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Abstract

The impact of goethite on air-oxidation of PAH-contaminated soils was studied through two sets of experiments. (i) Soil extractable organic matter (EOM) and (ii) whole coking plant soils were oxidized at 60 and 100 °C for 160 days, with/without goethite. Organic matter (OM) mineralization was monitored via CO_2 production and polycyclic aromatic compounds (PACs) oxidation was investigated by GC-MS analyses. The decrease in EOM and PAH contents, and the oxygenated-PAC production observed during EOM oxidation, were enhanced by the presence of goethite. PACs were likely transformed at the goethite surface through electron transfer process. Mass carbon balance revealed a transfer from EOM to the insoluble organic fraction indicating condensation/polymerization of organics. Soil oxidation induced a decrease in EOM, PAH but also in oxygenated-PAC contents, underscoring different oxidation or polymerization behavior in soil. The goethite addition had a lesser impact suggesting that indigenous minerals played an important role in PAC oxidation.

Keywords: contaminated soil; polycyclic aromatic compound (PAC); oxygenated-PAC; goethite; oxidation

1. Introduction

Iron oxides are the most abundant metallic oxides in soils (Schwertmann and Taylor, 1989), they are present in most soils and encompass oxides, oxyhydroxides and hydrated oxides. Fe-minerals are known to play an active part in the organic contamination fate as they represent strong sorption surfaces for pollutants and they catalyze many important redox transformations (Borch et al., 2009). During the past decades their ability to participate in such redox reactions was involved in remediation strategies for organic contamination. For instance Fe-minerals are associated with H_2O_2 to produce hydroxyl radicals that can degrade organic compounds in Fenton-like reactions. Soil iron minerals i.e. magnetite, hematite, goethite, and ferrihydrite, are all able to catalyze H_2O_2 (Yap et al., 2011).

Fenton-like reaction has been investigated for the remediation of water and soil contaminated with halogenated solvent, pesticides and petroleum hydrocarbons (Watts and Stanton, 1999; Usman et al., 2013). Fenton-like reaction shows also a great potential for polycyclic aromatic hydrocarbon (PAH, compounds constituted of two, or more, fused benzene rings) degradation in contaminated soils (Nam et al., 2001; Usman et al., 2012). The catalytic role of iron oxides for Fenton-like reaction is extensively studied for chemical remediation purpose. However such treatments are not automatically applied to contaminated soils and little is known about the involvement of iron oxide in processes occurring during natural attenuation of contaminated soils, especially abiotic oxidation. Some authors studied iron oxide-mediated oxidative transformations of organic compounds (Zhang and Huang, 2007; Lin et al., 2012) but the experiments were designed with solids suspended in aqueous solution which is not representative of real soil conditions. Wang et al. (2009) studied pyrene degradation on iron oxide under UV radiation and evidenced photocatalytic effect of several iron oxide. In real

soils UV light affects only the surface layers since its intensity decays rapidly in the solid phase. Abiotic oxidation still occurs in deeper layer but so far this process was scarcely investigated, probably due to the difficulty to study this process independently to others. This difficulty can be bypassed using experimental simulation. Indeed low-temperature oxidations (60-130 °C) are proven to successfully mimic long-term abiotic oxidation of fossil organic matter (OM) (Faure et al., 1999; Elie et al., 2000; Blanchart et al., 2012). Such experiments were extensively used in the 1980s to study coal weathering and its impact on coal heating properties (Gethner, 1987; Calemma et al., 1988; Jakab et al., 1988). More recently, low-temperature oxidations of PAH-contaminated matrices showed that minerals (e.g. clay minerals and calcite) play an important role on the contamination fate (Ghislain et al., 2010; Biache et al., 2011; Biache et al., 2014). Indeed, oxidation causes a production of oxygenated-polycyclic aromatic compounds (O-PACs: PAH with oxygenated moieties e.g. alcohol, ketone, aldehyde groups) and formation of an insoluble carbonaceous residue, supposedly through oxidative polymerization, leading to the contamination stabilization. PAH-contaminated soils often contain high proportion of iron oxide and other metal oxides (Biache et al., 2014), however their influence on PAC oxidation has never been investigated in such context.

Therefore, this study reported a first investigation on the role of iron oxide (goethite) on PAC fate (including PAHs and O-PACs) during abiotic air-oxidation of contaminated soils. Its aim was to determine which mechanisms were involved during this major process involved in natural attenuation. Goethite (α-FeOOH) was selected because it is one of the most thermodynamically stable and the most abundant iron (oxy)(hydr)oxide in natural environments (Schwertmann and Cornell, 2007).

