



Low temperature oxidation of a coking plant soil organic matter and its major constituents: An experimental approach to simulate a long term evolution

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ABSTRACT

In contaminated soils, several natural processes (biodegradation, oxidation, etc.) can induce degradation of organic pollutants. The aim of this work was to evaluate the impact of an abiotic low-temperature oxidation on a coking plant soil and its main organic constituents (coal, coke, coal tar and road asphalts) in order to understand its long term evolution. This natural process was experimentally reproduced by oxidizing the soil and isolated organic matrices at 100 °C during 180 days. The samples were analyzed by total organic carbon measurements and elemental analyses, and the solvent-extractable organic matter was quantified by GC–MS (gas chromatography–mass spectrometry). Oxidation experiments on coal, coal tar and coking plant soil samples lead to the decrease in polycyclic aromatic hydrocarbon (PAH) concentrations correlated to an incorporation of oxygen evidenced by the production of oxygenated PAHs. The increasing amount of polar macromolecules and the decrease in solvent-extractable organic matter suggest a molecular growth through ether/ester cross-linking. The chemical environment of organic compounds and the presence of a reactive mineral fraction are important parameters that improve the efficiency of oxidation. This work reveals that abiotic low temperature oxidation, can strongly contribute to pollutant removal especially by a stabilization process and should be considered in the long term evolution of a soil.

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1. Introduction

Many organic components such as coke, coal tar, coal, road asphalts and, in a lesser extent, natural organic matter are the major constituents of coking plant soils that can contain up to 20% of organic carbon. Organic matter is known to be reactive toward organic and metallic contaminants [1–3]. It acts as a source of micropollutants, mainly polycyclic aromatic hydrocarbons (PAHs), and can trap, temporarily or not, organic and metallic pollutants through sorption processes. The composition and the reactivity of organic matter evolve through time via weathering processes that can modify the fate of contaminants in soils. These weathering processes play a major role for natural attenuation. According to USEPA [4], it is the result of several “physical, chemical and biological processes that, under favorable conditions, act without human intervention, to reduce the mass, toxicity, mobility, volume or concentration of contaminants in soils or groundwater”. It includes oxidation, biodegradation and water leaching occurring simultaneously in soils on long time scales.

Among the different processes involved in natural attenuation occurring in contaminated soils, biodegradation [5–7] as well as

water leaching [6,8] are largely studied whereas no work deals with the natural abiotic air oxidation of organic matter in polluted soils. Studies dealing with low temperature oxidation and weathering of soils or sediments mainly focused on coals in the 80s to evaluate the alteration of their heating values [9–12]. The authors evidenced mainly an oxygen incorporation with the formation of ketones, carboxylic acids and/or alcohols. Some authors proposed oxidation pathways to explain their observations. For example, Rhoads et al. [13] suggest that the oxidation of methylene bridges linking aromatic units (Ar–CH₂–Ar) results in the formation of Ar–(CO)–Ar groups. Tognotti et al. [14] proposed more detailed pathways for aliphatic and aromatic structures oxidation involving radical reaction, based on the observation of the FTIR spectra of coal samples and their pyridine extracts.

In the late 90s, some works focused on the oxidation of sedimentary rocks to study the evolution of their properties as natural barriers in waste storage [15,16]. The authors show that the oxidation of immature organic matter lead to an increase in polar compounds and incorporation of oxygen in the kerogen structure, leading to a partial breakdown of organic matter and a production of polar and saturated hydrocarbons.

In the last decade, studies dealing with oxidation of contaminated soils mainly concentrated on the development of a new remediation technology mediated by chemical oxidizers such as hydroxyl radical, ozone and Fenton reagent [17–22]. But finally, few

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are known on the effect of low temperature oxidation or weathering of contaminated soils.

In order to study the long term behavior of organic matter during oxidation, natural series of samples can be collected [9,11,23] but the difficulty to obtain complete series of increasing oxidation degrees or homogeneous samples limits this field approach. Furthermore, oxidation by-products (especially oxygenated compounds) may have migrated and can be partially removed in the natural samples. In order to circumvent these difficulties, experimental simulations are carried out at laboratory scale allowing to work at higher temperature in order to accelerate the kinetics of oxidation reactions [10,13,24] and also to recover the generated compounds. Different experimental studies have suggested that temperatures lower than 130 °C in ventilated oven and especially those close to 100 °C were able to simulate the reactions occurring during natural oxidation [15,16,24].

The aim of this work was to evaluate the impact of abiotic oxidation in the natural evolution of a contaminated soil and focused on the decrease of micropollutant content and the formation of byproducts. Oxidation was simulated experimentally following the protocol proposed by Faure et al. [16]. Since the organic fraction of such soils presents a high complexity and contains several constituents such as coal-tar, coal, asphalts and coke, the experiments were performed on a contaminated soil but also on its isolated organic constituents and model molecules. The transformations induced by air oxidation are discussed based on elemental, molecular and spectroscopic analysis. This approach at different scales (from the isolated molecules to the soil organic matter) allows (i) distinguishing the specific response of isolated constituents, (ii) evaluating their possible interactions (iii) identifying the role of mineral phases in the case of the soil

2. Experimental

2.1. Soil and isolated matrices

Isolated matrices used in the oxidation experiments were a coke and a coal tar (from the Marienau Pyrolysis Center, France), a type III coal (Merlebach, France) and a fresh road asphalt (Nancy). The coking plant soil was sampled in a former coking plant site in Homécourt (Lorraine, France). The physico-chemical parameters of the coking plant soil are described in [25].

Coal and coke samples were crushed to 40 µm and the coking plant soil sample was crushed to 500 µm. The coal tar was previously spread out on silica (4%) in order to increase the surface contact with air oxygen. Because of the occurrence of mineral charge increasing surface contact with air, the road asphalt was used without any pretreatment.

The phenanthrene, fluoranthene and pyrene were supplied by Aldrich (assay = 98%) and the anthracene was purchased at Fluka (purity ≥ 99%).

2.2. Oxidation experiments

Two solutions were made by dissolving the PAH couples in DCM (dichloromethane) at a unitary concentration of 10 mg mL⁻¹. The PAH were spread out in 100 mL Schott glass bottle by transferring 25 mL of solution in the bottle and evaporating the solvent under N₂ stream.

