a soil/Na$_2$SO$_4$ homogenate (1:9, w/w). The cell was topped with sodium sulphate and extracted with *n*-hexane/dichloromethane (9:1, v/v). Extracts were reconstituted in 1 ml of toluene under a gentle stream of nitrogen and finally, 50 μl recovery standard (RS) was added to each sample.

2.7. Instrumental analysis

All samples were analysed using a Fisons GC 8000 Top gas chromatograph (GC) coupled to an electron impact (EI), Fisons MD800, low resolution mass spectrometer (LRMS). One microlitre aliquots were splitless injected (250 °C) into the GC by an auto injector. Helium was used as the carrier gas at a head pressure of 14 psi. The GC column temperature program was as follows: 2 min at 80 °C, 8 °C/min up to 300 °C, and 10 min at 300 °C. The 24 target compounds were separated on a 30-m DB-5 capillary column (25 mm × 0.25 μm, J&W Scientific/Agilent Technologies, Folsom, CA, USA) and identified by mass spectrometry using relative retention time comparisons with reference standards. The MS was operated in splitless mode and data were collected in full scan mode for identification and single ion monitoring (SIM) mode for quantification. PAH concentrations in samples were determined by comparing peak area ratios of the target compounds in samples and in reference standard, by using the internal standard technique. The concentrations in the soils prior to and after oxidation were used for calculating the degradation efficiencies.

2.8. Statistical evaluation

Partial least squares projections to latent structures (PLS) is a multivariate regression technique capable of handling both large data matrices and in contrast to traditional methods, noisy and missing data [39]. Briefly, PLS considers two matrices simultaneously, a descriptor matrix *X* (here, physico-chemical parameters or soil characteristics) and a response matrix, *Y* (here, degradation efficiency). Separate PLS components for the *X* and *Y* matrices are calculated, and these indicate the systematic variation in the matrices and the relationships between them.

Two PLS models were calculated to evaluate factors influence on the degradation efficiency. The factors investigated were (a) physico-chemical properties of the PAHs and (b) soil characteristics. In PLS model one, the degradation efficiency was calculated for all of the 24 determined PAHs in each soil sample. The mean values for the 24 PAHs in the 10 soil samples were then used as the response data. The data were pre-processed by means of auto-scaling and mean centring prior to the PLS calculations,

