

Sources, Fate, and Toxic Hazards of Oxygenated Polycyclic Aromatic Hydrocarbons (PAHs) at PAH- contaminated Sites

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Sources, Fate, and Toxic Hazards of Oxygenated Polycyclic Aromatic Hydrocarbons (PAHs) at PAH-contaminated Sites

In this paper we show that oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) are important cocontaminants that should be taken into account during risk assessment and remediation of sites with high levels of PAHs. The presented data, which have been collected both from our own research and the published literature, demonstrate that oxy-PAHs are abundant but neglected contaminants at these sites. The oxy-PAHs show relatively high persistency and because they are formed through transformation of PAHs, their concentrations in the environment may even increase as the sites are remediated by methods that promote PAH degradation. Furthermore, we show that oxy-PAHs are toxic to both humans and the environment, although the toxicity seems to be manifested through other effects than those known to be important for polycyclic aromatic compounds in general, that is, mutagenicity and carcinogenicity. Finally, we present data that support the hypothesis that oxy-PAHs are more mobile in the environment than PAHs, due to their polarity, and thus have a higher tendency to spread from contaminated sites via surface water and groundwater. We believe that oxy-PAHs should be included in monitoring programs at PAH-contaminated sites, even if a number of other toxicologically relevant compounds that may also be present, such as nitro-PAHs and azaarenes, are not monitored. This is because oxy-PAH levels are difficult to predict from the PAH levels, because their environmental behavior differs substantially from that of PAHs, and oxy-PAHs may be formed as PAHs are degraded.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of contaminants commonly found at contaminated sites. In many cases, these compounds originate from coal tar formed as a by-product at gasworks (i.e., coal gas manufacturing) and coke production sites or from creosote used as a preservative to impregnate wood at wood preservation sites (1). The sites are of environmental concern because PAHs are known to be toxic, mutagenic, and carcinogenic (2, 3), and during risk assessment of the sites a small subset of 16 PAHs, often referred to as the "priority PAHs," are generally monitored. However, it has been recognized that the priority PAHs are not the only contaminants present at these sites, and that other classes of polycyclic aromatic compounds (PACs) also may contribute significantly to the load of toxic contaminants and thus the risk the sites pose to the environment (1, 4).

Contaminants that may be relevant in this context are the oxygenated PAHs (oxy-PAHs). These compounds are defined as PAHs with one or more carbonylic oxygen(s) attached to the

aromatic ring structure, and in some cases they also contain other chemical groups, such as alkyl groups and hydroxyl groups (Figure 1). Oxygenated PAHs are emitted from the same sources as PAHs, because they are both products of incomplete combustion (5–8). However, oxy-PAHs may also be formed through postemission oxidation of PAHs in the environment. This may occur through chemical oxidation, photooxidation, or biological transformation (9–11).

The chemical oxidation pathways generally involve oxidants, such as singlet oxygen, peroxides, peroxy radicals, and hydroxyl radicals, which are primarily formed through photochemical processes (10, 12). However, the PAHs themselves may also absorb light and undergo direct photooxidation through reactions with ground state oxygen (11, 13). Biological transformations of PAHs in the environment are generally catalyzed by enzymatic systems of microorganisms, such as bacteria and fungi, which are involved in various intra- or extracellular processes (9, 14). Some microorganisms are capable of using PAHs as a carbon and energy source and may thus transform the contaminants into molecules that can enter the organisms' central metabolic pathways. Other microorganisms simply transform PAHs into nontoxic excretable products. Polycyclic aromatic hydrocarbons may also be transformed through cometabolism, in which the microorganisms transform the PAHs coincidentally while living on another available substrate (15, 16).

In all these environmental processes, a wide variety of transformation products are formed, including oxygenated and hydroxylated PAHs, as well as ring cleavage products, such as aldehydes and carboxylic acids (9–11, 13, 15), raising questions about whether (and if so why) the oxy-PAHs should be considered more important to study than other compounds. One reason is that the oxy-PAHs seem to be more persistent than other transformation products, which often appear as ephemeral intermediates. Oxygenated PAHs have thus been proposed to be "dead-end products" of many biological and chemical degradation pathways (9, 10, 15, 17–20) and could potentially accumulate as PAHs are degraded (4, 21, 22). This is of particular concern when degradation processes are used for remediation purposes, which has become increasingly popular for contaminated soil and water systems (23, 24). In the worst cases, such treatments may lead to the formation of new, even more toxic contaminants in the remediated material. Another indication of the persistency of oxy-PAHs is their widespread occurrence in the environment. Indeed, many oxy-PAHs have been found at significant levels in diesel and gasoline exhaust (25–28), flue gases from various combustion processes (29, 30), fly ash (31), urban aerosols (5–8, 26, 32–39), sediments (40–43), river and coastal waters (44, 45), sewage sludge (46), industrial waste (47), and soil (4, 22, 48–53).

Another reason to study oxy-PAHs is that they seem to be considerably toxic. Although the available literature data are limited and the effects are far from fully understood, there is

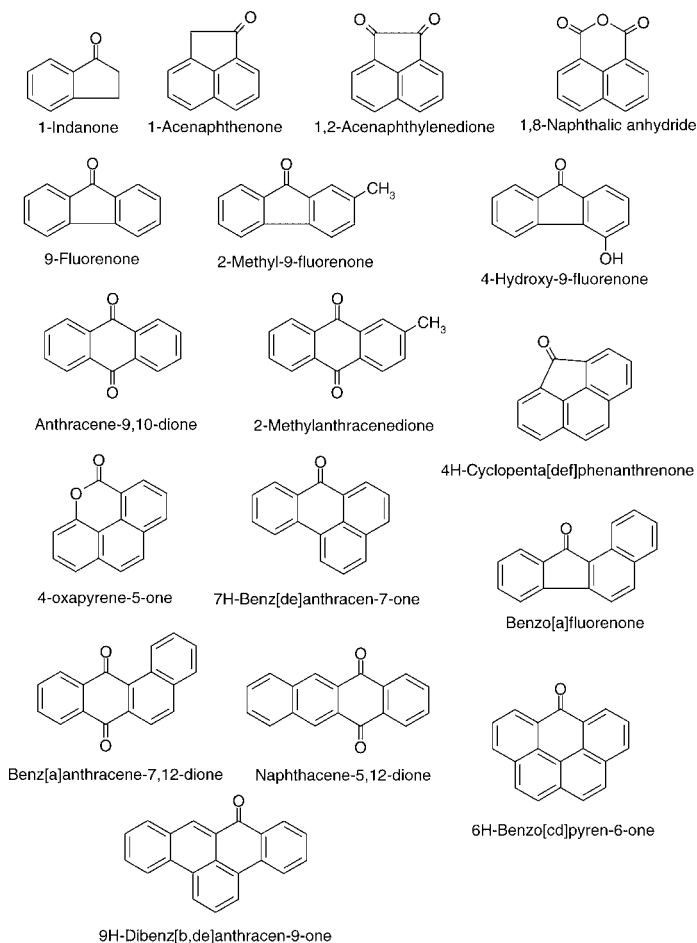


Figure 1. Structures of selected oxygenated polycyclic aromatic hydrocarbons.

substantial evidence indicating that oxy-PAHs are hazardous for both humans and the environment (see below). A third reason to study oxy-PAHs is their supposed mobility in the soil environment (11, 51, 54–56). The carbonyl groups added to the PAH molecules make oxy-PAHs relatively polar and more water soluble than the PAHs themselves. This increases their tendency to spread to the surroundings and hence the risk of adverse environmental effects.

In this paper, we discuss the relevance of oxy-PAHs as cocontaminants at sites previously highlighted for PAH contamination. We present data on the occurrence of oxy-PAHs at contaminated sites, their possible formation during remediation processes, their toxicity, and finally their mobility in soil. However, first we provide a brief summary of the methods used to analyze oxy-PAHs in soil. The data presented include a review of the published literature, as well as recent results from our own research.

ANALYSIS OF OXYGENATED POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL

Analysis of oxy-PAHs in soil generally involves exhaustive extraction techniques, such as Soxhlet (51), pressurized liquid extraction (4, 57), and ultrasonic extraction (56), in combination with solvent mixtures of different polarities, which will release both PAHs and oxy-PAHs from the soil matrix. After that, the oxy-PAHs are separated from the PAHs and other interfering compounds by open-column adsorption chromatography or solid-phase extraction using silica or alumina as the chromatographic material (4, 51, 52, 56). The semipolar fraction, containing the oxy-PAHs, may then be accurately

analyzed using methods based on either liquid chromatography (LC) (51, 58) or gas chromatography (GC) (4, 51, 52, 56, 57), usually coupled with mass spectrometry (MS). Gas chromatography mass spectrometry is most commonly used and has the advantages of being sensitive and producing unique mass spectra for several oxy-PAHs (generally more unique than the spectra obtained from PAHs). However, some oxy-PAHs are less successfully analyzed by GC/MS, probably because they are thermally labile, their volatility is too low, or their carbonyl groups interact too strongly with the stationary phase in the GC column (58). In those cases, LC/MS may be more useful.

An alternative method to be used prior to the GC or LC analysis is a combined extraction and separation method that was recently developed by our group (50). This method is based on pressurized liquid extraction with silica-packed extraction cells. The soil is placed on top of the silica gel in the cell, and the PAHs and oxy-PAHs can then be selectively extracted into 2 separate fractions using solvents of increasing polarity.

A limitation in today's analyses of oxy-PAHs is the shortage of authentic reference compounds. Not all oxy-PAHs that have been found in the environment are thus commercially available as pure compounds, which mean that they have to be determined by other means. Usually these oxy-PAHs are identified by their mass spectra and subsequently quantified against a similar oxy-PAH in the standard mixture (22, 50). This procedure will, of course, reduce the certainty of the results but is currently the only way to go for these compounds.