For each matrices and coking plant soil, 15 g were introduced into closed 100 mL Schott bottles. Six repetitions of each sample were realized and placed into an oven at 100 °C. Duplicates were taken at 60, 120 and 180 days. The released CO₂ concentration during the oxidation was determined every 15 days with an infrared absorbance measurement ($\lambda = 2325.6 \text{ cm}^{-1}$) performed

with an infrared Binos analyzer. After each measurement, the bottles were opened to renew the flask atmosphere (especially air oxygen) [26–29]. After the oxidation time, samples were stored at –18 °C before analysis.

2.3. Organic analyses

2.3.1. Elemental analysis

The C, H, and O elemental analysis of non-oxidized and oxidized samples were performed on an elementary analyzer Thermo Finnigan EA 1112. In order to determine the TOC (total organic carbon) value of the coking plant soil, a set of decarbonated samples was also analyzed. Because it was impossible to crush the road asphalt, the TOC content of the sample was calculated from the EOM (extractable organic matter) and the solid residue TOC contents.

2.3.2. Organic extract isolation and fractionation

The samples of oxidized PAH couples were dissolved with 20 mL of DCM and then diluted 5000 times, using serial dilution, before analyzes.

The organic extractions of the isolated matrices and the coking plant soil were carried out on 3–9 g of matrices, according to the TOC concentration, with an automated extractor Dionex[®] ASE (Accelerated Solvent Extractor) 200 (DCM, 130 °C, 130 bars).

Copper powder, to eliminate the molecular sulfur, Na₂SO₄, to remove the remaining molecules of water, and Fontainebleau sand, to increase the extraction yield, were added to the samples prior to the extraction. Then, the extracts were diluted with DCM to 20 mL and an aliquot was sampled and dried under nitrogen to determine the solvent EOM yield.

The fractionation of aliphatic, aromatic and polar families was performed on alumina and silica columns as described by Jeanneau et al. [30]. The aliphatic, aromatic and low molecular weight polar compounds were isolated from polar macromolecules on an alumina column, eluted successively with DCM and a mixture of DCM/methanol (1/1, v/v). The DCM fraction was then eluted on a silica column successively with *n*-heptane, a mixture of *n*-heptane/DCM (2/1, v/v), and a mixture of DCM/methanol (1/1, v/v), to recover, respectively, aliphatic HC (hydrocarbons), aromatic HC and polar fractions. The recovered fractions were then diluted to 5 mL with DCM and an aliquot was dried and weighed to determine the mass proportion of each fraction. The mass balance between amount of EOM and of collected fractions (aliphatic, aromatic and polar compounds) allowed to quantify a fourth fraction attributed to highly polar macromolecules trapped in the columns.

2.3.3. Molecular analysis and quantification

An internal *n*-alkanes standard mix (C₁₆D₃₄, C₂₀D₄₂, C₂₄D₅₀ and C₃₀D₆₂) was added into the aliphatic fractions and an internal PAH standard mix (naphthalene d8, acenaphthene d10, phenanthrene d10, chrysene d12, perylene d12) was added to the diluted polar and aromatic fractions, and to the diluted PAH solutions before being injected in a gas chromatograph coupled with a mass spectrometer (GC–MS). The GC–MS was previously calibrated with mixtures of 16 PAHs (listed by the US-EPA), 5 oxygenated polyaromatic compounds (PACs), 2 nitrogenous PACs, 29 *n*-alkanes and 2 isoprenoids. The GC used was a Hewlett Packard G1800A equipped with a capillary column in silica glass DB5–MS coupled to a MS Hewlett Packard GCD System detector on the fullscan mode. The temperature program was the following: from 70 °C to 130 °C at 15 °C min⁻¹, then from 130 °C to 315 °C at 3 °C min⁻¹ and then a 15 min hold at 315 °C. The carrier gas was helium at 1.4 mL min⁻¹ constant flow.

In order to improve the chromatographic resolution of polar compounds (especially alcohols and carboxylic acids), a supplementary derivatization step using BSTFA+TMCS (N, O-

Table 1
Evolution of the sample organic characteristics in $\text{mg g}^{-1} \text{ dw} \pm \text{SD}$, during the oxidation experiment.

			T=0	T=60 days	T=120 days	T=180 days
Coal	Total organic carbon		765.5 ± 0.1	766.3 ± 2.9	757.1 ± 7.6	747.0 ± 1.1
	Oxygen content		76.9 ± 1.2	93.9 ± 1.1	104.9 ± 0.7	114.8 ± 0.8
	EOM		41.7 ± 3.9	47.9 ± 0.2	38.5 ± 4.3	35.5 ± 1.7
	Aliphatic HC		4.0 ± 0.2	6.4 ± 1.7	3.2 ± 0.0	2.1 ± 0.7
	Aromatic HC		9.9 ± 1.1	8.6 ± 0.4	8.4 ± 0.2	6.8 ± 2.5
	Polar compounds		22.8 ± 1.1	28.3 ± 0.8	21.5 ± 2.6	17.1 ± 1.4
	Polar macromolecules		5.0 ± 3.6	4.5 ± 2.0	5.4 ± 1.8	9.4 ± 1.5
Coke	Total organic carbon		861.0 ± 1.6	855.7 ± 1.2	853.0 ± 1.7	845.9 ± 17.2
	Oxygen content		7.2 ± 0	3.7 ± 0.3	3.3 ± 0.4	4.5 ± 0.1
	EOM		0.05 ± 0.03	–	–	–
Coal tar/silica	Total organic carbon		42.5 ± 0.8	34.8 ± 0.2	34.5 ± 0.0	33.3 ± 1.2
	EOM		28.1 ± 0.2	25.5 ± 0.6	26.5 ± 0.4	20.8 ± 3.3
	Aliphatic HC		0.3 ± 0.4	1.0 ± 0.6	1.9 ± 1.0	0.4 ± 0.6
	Aromatic HC		18.5 ± 1.0	11.7 ± 0.6	10.2 ± 0.3	7.9 ± 1.5
	Polar compounds		5.9 ± 0.8	11.1 ± 4.3	9.3 ± 0.6	6.5 ± 0.8
	Polar macromolecules		3.5 ± 0.9	2.6 ± 3.7	5.1 ± 2.0	6.0 ± 0.3
	EOM		59.2 ± 11.2	47.5 ± 6.8	45.1 ± 2.7	37.0
Road asphalt	Total sample	Total organic carbon	48.7 ± 0.02	42.2 ± 0.1	34.1 ± 0.1	40.5 ± 0.5
		Oxygen content	16.5 ± 0.6	78.3 ± 0.3	92.1 ± 0.1	91.2 ± 0.1
		Aliphatic HC	14.6 ± 3.6	9.7 ± 0.0	5.7 ± 0.3	6.5
		Aromatic HC	26.4 ± 9.5	6.4 ± 1.3	5.4 ± 0.2	5.5
		Polar compounds	11.3 ± 0.4	16.2 ± 2.4	11.1 ± 1.6	8.0
		Polar macromolecules	0.0 ± 0.0	17.6 ± 2.1	22.9 ± 1.1	17.1
		EOM	59.2 ± 11.2	47.5 ± 6.8	45.1 ± 2.7	37.0
	Solid residue	Total organic carbon	0.5 ± 0.4	1.8 ± 0.1	1.8 ± 0.2	13.0 ± 1.6
		Total organic carbon	833.4 ± 2.7	776.0 ± 1.1	751.4 ± 0.1	755.5 ± 1.8
		Total organic carbon	100.1 ± 1.4	108.7	95.8	93.8
		EOM	42.4 ± 2.1	31.5	32.0	31.9 ± 1.02
		Aliphatic HC	2.0 ± 0.9	0.7	2.1	0.8 ± 0.2
		Aromatic HC	8.5 ± 0.6	4.0	4.3	4.0 ± 0.7
Coking plant soil	Polar compounds		18.9 ± 1.5	18.2	20.0	14.8 ± 0.1
	Polar macromolecules		6.2 ± 0.5	8.5	5.7	12.4 ± 0.0