Two sets of experiments were performed. The first one was conducted on extractable organic matter (EOM) previously isolated from PAC-contaminated soils. Afterwards, EOM was

mixed with goethite or silica sand; the latter was used as inert support since its reactivity towards organic compounds is limited (Ghislain et al. 2010). The second experiment was performed directly on soils, raw or supplemented with goethite. These two sets allowed investigating two levels of increasing complexity by studying the influence of an iron oxide on the soil EOM, which could give more precise information on the involved mechanisms, and on the whole soil including indigenous minerals, which is more complex but also more realistic. Oxidations were performed at 60 and 100 °C, the latter allowing more advanced oxidation and the first one representing an intermediate between 100 °C and field temperatures.

2. Materials and Methods

2.1. Samples

Soils were sampled at two former coking plant sites (Homécourt and Neuves-Maisons, France), then freeze-dried, sieved (2 mm) and crushed (500 µm). EOM was recovered by extracting parts of the soils in Soxhlet apparatus ($CHCl_3$, 24 h), it contains PACs and other organics of various size, from macromolecules (asphaltenes) to mono-aromatic units. Neuves-Maisons and Homécourt EOMs were concentrated at 1.4 and 2.4 mg/mL, respectively. Soils were also used directly or mixed with goethite.

2.2. Minerals

The silica sand was Fontainebleau sand (180-500 µm, Carlo Erba) used as a non-reactive reference in the EOM experiment.

Goethite (α-FeOOH) was synthesized according to Schwertmann and Cornell (2007). Briefly, sample was prepared by air-oxidation of a hydrolyzed $FeSO_4$ solution according to Prélot et al. (2003) (cf. supporting information).

Minerals were washed with dichloromethane prior experiments to prevent organic contamination.

2.3. Oxidation experiment

EOMs and soils were mixed with minerals according to the following proportions: silica sand (2 g) and goethite (0.5 g) mixed with Homécourt (47.1 mg) and Neuves-Maisons (48.7 mg) EOMs, Homécourt (2.5 g) and Neuves-Maisons (5 g) soils taken alone or mixed with goethite (0.5 g) (Table S1). Soils and minerals were placed in 100 mL glass bottles equipped with open caps and PTFE/silicone septa. EOM aliquots were added to the minerals to reach the mineral/EOM proportions specified in Table S1. Bottles were left open in a ventilated hood until complete evaporation of the solvent.

Two sample sets were prepared and placed in ovens at 60 and 100 °C. CO_2 released in the bottles was measured weekly by an infrared absorbance measurement (λ = 2325.6 cm^{-1}) with an infrared Binos analyzer. The measured CO_2 was normalized to the initial sample total organic carbon (TOC) content. After each measurement bottles were opened to renew the atmosphere and the septa were replaced. After 160 days, samples were removed from the ovens and, after CO_2 measurements, were stored at -18 °C prior analyses.

2.4. Extraction

Samples were transferred to 250 mL boiling flasks and chloroform (100 mL) was added to each flask. The mixtures were heated at 60 °C and stirred for 45 min before being filtered on GF/F Whatman glass-fiber filters. The filtrates were concentrated under a gentle nitrogen flow and volumes were adjusted to 20 mL. For each sample, an EOM fraction (3 mL) was transferred to a pre-weighed bottle and the EOM content was determined after solvent evaporation.

2.5. PAC quantification

An internal PAH standard mix of [$^2H_8$]naphthalene, [$^2H_{10}$]acenaphthene, [$^2H_{10}$]phenanthrene, [$^2H_{12}$]chrysene, [$^2H_{12}$]perylene (25 µL at 16 µg/mL, Cluzeau) was added to the EOM (75 µL) before being injected in a gas chromatograph coupled with a mass spectrometer (GC-MS). The GC-MS was previously internally calibrated with the internal standards listed above for 16 PAHs plus 4 O-PACs (Table 1) at 6 concentrations (0.5, 1, 2, 4, 6 and 8 µg/mL). The GC was a Shimadzu GC-2010 Plus, equipped with a silica-glass capillary column DB-5MS (60 m × 0.25 mm i.d. × 0.1 µm film thickness) coupled with a QP2010-Ultra (Shimadzu) MS in fullscan mode with a transfer line heated at 300 °C. The oven temperature program was as follow: 70 °C for 2 min, from 70 to 130 °C at 15 °C/min, then from 130 to 315 °C at 3 °C/min and then a 15-min hold at 315 °C. Helium was used as carrier gas in constant flow mode (1.4 mL/min).

2.6. TOC content

TOC contents were determined in soils and EOM/mineral mixtures with a total carbon analyser TOC-V CSH (Shimadzu) associated with a solid sample module SSM-5000A (Shimadzu).