OCCURRENCE OF OXYGENATED POLYCYCLIC AROMATIC HYDROCARBONS (PAH) IN PAH-CONTAMINATED SOILS

Oxygenated PAHs have only been included among the compounds analyzed at contaminated sites in a few cases. However, existing literature data, including data we have published, indicate that these compounds are relatively abundant in the soil at many sites. In our most recent study (50), we quantified oxy-PAHs in soils from 7 different PAH-contaminated sites (Table 1): a gasworks site, a coke production site, and 4 wood preservation sites in Sweden and a Superfund site in the US (CRM 103–100, RTC, Laramie, WY). In all these soils, the oxy-PAH levels were comparable to the PAH levels. In 6 of the 7 soils, the total concentration of 17 oxy-PAHs varied between 10% and 30 % of the total concentration of the 16 US Environmental Protection Agency PAHs (Table 1). In the seventh soil, from the wood preservation site in Boden, the oxy-PAH load was even higher and 66% of the PAH concentration. However, in this case the PAH concentrations were much lower, and it is possible that a significant fraction of the contamination at this site originated from atmospheric deposition instead of direct inputs of creosote. Atmospheric input may lead to higher proportions of oxy-PAHs, because PAHs in the atmosphere are more susceptible to photochemical transformation than PAHs in soil (43). It should also be noted that whereas all compounds listed in Table 1 were analyzed by GC/MS, not all of them were quantified using authentic reference compounds; some had to be quantified against other compounds due to lack of authentic standards, such as, 4H-cyclopenta[def]phenanthrene, which constituted one of the major oxy-PAH-peaks in all chromatograms. Nevertheless, the oxy-PAH levels were too high to be neglected in any of the soils. In some cases the concentrations of individual oxy-PAHs were even higher than the concentrations of the PAHs from which they most likely originated, that is, the parent PAH. For example, this was the case for 9-fluorenone/fluorene in the soils from Husarviken, Boden, and Luleå.

The gasworks soil from Husarviken has also been analyzed for oxy-PAHs in 2 other studies by our group (4, 22), which were carried out prior to remedial treatments of the soil (see

Table 1. Concentrations ($\mu\text{g g}^{-1}$ dry soil) of polycyclic aromatic hydrocarbons (PAHs) and oxygenated PAHs (oxy-PAHs) in soil samples collected from PAH-contaminated gasworks, coke production, and wood preservation sites in Sweden and from a Superfund site in the US (CRM 103-100). Data from Lundstedt et al. (50).

	Gasworks site (Husarviken)	Coke production site	Wood preservation site 1 (Holmsund)	Wood preservation site 2 (Boden)	Wood preservation site 3 (Forsmo)	Wood preservation site 4 (Hässleholm)	Superfund site (CRM 103-100)
PAHs							
Naphthalene	12	7.1	2.7	0.075	0.54	0.64	20
Acenaphthylene	28	2.9	2.2	0.26	1.3	3.8	16
Acenaphthene	2.8	10	28	0.020	11	38	630
Fluorene	38	17	20	0.079	26	26	370
Phenanthrene	410	71	29	0.17	12	5.0	1770
Anthracene	74	12	38	0.95	53	48	420
Fluoranthene	530	57	665	1.6	697	563	1270
Pyrene	370	37	391	1.2	536	298	1070
Benzo[a]anthracene	240	24	96	0.54	125	130	250
Chrysene	230	26	113	0.76	135	139	320
Benzo[b]fluoranthene	270	34	58	3.7	73	82	140
Benzo[k]fluoranthene	110	11	21	0.89	30	29	51
Benzo[a]pyrene	160	18	16	1.0	37	39	96
Dibenz[a,h]anthracene	44	3.8	2.4	0.35	4.4	4.2	12
Indeno[1,2,3-cd]pyrene	140	15	7.9	1.6	15	15	31
Benzo[ghi]perylene	120	13	5.7	1.3	12	11	30
Oxy-PAHs							
1-indanone	0.46	0.11	0.38	0.074	0.65	0.45	0.42
1-acenaphthenone ^a	2.3	0.30	1.8	0.49	1.0	1.7	11
9-fluorenone	83	48	16	0.70	6.5	5.3	340
Methyl-9-fluorenone (Σ 4 peaks) ^a	13	23	6.4	0.085	8.5	2.2	110
Anthracene-9,10-dione	51	6.4	15	2.1	15	3.8	250
4H-cyclopenta[def]phenanthrenone ^a	78	5.3	134	1.3	139	75	180
2-methylanthracenedione	6.8	0.75	4.9	0.34	9.9	1.7	44
4-oxapyrene-5-one ^a	3.3	0.18	2.7	0.30	3.5	5.6	3.7
Benzo[fluorenone (Σ 2 peaks) ^a	84	10	21	0.31	28	18	120
7H-benz[de]anthracen-7-one	22	2.8	4.1	0.049	0.95	1.7	5.5
Benz[a]anthracene-7,12-dione	6.3	0.71	7.6	0.64	9.0	4.7	15
Naphthacene-5,12-dione	9.5	0.41	17	0.55	29	11	52
Benzo[cd]pyrene ^a	67	8.8	22	2.4	26	21	51

^a Authentic reference compounds were not available for these compounds. 1-acenaphthenone, methyl-9-fluorenone, and 4H-cyclopenta[def]phenanthren-4-one were quantified using the response factor of 9-fluorenone, 4-oxapyrene-5-one, and benzo[fluorenone using the response factor of 7H-benz[de]anthracen-7-one and benzo[cd]pyrene using the response factor of benz[a]anthracene-7,12-dione.

below). The relative proportions of PAHs and oxy-PAHs were similar in these samples compared with the sample used in the aforementioned study (50), although the soils sampled for remedial treatments contained somewhat lower concentrations of both PAHs and oxy-PAHs. On the other hand, we detected some additional oxy-PAHs in these studies compared with the study from which Table 1 is taken, such as acenaphthylene-1,2-dione, 1,8-naphthalic anhydride, 1-methylanthracenedione, 4-hydroxy-9-fluorenone, and dibenzanthracene.

Other researchers have also quantified oxy-PAHs in contaminated soil. In fact, Eriksson et al. (49) have even analyzed such compounds in the soil at the aforementioned gasworks site at Husarviken, which they conducted prior to a biodegradation study. Although the samples examined in their study were less contaminated and the overall concentrations they found were lower than the concentrations we found, the relative proportions of PAHs and oxy-PAHs were similar. However, it should be noted that Eriksson et al. only quantified 4 oxy-PAHs in the soil, *vis-a-vis* 9-fluorenone ($28 \mu\text{g g}^{-1}$), 4H-cyclopenta[def]phenanthrenone ($35 \mu\text{g g}^{-1}$), 4-hydroxy-9-fluorenone ($15 \mu\text{g g}^{-1}$), and 9,10-phenanthrene-9,10-dione ($17 \mu\text{g g}^{-1}$), 2 of which we did not analyze in the study from which the data in Table 1 are taken. Furthermore, while validating a new fractionation protocol for PACs, Meyer et al. (51) quantified 4 oxy-PAHs (9-fluorenone, anthracene-9,10-dione, 7H-benz[de]anthracen-7-one, and benz[a]anthracene-7,12-dione) in 2 different creosote-contaminated soils from wood preservation sites in Germany. The oxy-PAH levels found in that study were in the same range as the levels we found in the soils listed in Table 1, with similar PAH-levels, that is, between 1.3 and $20 \mu\text{g g}^{-1}$ of the individual oxy-PAHs in soils with total PAH concentrations of 1200 – $1400 \mu\text{g g}^{-1}$.

In addition to these quantitative determinations, oxy-PAHs have been identified in PAH-contaminated soil in at least 2 other studies, both of which were conducted prior to biodegradation experiments. In the first, by Brooks et al. (48), 9-fluorenone, anthracene-9,10-dione, 7H-benz[de]anthracen-7-one, and 4H-cyclopenta[def]phenanthrenone were identified in a creosote-contaminated soil from a Superfund site in Minnesota, while in the second, by Saponaro et al. (53), anthracene-9,10-dione and 2 isomers of benzanthracenone were identified in a soil from a former gasworks site in Italy. The oxy-PAHs in these studies were all tentatively identified only by their mass spectra, which to some degree reduces the certainty of the identification. On the other hand, this fact supports the hypothesis that oxy-PAHs are relatively abundant in these types of soils, because relatively high concentrations of sample components are required for mass spectral identification in such complex mixtures.

In summary, we can conclude that oxy-PAHs are indeed relatively abundant in soil at PAH-contaminated sites, and considering their toxic hazards, that in some cases can be greater than those of PAHs, it is reasonable to assume that oxy-PAHs make a significant contribution to the total hazard of toxic compounds at these sites.

FORMATION OF OXYGENATED POLYCYCLIC AROMATIC HYDROCARBONS (PAH) DURING REMEDIAL DEGRADATION OF PAHS

As mentioned above, oxy-PAHs may be formed as stable intermediates and persistent dead-end products during both biological and chemical degradation processes in the environment (9, 10, 15, 17–20). Analogously, they may also conceivably