bis(trimethylsilyl) trifluoroacetamide) was carried out prior to GC–MS analysis.

2.3.4. Infrared spectroscopy analysis

The micro Fourier Transform Infrared (μFTIR) spectroscopic analysis were performed on an infrared spectrometer Bruker IFS55 coupled with a Multipurpose Bruker IR microscope equipped with a MCT detector cooled with liquid N_2 . EOM were analyzed as described by Faure et al. [16] using a diamond window in order to avoid drawbacks usually encountered when using bulk infrared on KBr pellets, such as contamination by water adsorbed on the highly hygroscopic KBr [31]. The spectra were recorded with the following conditions: size of the analyzed area $60 \mu\text{m}^2$, 64 accumulations (32 s), spectral resolution 4 cm^{-1} , gain 4.

3. Results

3.1. Characterization of the initial matrices

3.1.1. TOC values in matrices, EOM and EOM fractions contents

The TOC content was very similar in coke and coal samples. The TOC values of the road asphalt and the coal tar on silica were also close. The TOC content of the coking plant soil showed an intermediate value. The amount of EOM was in the same range for all the samples except for coke which showed no EOM.

The organic extract composition, in terms of aliphatic, aromatic, polar compounds and polar macromolecule amounts, is presented in Table 1. Because of the very low amount of EOM, no fractionation was performed on the coke. The coal and coking plant soil samples showed EOM dominated by the polar compounds. The coal tar EOM was enriched in aromatic compounds. In the road asphalt EOM, approximately the same proportion of aliphatic, aromatic and polar compounds was observed. In all EOM, the polar macromolecules contents were relatively low.

3.1.2. Molecular quantification

The identified and quantified molecular families are shown in Table 2 and consist of *n*-alkanes, alkyl-cyclohexanes, pentacyclic triterpanes, PAHs, alkylated PAHs (alk-PAHs), aromatic ketones, aromatic aldehydes, aromatic alcohols, oxaarenes, azaarenes and thiaarenes. No aliphatic HC (i.e. *n*-alkanes, alkyl cyclohexanes and pentacyclic triterpanes) was present in the coal tar samples but the PAH concentration was very high and represented up to 35% of the EOM. *n*-Alkanes and pentacyclic triterpanes were the only quantifiable compounds in the road asphalt extract and made up less than 1% of the EOM. The chromatogram of the aliphatic fraction of this sample was dominated by an UCM (unresolved complex mixture) corresponding to a complex mixture of iso- and cyclo-alkanes not separated by conventional gas chromatographic column [32]. The coal extracts were dominated by alk-PAHs and, to a lesser extent, by *n*-alkanes and PAHs. Almost all molecular families were found in the EOM of the coking plant soil with a marked predominance of PAHs. The proportion of oxygenated PAHs was also higher than in the other samples and represented more than 20% of the quantifiable molecules.

3.1.3. Infrared spectroscopy on EOM

The infrared spectra of the initial samples were consistent with the data obtained from the molecular analysis (Fig. 1). Road asphalts and to a lesser extent coal were dominated by aliphatic bands ($\nu\text{CH}_{\text{ali}}$ and $\delta\text{CH}_{\text{ali}}$) whereas coal tar was dominated by aromatic bands ($\nu\text{CH}_{\text{aro}}$, $\nu\text{C}=\text{C}$, $\gamma\text{CH}_{\text{aro}}$). Coking plant soil showed an intermediate signature.

3.2. Oxidation experiments

3.2.1. CO_2 measurement

The oxidation efficiency evaluated by the mineralization of organic matter was monitored with the amount of CO_2 released

Table 2
Evolution of the molecule concentrations in $\mu\text{g g}^{-1} \text{ dw} \pm \text{SD}$, during the oxidation experiment. 16 PAHs: concentrations of the 16 PAHs listed by the US-EPA as priority pollutant, alk-PAH: concentrations of all the alkylated PAHs.