3. Results

3.1. EOM/minerals mixture

3.1.1. CO_2 production

For both samples, CO_2 production of the EOM/mineral mixture followed the same trend (Figure 1a,b). The maximum production was observed for the EOM/goethite mixtures

oxidized at 100 °C and reached about 6 and 5‰ of TOC for Homécourt and Neuves-Maisons, respectively. It was followed by the CO_2 produced by the EOM/goethite mixture during the 60 °C oxidation. Smaller amount of CO_2 were observed for the EOM/sand mixture oxidations.

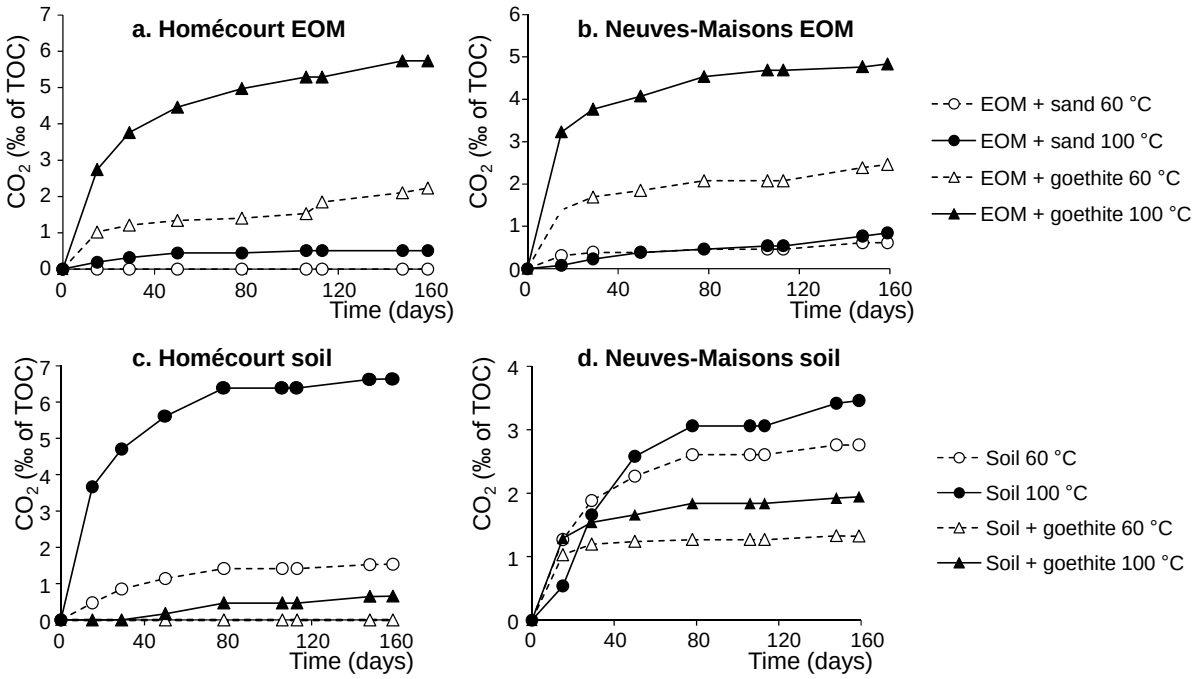
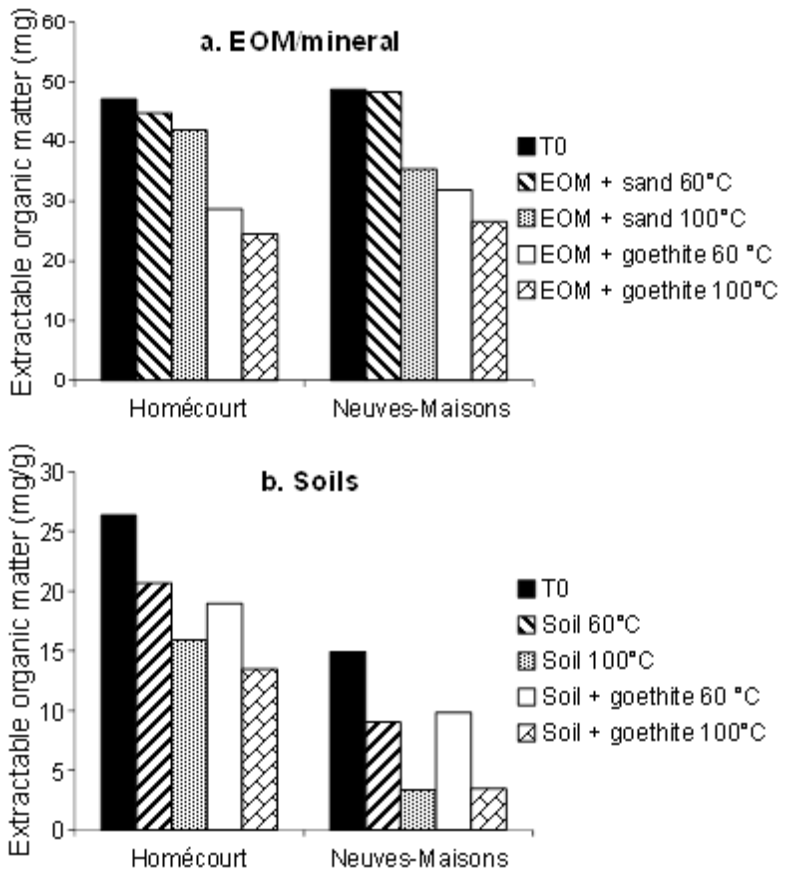