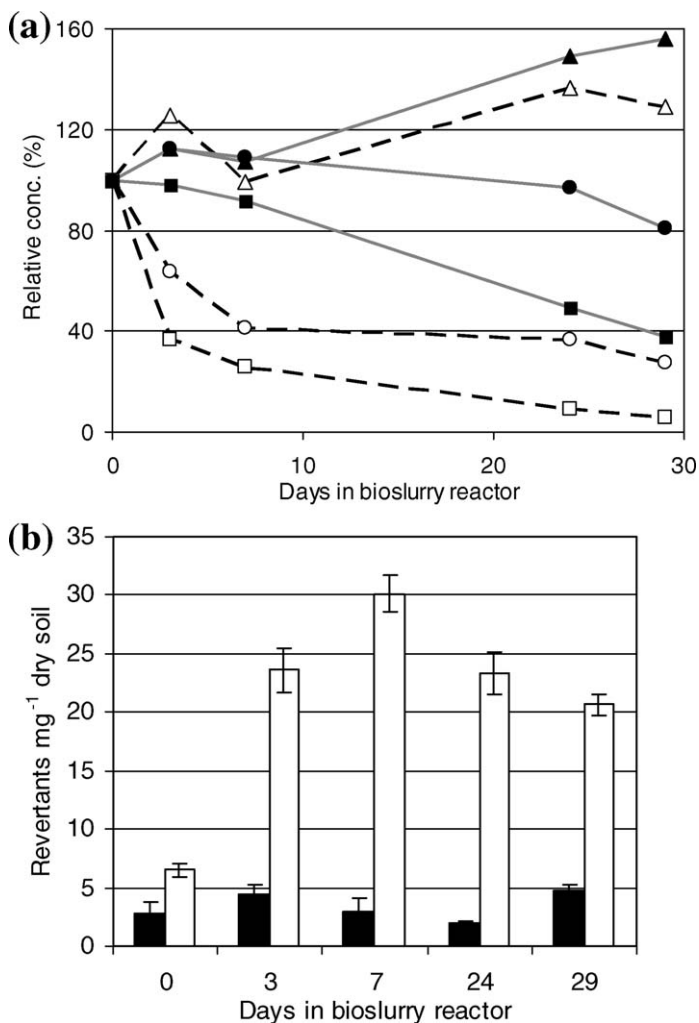


Figure 2. Changes in concentrations of polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs, and *Salmonella* mutagenicity during bioslurry treatment of a gasworks soil, from Lundstedt et al. (4) and Lynes (76). (a) Relative concentrations of PAHs with 3 fused rings (○), oxy-PAHs with 3 fused rings (○), 1-acenaphthenone (△), PAHs with 4 fused rings (■), oxy-PAHs with 4 fused rings (●), and 4-oxapyrene-5-one (▲). (b) Mutagenic potencies of the semipolar (oxy-PAH containing) fraction measured by the *Salmonella* reverse mutation assay using the strains TA98 (■) and YG1041 (□) in the presence of exogenous metabolic activation (+S9). Figure 2a is reprinted with permission. Copyright 2003, SETAC, Environmental Toxicology and Chemistry.

accumulate during remediation processes that promote PAH degradation, particularly because bottlenecks in the degradation pathways may become even more pronounced during the course of such treatments.

Accumulation of oxy-PAHs has indeed been demonstrated in several soil remediation studies. For example, Andersson and Henrysson (59) showed that anthracene-9,10-dione accumulated during treatment of an artificially PAH-contaminated soil with various white-rot fungi. Under certain conditions in their study, almost all of the anthracene in the soil was converted to anthracene-9,10-dione, which accumulated during the process. In another study, by Wischmann and Steinhart (56), 4 oxy-PAHs (9-fluorenone, anthracene-9,10-dione, 2-methylanthracene-9,10-dione, and benz[a]anthracene-7,12-dione) were found to accumulate during biodegradation of PAHs in an artificially contaminated soil. In a soil with no additives, the oxy-PAH concentrations increased steadily as the PAHs were degraded, although none of the oxy-PAHs reached levels higher than 5.7% of the original levels of their parent PAHs. In contrast, in a compost-amended soil, some oxy-PAHs reached levels up to 35% of the original PAH levels, but here the accumulation was

only temporary, and by the end of the study the oxy-PAHs had also been degraded. Furthermore, Lee et al. (60) and Lee and Hosomi (61) found anthracene-9,10-dione and benz[a]anthracene-7,12-dione to accumulate during ethanol-Fenton treatment of soils artificially contaminated with anthracene and benz[a]anthracene, respectively. More than 97% of the PAHs were removed in these studies, but 68% and 39% respectively, were just converted to their corresponding oxy-PAHs. In a study by Meyer and Steinhart (62), accumulation of 1,2-acenaphthenedione, 1,8-naphthalic anhydride, 4-hydroxy-9-fluorenone, and 9-fluorenone was demonstrated during biodegradation of PAHs in an artificially PAH-contaminated soil amended with compost. Although none of the oxy-PAHs reached levels higher than 10% of the original PAH levels during the time the PAHs were depleted, some oxy-PAH concentrations were still increasing at the end of the study. In the aforementioned study by Eriksson et al. (49), the 4 oxy-PAHs identified in the gasworks soil were found to accumulate as the soil was biotreated under various conditions. In most cases the accumulation was low, but under some conditions the concentration of 4-hydroxy-9-fluorenone increased up to 550% of its initial concentration. Finally, Saponaro et al. (53) reported that concentrations of the oxy-PAHs they identified in the soil increased as it was treated biologically in slurry reactors for 91 days. However, they did not report the magnitude of the increase.

In our own studies, we have demonstrated oxy-PAH accumulation during 3 different remedial processes: a bioslurry treatment (4), treatment with wood-rotting fungi (21), and treatment with a combination of ethanol and Fenton's reagent (22). In the first process, a soil from the aforementioned Swedish gasworks site at Husarviken was treated in a pilot-scale (~1 m³) bioslurry reactor for 29 days. Although the overall PAH removal in this study was relatively poor (~40%), oxy-PAHs were found to accumulate in the process (Fig. 2a). The accumulated compounds, 1-acenaphthenone and 4-oxapyrene-5-one, were also present in the untreated soil, but their concentrations were significantly higher at the end of the treatment than before it. Consequently, these 2 compounds must have been formed to a greater extent than they were degraded. Furthermore, as shown in Figure 2a, other oxy-PAHs were generally depleted more slowly than PAHs with the same number of fused rings (including their parent compounds), indicating a continuous formation of these oxy-PAHs during the treatment. Some of these compounds were also seen to accumulate temporarily during the first days of the process. Other oxy-PAHs that were probably formed to a minor extent, because of a lack of parent PAHs, showed remarkable persistency. For example, naphthacene-5,12-dione was found at a relatively constant concentration throughout the treatment.

In the second study (21), a soil artificially contaminated with fluorene, phenanthrene, pyrene, and benzo[a]anthracene was inoculated with wood-rotting fungi. These fungi excrete extracellular enzymes that degrade lignin in wood. However, the enzymes are also capable of breaking up the aromatic structures of organic contaminants. Two fungi were examined in this study, and the one that enhanced the degradation rate the most caused concentrations of oxy-PAHs in the soil to increase. Thus, 9-fluorenone, 4-hydroxy-9-fluorenone, benzo[a]anthracene-7,12-dione, and 4-oxa-5-pyrenone were found to accumulate as the PAHs were degraded. Figure 3 shows time courses of the accumulation of benzo[a]anthracene-7,12-dione and the degradation of benzo[a]anthracene. The accumulation of 9-fluorenone showed similar trends, although its parent compound, fluorene, was almost completely depleted during the process. However, the other 2 oxy-PAHs accumulated to lesser degrees. The other fungus examined was less effective in

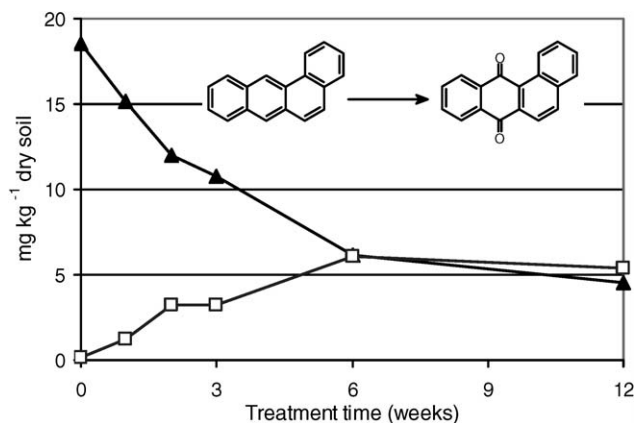


Figure 3. Degradation of benzo[a]anthracene (▲) and accumulation of benzo[a]anthracene-7,12-dione (□) in soil inoculated with the white-rot fungus *Pleurotus osteratus* from Andersson et al. (21), reprinted with permission. Copyright 2003, SETAC, Environmental Toxicology and Chemistry.

enhancing PAH degradation, but on the other hand, no oxy-PAHs were accumulating during this treatment. The accumulation of oxy-PAHs during the first treatment was probably due to an inhibition of indigenous soil bacteria by the fungus examined. These bacteria may be necessary for complete degradation of the PAHs, which probably occurs through a sequential process involving both bacteria and fungi.

In the third study (22), soil from the Husarviken gasworks site (i.e., the soil used in the bioslurry study) was chemically treated in slurries with a combination of ethanol and Fenton's reagent. The latter consists of hydrogen peroxide catalytically decomposed by ferrous iron (Fe^{2+}), producing hydroxyl radicals capable of oxidizing organic compounds. Ethanol was added to increase the dissolution and thus the chemical availability of the PAHs. The combined ethanol and Fenton's reagent treatment was found to deplete the PAHs in the soil more than similar treatments with water only and traditional Fenton conditions, that is, without ethanol. However, the increased PAH removal was accompanied by the accumulation of oxy-PAHs. For instance, anthracene-9,10-dione, 1-methylantracene-9,10-dione, 2-methylantracene-9,10-dione, benzo[a]anthracene-7,12-dione, and 4-hydroxy-9-fluorenone were found at higher concentrations in the soil after the treatment than before the treatment (Fig. 4). These compounds were also found in considerable amounts in the liquid phase after the treatment. Analysis of the liquid phase also revealed that the total amounts of 1-indanone and 1,8-naphthalic anhydride had increased during the treatment and that a second isomer of hydroxyl-9-fluorenone had been formed.

All these studies show that many oxy-PAHs have the potential to accumulate during degradation of PAHs in soil, which may lead to new environmental threats even if the original contaminants are eliminated. Some of the oxy-PAHs that were seen to accumulate in the aforementioned studies may well be ephemeral, and their abundance in the soil might decrease if, for instance, the process time was extended. However, because most of the compounds are also found in untreated soils (4, 50) and other environmental matrices (8, 26, 30, 31, 40, 44, 46, 47), they can be considered to be relatively persistent and may therefore remain in the soil a long time after remedial treatment ends.

TOXIC EFFECTS OF OXYGENATED POLYCYCLIC AROMATIC HYDROCARBONS

The toxic effects of PAHs have been the subject of many studies; however, less is known about the toxicity of oxy-PAHs.