	$\mu\text{g g}^{-1} \text{ dw}$	T=0	T=60 days	T=120 days	T=180 days	
Coal	<i>n</i> -Alkanes	271 ± 66	278 ± 10	244 ± 1	273 ± 0	
	Alkyl-cyclohexanes	29 ± 7	32 ± 1	28 ± 1	15 ± 1	
	Pentacyclic triterpanes	47 ± 10	107 ± 4	94 ± 2	41 ± 4	
	Total parent-PAHs	221 ± 45	96 ± 4	82 ± 7	90 ± 6	
	16 PAHs	188 ± 43	72 ± 5	64 ± 6	73 ± 3	
	Alk-PAHs	630 ± 89	436 ± 60	330 ± 26	294 ± 30	
	Aromatic ketones	51 ± 1	225 ± 24	138 ± 13	595 ± 127	
	Aromatic aldehydes	71 ± 17	66 ± 0	70 ± 4	309 ± 21	
	Aromatic alcohols	40 ± 3	33 ± 0	26 ± 2	58 ± 4	
	Oxaarenes	173 ± 25	114 ± 1	97 ± 5	91 ± 15	
	Azaarenes	58 ± 7	30 ± 6	50 ± 6	108 ± 52	
	Thiaarenes	3 ± 1	2 ± 0	0 ± 0	0 ± 0	
	Coal tar	Total parent-PAHs	10,242 ± 883	5513 ± 336	5195 ± 258	5074 ± 566
		16 PAHs	8397 ± 784	4681 ± 306	4392 ± 247	4338 ± 449
Alk-PAHs		766 ± 83	316 ± 27	286 ± 30	295 ± 29	
Aromatic ketones		326 ± 170	2019 ± 6	1984 ± 19	1911 ± 264	
Aromatic aldehydes		33 ± 7	53 ± 1	50 ± 0	30 ± 2	
Aromatic alcohols		302 ± 69	231 ± 5	217 ± 5	182 ± 38	
Oxaarenes		675 ± 66	490 ± 19	488 ± 11	466 ± 73	
Azaarenes		1938 ± 583	917 ± 0	530 ± 28	570 ± 113	
Thiaarenes		248 ± 56	155 ± 6	151 ± 7	165 ± 21	
Road asphalt		<i>n</i> -Alkanes	193 ± 24	67 ± 4	59 ± 4	124 ± 49
		Pentacyclic triterpanes	131 ± 31	95 ± 13	84 ± 4	120 ± 58
		<i>n</i> -Alkanes	27 ± 4	4	7	4 ± 1
Coking plant soil		Total parent-PAHs	1956 ± 157	943	938	801 ± 87
		16 PAHs	1531 ± 133	844	840	702 ± 72
	Alk-PAHs	384 ± 70	48	87	31 ± 11	
	Aromatic ketones	704 ± 64	1133	1028	1042 ± 101	
	Aromatic aldehydes	72 ± 8	21	55	27 ± 6	
	Aromatic alcohols	119 ± 16	65	79	60 ± 2	
	Oxaarenes	370 ± 89	202	238	184 ± 26	
	Azaarenes	104 ± 50	0	0	0 ± 0	
	Thiaarenes	82 ± 11	30	30	33 ± 4	

during the experiment, normalized to the initial TOC of each sample (Fig. 2).

The most important evolution of the CO_2 /initial TOC ratio was observed for the coking plant soil, especially in the beginning of the oxidation experiment. The amount of released CO_2 was in the same range for the coal tar and the road asphalt but the curve shapes were different. Whereas the CO_2 evolution of coal tar was similar to the coking plant soil following a logarithmic curve, the road asphalt showed a linear CO_2 release.

The amount of CO_2 produced by the coke and the coal were significantly lower than the other samples. The curve shape of CO_2 production from coke was similar to the coal tar and the coking plant soil whereas the curves were linear for the coal.

The amounts of CO_2 released during the oxidation of the PAH couples were very low and reached only 0.25% of the TOC after 180 days of experiment (Fig. 2).

3.2.2. TOC values in matrices and elemental analysis in EOM

The TOC contents decreased of 2.4%, 1.8%, 21.6%, 16.8% and 6.3%, respectively, for the coal, the coke, the coal tar, the road asphalt and the coking plant soil samples during oxidation experiments (Table 1). The solid residue of the road asphalt increased up to $12.5 \text{ mg g}^{-1} \text{ dw}$. The EOM content (Fig. 3) showed the same trend with a decrease during the oxidation experiment of 0.62%, 0.73%, 2.22% and 1.05%, respectively, for the coal, the coal tar, the road asphalt and the coking plant soil samples.

Table 1 also shows the evolution of the oxygen content during oxidation in the samples for which the oxygen analysis was relevant (i.e. with no mineral phases which could contain oxygen such as silica or carbonate). It concerns the coke, the coal and the road asphalt EOM. A significant increase in the oxygen content was observed during oxidation in coal and road asphalt EOM.

3.2.3. Infrared spectroscopy on EOM

The oxidation induced an increase in the band intensity corresponding to $\nu\text{C}=\text{O}$ and $\nu\text{C}-\text{O}/\delta\text{O}-\text{H}$ groups in all the samples (Fig. 1). A slight decrease in the band intensity corresponding to $\nu\text{CH}_{\text{all}}$ and $\delta\text{CH}_{\text{all}}$ of the coal and coking plant soil samples was also observed.

3.2.4. Organic fraction evolution

Whatever the samples, the oxidation induced an important increase in the polar macromolecule contents (Table 1). Moreover, for the coal, as well as for the coking plant soil sample, the aliphatic and aromatic fraction proportions remained stable but the proportion of polar compounds decreased during oxidation (Fig. 4). This decrease was observed from the beginning of the experiment for the coking plant soil and from 60 days of experiment for the coal sample. The coal tar aromatic fraction percentage decreased during the oxidation whereas the proportion of the aliphatic fractions remained unaffected. The polar fraction of this sample increased for 60 days of experiment and then slightly decreased. The aliphatic, aromatic and polar compounds proportions in the road asphalt samples decreased during the experiment.

3.2.5. Molecular quantification

Oxidation experiments induced also modifications at a molecular level (Table 2).

In the coal samples, the aliphatic fraction (i.e. *n*-alkanes and pentacyclic triterpanes) was not affected, but the aromatic compound content, such as parent PAHs, alk-PAHs and oxaarenes, decreased considerably. The aromatic ketones (Fig. 5), aldehydes and alcohols compounds increased significantly.