Figure 1: CO_2 production during the 60 and 100 °C oxidation experiments of the extractable organic matter (EOM) from (a.) Homécourt and (b.) Neuves-Maisons samples, mixed with silica sand and goethite, and (c.) Homécourt and (d.) Neuves-Maisons soils and soils mixed with goethite.

3.1.2. EOM contents

Overall, oxidations induced a decrease in the EOM content of the EOM/mineral mixtures (Figure 2a). It was limited for the EOM/sand mixtures oxidized at 60 °C and was more important for the same mixture oxidized at 100 °C but clearly lower than the EOM/goethite mixtures. The decrease was similar for both Homécourt and Neuves-Maisons samples at 100 °C and went from 47.1 to 24.5 mg and from 48.7 to 26.6 mg, respectively.



178

179 *Figure 2: Extractable organic matter (EOM) contents after the 60 and the 100 °C oxidation*
180 *experiment of (a.) Homécourt and Neuves-Maisons EOM/mineral mixtures, and (b.) Homécourt and*
181 *Neuves-Maisons soil and soil/goethite mixtures.*

182

183 *3.1.3. PAH contents*

184 Overall, EOM/mineral mixture oxidations induced a decrease in PAH concentrations. For
185 Homécourt EOM/sand mixture it was limited to 5% after the 60 °C experiment (Table 1). It
186 was more important at 100 °C (49%), mostly because of the loss of low molecular weight
187 (LMW) compounds compared to high molecular weight (HMW), as shown by the
188 LMW/HMW ratio which went from 3.1 to 1 (Table 1). The 60 and 100 °C experiments
189 induced a decrease in PAH content of 27% and 59% for Homécourt EOM/goethite mixture,
190 respectively. It affected again mainly LMW PAHs, especially the 2- and 3-ring PAHs (Table
191 1, Figure S3).

192 Contrary to the Homécourt EOM/sand mixture, PAHs decreased notably (40%; Table 1) after
193 the 60 °C oxidation of the Neuves-Maisons EOM/sand mixture. This decrease affected both
194 LMW and HMW compounds (Table 1, Figure S4). It was confirmed by the LMW/HMW ratio
195 which was barely modified (Table 1). At 100 °C, the PAH decrease was more important and
196 reached 61%. The LMW PAH, especially the 2- and 3-ring compounds were more affected
197 (Table 1, Figure S4). Neuves-Maisons EOM/goethite mixture oxidations induced also a
198 decrease in the PAH contents. It was relatively close whatever the temperature (63% at 60 °C
199 and 66% at 100 °C; Table 1)

200

201 *3.1.4. O-PAC contents*

202 Overall, oxidations induced an increase in the O-PAC contents (Table 1). For Homécourt
203 EOM, it was more important at 60 °C than at 100 °C. It was also higher when the EOM was
204 mixed with goethite than when mixed with sand (Table 1). The O-PAC production concerned
205 mostly 9-fluorenone and anthracene-9,10-dione (Table 1, Figure S5). The increase in O-PAC
206 concentrations in Neuves-Maisons EOM/mineral mixtures was higher at 100 °C than at 60 °C
207 (Table 1). The maximum O-PAC production reached 203% when Neuves-Maisons EOM was
208 mixed with goethite and oxidized at 100 °C (Table 1). This increase affected mostly
209 benzo[*de*]anthracene-7-one and benz[*a*]anthracene-7,12-dione (Table 1, Figure S6).

210 .