Table 4
PAH property values

PAH	NOR	NOAR	5 ring	HOMO	LUMO	Ip-homo	Ea-lumo	MP	BP	Hvap	L/B	F	log Sw	m.vol.	TSA	log Kow	log Koc	Area	Vol	Ref	Pol	Mw
Naphthalene	2	2	0	24	25	-8,711	-0,265	81	218	43,2	1,2	5	0,24	148	193,5	3,4	3,11	313,1	455	42,5	17,7	128,2
2-Methylnaphthalene	2	2	0	27	28	-8,620	-0,246	35	241	45,3		6	0,18	149,7	176,6	3,99	3,64	341,8	506,9	47,6	19,5	142,2
1- Methylnaphthalene	2	2	0	27	28	-8,584	-0,267	-22	245	54,8		6	0,2	154,4	173,3	3,97	3,36	335,8	500	47,6	19,5	142,2
Biphenylene	3	2	0	28	29	-8,443	-0,437	71	255	48		6	0,062	184,6	196,4	3,96	3,27	351,5	517,6	50,3	19,3	152,2
2-6-Dimethylnaphthalene	2	2	0	30	31	-8,531	-0,218	110	262			7	0,01	199	198,1	4,34		370,5	558,7	52,6	21,4	156,2
Acenaphthylene	3	2	1	28	29	-8,943	-0,936	95	270	50,4	1,1	6	0,04		182	3,95	3,83	337,6	503,2	51,9	20,4	152,2
Acenaphthene	3	2	1	29	30	-8,495	-0,021	96,2	279	51,1	1,1	6	0,029	173	177,9	4,04	3,79	346,5	519,5	50,8	20,6	154,2
2-3-5-Tri methylnaphthalene	2	2	0																			170,3
Fluorene	3	2	1	31	32	-8,711	-0,219	116	294	58,2	1,6	7	0,012	188	193,8	4,22	3,7	367,7	554,6	54,9	21,2	166,2
Phenanthrene	3	3	0	33	34	-8,617	-0,408	101	338	52,7	1,5	7	0,0072	199	271	4,5	4,28	374,6	573,5	59	25	178,2
Anthracene	3	3	0	33	34	-8,123	-0,840	216	340	52,4	1,6	7	0,00037	197	244,7	4,46	4,27	381,6	580,2	59	25	178,2
1- Methylphenanthrene	3	3	0			-8,533	-0,404	123	359		1,5	8	0,0014		217	5,14		397,3	618,3	64	26,8	192,3
Fluoranthene	4	3	1	37	38	-8,631	-0,929	109	383	66,5	1,2	8	0,0013	271	218,2	5,2	4,62	402,1	625,4	66,7	28,8	202,3
Pyrene	4	4	0	38	39	-8,885	-0,243	150	393	65,8	1,3	8	0,00072	241	261,5	5,06	4,66	392,9	612,9	66,7	28,8	202,3
Benzo[a]anthracene	4	4	0	42	43	-8,206	-0,813	161	425	65,6	1,6	9	6,8E-05		244,3	5,82	5,3	442,8	698,7	75,4	32,2	228,3
Chrysene	4	4	0	42	43	-8,371	-0,675	254	431	65,8	1,7	9	1,3E-05	251	207,4	5,81	5,37	436,6	691,7	75,4	32,2	228,3
Benzo[b]fluoranthene	5	4	1	46	47	-8,567	-0,965	168	481		1,4	10	3,1E-05	268,9	260,8	6,29	5,89	464,9	744,1	83,2	36	252,3
Benzo[k]fluoranthene	5	4	1	46	47	-8,300	-0,909	271	481		1,5	10	0,0036	268,9	265	6,59	5,89	468,6	749,8	83,2	36	252,3
Benzo[e]pyrene	5	5	0	46	47	-8,219	-0,855	179	493	70,8	1,1	10	2,5E-05	263	227,8	6,92	5,71	448,5	724,3	83,2	36	252,3
Benzo[a]pyrene	5	5	0	46	47	-7,922	-1,111	178	496	71,1	1,5	10	1,5E-05	263	255,8	6,3	5,71	454	731,3	83,2	36	252,3
Perylene	5	5	0	46	47	-7,858	-1,156	278	497	71,3	1,3	10	1,2E-05	263	251,5	6,12	5,89	448	724,4	83,2	36	252,3
Dibenz[a,h]anthracene	5	5	0	51	52	-8,283	-0,797	206	535	75,2	1,2	11	8,2E-05	300		7,16		499,7	809,8	91,9	39,5	278,4
Indeno[cd]pyrene	6	5	1	50	51	-8,137	-1,283	164	536		1,4	11				6,14		481,8	783,6	90,9	39,8	276,3
Benzo[ghi]perylene	6	6	0	50	51	-8,024	-1,065	278	542	75,8	1,1	11	2,0E-05	277	266,9	7		465,9	763,7	90,9	39,8	276,3