In the coal tar, the PAHs, the alk-PAHs and the oxaarenes showed a sharp decrease in abundance after 60 days of oxidation and then

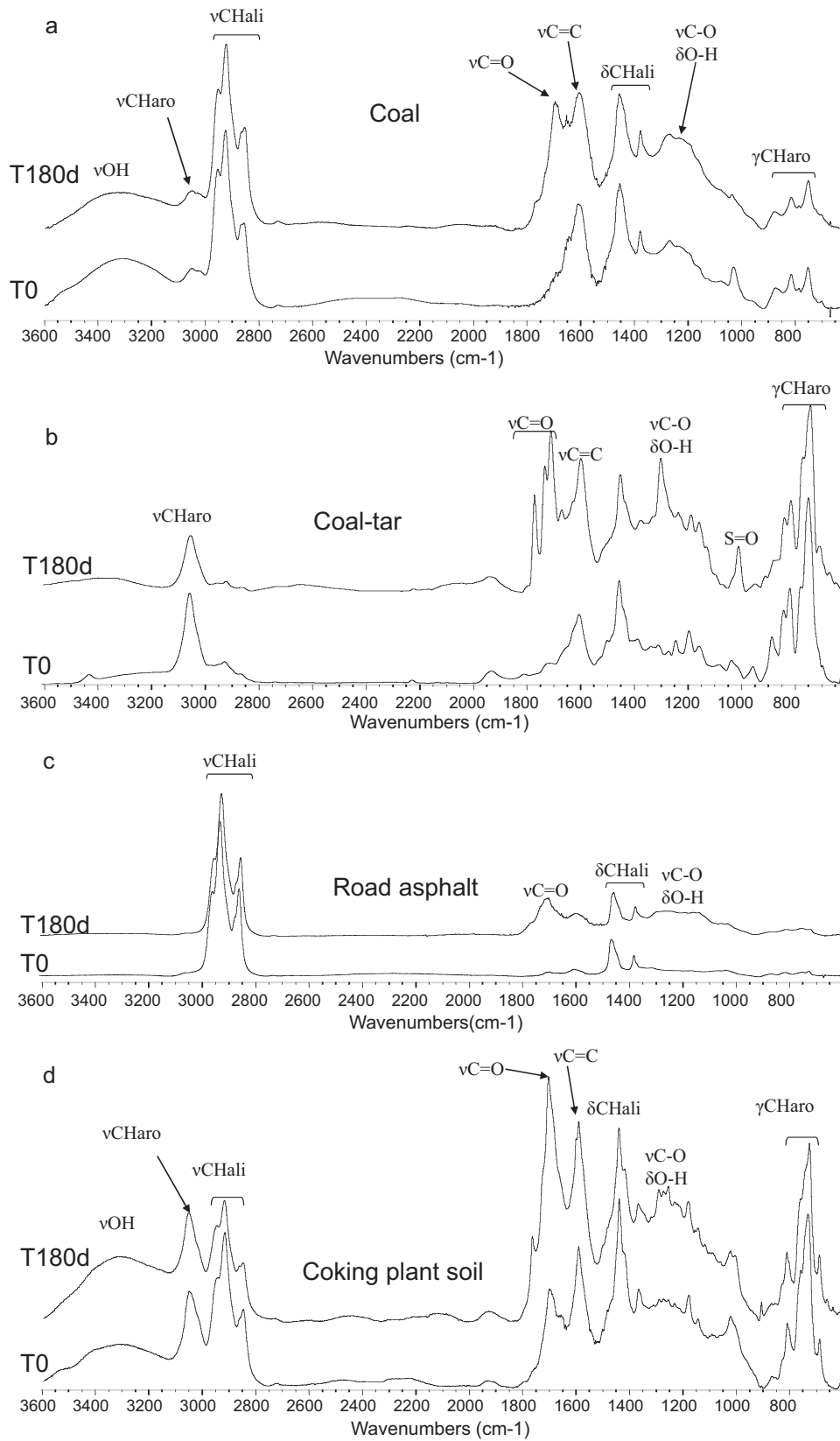


Fig. 1. FTIR spectra of the initial and 180d oxidized EOM of the samples.

remained stable. The aromatic aldehyde concentration increased after 60 days of oxidation and then decreased between 120 and 180 days. The aromatic ketones concentration also increased until 60 days and then remained stable (Fig. 5).

In the coking plant soil sample, the aromatic ketone contents increased during oxidation (Fig. 5) whereas the amounts of the majority of the detected compounds (*n*-alkanes, parent and alk-PAHs, arenes, aromatic aldehydes and alcohols) decreased.

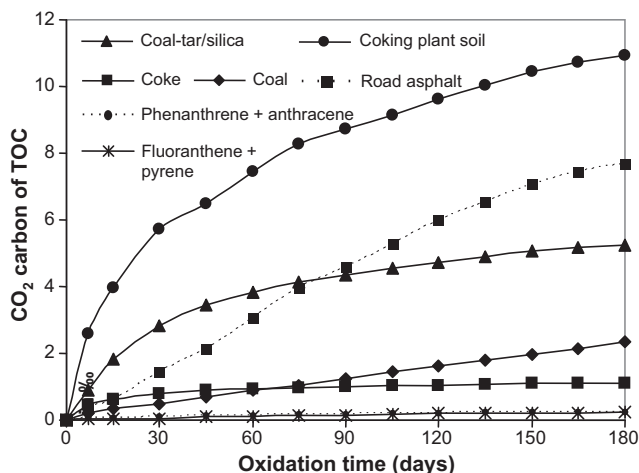


Fig. 2. Amount of CO₂ carbon released during the oxidation experiment, normalized to the initial samples TOC content.

The evolution of the distribution of the 16 PAHs (Table 3) shows that the decrease of PAH concentrations affected low molecular compounds especially fluorene, acenaphthene and anthracene. However, some high molecular weight compounds showed elevated degradation rate, even if the initial concentration was

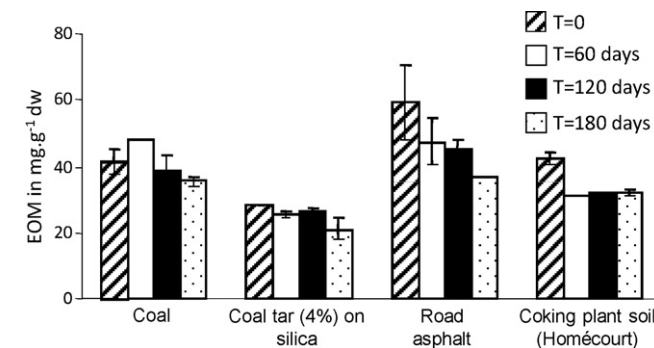


Fig. 3. Evolution of the EOM amounts of the different samples during oxidation, error bars represent standard deviation.

important. For example benzo(a)pyrene ($M_w = 252$) decreased of 94% with a high initial concentration of about $300 \mu\text{g g}^{-1}$ dw in the coal-tar sample.