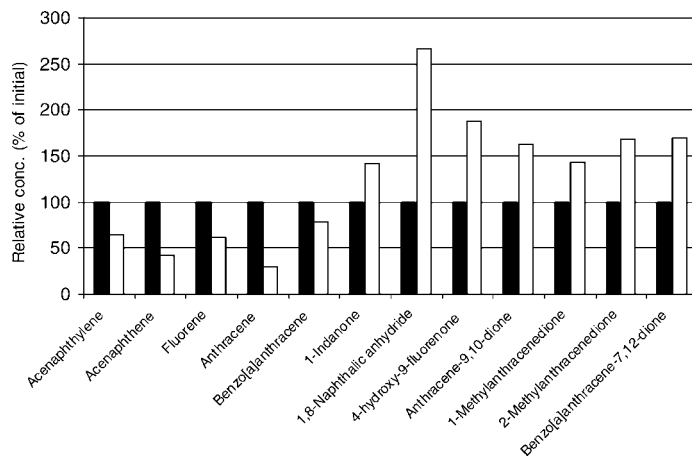


Figure 4. Relative concentrations of selected polycyclic aromatic hydrocarbons (PAHs) and oxygenated PAHs before (■) and after (□) combined ethanol-Fenton's reagent treatment of a gasworks soil, from Lundstedt et al. (22). Percentage values are relative to the initial concentration found in the soil.

Nevertheless, several studies have demonstrated that they can adversely affect a variety of organisms in the environment (Table 2a and 2b), even if the nature of the effects, such as those associated with PAHs, vary from compound to compound. For example, several studies have shown that a number of oxy-PAHs are acutely toxic to the marine bacterium *Vibrio fischeri* (45, 55, 63), the aquatic invertebrate *Daphnia magna* (64, 65), various microalgae (63, 66), and the aquatic and terrestrial plants *Lemna gibba* (54, 55) and *Brassica napus* (67). Oxygenated PAHs have also been shown to induce oxidative stress (68–70), endocrine system disruptions (42, 45), and cytotoxic effects (71) in mammalian cell systems. In addition, several oxy-PAHs have been shown to elicit mutagenic effects (29, 63, 72–78), which are generally considered to be the most alarming effect elicited by PACs in general. The mutagenic activity has usually been assessed through bacterial assays systems, such as the *Salmonella* reverse mutation assay or similar tests. However, mutagenic activity of oxy-PAHs has also been observed in mammalian cells (73).

The mechanisms underlying the toxicity of oxy-PAHs are complex and far from fully understood. Some oxy-PAHs, such as the quinones, may be converted to electrophilic intermediates that may form adducts with essential macromolecules, such as proteins and DNA. This may lead to genotoxic effects through DNA adduct formation and possibly also cytotoxic effects via the depletion of reduced glutathione (79). In addition, quinones may undergo enzymatic (i.e., P450/P450-reductase) and non-enzymatic redox cycling with their corresponding semiquinone radicals and as a result generate reactive oxygen species in target cell populations. Production of reactive oxygen species is responsible for severe oxidative stress within cells through the formation of oxidized macromolecules, including lipids, proteins, and DNA. Furthermore, reactive oxygen species can activate a number of signaling pathways and cellular events that may be involved in or responsible for several of the toxic effects associated with oxy-PAHs (79).

The potencies of oxy-PAHs vary from compound to compound and with the toxicological end point studied. However, in many cases the oxidation products are more toxic than their parent compounds (Table 2). For example, there are several studies showing that photolytic oxygenation of PAHs leads to transformation products with increased toxicity to aquatic and terrestrial plants (54, 55, 67, 80, 81), marine bacteria (55, 63), and aquatic invertebrates (45, 64, 65). There are also studies showing that some oxy-PAHs may have higher

Table 2a. Compilation of the published data on the toxicity of oxygenated polycyclic aromatic hydrocarbons (PAHs). Data for some PAHs are also included for comparison. The footnotes indicate the sources of the data. Please see Table 2b for definitions of footnotes.

	Acute toxic effects		Aq. Plants <i>Lemna gibba</i> , EC50 ($\mu\text{g L}^{-1}$)	Algae EC50 ($\mu\text{g L}^{-1}$)	Mammalian cells survival (%)	Oxidative stress	Endocrine disruption
	Bacteria <i>Vibrio fischeri</i> , EC50 ($\mu\text{g L}^{-1}$)	Aq. Invertebrates <i>Daphnia magna</i> , EC50 ($\mu\text{g L}^{-1}$)				Mammalian cells EC50 ($\mu\text{g L}^{-1}$)	Mammalian and yeast cells EC50 ($\mu\text{g L}^{-1}$)
Phenalen-1-one				nv ^g	24 ^h		
Naphthalene-1,2-dione						777 ^l	
Naphthalene-1,4-dione						1781 ^l	
1,8-naphthalic anhydride					92 ^h		
2-hydroxy-9-fluorenone							186 ^{c1}
9,10-phenanthrene-9,10-dione	102 ^a	358 ^d 358 ^e	530 ^a		0 ^h	349 ^l nv ^k nv ^l	
Anthracene-9,10-dione		231 ^d	500 ^f	750 ^b	90 ^h	6177 ^l nv ^k	nd ^c $7.7 \times 10^{-7} \text{ m}^1$
Anthracene-1,4-dione	3.7 ^b	28 ^d					
1-hydroxyanthracene-9,10-dione		nd ^d	2400 ^f				47 ^{c2}
2-hydroxyanthracene-9,10-dione		nd ^d	50 ^f				119 ^{c1}
1,2-dihydroxyanthracene-9,10-dione		2928 ^d	2800 ^f				2620 ^{c1} 59 ^{c2}
1,3-dihydroxyanthracene-9,10-dione			2500 ^f				
1,4-dihydroxyanthracene-9,10-dione		29.5 ^d	6500 ^f				nd ^c
1,5-dihydroxyanthracene-9,10-dione			>10 000 ^f				nd ^c
1,8-dihydroxyanthracene-9,10-dione		192 ^d	2500 ^f			nv ^k	nd ^c
2,6-dihydroxyanthracene-9,10-dione			>10 000 ^f				427 ^{c1}
1,2,4-trihydroxyanthracene-9,10-dione	2340 ^c	50.4 ^d	6000 ^f				nd ^c
1,2,5,8-tetrahydroxyanthracene-9,10-dione		186 ^d	9500 ^f				
9(10H)-anthracenone						nv ^k	
10-hydroxy-9-anthracenone				nv ^b			
4H-cyclopenta[def]-phenanthrenone					69 ^h		
7H-benz[de]anthracen-7-one					68 ^h		$1.0 \times 10^{-4} \text{ m}^2$ $3.0 \times 10^{-6} \text{ m}^1$
Benz[a]anthracene-7,12-dione		3.82 ^d			73 ^h		$1.8 \times 10^{-3} \text{ m}^2$ $1.4 \times 10^{-6} \text{ m}^1$
Naphthacene-5,12-dione		nd ^d			71 ^h		
Chrysene-1,4-dione							
Benzo[a]pyrene-1,6-dione		1.94 ^d			26 ^h 6 ^j		
Benzo[a]pyrene-3,6-dione		2.90 ^d			25 ^h 80 ^j 55 ^h		
Benzo[a]pyrene-4,5-dione					75 ^j		
Benzo[a]pyrene-6,12-dione					78 ⁱ		
Benzo[a]pyrene-7,8-dione					74 ^h		
6H-benzo[cd]pyren-6-one					23 ^h		
Cyclopenta[c,d]pyren-3(4H)-one					54 ^h		
7H-dibenz[de,j]anthracen-7-one					90 ^h		
Anthanthrenequinone							
Phenanthrene	530 ^a	698 ^d 949 ^e	>5000 ^a			5504 ^l	
Anthracene		19.6 ^d	800 ^f			4324 ^l	nd ^c
Benzo[a]anthracene		1.48 ^d					0.109 ^{m2} $7.9 \times 10^{-7} \text{ m}^1$
Benzo[a]pyrene		1.62 ^d			95 ⁱ		

estrogenic activity than their parent compounds (42, 45). However, in terms of mutagenic activity, oxy-PAHs are generally less potent than the unsubstituted PAHs (29, 73, 75–77), although there are some studies showing that oxy-PAHs are more potent (63, 78). It should also be noted that oxy-PAHs do not always require exogenous mammalian metabolic activation to manifest their mutagenicity in bacterial systems but appear to react with DNA and other biomolecules directly (29, 63, 76–78). Although mammalian metabolic processes may enhance the mutagenic activity of oxy-PAHs, such metabolism is always required for the induction of a mutagenic response for unsubstituted PAHs (3, 11).

In our own work, we have observed *Salmonella* mutagenic activity for some pure oxy-PAHs, although the responses have been fairly weak (75). We have also seen strong indications that mixtures of oxy-PAHs contribute significantly to the total mutagenic activity of PAH-contaminated soil samples (82). During these studies, in which chemical separation methods were combined with biological tests for toxicity assessment (i.e.,

effect directed chemical fractionation), we found the semipolar (oxy-PAH containing) fraction to be almost as mutagenic as the PAH-containing fraction (Fig. 5). Further fractionation of the semipolar fraction, from one of the soils, revealed that several groups of PAH derivatives probably contributed to the mutagenic activity (Fig. 6). The subfractions containing oxy-PAHs, nitro-PAHs, and azaarenes all contributed to the total genotoxicity of the semipolar fraction. Nevertheless, the oxy-PAH-enriched subfraction (subfraction 3 in Fig. 6) contributed at least as much as the other fractions (Lundstedt and Lemieux, unpublished data). Other researchers who have used effect-directed chemical fractionation to investigate complex environmental matrices have come to the same conclusion about oxy-PAHs, that is, that they predominate in the most toxic fractions of samples containing PACs (25, 34–36, 40).

Furthermore, the formation of oxy-PAHs may be responsible for the increase in toxicity that has been seen during remedial treatments of some PAH-contaminated soils (48, 83–86), including our bioslurry treatment of the Husarviken gasworks

Table 2b. Compilation of the published data on the genotoxicity of oxygenated polycyclic aromatic hydrocarbons (PAHs). Data for some PAHs are also included for comparison. The footnotes indicate the source of the data.