Table 5
Characteristics of soil samples included in this study

Soil characteristic	Soil sample									
	1	2	3	4	5	6	7	8	9	10
Age (years)	40	40	40	–	62	62	48	48	71	71
Clay (%)	0.00	0.30	0.20	0.40	0.00	0.00	0.00	0.00	0.20	[a]
Silt (%)	5.6	4.9	7.4	15	4.8	36	3.7	0.1	7.6	[a]
Sand (%)	94	95	92	85	95	64	96	>99	92	[a]
Spec surface (m^2/m^3 soil)	1100	1100	1200	1600	1000	2600	980	800	1200	[a]
LOI (%)	9.8	6.9	2.7	13	2.6	13	6.8	2.2	19	12
pH (H_2O)	6.9	7.2	7.5	11	7.9	7.6	7.2	7.5	7.8	[a]
pH ($CaCl_2$)	6.9	7.5	5.1	11	4.8	4.7	6.6	6.7	7.1	[a]
Cond (mV)	5.0	−11	−30	−230	−98	30	−12	−28	−50	[a]
Al CD (g/kg)	0.40	[a]	[a]	0.50	0.20	1.8	0.40	0.10	0.60	[a]
Al Ox (g/kg)	0.50	[a]	[a]	1.1	0.17	2.0	0.46	0.24	1.4	[a]
Fe CD (g/kg)	2.0	[a]	[a]	15	1.2	5.3	7.4	0.60	23	[a]
Fe Ox (g/kg)	1.1	[a]	[a]	6.3	0.44	4.2	4.3	0.18	18	[a]
Mn CD (g/kg)	0.10	[a]	[a]	0.20	0.00	0.10	0.70	0.00	0.20	[a]
Mn Ox (g/kg)	0.05	[a]	[a]	0.00	0.00	0.08	0.34	0.00	0.09	[a]

[a] Not analysed.

and some data were also log-transformed in order to achieve a better approximation to a normal distribution. The number of significant components was confirmed by cross-validation [40]. All calculations were performed using the multivariate statistics software *Simca* 10.0 (Umetrics AB, Umeå, Sweden).

3. Results and discussion

3.1. Soil characterisation

The soil samples originated from sites representing three types of industrial activities, i.e. wood impregnation (samples 1–3 and 5–8), coke production (sample 4) and gas works (samples 9 and 10), and their characteristics are listed in Table 5. The mean of the time since the contaminating activity started and stopped, referred to for convenience as the 'age' of the soil, ranged from 40 to 71 years. All soil samples contained very low percentages of clay (0.0–0.4%), so the specific surface area (spec_surface) was mainly determined by the sand and silt contents of the soils. The organic matter content (measured as LOI)

varied greatly between the samples, ranging from 2.2 to 19%. The pH measurements of the soils, in distilled water and calcium chloride solutions, gave similar results. Lime had been used at site 4, resulting in the corresponding soil sample having a pH of 11, and this is also the most likely the reason for the high conductivity (cond) measured in this sample. Manganese oxides and chlorides (MnOx/CD) were not present to a large extent in any of the soil samples. The highest iron oxide (FeOx) and chloride (FeCD) contents were found in sample 9 (18 and 23 g/kg, respectively), and sample 6 contained the highest aluminium oxide (AlOx) and chloride (AlCD) content, 2.0 and 1.8 g/kg, respectively (Table 5).

3.2. PAH concentrations and profiles

The soil samples were collected both from "hot spots" and from areas presumed to be less contaminated, in order to obtain soil samples with varying degrees of contamination and contaminant profiles. The total PAH concentrations and the PAH profiles in the soil samples before oxidation are shown in Table 6. The

Table 6
Soil PAH concentrations and standard deviations (based on triplicate measurements) and relative abundance of two to six ring PAHs before treatment with Fenton's reagent

Soil sample	Concentration of PAHs before oxidation[a] (mg/kg ± S.D.)	Ring distribution (%)				
		Two rings	Three rings	Four rings	Five rings	Six rings
1	1300 ± 42	0.18	3.7	62	31	3.1
2	7300 ± 220	1.1	25	66	6.7	0.92
3	1700 ± 92	0.34	11	80	8.2	1.1
4	440 ± 53	4.1	33	35	20	7.5
5	1800 ± 290	1.4	11	76	9.4	1.8
6	3400 ± 550	0.55	5.4	76	14	3.4
7	690 ± 250	0.04	6.6	32	52	9.6
8	1300 ± 160	0.58	11	74	12	2.3
9	90 ± 34	0.58	21	41	28	9.4
10	1600 ± 100	0.62	32	42	18	7.0

[a] Napthalene, 2-methylnaphthalene, 1-methylnaphene, biphenyl, and acenapthylene excluded, due to low recoveries.

total PAH concentrations (i.e. the sum of all 24 PAHs) ranged from 90 to 7300 mg/kg. We found that the soil samples from wood impregnation sites principally contained PAHs with two to four fused aromatic rings (>80%), those with four rings predominating (>60%). Considering that wood impregnation sites have previously been observed to be dominated by LMW PAHs [15], soil samples 1 and especially 7, both from wood impregnation sites, contained higher concentrations of HMW PAHs than expected.