The oxidation of the pure compounds induced a very low decrease in PAH quantities with a preferential degradation in phenanthrene and fluoranthene compared, respectively, to anthracene and pyrene (Fig. 6). In both cases, no by-products were detected.

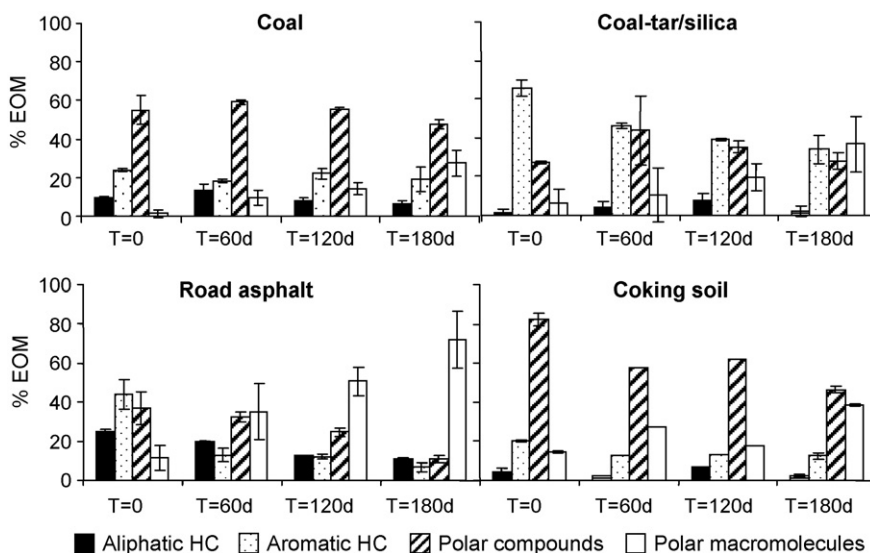


Fig. 4. Variation of the aliphatic hydrocarbons, aromatic hydrocarbons, polar compounds and polar macromolecules proportions of EOM during oxidation.

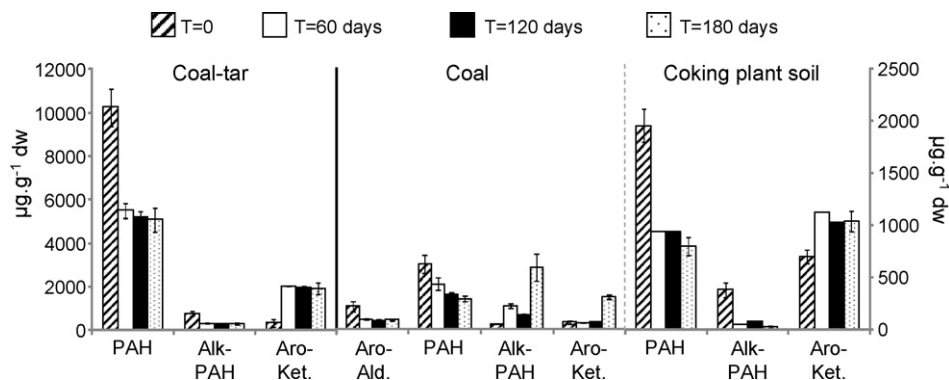


Fig. 5. Evolution of the PAH, alk-PAH, aromatic ketones (aro-Ket.) and aldehydes (aro-Ald.) contents during oxidation, error bars represent standard deviation.

Table 3
16 PAH concentrations ($\mu\text{g g}^{-1}$ dw \pm SD) in the coal, coal-tar and coking plant soil samples before and after the oxidation experiment.

	Coal			Coal-tar			Coking plant soil		
	T0	T180d	%deg	T0	T180d	%deg	T0	T180d	%deg
Naphthalene	39 \pm 22	24 \pm 1	38	976 \pm 149	614 \pm 146	37	5 \pm 3	0 \pm 0	100
Acenaphthylene	0 \pm 0	0 \pm 0	–	757 \pm 54	18 \pm 5	98	207 \pm 33	108 \pm 14	48
Acenaphthene	0 \pm 0	0 \pm 0	–	23 \pm 3	0 \pm 0	100	190 \pm 44	0 \pm 0	100
Fluorene	9 \pm 3	0 \pm 0	100	562 \pm 26	0 \pm 0	100	159 \pm 16	17 \pm 1	90
Phenanthrene	42 \pm 6	17 \pm 2	59	1662 \pm 178	1256 \pm 184	24	327 \pm 42	235 \pm 25	28
Anthracene	2 \pm 1	0 \pm 0	100	581 \pm 83	83 \pm 19	86	131 \pm 28	53 \pm 8	60
Fluoranthene	5 \pm 1	2 \pm 0	60	1135 \pm 136	881 \pm 132	22	148 \pm 19	91 \pm 5	38
Pyrene	4 \pm 1	2 \pm 0	33	877 \pm 112	509 \pm 82	42	91 \pm 14	40 \pm 4	56
Benzo(a)anthracene	11 \pm 2	3 \pm 0	73	356 \pm 46	157 \pm 28	56	49 \pm 7	13 \pm 2	73
Chrysene	11 \pm 2	4 \pm 1	69	303 \pm 21	246 \pm 39	19	49 \pm 6	36 \pm 4	26
Benzo(b)fluoranthene	9 \pm 2	6 \pm 0	28	286 \pm 22	217 \pm 40	24	45 \pm 9	37 \pm 3	19
Benzo(k)fluoranthene	5 \pm 2	3 \pm 0	42	115 \pm 7	83 \pm 13	28	19 \pm 3	13 \pm 1	34
Benzo(a)pyrene	11 \pm 2	6 \pm 0	45	298 \pm 38	18 \pm 4	94	37 \pm 5	9 \pm 1	76
Indeno(1,2,3-c,d)pyrene	11 \pm 4	2 \pm 0	84	271 \pm 43	168 \pm 33	38	37 \pm 7	28 \pm 3	25
Benzo(g,h,i)perylene	14 \pm 4	4 \pm 0	74	153 \pm 11	62 \pm 11	59	23 \pm 3	16 \pm 1	32
Dibenzo(a,h)anthracene	15 \pm 6	0 \pm 0	100	42 \pm 2	27 \pm 4	37	13 \pm 4	8 \pm 0	41