	Bacterial tests (<i>Salmonella typhimurium</i>)							Human cells	
	umuC test TA1535/ pSK1002 EC1.5 (mgL ⁻¹)	Ames test TA98 +S9, potency (rev μg ⁻¹)	Ames test TA98 -S9, potency (rev μg ⁻¹)	Ames test TA100 +S9, potency (rev μg ⁻¹)	Ames test TA100 -S9, potency (rev μg ⁻¹)	Ames test TA97 +S9, potency (rev μg ⁻¹)	Ames test TA97 -S9, potency (rev μg ⁻¹)	Other strain, potency (rev μg ⁻¹)	h1A1v2 cells, relative mutational activity
Phenalen-1-one								nv ^t	0.0018 ^h
1,8-naphthalic anhydride									nd ^h
9,10-phenanthrenequinone								nv ^u	nd ^h
2-methylanthracenedione								0.45 ^{r1}	
								0.49 ^{r2}	
1-hydroxyanthracene-9,10-dione	15.7 ^b								
1,4-dihydroxyanthracene-9,10-dione	3.95 ^b								
9H-anthrone		nd ^o	0.4 ^o	<0.2 ^o	<0.2 ^o				
			0.4 ^q	<0.2 ^q	<0.2 ^q				
Anthracene-9,10-dione		nd ^s	nd ^s	nd ^s	nd ^s	nd ^s	nd ^s		nd ^h
2-methylanthracenedione		nd ^s	nd ^s	nd ^s	nd ^s	nd ^s	nd ^s		
4H-cyclopenta[def]-phenanthrene									nd ^h
Benzo(a)fluorenone		nd ^q	nd ^q	nd ^q	nd ^q				
Benzo(c)fluorenone		<0.3 ^o	<0.2 ^o	2.0 ^o	nd ^o				
		<0.3 ^q	<0.2 ^q	2.0 ^q					
Benzo(b)fluorenone		1.0 ^o	0.5 ^o	0.3 ^o	0.1 ^o				
		1.0 ^q	0.5 ^q	0.3 ^q	0.1 ^q				
7H-benz[de]anthracen-7-one		<0.3 ^o	<0.2 ^o	3.0 ^o	nd ^o				0.0039 ^h
		<0.3 ^q	<0.2 ^q	3.0 ^q					
6H-benzo[cd]pyren-6-one		<0.6 ^o	nd ^o	nv ^q	nd ^q				0.32 ^h
		nv ^q	nd ^q						
7H-dibenz[de,j]anthracen-7-one		nv ^q	nd ^q	nv ^q	nd ^q				
4-oxapyrene-5-one		3.7 ^p	4.7 ^p						
1,6-pyrenequinone		7.0 ^q	nd ^q	nd ^s	nd ^s	275 ^s	302 ^s	nv ^u	
		nd ^s	nd ^s						
1,8-pyrenequinone		nd ^s	nd ^s	nd ^s	nd ^s	236 ^s	260 ^s	nv ^u	
13H-dibenzo[c,g]fluoren-13-one		nv ^q	nd ^q	nv ^q	nd ^q				
7H-dibenzo[c,g]fluoren-7-one		7.0 ^q	nd ^q	22 ^q	nd ^q				
Naphthacene-5,12-dione				7.8 ^f					nd ^h
Chrysene-1,4-dione									nd ^h
Benz[a]anthracene-7,12-dione							1.4 ^{r3}		nd ^h
Benzo[a]pyrene-1,6-dione							nv ^u		nd ^h
Benzo[a]pyrene-3,6-dione							nv ^u		nd ^h
Benzo[a]pyrene-4,5-dione									nd ^h
Benzo[a]pyrene-6,12-dione							nv ^u		nd ^h
Cyclopenta[c,d]pyren-3(4H)-one									0.0050 ^h
Anthanthrenequinone									0.018 ^h
Pyrene						315 ^s	nd ^s		nd ^h
Benzo[a]anthracene			32 ^f					0.08 ^{r3}	0.082 ^h
								0.31 ^{r1}	
								0.36 ^{r2}	
Cyclopenta[cd]pyrene									6.9 ^h
Benzo[a]pyrene		125 ^o	nd ^o	250 ^o	nd ^o	1031 ^s	nd ^s		1.0 ^h
		700 ^p	nd ^p	208 ^q	nd ^q				
		74 ^q	nd ^q						

nd = tested but no detected effect. nv = observed effect but no value. ^a McConkey et al. (55). Inhibition of the luminescence of the marine bacterium *Vibrio fischeri* (*Photobacterium phosphoreum*) and the growth of the aquatic plant *Lemna gibba*. ^b Brack et al. (63). Inhibition of the luminescence of the marine bacterium *Vibrio fischeri* and the reproduction of the green alga *Scenedesmus vacuolatus*. Mutagenic effects measured by the *umuC* test using the *Salmonella typhimurium* strain TA1535/pSK1002. Mutagenicity expressed as EC1.5, that is, the concentration at which an induction factor of 1.5 was obtained. ^c Kurihara et al. (45). Inhibition of the luminescence of the marine bacterium *Vibrio fischeri*. Estrogenic activity in a yeast 2-hybrid assay. ^d Agonist-concentration at which the chemiluminescence is 10 times the controls. ^e Antagonistic EC50 inhibition of the chemiluminescent signal of 17β-estradiol. ^f Lampi et al. (64). Inhibition of the mobility of the cladoceran *Daphnia magna* under visible light for the oxy-PAHs and visible + UVA light for the PAHs. ^g Xie et al. (65). Inhibition of the mobility of the cladoceran *Daphnia magna*. ^h Mallakin et al. (54). Growth inhibition of the aquatic plant *Lemna gibba*. ⁱ Winters et al. (66). Various acute toxic effects on blue-green and green algae. ^j Durant et al. (73). Mutagenic activity relative to benzo[a]pyrene determined in a forward mutation assay based on human lymphoblastoid cells (*h1A1v2*). Cytotoxicity was also measured during the test, here presented as survival of the cultured cells. ^k Zhu et al. (71). Survival of bone marrow stromal cells from DBA/2 mice. ^l Shimada et al. (70). Inhibition of the stereoselective reduction of 4-benzoylpyridine to S(-)-α-phenyl-4-pyridylmethanol. EC50 was determined for phenanthrene-9,10-dione. The other EC50 values were calculated from their relative inhibition at the 10-μM level. ^m Kubatova et al. (68). Depletion of glutathione in murine macrophages (RAW 264.7). No values presented, only positive or negative response. ⁿ Kumagai et al. (69). Oxidation of protein sulfhydryls and the potential generation of harmful oxidants. No values presented. ^o Machala et al. (42). Estrogenic and aryl hydrocarbon receptor (AhR)-mediated activities. ^{m1} Estrogenic potency expressed as induction equivalency factors (IEFs), that is, the ratio between the EC25 of 17β-estradiol and an oxy-PAH concentration giving equal levels of luciferase activity. ^{m2} AhR-mediated potency expressed as IEFs, that is, the ratio between the EC25 of 2,3,7,8-tetrachlorodibenzo-p-dioxin and an oxy-PAH concentration giving equal levels of luciferase activity. ^o Ramdahl (29). Mutagenic activity determined by the Ames *Salmonella*/microsome assay, using the strains TA98 and TA100, with (+S9) and without (-S9) exogenous metabolic activation. Potencies expressed as revertants μg⁻¹. ^p Pitts et al. (77). Mutagenic activity determined by the Ames *Salmonella*/microsome assay, using the strain TA98, with (+S9) and without (-S9) exogenous metabolic activation. Potencies expressed as revertants μg⁻¹. ^q Moller et al. (76). Mutagenic activity determined by the Ames *Salmonella*/microsome assay, using the strains TA98 and TA100, with (+S9) and without (-S9) exogenous metabolic activation. Potencies expressed as revertants μg⁻¹. ^r Lynes (75). Mutagenic activity determined by the Ames *Salmonella*/microsome assay, using the strains TA100, YG1041, CFT509, and CFA509 with (+S9) and without (-S9) exogenous metabolic activation. Potencies expressed as revertants μg⁻¹. ^{r1} CFT509, ^{r2} CFA509, ^{r3} YG1041, all -S9. ^s Sakai et al. (78). Mutagenic activity determined by the Ames *Salmonella*/microsome assay, using the strain TA97, with (+S9) and without (-S9) exogenous metabolic activation. Potencies expressed as revertants μg⁻¹. ^t Leary et al. (74). Mutagenic activity determined in *Salmonella typhimurium*, strain TM677, using 8-azaguanine resistance as the genetic end point. No potency values were presented. ^u Chesis et al. (72). Mutagenic activity determined by the Ames *Salmonella*/microsome assay, using the strain TA104 in the presence of exogenous metabolic activation. Potencies expressed as revertants μg⁻¹.

soil (4, 75). In that study, the net *Salmonella* mutagenic activity (i.e., final minus initial) increased during the course of the treatment, although the results were somewhat ambiguous and the response was not very well correlated with the accumulation and elimination of analyzed oxy-PAHs (Fig. 2).