Weathered soils originating from gas works and coke production sites are generally characterised by relatively high concentrations of HMW PAHs [41,42], and the soil samples of this type (4, 9 and 10) did indeed contain larger proportions of HMW PAHs with five or six fused rings. Coke production was still in operation at the time of sampling (sample 4), so the relatively even distribution of PAHs with between two and six rings in this sample may reflect this more recent contamination. Earlier studies have reported a depletion of LMW PAHs over time due to environmental processes such as evaporation, oxidation and biological degradation [17,42,43].

3.3. Efficiency of PAH degradation

It has been shown in previous studies that PAHs may be directly oxidised from a sorbed state under strong oxidizing conditions [35]. Therefore, in order to be able to reveal the parameters influence on the PAH sequestration in various soils, the soil samples in this study were subjected to a relatively mild Fenton treatment. Previous studies performed on dissolved PAHs in the liquid phase indicates that desorbed PAHs are quickly oxidised [34]. The mean PAH concentrations in the soil prior to and after oxidation were therefore used to calculate the degradation efficiencies (the percentage of PAHs degraded during the treatment). Degradation efficiencies in the 10 soils, for PAHs consisting of two to six rings, are listed in Table 7. The treatments resulted in low overall degradation efficiency (0–43%). However, the degradation efficiency was generally higher for low molecular weight PAHs. Up to 89 and 59% degradation was observed for PAHs with two and three rings,

respectively, whereas for PAHs with four, five, and six rings the corresponding figures varied between zero and 38%. Thus, as a result of the higher degradation efficiency for LMW PAHs, the relative proportions of HMW PAHs were greater after Fenton's treatment.

3.4. Multivariate evaluation of PAH degradation

3.4.1. The influence of physico-chemical parameters and semi-empirical descriptors on the degradation efficiency

The relationships between the 20 physico-chemical properties of the PAHs (Table 4) and the degradation efficiency were evaluated with PLS. As response data the mean values for individual PAHs in the 10 soil samples were used. Fig. 2 shows the score and loading plots for the PLS calculations, from which two principal components (PCs) were calculated.

From the score plot it is evident that molecular size is strongly influencing the PAH removal efficiency. PAHs consisting of two and three rings have high principal component one (PC1) scores, and are situated to the right in the score plot, while those with five and six rings have low PC1 scores, and are located to the left. Judging by the appearance of the corresponding loading plot, the PAH availability is the key parameter affecting the PAH removal. Parameters reflecting size (e.g. M_w and TSA) and hydrophobicity (e.g. log K_{ow}) are found to the left, and are negatively correlated with PAHs that were removed to a large extend, while water solubility is found to the right and is, thus, positively correlated to the same.

The second PC of the loading plot indicate that the PAH reactivity is the second most important factor for the PAH removal efficiency. The ionisation potential (Ip-homo), which is a good measure of the PAH reactivity and the electron affinity (Ea-lumo) are both positively correlated with the Fenton removal efficiency (as they all appear in the upper part of the plot).

Thus, the PAH removal efficiency appears to be favoured by increasing water solubility (log S_w) and, to a lesser extend by increasing reactivity, but strongly impeded by a high hydrophobicity. This may be interpret as the desorption of PAHs from the soil particles, at least in most cases, is the rate limiting

Table 7

Degradation of PAHs with between two and six rings with Fenton's reagent and standard deviation in total degradation

Soil sample	Degradation (%)						S.D. (%)
	Two rings[a]	Three rings	Four rings	Five rings	Six rings	Total[a]	
1	20	30	2.2	38	33	25	14[b,c]
2	54	24	8.7	27	23	27	6.6
3	63	59	32	35	25	43	1.5
4	18	31	9.9	13	2.6	15	37[c]
5	72	47	13	19	0.5	30	9.7
6	29	27	13	21	21	22	24[c]
7	0	30	7.7	5.5	10	11	20[c]
8	89	56	15	27	25	42	12
9	13	12	9.2	10	0	8.8	48[c]
10	47	36	12	9.4	7.9	22	13

[a] Napthalene, 2-methylnaphthalene, 1-methylnaphene, biphenyl, and acenapthylene excluded, due to low recoveries.