4. Discussion

4.1. Does low temperature oxidation simulate the long term evolution of a contaminated soil?

The experimental approach developed in this study was first applied to the understanding of the long-term evolution of coal submitted to weathering [15,24,33]. Low temperatures were used to accelerate oxidation reactions and then compensate the long time of oxidation (several years) that could not be reproduced in laboratory experiments. This approach was also used to simulate the weathering of immature sedimentary rocks that never reached temperatures higher than 50 °C in the sedimentary basin

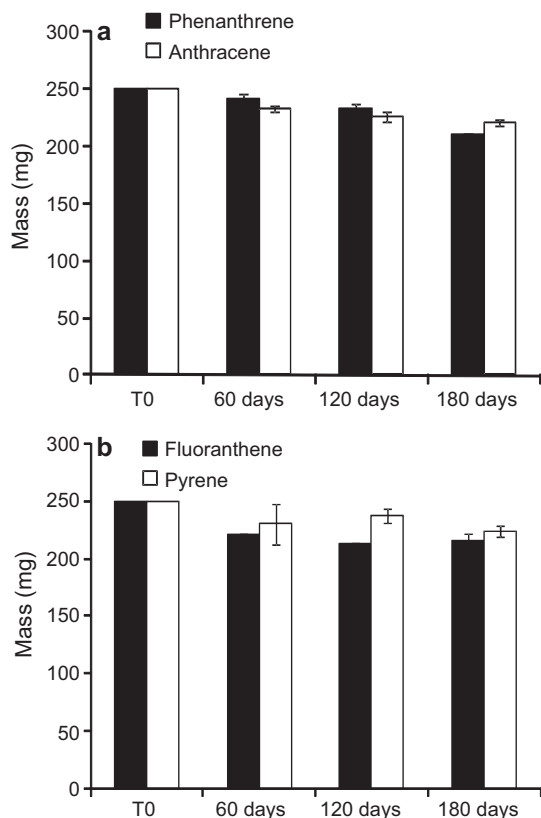


Fig. 6. Evolution of the PAH amounts during the oxidation of pure compounds, error bars represent standard deviation.

[9,34]. It was validated by the comparison to a natural oxidation series of samples [15,16]. These sedimentary rocks, containing some thermolabile compounds, showed comparable quantitative and molecular trends in artificial (130 °C – 45 days) and natural oxidation series (from 10 to 40 years of air exposure) [15] and thus validated the representativeness of the low temperature oxidation for simulating natural air oxidation.

In this study, we chose to apply this low-temperature oxidation approach to contaminated soils considering that most of the organic matter is highly condensed and is inherited either from diagenesis (for coal) or from high-temperature processes (high temperature pyrolysis or distillation for coke, coal tar and road asphalt). In our contaminated soil, the high TOC (10%) is mainly due to the major contribution of coke, coal and coal tar. No molecule related to recent organic matter contribution has been detected by GC–MS. Moreover, considering the results obtained after the experiment performed on pure compounds, isolated PAHs seemed insensitive to the thermal treatment applied in this experiment. Consequently, we can assume that the low temperature used in our experiments allows enhancing oxidation reactions without inducing thermal decomposition of organic matter.

4.2. Case of the coke

The lack of EOM, the very limited CO₂ production during the oxidation experiment and the invariable C and O concentrations of the coke sample showed that this constituent is insensitive to oxidation and seems to be a very stable organic material. However, coke is known to be a highly porous material and to exhibit high sorptive properties (specific areas: 9.8 m² g⁻¹) toward metallic elements and hydrophobic organic compounds [35]. Even if the coke seemed unaffected by air oxidation, it must be considered as a potential trap for micropollutants, organic as well as metallic, available or released by other materials during natural attenuation.

4.3. PAH degradation and limitation

After 180 days of oxidation, the PAH (parents + alkylated) degradation rates were relatively important with 55%, 51% and 64%, respectively, for the coal, the coal tar and the coking plant soil. In the same context, other treatments currently used to eliminate PAHs from contaminated soils (such as biodegradation and chemical oxidation) appeared to be less efficient. For example, Canet et al. [36] studied the biodegradation of the 16 PAHs in a coal tar contaminated soils and obtained, at best, a degradation rate of 17%. In the same way, Lundstedt et al. [18] obtained a decrease of 22% in

the PAH concentration of an aged gasworks' soil with an ethanol-Fenton treatment.

In our experiment, higher degradation efficiency is observed for some PAH such as fluorene, acenaphthene and anthracene. Lundstedt et al. [18] have already observed the same evolution. These compounds have preferential sites for a radical oxidation mechanism [37] that enhances their reactivity and explains the better efficiency of oxidation on these compounds. However, the oxidation affected not only low molecular weight compounds but also high molecular weight compounds. These high molecular weight PAHs are yet known to be resistant to degradation (especially biodegradation). So, these results suggest that oxidation is probably an important degradation mechanism occurring in PAH contaminated soils in a long-term time scale.

Like the degradation rate, the CO₂ evolution during the experiment was higher for the coking plant soil than for the other samples. Mineral phases such as clays and ferric minerals, are known to have a catalytic effect in the oxidation reactions [38] and the PAH degradation [39]. The occurrence of such minerals in the soil can explain the higher reactivity of this latter face to oxidation compared to the isolated constituents free from any reactive mineral surfaces.

The logarithmic shape of the CO₂ production of the coking plant soil and the coal tar suggests a limitation in the oxidation reaction. This observation is consistent with the PAH degradation, important until 60 days and negligible for higher oxidation time.

As the oxidation is a surface phenomenon, it affects only the thin external layer coating the grains while the compounds inside the grain are preserved from oxidation. The limited access of O₂ to the organic compounds could explain why the CO₂ production and PAH degradation are stabilized after 60 days. Moreover, the hydrophobic contaminants, like PAHs, tend to bind to organic matter or mineral clay [4]. In fact, organic matter known as "glassy" type i.e. condensed material and diagenetically older, exhibits numerous pores inside which the sorption occurs rather than at the surface of the material. The trapping (i.e. the sorption inside the porosity) preserves compounds from oxidation [40]. It also prevents migration of the contaminant, which contributes to a stabilization process. Several studies also showed that with time, organic compounds become more resistant to desorption and mineralization [5,41,42]. The limited accessibility of organic compounds to oxygen seems to be a valid explanation for the limitation in the oxidation reaction.