All these toxicological data support the hypothesis that oxy-PAHs make a significant contribution to the toxic hazards of complex environmental matrices contaminated with PACs, including PAH-contaminated land. Consequently, exclusive monitoring of priority PAHs at contaminated sites may result

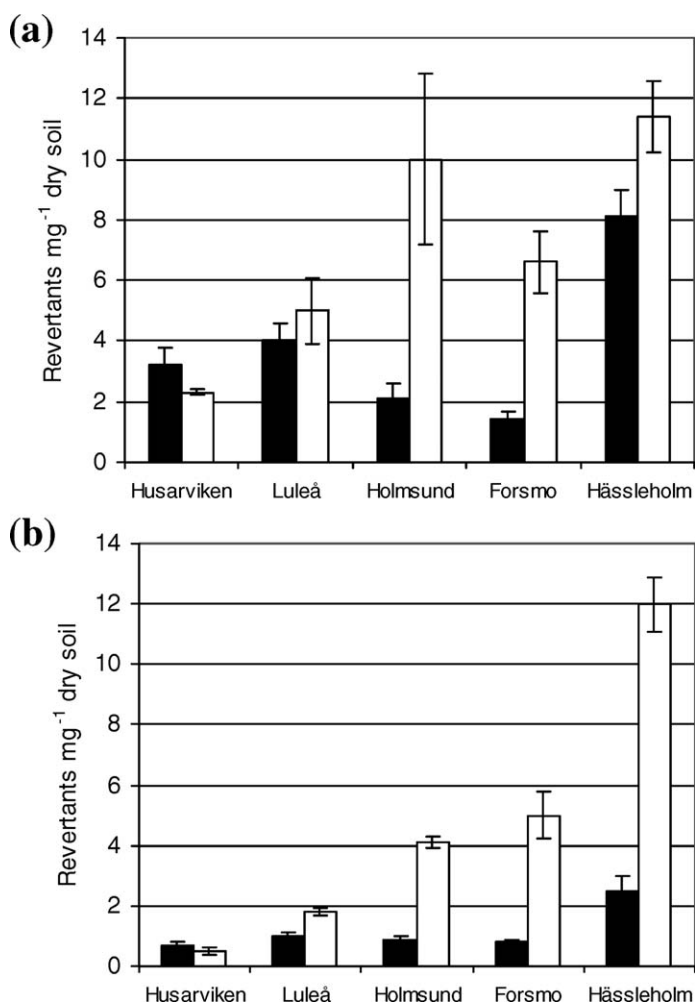


Figure 5. Mutagenic potencies measured in (a) the nonpolar (polycyclic aromatic hydrocarbon [PAH]) fraction and (b) the semipolar (oxygenated PAH) fraction of extracts of soil from various PAH-contaminated sites in Sweden. The mutagenicity was measured by the *Salmonella* reverse mutation assay using the strains TA98 (■) and YG1041 (□) in the presence of exogenous metabolic activation (+S9). Data from Lemieux et al. (82).

in underestimations of actual hazard and risk, and this underestimation may be particularly acute during and after remedial treatments.

MOBILITY OF OXYGENATED POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL

Because oxy-PAHs contain oxygen atoms, they are more polar than unsubstituted PAHs that contain only carbon and hydrogen atoms. A direct consequence of this structural difference is that the oxy-PAHs are more water soluble and less lipophilic than the PAHs with the same number of aromatic rings (Table 3). Thus, oxy-PAHs should theoretically have higher mobility in the environment than PAHs, because they are more likely to be transported in aqueous phases. This has been postulated in several studies (11, 51, 54–56) but only recently demonstrated. In a study in our laboratory, we compared the leachability of oxy-PAHs and PAHs from a contaminated soil using column experiments (Lundstedt and Karlsson, in prep.). Soil samples from the wood impregnation site in Holmsund, Umeå, Sweden (Table 1), were packed in glass columns (36 cm \times 2.5 cm internal diameter) and percolated with water at 0.13 mL min⁻¹ for 19 d. The effluent was collected and analyzed for PAHs and oxy-PAHs after leaching periods of 42 hr and 5, 12, and 19 d, corresponding to liquid/solid ratios (L/S) of approximately 1, 3, 7, and 11, respectively. The results showed

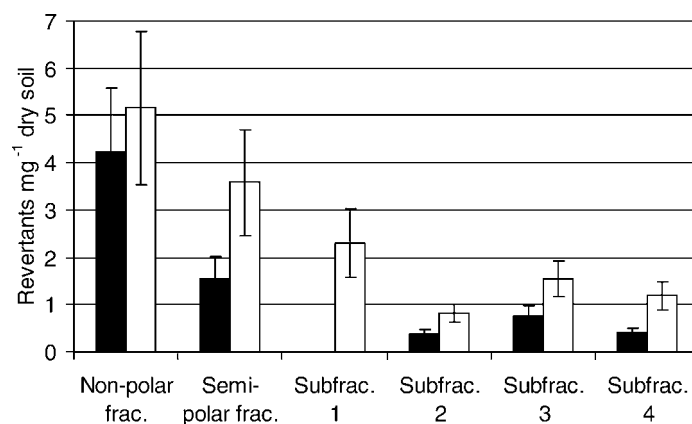


Figure 6. Mutagenic potencies measured in the nonpolar (polycyclic aromatic hydrocarbon [PAH]) fraction, semipolar (oxygenated PAH) fraction, and high-performance liquid chromatography subfractions of the semipolar fraction of an extract of soil sampled at a wood preservation site (Holmsund, Sweden). Mutagenicity was measured by the *Salmonella* reverse mutation assay using the strains TA98 (■) and YG1041 (□) in the presence of exogenous metabolic activation (+S9). Subfraction 1 contains mononitro-PAHs and carbazole-type azaarenes; subfraction 2, dinitro-PAHs and early eluting oxy-PAHs; subfraction 3, the bulk of oxy-PAHs and oxy-nitro-PAHs; and subfraction 4, acridine-type azaarenes.

that the oxy-PAHs leached to a much higher degree than the corresponding PAHs. Figure 7 compares the accumulated leached fraction of PAHs and oxy-PAHs containing 3 fused rings. The data clearly show that the oxy-PAHs leach much more readily than the PAHs. After 19 d, that is, at L/S 11, almost 2% of the oxy-PAHs had leached from the soil while less than 0.5% of the corresponding PAHs were found in the leachate. The pattern was similar for other groups of PAHs and oxy-PAHs, although lighter compounds, on the whole, tended to leach to a greater extent than heavier compounds.

The differences in leachability can also be seen when comparing the soil organic carbon-water partitioning coefficients (K_{oc}) determined during the study (Table 3). The K_{oc} values were generally lower for the oxy-PAHs than for the corresponding PAHs, meaning that the oxy-PAHs were distributed in the water phase to a higher degree than the PAHs. The biggest difference was seen for anthracene and anthracene-9,10-dione, for which the K_{oc} values differed almost an order of magnitude. Furthermore, the study showed that the PAHs were bound to small particles in the leachate to a greater extent than the oxy-PAHs. When the leachate, which already had been filtered through a 1.2- μ m filter at the outlet of the columns, was centrifuged, a larger fraction of the PAHs than of the oxy-PAHs was lost with the fine particles.

The results strongly indicate that oxy-PAHs have higher mobility in soil compared with unsubstituted PAHs. Due to their higher water solubility and lower lipophilicity (expressed as octanol water partitioning coefficients, K_{ow} , in Table 3), the oxy-PAHs tend to be distributed in the water phase to a greater extent than the PAHs. Although this may not be unexpected, it emphasizes the significance of oxy-PAHs as a class of compounds that should be taken into account during risk assessments of contaminated sites.

CONCLUSIONS

The data reviewed in this paper show that oxy-PAHs are important cocontaminants at PAH-contaminated sites. They are present in the soil at levels that are not far below the PAH levels, and there is ample evidence showing that they are considerably toxic to both humans and the environment. The levels of oxy-PAHs are maintained partly because of their

Table 3. Physicochemical properties of selected polycyclic aromatic hydrocarbons (PAHs) and oxygenated PAHs. The aqueous solubility data and the octanol-water partition coefficients (log K_{ow}) were collected from the PhysProp database and EPI Suite™ v.3.12, US Environmental Protection Agency. The soil organic carbon-water partitioning coefficients (log K_{oc}) were determined in the column leaching study by Lundstedt and Karlsson (in prep.).

	CAS number	Molecular weight	Aqueous solubility (mg L ⁻¹)	Log K_{ow}	Log K_{oc} (measured)
Naphthalene	91-20-3	128	31	3.30	-
Acenaphthylene	208-96-8	152	16	3.94	4.52
Acenaphthene	83-32-9	154	3.9	3.92	4.08
Fluorene	86-73-7	166	1.69	4.18	4.43
Phenanthrene	85-01-8	178	1.15	4.46	4.96
Anthracene	120-12-7	178	0.043	4.45	5.17
Fluoranthene	206-44-0	202	0.26	5.16	5.53
Pyrene	129-00-0	202	0.135	4.88	5.63
Benzo[a]anthracene	56-55-3	228	0.0094	5.76	6.34
Chrysene	218-01-9	228	0.002	5.81	6.61
Benzo[b]fluoranthene	205-99-2	252	0.0015	5.78	6.76
Benzo[k]fluoranthene	207-08-9	252	0.0008	6.11	6.49
Benzo[a]pyrene	50-32-8	252	0.00162	6.13	6.74
Dibenz[a,h]anthracene	53-70-3	278	0.00249	6.75	6.55
Indeno[1,2,3-c,d]pyrene	193-39-5	276	0.00019	6.70 ^b	6.72
Benzo[g,h,i]perylene	191-24-2	276	0.00026	6.63	6.63
1-indanone	83-33-0	132	1427 ^a	2.11 ^b	3.81
1-acenaphthenone	2235-15-6	168	20 ^a	2.79 ^b	3.89
1,2-acenaphthylenedione	82-86-0	182	90 ^a	1.95	
1,8-naphthalic anhydride	81-84-5	198	5.9 ^a	3.24 ^b	
9-fluorenone	486-25-9	180	3.7 ^a	3.58	4.59
2-methyl-9-fluorenone	2840-51-9	194	1.2 ^a	4.10 ^b	
4-hydroxy-9-fluorenone	1986-00-1	196	32 ^a	3.07 ^b	
Anthracene-9,10-dione	84-65-1	208	1.4	3.39	4.19
2-methylanthracenedione	84-54-8	222	1.2 ^a	3.89 ^b	4.66
4H-cyclopenta[def]phenanthrenone	5737-13-3	204	0.94 ^a	4.14 ^b	4.85
4-oxapyrene-5-one		220	—	—	4.76
7H-benz[de]anthracen-7-one	82-05-3	230	0.18 ^a	4.81	5.45
Benzo[a]fluorenone	479-79-8	230	0.22 ^a	4.73 ^b	5.76
Benz[a]anthracene-7,12-dione	2498-66-0	258	0.29 ^a	4.40	5.94
Naphthacene-5,12-dione	1090-13-7	258	0.23 ^a	4.52 ^b	5.74
6H-benzo[cd]pyren-6-one	3074-00-8	254	0.050 ^a	5.31 ^b	6.43
9H-dibenz[b,de]anthracen-9-one	86854-05-9	280	0.011 ^a	5.90 ^b	

^a Estimated value using WSKOW v1.67; ^b estimated value using KOWWIN v1.67.