[b] One triplicate excluded due to low recoveries.

[c] Total degradation not statistically significant ($p = 0.1$, one-tailed t-test) from start concentration.
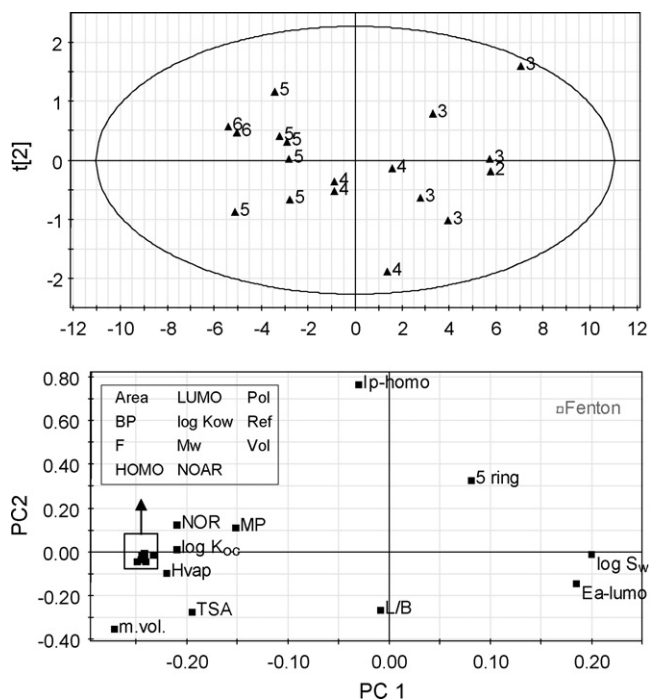
Fig. 2. Score (upper) and loading (lower) plots of PC1 and PC2, showing the influence of PAH physico-chemical properties on chemical degradability with Fenton's reagent. Mean degradation efficiencies of the 24 PAHs in the 10 soil samples were used as response data. 2,3,5-Trimethylnaphthalene was excluded from the model since data for this compound were missing in more than 60% of the cases. The PLS calculations resulted in two principal components, explaining 81% of the variation in the data and a predictability (Q^2) of 56%.

step; which makes sense as hydroxyl radicals are known to react with aromatic compounds at rates approaching the diffusion controlled limit [44]. However, there were some exceptions to this; for example, oxidation of benzo(a)pyrene and perylene (five rings) was considerably greater than for other structurally similar PAHs (see Fig. 3). These compounds possess higher ionisation potential (Ip-homo) than other PAHs with five rings, so their higher rates of degradation can be explained by their higher chemical reactivity [45]. In fact, benzo(a)pyrene and perylene were more efficiently removed than some PAHs with considerably lower log K_{ow} values. Further, although phenanthrene and anthracene are structurally similar and possess similar log K_{ow} values anthracene was degraded to a greater extent (37%) than phenanthrene (23%) [43,46], which might be explained by the fact that anthracene possesses a linear configuration (as opposed to phenanthrenes angular configuration) and higher ionisation potential (and higher reactivity towards hydroxyl radicals) [45]. Finally, acenaphthene, which combines the lowest log K_{ow} value (Fig. 3) with a high electron affinity, was the most efficiently degraded of the PAHs included in the study.