211 *Table 1: PAH and O-PAC contents (in µg/g) of the initial and oxidized (60 °C and 100 °C) extractable organic matter (EOM)/mineral mixture*

µg/g	Homécourt					Neuves-Maisons				
	Initial	EOM/sand 60°C	EOM/sand 100°C	EOM/goet. 60°C	EOM/goet. 100°C	Initial	EOM/sand 60°C	EOM/sand 100°C C	EOM/goet. 60°C	EOM/goet. 100°C
Naphthalene	17	2.0	n.d.	n.d.	n.d.	240	7.6	n.d.	n.d.	n.d.
Acenaphthylene	290	250	160	160	93	170	99	26	49	24
Acenaphthene	600	410	n.d.	61	n.d.	150	71	n.d.	n.d.	n.d.
Fluorene	410	260	20	39	22	120	65	2.5	7.0	1.3
Phenanthrene	750	760	150	720	320	390	270	21.1	130	34
Anthracene	220	260	120	150	67	170	150	37	39	31
Fluoranthene	400	550	300	560	260	550	440	220	320	220
Pyrene	290	320	240	310	200	450	290	180	200	150
Benz[*a*]anthracene	190	150	140	140	46	480	290	220	160	160
Chrysene	150	180	190	180	170	500	330	310	240	310
Benzo[*b*]fluoranthene	210	180	260	170	190	650	360	350	300	340
Benzo[*k*]fluoranthene	61	57	71	54	56	320	210	200	140	170
Benz[*a*]pyrene	140	130	39	94	4.9	500	290	110	150	0.6
Indeno[*cd*]pyrene	110	85	100	83	74	490	260	260	190	230
Dibenz[*a,h*]anthracene	34	63	69	68	44	170	81	110	58	92
Benzo[*ghi*]perylene	84	120	140	110	89	370	210	200	160	190
Sum of PAHs	3956	3777	1999	2899	1636	5720	3424	2247	2143	1953
PAH decrease (%)		5	49	27	59		40	61	63	66
LMW/HMW[a]	3.1	2.9	1.0	2.2	1.4	0.6	0.7	0.3	0.5	0.3
9-Fluorenone	530	780	680	1500	1200	160	180	48	180	130
Anthracene-9,10-dione	140	240	190	420	450	110	110	47	120	97
Benzo[*de*]anthracene-7-one	5.7	78	n.d.	82	n.d.	130	350	530	240	550
Benz[*a*]anthracene-7,12-dione	n.d.	n.d.	120	71	n.d.	64	130	430	150	630
Sum of O-PACs	676	1098	990	2073	1650	464	770	1055	690	1407
O-PAC production (%)		62	46	207	144		66	127	52	203
%O-PAC (/total PAC)	15	23	33	42	50	8	18	32	24	42

212 [a]LMW/HMW = ratio of sum of naphthalene to pyrene relative to sum of benzo[*a*]anthracene to benzo[*ghi*]perylene

213 3.2. Soils and soil/goethite mixtures

214 *3.2.1. CO_2 production*

215 For Homécourt soil, the CO_2 production was higher when the raw soil was oxidized at 100 °C
216 and reached 7‰ of the TOC at the end of the experiment (Figure 1c). The CO_2 production
217 was much lower at 60 °C and reached less than 2‰ of the TOC. It was followed by the
218 Homécourt soil/goethite mixture oxidized at 100 °C whereas the same mixture produced
219 nearly no CO_2 at 60 °C (Figure 1c).

220 Similar pattern was observed for the Neuves-Maisons soil with a maximum CO_2 production
221 for the raw soil oxidized at 100 °C which reached about 4‰ of the TOC. However the
222 differences between the modalities were less pronounced and the minimum CO_2 production
223 observed for the Neuves-Maisons/goethite mixture oxidized at 60 °C reached 1.3‰ of the
224 TOC (Figure 1d).

225 It should be noted that a part of the generated gas could result from CO_2 desorption from soil
226 solid surfaces (e.g. minerals, OM) over the soil thermal treatments, but this process may be
227 insignificant under our experimental conditions (Sumner, 2000).

228 *3.2.2. EOM contents*

229 Soil oxidations led to a decrease in the EOM contents (Figure 2b). For both soils and
230 soil/goethite mixtures, it was more important at 100 °C than at 60 °C. This decrease was
231 enhanced by the presence of goethite in the case of Homécourt samples for which the EOM
232 went from 26.4 to 19.0 and to 13.5 mg/g of soil after the 60 and the 100°C experiments,
233 respectively. Surprisingly, no difference was observed with goethite addition to the Neuves-
234 Maisons soil (Figure 2b).

235 *3.2.3. PAH contents*

Oxidations induced a strong decrease in the PAH concentrations for both soils. It was more important at 100 than at 60 °C and was maximum when goethite was added to the soil (92% of decrease for both samples; Table 2). For both samples, the 60 °C experiments affected slightly more HMW than LMW compounds, as shown by the increasing LMW/HMW ratios (Table 2). On the contrary, the 100 °C experiment induced a decrease in this ratio, indicating a preferential loss of the LMW PAHs (Table 2, Figures S7 and S8).