relatively high persistence in environmental matrices and partly through continuous inputs of newly oxidized PAHs. There is also convincing evidence to suggest that the enhanced PAH transformation occurring during certain remediation activities may lead to increasing concentrations of oxy-PAHs in the treated material and thus increase the risks posed by contaminants at the site. This is partly due to the toxicity of the oxy-

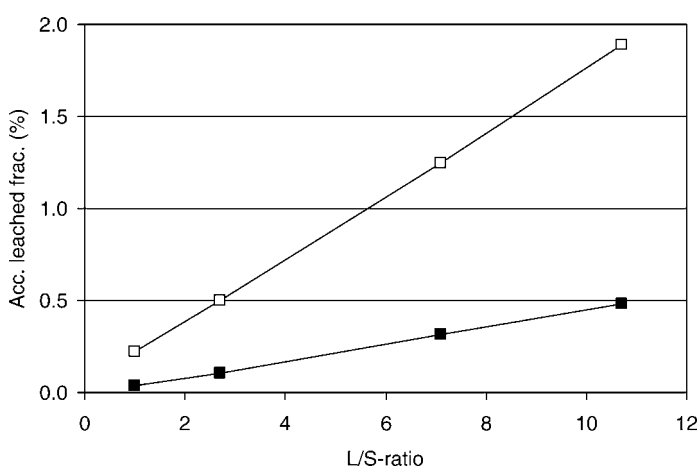


Figure 7. Accumulated leached fraction of polycyclic aromatic hydrocarbons (PAHs) (■) and oxygenated PAHs (□) containing 3 fused rings during column leaching of soil from a wood preservation site (Holmsund, Sweden). The soil was percolated with water for 19 d, reaching a liquid-solid ratio (L/S) of approximately 11. From Lundstedt and Karlsson (in prep.).

PAHs and partly due to their increased mobility in soil compared with the PAHs from which they are formed, which is expected to have an impact on bioavailability and exposure.

To avoid misapprehension of the actual risks posed by PAH-contaminated sites, we believe that further investigations to characterize the contribution of oxy-PAHs are essential. Moreover, once the culpable oxy-PAHs have been positively identified, using such techniques as effect-directed chemical fractionation, it will be necessary to include these compounds in the list of priority substances commonly monitored at sites undergoing risk assessment or remediation. Although there may be other toxicologically relevant compounds present at these sites (e.g., nitro-PAHs, azaarenes), the evidence accumulated to date indicates that oxy-PAHs may be one of the more important compound classes to include in programs monitoring contaminated sites.

References and Notes

- Howsam, M. and Jones, K.C. 1998. Sources of PAHs in the environment. In: *The Handbook of Environmental Chemistry*, Vol. 3, Anthropogenic compounds, Part I. PAHs and Related Compounds. Neilson, A.H. (ed). Springer-Verlag, Berlin, pp. 137–174.
- Delistraty, D. 1997. Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons. *Toxicol. Environ. Chem.* 64, 81–108.
- Pickering, R.W. 1999. A toxicological review of polycyclic aromatic hydrocarbons. *J. Toxicol. Cutan. Ocul. Toxicol.* 18, 101–135.
- Lundstedt, S., Haglund, P. and Öberg, L.G. 2003. Degradation and formation of polycyclic aromatic compounds during bio-slurry treatment of an aged gasworks soil. *Environ. Toxicol. Chem.* 22, 1413–1420.
- Castells, P., Santos, F.J. and Gaiceran, M.T. 2003. Development of a sequential supercritical fluid extraction method for the analysis of nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in urban aerosols. *J. Chromatogr. A* 1010, 141–151.
- Kallio, M., Hyötyläinen, T., Lehtonen, M., Jussila, M., Hartonen, K., Shimmo, M. and Riekkola, M.L. 2003. Comprehensive two-dimensional gas chromatography in the analysis of urban aerosols. *J. Chromatogr. A* 1019, 251–260.