The results of the PLS analyses clearly shows that the PAHs were primarily oxidised in solution and not in the sorbed state, which have been shown to dominate under aggressive Fenton treatments [28], and supports our previous suggestion that oxidation under relatively mild conditions is more dependent on desorption than on the reactivity of the individual PAHs [25].
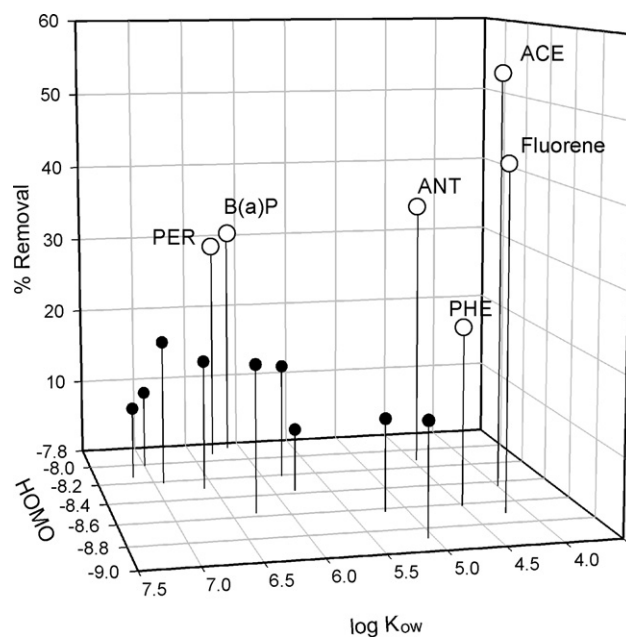

Fig. 3. Influence of log K_{ow} and HOMO energy (Ip-homo) values on the removal of PAHs (in 10 soils) following Fenton treatment. PAHs that are discussed in the text for their remarkably high removal efficiency are indicated by open circles. *Abbreviations*: PER, perylene; B(a)P, benzo(a)pyrene; ANT, anthracene; PHE, phenanthrene; ACE, acenaphthene.

3.4.2. The influence of soil characteristics on chemical degradation

The PLS loading plot (Fig. 4) shows the relationship between degradability of PAHs consisting of two to six rings and different soil parameters. Organic matter (measured as LOI) was the parameter with the strongest influence on the degradability of the PAHs; the degradability decreased as the LOI increased. This may be explained by increased competition for hydroxyl radicals. In many cases the hydroxy radicals are simply consumed by SOM before they had a chance to react with PAHs.

The organic matter content of the soils did, however, have a larger influence on the degradability of the LMW PAHs than on the degradability of the HMW PAHs. This may result from partial dissolution of the relatively water-soluble LMW PAHs, which would increase their susceptibility to oxidation by hydroxyl radicals. A higher organic matter content would favour partition of the LMW PAHs into soils, while the HMW PAHs, being poorly soluble in water and highly hydrophobic, will be strongly sorbed to the soil, even if the organic content is low. We infer, therefore, that the organic matter content of the soil has a greater impact on the degradability of LMW PAHs than of the HMW PAHs.

The degradability of the HMW PAHs (Fig. 5) was, on the other hand, more affected by the amount of degraded soil organic matter (%L LOI). This may be attributed to the non-specific nature of the Fenton oxidation process, which results in degradation of soil organic matter [47,48] and release and degradation of strongly sorbed HMW PAHs.