3.2.4. O-PAC contents

Overall, the soil and soil/goethite mixture oxidations induced a decrease in the O-PAC contents. For the raw Homécourt soils, it was limited to 3% after the 100 °C experiment and reached 12% after the 60 °C oxidation. This decrease was higher when Homécourt soil was mixed with goethite and attained 18% and 41% after the 60 and the 100 °C experiments, respectively (Table 2, Figure S9).

The abatement rates were higher for the Neuves-Maisons soil with 54% and 60% after the 60 and the 100 °C experiment on the raw soil, respectively. Goethite supplementation also enhanced this decrease but the proportion of O-PAC abatement was similar for both temperatures (71%; Table 2, Figure S10).

252 *Table 2: PAH and O-PAC contents (in µg/g) of the initial and oxidized (60 °C and 100 °C) soils and soil/mineral mixtures*

µg/g	Homécourt					Neuves-Maisons				
	Initial	Soil 60°C	Soil 100°C	Soil/goet. 60°C	Soil/goet. 100°C	Initial	Soil 60°C	Soil 100°C C	Soil/goet. 60°C	Soil/goet. 100°C
Naphthalene	9.4	4.5	0.3	3.6	n.d.	74	26	3.6	12	n.d.
Acenaphthylene	160	65	48	57	40	52	15	4.0	13	4.0
Acenaphthene	340	18	n.d.	13	n.d.	46	2.0	n.d.	1.6	n.d.
Fluorene	230	26	13	22	9.1	36	2.4	0.3	1.9	0.2
Phenanthrene	420	240	140	200	14	120	47	19	28	6.3
Anthracene	130	47	24	40	21	52	18	3.3	10	2.9
Fluoranthene	220	120	68	120	15	170	94	33	73	17
Pyrene	160	73	26	61	n.d.	140	68	11	44	n.d.
Benz[*a*]anthracene	110	32	15	20	3.6	150	55	10	22	1.7
Chrysene	81	34	25	31	6	150	57	33	45	15
Benzo[*b*]fluoranthene	120	37	39	38	23	200	81	53	75	42
Benzo[*k*]fluoranthene	34	13	9.5	12	5.3	97	27	15	25	9.0
Benz[*a*]pyrene	77	22	6.4	18	5.0	150	31	2.3	15	0.9
Indeno[*cd*]pyrene	61	14	17	14	14	150	39	23	33	20
Dibenz[*a,h*]anthracene	19	4.5	4.9	4.2	3.0	52	10	7.6	n.d.	5.3
Benzo[*ghi*]perylene	47	12	13	12	11	120	32	17	28	15
Sum of PAHs	2218	762	449	666	170	1759	604	235	427	139
PAH decrease (%)		66	80	70	92		66	87	76	92
LMW/HMW[a]	3.1	3.5	2.4	3.5	1.4	0.6	0.8	0.5	0.8	0.3
9-Fluorenone	300	270	280	250	170	48	34	22	18	14
Anthracene-9,10-dione	72	50	60	45	40	33	17	11	11	7.9
Benzo[*de*]anthracene-7-one	3.2	5.0	n.d.	5.0	n.d.	39	6.5	4.2	4.9	n.d.
Benz[*a*]anthracene-7,12-dione	n.d.	5.5	22	5.9	11	20	6.3	19	5.8	18
Sum of O-PACs	375	331	362	306	221	140	64	56	40	40
O-PAC decrease (%)		12	3	18	41		54	60	71	71
%O-PAC (/total PAC)	14	30	45	31	57	7	10	19	9	22

253 [a]LMW/HMW = ratio of sum of naphthalene to pyrene relative to sum of benzo[*a*]anthracene to benzo[*ghi*]perylene

4. Discussion

4.1. Mechanisms of goethite-activated EOM oxidation

Overall, goethite showed a high reactivity during the EOM oxidation as CO_2 production and the PAH degradation rate were enhanced by its presence. However, it should be noted that the mineralization was of less importance because the amount of produced CO_2 during the experiment remained very low (< 7‰ of TOC).

To give a better insight into the main process involved in the reduction of the PAH and EOM contents, a carbon mass balance was performed (Figure 3). It showed that most of the carbon from the initial EOM was transferred to the insoluble compartment. Such observations were made in previous studies (Ghislain et al., 2010; Biache et al., 2011; Biache et al., 2014) where air-oxidation of PAH associated with active minerals led to the decrease in EOM content and to the formation of an insoluble carbonaceous residue resulting from oxidation-induced polymerization.