Contrary to coal-tar and coking plant soil samples, the curve of the CO₂ released during the coal oxidation showed a linear trend. It suggests no limitation of the oxidation for this sample and it was consistent with the continuous decrease of the alk-PAH contents. Because the coal powder was extremely fine (40 μm) and PAHs are disseminated homogeneously in the coal, it offered a higher surface to oxidation than other samples (a specific area of 3.5 m² g⁻¹) and the oxidation was more extended.

4.4. Oxygen incorporation and oxygenated by-products

Several evidences of the oxygen incorporation in the coal, the coal tar, the road asphalt EOM and the coking plant soil during oxidation experiments were demonstrated through the elementary analysis, the FTIR spectra and the molecular analysis results. The increasing oxygen content with oxidation progress was already observed by several authors in artificial oxidation context on a shale kerogen [16] and in natural conditions on black carbon [43] and on coals [10,12,44,45].

Considering the FTIR spectra and molecular data, the major products generated during the oxidation were oxygenated compounds and more precisely aromatic ketones in the case of coal tar and coking plant soil, and also aromatic aldehydes and alcohols for the coal samples. After 180 days of oxidation, the aromatic ketones concentrations increased of 1067%, 486% and 48% for the coal, the

coal tar and the coking plant soil samples, respectively. In the case of the coal, the degradation of PAH is fully compensated by the formation of aromatic ketones.

Reactions involved in chemical oxidation [18,20,21,46] as well as air oxidation [38] imply, most of the time, radical reactions like in auto-oxidation reaction. The reaction products found in those studies are similar to those encountered here, i.e. ketones and quinones. In the case of coal sample, a great amount of aromatic aldehydes were also produced during oxidation contrary to the other samples. It can be explained by the difference in the composition of the initial samples. Indeed, the initial coal sample contains high alk-PAH concentrations. The oxidation of a methyl group substituted on these aromatic rings could produce aromatic-aldehydes. However, as most of the literature focuses on the oxidation of parent PAHs, there is no study considering the natural oxidation pathways of an alk-PAH that could confirm our hypothesis.

Because of the oxygen group, aromatic oxygenated compounds are more reactive and potentially more mobile in soils than their apolar counterparts [47,48]. Moreover, these compounds are known to present toxic, mutagenic and carcinogenic properties [28,29,49] and must be taken into account in the rehabilitation prospective of contaminated sites.

4.5. Evidence of organic condensation

The oxidation experiment also induced a decrease in the EOM yield. This observation was previously made by authors who studied coal weathering process [10,50]. The decrease in the EOM content cannot be explained only by the CO₂ production which represents a maximum of 1% of the initial TOC in the case of coking plant soil. As a matter of fact, only molecular condensation can explain such EOM content reduction.

The molecular growth has been already evidenced during thermal treatment of PAH contaminated soil [25]. The decrease in EOM yield, associated with the increasing TOC in the road asphalt residue and the increasing proportion of polar macromolecules in the EOM during oxidation suggests that oxidation leads to a molecular condensation. The increasing intensity of the νC–O/δO–H bands in the EOM infrared spectra suggests that ether or ester cross-linking bonds could be formed and leads to increase the molecular weight. This molecular size enhancement is consistent with coal oxidation studies through IRTF analysis [10,11,13,44,51].

A recent work focusing on fluoranthene oxidation on mineral surfaces, demonstrates that the main reaction is the formation of high molecular weight compounds leading to the formation of a carbonaceous residue insoluble in commonly used organic solvents [52].

4.6. Are pure compound experiments representative of oxidation process?

As mentioned before, pure compounds were quite insensitive to the oxidation. The only modification observed during the experiment was a preferential decrease of the phenanthrene and fluoranthene amounts compared, respectively, to anthracene and pyrene. This evolution is related to the physico-chemical properties of the compounds. The phenanthrene and the fluoranthrene being more volatile than their respective isomers [49], the preferential decrease of these compound amounts was due to volatilization during the experiment preparation. As a matter of fact, these experiments carried out on isolated compounds in order to identify precise chemical processes are not able to simulate their evolution in soils. The contrasted efficiency of oxidation on complex samples suggests that the chemical environment plays an important part in oxidation reaction, particularly through the presence of mineral phases and the high diversity of organic compounds (in terms of

molecular mass and chemical structure) which can act as initiator and/or catalyst in radical chain reactions involved during the oxidation.

5. Conclusion

In order to evaluate the influence of natural oxidation on coking plant soils, low temperature oxidation were carried out on a coking plant soil and its isolated organic constituents (coal, coal tar, asphalts and coke). Among these constituents, the coke seems stable toward oxidation but its influence on the sorption of organic compounds or/and metallic element during oxidation should not be neglected. On the contrary, the coal and the coal tar seem to be the major organic constituents impacting the composition and the behavior of the coking plant soil during low temperature oxidation. For these materials, oxidation leads to an important decrease in the PAH concentrations (~50% of elimination) including the high molecular weight PAH particularly difficult to remove by biological processes. It appears then that the natural oxidation is an important process to take into account for long term evolution. However, this PAH decrease is observed for short time experiment (60 days) and then concentration remains stable suggesting a limitation due to restricted oxygen accessibility.

The PAH reduction is associated with a generation of aromatic ketones in the coal, the coal tar as well as in the coking plant soil samples with concentration in the same range as the PAH removal. The coal oxidation also induced an important production of aromatic aldehydes. This can be related to the specific sample composition, the coal being enriched in alkylated-PAHs, the oxidation of the methyl group could lead to the aldehyde formation.

Some of these oxygenated compounds are equally toxic, more mobile (water solubility) and more reactive in soils than their apolar counterparts and therefore must be taken into account in the rehabilitation prospective of contaminated sites.

In parallel to the oxygenated byproducts formation, a molecular condensation is suggested through ether and/or ester cross-linking leading to an increase in the insoluble organic fraction and a stabilization of the organic matter.

PAH in the studied complex matrices (coal, coal-tar and soils) showed a high reactivity, whereas pure model compounds were insensitive to oxidation. This emphasizes the major influence of the reacting medium (complex organic matrixes and mineral phases) for PAH oxidation effectiveness.

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