The specific surface area and the metal oxide content of the soil also showed some negative correlation with the degradation of the PAHs. The lack of positive correlation between FeOx and
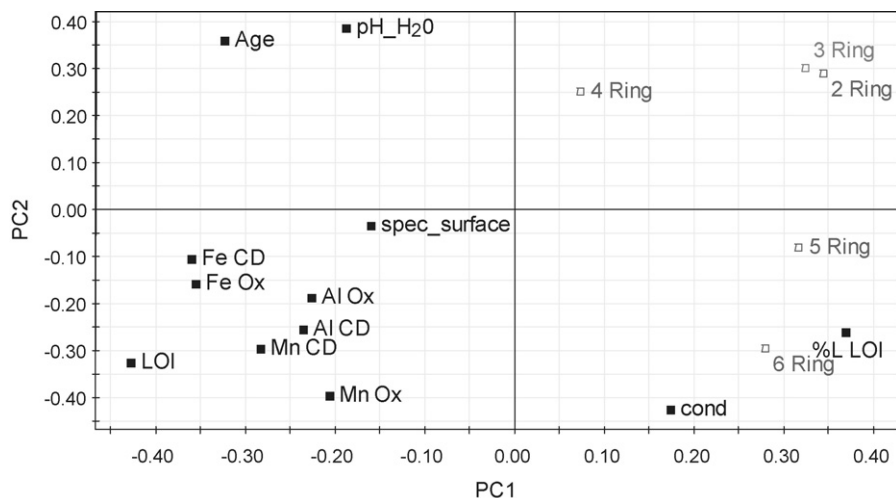
Fig. 4. PLS calculations of the influence of different soil characteristics on PAH degradation efficiency with Fenton's reagent. Soil sample 10 was excluded since data for this compound were missing in more than 60% of the cases. The PLS calculations resulted in two principal components, explaining 81% of the variation in the data and a predictability (Q^2) of 24%.
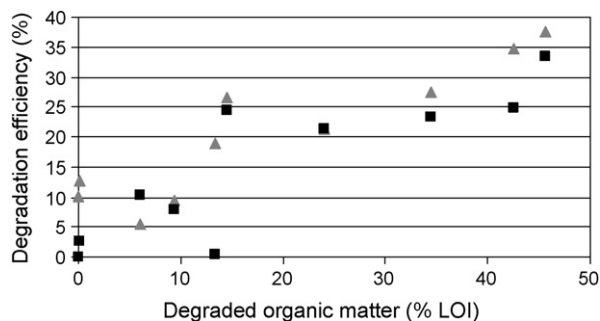

Fig. 5. Correlation between degradation of PAHs consisting of five (▲) and six (■) rings and degraded organic matter (% LOI).

Fenton treatment indicates that added ferrous ions were more important for the hydroxyl ion generation process than metal ions leaching out of the soil; which has previously been suggested to be of importance in modified Fenton systems [23–25].

Finally, the age of the contamination was negatively correlated to the PAH removal efficiency, and it appears to influence HMW PAHs more than LMW PAHs. This might be attributed to the lower diffusivity of the former, which would then take longer to penetrate the soil aggregates and particles than the LMW PAHs. Recently deposited HMW PAHs would then be relatively more accessible than earlier deposited PAHs.

4. Conclusions

This study shows that the efficiency of the chemical oxidation of PAHs in soils depends on a complex interplay of factors, including the properties of the specific PAHs present and the soil characteristics. Smaller PAHs with relatively high water solubilities, and PAHs with particularly high reactivity (and high ionisation potential), are most susceptible to chemical oxidation. Over time, the PAH composition is generally displaced towards HMW PAHs as a result of more extensive degradation of the smaller PAHs. The measured soil characteristics were found to affect the availability of the each type of PAH to different degrees. The organic matter content, oxide content and specific surface area all had a greater negative impact on the degradation of LMW PAHs, whereas the age of the contamination and pH were more negatively correlated to the degradation efficiency of PAHs with five or six fused rings. The degraded organic matter content was clearly positively correlated with degradation of large PAHs, indicating that they are released and degraded upon oxidation of the soil organic matter.

Despite the relatively low amounts of degradation observed, the use of multivariate statistics enabled us to evaluate a relatively complex dataset and draw general conclusions about the parameters affecting the degradation of PAHs in soils.

Our results indicate that coarse soils with a high percentage of LMW PAHs, low organic matter content and low percentages of iron aluminium and manganese oxides and chlorides are suitable for Fenton's treatments; especially if the soils were recently contaminated. Pilot studies are however still recommended to ensure sufficient treatment efficiency. These should also include analysis of potential by-produces, such as carbonyls, diol- and epoxy-PAHs to ensure that these are not formed to any major extend.

Future researches are however still recommended to further explore the factors of importance for the treatment success. It may, for instance, target the contaminant sequestration process and therefore include a more detailed characterisation of the soil organic matter.

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