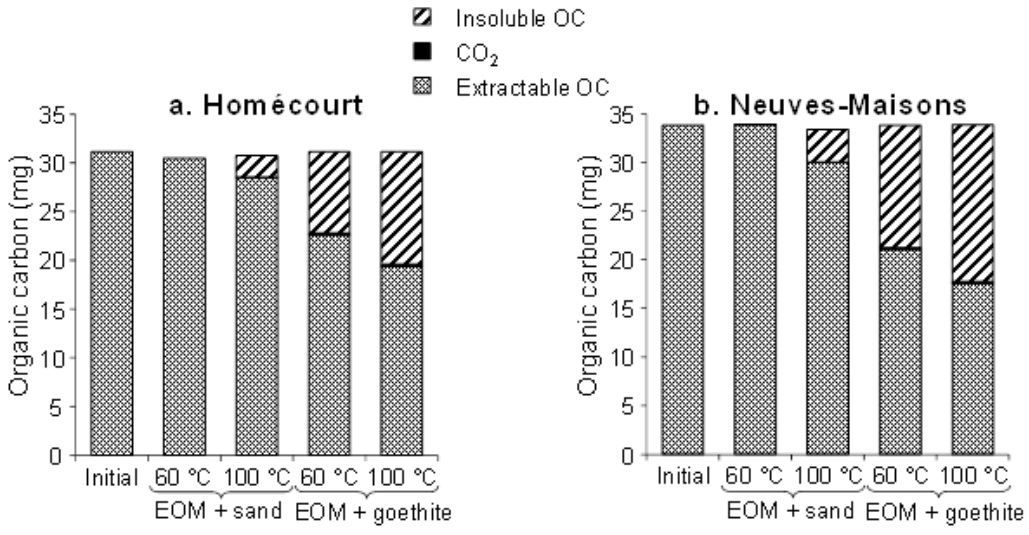


Figure 3: Carbon mass balance of the initial and oxidized samples of extractable organic matters (EOMs) mixed with mineral phases (OC: organic carbon).

271 EOM oxidations also induced an O-PAC production (ketones). Such compounds are known to
272 be produced during PAH oxidation in various contexts i.e. chemical oxidation (Lundstedt et
273 al., 2006), photo-degradation (Barbas et al., 1996) and biodegradation (Kazunga and Aitken,
274 2000). As the O-PAC production was much more important in the EOM/goethite mixture than
275 in the EOM/sand mixture, goethite seems to play an active part in the oxidation process. The
276 oxidation of organic compounds on goethite is known to be initiated by the sorption and then
277 formation of inner-sphere surface complexes with Fe^{III} surface sites (Pizzigallo et al., 1998).
278 This chemical coordination at the goethite surface is a prerequisite for the electron transfer
279 process (Stone and Morgan, 1987). Indeed, the sorbed molecule transfers an electron to Fe^{III}
280 site at goethite surfaces, leading to the formation of a very reactive cation radical that in turn
281 interacts with oxygen to produce oxygenated species (McBride, 1987). Finally, dissociation of
282 surface complexes and release of oxygenated species may occur, while the newly generated
283 Fe^{II} may be rapidly oxidized by O_2. Such mechanism was suggested for room temperature
284 oxidation of organic compounds by Mn^{VI}-Mn^{III}-oxides and Fe^{III}-oxides (McBride, 1987;
285 Stone and Morgan, 1987).

286 Our observations, i.e. important decrease in PAH contents and important production of O-
287 PACs, were consistent with the previously mentioned mechanism. This oxidation mechanism
288 must be favored by the increasing temperature, since more decay in EOM and PAH contents
289 and more O-PAC production were noted at 100 than at 60°C. Generally, the electron transfer
290 process induced by chemical complexation is considered as endothermic and therefore
291 improved by increasing temperature (Chidsey, 1991).

292 Moreover, several studies dealing with the Fe^{III}- or $Mn^{III/IV}$-induced oxidation of aromatic
293 compounds have pointed out same polymerization/condensation process as observed in this
294 study (Li et al., 2003; Arroyo et al., 2005; Russo et al., 2005).

295

296 4.2. Impact of goethite addition on the soil contamination.

297 When comparing the PAH decrease rates of both experiments (EOMs and soils), whole soils
298 seemed to be more reactive. Goethite addition had a different impact on the whole soil vs the
299 isolated EOM. While more decay in PAH concentration was observed in the presence of
300 goethite, less CO_2 was produced and O-PAC concentrations decreased. The EOM content did
301 not change significantly compared to the soil without goethite. The first explanation for these
302 differences is the presence in the soils of other –mineral and organic– reactive surfaces.
303 Previous studies dealing with biotic and abiotic oxidation of PAH contaminated matrices have
304 already pointed out a high reactivity of complex soil systems (Biache et al., 2011; Biache et
305 al., 2013; Biache et al., 2014) which has been attributed to the presence of reactive phases
306 such as clay minerals, metal oxides and organic macromolecules. Both soils contain such
307 reactive minerals (Biache et al., 2014), which may explain why the decrease in PAH and
308 EOM contents were already high in the soil without goethite addition. Similar mechanisms of
309 PAH oxidation could be involved here as in the EOM experiment but other by-products may
310 be formed. The decrease in O-PAC contents may be explained by a strong
311 sorption/sequestration in the soil and/or incorporation in the macromolecular network via
312 polymerization. The high decay of EOM in the whole soil compared to the EOM/mineral
313 mixture tends to support this hypothesis.

314 The goethite major impact was to reduce the CO_2 production in the whole soil experiment
315 even if the CO_2 amount remained very low in all investigated experiments (less than 7‰ and
316 4‰ of the Homécourt and Neuves-Maisons soils, respectively). This slight discrepancy "soil
317 *vs* soil/goethite" might be due to CO_2 adsorption on goethite surfaces, but this process cannot
318 be quantitatively evaluated in soil complex systems (Russell et al., 1975).

4.3. Impact of initial soil composition on the OM reactivity

While both EOMs exhibited similar global trends during oxidations, some molecular-level differences can be observed. For example during the mineral/EOM oxidation, O-PAC compounds were produced for both EOMs; however the distribution of the generated compounds was different (Table 1, Figures S5 and S6). Indeed, the main O-PACs produced during Homécourt EOM oxidation were 3-ring O-PACs (9-fluorenone and anthracene-9,10-dione) whereas for Neuves-Maisons EOM oxidation, 4-ring O-PACs (benzo[*de*]anthracene-7-one and benz[*a*]anthracene-7,12-dione) were predominantly generated. These discrepancies can be attributed to differences in the initial PAH soil composition; Homécourt sample being dominated by 3-ring PAHs (Table 1, Figure S3) and Neuves-Maisons being dominated by 4- and 5-ring PAHs (Table 1, Figure S4). It is worthwhile noting that PAHs are known to be precursors of O-PAC formation. For instance 9-fluorenone is known to be one of the oxidation product of fluorene (Lee et al., 2001) which occurs in high concentration in Homécourt sample and, similarly, benz[*a*]anthracene-7,12-dione can be generated during benz[*a*]anthracene oxidation (Lee et al., 2001) which is one of the major PAHs of Neuves-Maisons sample.

Difference of the initial sample composition also seems to influence the sample response to oxidation. For both EOM/mineral and soil oxidations, the decrease in EOM contents was more important for Neuves-Maisons samples than for Homécourt (Figure 2). As discussed, this decrease was a transfer of the organic carbon from the EOM to the insoluble fraction which was more important for Neuves-Maisons than for Homécourt (Figure 3). The latter observation can be due to the fact that Neuves-Maisons sample presented higher proportion of

342 HMW compounds than Homécourt and HMW compounds are more inclined to be stabilized
343 (condensed) in the non-extractable fraction (Northcott and Jones, 2001).

344

345 **5. Summary and conclusion**

346 In all experiments, oxidation led to (i) a decrease in PAH concentrations, (ii) a low production
347 of CO_2 and (iii) a decrease in EOM content due to a condensation/polymerization
348 phenomenon evidenced by a carbon mass balance. Oxidation of the EOM/minerals also led to
349 a production of O-PACs, the initial PAH soil composition governing the type of generated
350 compounds. The oxidation effects were more pronounced for EOM/goethite mixture than for
351 EOM/silica sand mixture. These observations are consistent with the famous goethite-induced
352 transformation mechanism of organic compounds. After PAC sorption on goethite surfaces,
353 electron transfer process occurs leading to the formation of reactive cation radical that in turn
354 interacts with oxygen or oxygen-species yielding oxidized products.

355 As in EOM experiments, goethite addition to the whole soils affected OM oxidation, but in a
356 lesser extent. This limited effect was likely due to the presence of a significant amount of
357 reactive phases naturally occurring in the soils. The soil initial composition also impacted its
358 evolution during oxidation; higher abundance of HMW compounds favoring the formation of
359 an insoluble residue and therefore EOM stabilization.

360 These conclusions showed that goethite may play a part in natural attenuation of PAH
361 contaminated soils as it contributes to contamination stabilization during low-temperature air-
362 oxidation. This work provides first results of the mechanisms involved and also underlined
363 the potential of indigenous reactive minerals to stabilize organic contamination. Therefore
364 their impact on the fate and transformation of PAHs in soils under different conditions
365 (humidity, temperature, oxygen concentrations) more representative of the field should be

366 investigated , and the long-term behavior of the refractory compounds generated during
367 oxidation (e.g. insoluble carbonaceous residues) should be explored.

368

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373

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