7. Nicol, S., Dugay, J. and Hennion, M.C. 2001. Determination of oxygenated polycyclic aromatic compounds in airborne particulate organic matter using gas chromatography tandem mass spectrometry. *Chromatographia* 53, S464-S469.
8. Sienna, M.D. 2006. Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter. *Atmos. Environ.* 40, 2374-2384.
9. Cerniglia, C.E. 1992. Biodegradation of polycyclic aromatic hydrocarbons. *Biodegradation* 3, 351-368.
10. Kochany, J. and Maguire, R.J. 1994. Abiotic transformations of polynuclear aromatic hydrocarbons and polynuclear aromatic nitrogen heterocycles in aquatic environments. *Sci. Total Environ.* 144, 17-31.
11. Yu, H. 2002. Environmental carcinogenic polycyclic aromatic hydrocarbons: photochemistry and phototoxicity. *J. Environ. Sci. Health C20*, 149-183.
12. Kotzias, D. and Brüssel, C. 1999. Fate of polycyclic aromatic hydrocarbons (PAHs) in ambient air. *Fresenius Environ. Bull.* 8, 518-522.
13. Mallakin, A., Dixon, D.G. and Greenberg, B.M. 2000. Pathway of anthracene modification under simulated solar radiation. *Chemosphere* 40, 1435-1441.
14. Sutherland, J.B., Rafii, F., Khan, A.A. and Cerniglia, C.E. 1995. Mechanisms of polycyclic aromatic hydrocarbon degradation. In: *Series in Ecological and Applied Microbiology: Microbial Transformation and Degradation of Toxic Organic Chemicals*. Young, L.Y. and Cerniglia, C.E. (eds). Wiley-Liss Inc, New York, pp. 269-306.
15. Cerniglia, C.E. 1997. Fungal metabolism of polycyclic aromatic hydrocarbons: past, present and future applications in bioremediation. *J. Ind. Microbiol. Biotechnol.* 19, 324-333.
16. Kanaly, R.A. and Harayama, S. 2000. Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. *J. Bacteriol.* 182, 2059-2067.
17. Koeber, R., Bayona, J.M. and Niessner, R. 1997. Analysis of ozonolysis products of benzo[a]pyrene with capillary gas chromatography mass spectrometry and liquid chromatography mass spectrometry. *Int. J. Environ. Anal. Chem.* 66, 313-325.
18. Wunder, T., Marr, J., Kremer, S., Sterner, O. and Anke, H. 1997. 1-methoxyppyrene and 1,6-dimethoxyppyrene: two novel metabolites in fungal metabolism of polycyclic aromatic hydrocarbons. *Arch. Microbiol.* 167, 310-316.
19. Yao, J.J., Huang, Z.H. and Masten, S.J. 1998. The ozonation of benz[a]anthracene: pathway and product identification. *Water Res.* 32, 3235-3244.
20. Yao, J.J., Huang, Z.H. and Masten, S.J. 1998. The ozonation of pyrene: pathway and product identification. *Water Res.* 32, 3001-3012.
21. Andersson, B.E., Lundstedt, S., Tornberg, K., Schnurer, Y., Öberg, L.G. and Mattiasson, B. 2003. Incomplete degradation of polycyclic aromatic hydrocarbons in soil inoculated with wood-rotting fungi, and their effect on the indigenous soil bacteria. *Environ. Toxicol. Chem.* 22, 1238-1243.
22. Lundstedt, S., Persson, Y. and Öberg, L. 2006. Transformation of PAHs during ethanol-fenton treatment of an aged gasworks' soil. *Chemosphere* 65, 1288-1294.
23. Freeman, H.M. and Harris, E.F. (eds). 1995. *Hazardous Waste Remediation: Innovative Treatment Technologies*. Technomic Publishing Company, Lancaster.
24. Hamby, D.M. 1996. Site remediation techniques supporting environmental restoration activities: a review. *Sci. Total Environ.* 191, 203-224.
25. Alsbeg, T., Stenberg, U., Westerholm, R., Strandell, M., Rannug, U., Sundvall, A., Romert, L., Bernson, V., et al. 1985. Chemical and biological characterization of organic material from gasoline exhaust particles. *Environ. Sci. Technol.* 19, 43-50.
26. Cho, A.K., Di Stefano, E., You, Y., Rodriguez, C.E., Schmitz, D.A., Kumagai, Y., Miguel, A.H., Eiguren-Fernandez, A., et al. 2004. Determination of four quinones in diesel exhaust particles, SRM 1649a, an atmospheric PM_{2.5}. *Aerosol Sci. Technol.* 38, 68-81.
27. Choudhury, D.R. 1982. Characterization of polycyclic ketones and quinones in diesel emission particulates by gas-chromatography mass-spectrometry. *Environ. Sci. Technol.* 16, 102-106.
28. Spitzer, T. and Takeuchi, T. 1995. Determination of benzanthrone in environmental samples. *J. Chromatogr. A* 710, 109-116.
29. Ramdahl, T. 1985. Characterization of polar compounds such as polycyclic aromatic ketones in air pollution including wood smoke. *Environ. Int.* 11, 197-203.
30. Sidhu, S., Gullett, B., Striebeck, R., Klosterman, J., Contreras, J. and DeVito, M. 2005. Endocrine disrupting chemical emissions from combustion sources: diesel particulate emissions and domestic waste open burn emissions. *Atmos. Environ.* 39, 801-811.
31. Akimoto, Y., Aoki, T., Nito, S. and Inouye, Y. 1997. Oxygenated polycyclic aromatic hydrocarbons from MSW incinerator fly ash. *Chemosphere* 34, 263-273.
32. Albinet, A., Leoz-Garziandia, E., Budzinski, H. and Villenave, E. 2006. Simultaneous analysis of oxygenated and nitrated polycyclic aromatic hydrocarbons on standard reference material 1649a (urban dust) and on natural ambient air samples by gas chromatography-mass spectrometry with negative ion chemical ionisation. *J. Chromatogr. A* 1121, 106-113.
33. Allen, J.O., Dookeran, N.M., Taghizadeh, K., Lafleur, A.L., Smith, K.A. and Sarofim, A.F. 1997. Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environ. Sci. Technol.* 31, 2064-2070.
34. Casellas, M., Fernandez, P., Bayona, J.M. and Solanas, A.M. 1995. Bioassay-directed chemical-analysis of genotoxic components in urban airborne particulate matter from Barcelona (Spain). *Chemosphere* 30, 725-740.
35. Durant, J.L., Lafleur, A.L., Plummer, E.F., Taghizadeh, K., Busby, W.F. and Thilly, W.G. 1998. Human lymphoblast mutagens in urban airborne particles. *Environ. Sci. Technol.* 32, 1894-1906.
36. Hannigan, M.P., Cass, G.R., Penman, B.W., Crespi, C.L., Lafleur, A.L., Busby, W.F., Thilly, W.G. and Simoneit, B.R.T. 1998. Bioassay directed chemical analysis of Los Angeles airborne particulate matter using a human cell mutagenicity assay. *Environ. Sci. Technol.* 32, 3502-3514.
37. König, J., Balfanz, E., Funcke, W. and Romanowski, T. 1983. Determination of oxygenated polycyclic aromatic hydrocarbons in airborne particulate matter by capillary gas chromatography and gas chromatography/mass spectrometry. *Anal. Chem.* 55, 599-603.
38. Moyano, E. and Galceran, M.T. 1997. Determination of oxy-, nitro- and hydroxy-polycyclic aromatic hydrocarbons in atmospheric aerosol samples. *Quim. Anal. (Barcelona)* 16, 159-164.
39. Oda, J., Nomura, S., Yasuhara, A. and Shibamoto, T. 2001. Mobile sources of atmospheric polycyclic aromatic hydrocarbons in a roadway tunnel. *Atmos. Environ.* 35, 4819-4827.
40. Fernandez, P., Grifoll, M., Solanas, A.M., Bayona, J.M. and Albaiges, J. 1992. Bioassay-directed chemical analysis of genotoxic components in coastal sediments. *Environ. Sci. Technol.* 26, 817-829.
41. Grifoll, M., Solanas, A.M. and Bayona, J.M. 1990. Characterization of genotoxic components in sediments by mass-spectrometric techniques combined with *Salmonella* microsome test. *Arch. Environ. Contam. Toxicol.* 19, 175-184.
42. Machala, M., Ciganek, M., Blaha, L., Minksova, K. and Vondrack, J. 2001. Aryl hydrocarbon receptor-mediated and estrogenic activities of oxygenated polycyclic aromatic hydrocarbons and azarenes originally identified in extracts of river sediments. *Environ. Toxicol. Chem.* 20, 2736-2743.
43. McKinney, R.A., Pruett, R.J. and Burgess, R.M. 1999. Ratio of the concentration of anthraquinone to anthracene in coastal marine sediments. *Chemosphere* 38, 2415-2430.
44. Grifoll, M., Solanas, A.M. and Bayona, J.M. 1992. Bioassay-directed chemical characterization of genotoxic agents in the dissolved and particulate water phases of the Besos and Llobregat rivers (Barcelona, Spain). *Arch. Environ. Contam. Toxicol.* 23, 19-25.
45. Kurihara, R., Shiraishi, F., Tanaka, N. and Hashimoto, S. 2005. Presence and estrogenicity of anthracene derivatives in coastal Japanese waters. *Environ. Toxicol. Chem.* 24, 1984-1993.
46. Bodzek, D., Janoszka, B., Dobosz, C., Warzecha, L. and Bodzek, M. 1997. Determination of polycyclic aromatic compounds and heavy metals in sludges from biological sewage treatment plants. *J. Chromatogr. A* 774, 177-192.
47. Mosi, A.A., Reimer, K.J. and Eigendorf, G.K. 1997. Analysis of polycyclic aromatic quinones in a complex environmental matrix using gas chromatography ion trap tandem mass spectrometry. *Talanta* 44, 985-1001.
48. Brooks, L.R., Hughes, T.J., Claxton, L.D., Austern, B., Brenner, R. and Kremer, F. 1998. Bioassay-directed fractionation and chemical identification of mutagens in bioremediated soils. *Environ. Health Perspect.* 106, 1435-1440.
49. Eriksson, M., Dalhammar, G. and Borg-Karlsson, A.K. 2000. Biological degradation of selected hydrocarbons in an old PAH/cresote contaminated soil from a gas work site. *Appl. Microbiol. Biotechnol.* 53, 619-626.
50. Lundstedt, S., Haglund, P. and Öberg, L. 2006. Simultaneous extraction and fractionation of polycyclic aromatic hydrocarbons and their oxygenated derivatives in soil using selective pressurized liquid extraction. *Anal. Chem.* 78, 2993-3000.
51. Meyer, S., Cartellieri, S. and Steinhart, H. 1999. Simultaneous determination of PAHs, hetero-PAHs (N, S, O), and their degradation products in creosote-contaminated soils: method development, validation, and application to hazardous waste sites. *Anal. Chem.* 71, 4023-4029.
52. Niederer, M. 1998. Determination of polycyclic aromatic hydrocarbons and substitutes (nitro-, oxy-PAHs) in urban soil and airborne particulate by GC-MS and NCI-MS/MS. *Environ. Sci. Pollut. Res.* 5, 209-216.
53. Saponaro, S., Bonomo, L., Petruzzelli, G., Romeo, L. and Barbaferi, M. 2002. Polycyclic aromatic hydrocarbons (PAHs) slurry phase bioremediation of a manufacturing gas plant (MGP) site aged soil. *Water Air Soil Pollut.* 135, 219-236.
54. Mallakin, A., McConkey, B.J., Miao, G.B., McKibben, B., Snieckus, V., Dixon, D.G. and Greenberg, B.M. 1999. Impacts of structural photomodification on the toxicity of environmental contaminants: anthracene photooxidation products. *Ecotoxicol. Environ. Saf.* 43, 204-212.
55. McConkey, B.J., Duxbury, C.L., Dixon, D.G. and Greenberg, B.M. 1997. Toxicity of a PAH photooxidation product to the bacteria *Photobacterium phosphoreum* and the duckweed *Lemna gibba*: effects of phenanthrene and its primary photoproduct, phenanthrenequinone. *Environ. Toxicol. Chem.* 16, 892-899.
56. Wischmann, H. and Steinhart, H. 1997. The formation of PAH oxidation products in soils and soil/compost mixtures. *Chemosphere* 35, 1681-1698.
57. Zdrahal, Z., Karasek, P., Lojkova, L., Buckova, M., Vecera, Z. and Vejrosta, J. 2000. Pressurized liquid extraction of ketones of polycyclic aromatic hydrocarbons from soil. *J. Chromatogr. A* 893, 201-206.
58. Letzel, T., Poschl, U., Wissiack, R., Rosenberg, E., Grasserbauer, M. and Niessner, R. 2001. Phenyl-modified reversed-phase liquid chromatography coupled to atmospheric pressure chemical ionization mass spectrometry: a universal method for the analysis of partially oxidized aromatic hydrocarbons. *Anal. Chem.* 73, 1634-1645.
59. Andersson, B.E. and Henrysson, T. 1996. Accumulation and degradation of dead-end metabolites during treatment of soil contaminated with polycyclic aromatic hydrocarbons with five strains of white-rot fungi. *Appl. Microbiol. Biotechnol.* 46, 647-652.
60. Lee, B.D., Hosomi, M. and Murakami, A. 1998. Fenton oxidation with ethanol to degrade anthracene into biodegradable 9,10-anthraquinone: a pretreatment method for anthracene-contaminated soil. *Water Sci. Technol.* 38, 91-97.
61. Lee, B.D. and Hosomi, M. 2001. A hybrid Fenton oxidation-microbial treatment for soil highly contaminated with benz[a]anthracene. *Chemosphere* 43, 1127-1132.
62. Meyer, S. and Steinhart, H. 2001. Fate of PAHs and hetero-PAHs during biodegradation in a model soil/compost-system: formation of extractable metabolites. *Water Air Soil Pollut.* 132, 215-231.
63. Brack, W., Altenburger, R., Kuster, E., Meissner, B., Wenzel, K.D. and Schuurmann, G. 2003. Identification of toxic products of anthracene photomodification in simulated sunlight. *Environ. Toxicol. Chem.* 22, 2228-2237.
64. Lampi, M.A., Gurska, J., McDonald, K.I., Xie, F., Huang, X.D., Dixon, D.G. and Greenberg, B.M. 2006. Photoinduced toxicity of polycyclic aromatic hydrocarbons to *Daphnia magna*: ultraviolet-mediated effects and the toxicity of polycyclic aromatic hydrocarbon photoproducts. *Environ. Toxicol. Chem.* 25, 1079-1087.
65. Xie, F., Koziar, S.A., Lampi, M.A., Dixon, D.G., Warren, N.P., Borgmann, U., Huang, X.D. and Greenberg, B.M. 2006. Assessment of the toxicity of mixtures of copper, 9,10-phenanthrenequinone, and phenanthrene to *Daphnia magna*: evidence for a reactive oxygen mechanism. *Environ. Toxicol. Chem.* 25, 613-622.
66. Winters, K., Batterton, J.C. and van Baalen, C. 1977. Phenalen-1-one: occurrence in a fuel oil and toxicity to microalgae. *Environ. Sci. Technol.* 11, 270-272.
67. Ren, L., Zeiler, L.F., Dixon, D.G. and Greenberg, B.M. 1996. Photoinduced effects of polycyclic aromatic hydrocarbons on *Brassica napus* (*Canola*) during germination and early seedling development. *Ecotoxicol. Environ. Saf.* 33, 73-80.
68. Kubatova, A., Dronen, L.C., Picklo, M.J. and Hawthorne, S.B. 2006. Midpolarity and nonpolar wood smoke particulate matter fractions deplete glutathione in RAW 264.7 macrophages. *Chem. Res. Toxicol.* 19, 255-261.
69. Kumagai, Y., Koide, S., Taguchi, K., Endo, A., Nakai, Y., Yoshikawa, T. and Shimojo, N. 2002. Oxidation of proximal protein sulfhydryls by phenanthraquinone, a component of diesel exhaust particles. *Chem. Res. Toxicol.* 15, 483-489.
70. Shimada, H., Oginuma, M., Hara, A. and Imamura, Y. 2004. 9,10-phenanthrenequinone, a component of diesel exhaust particles, inhibits the reduction of 4-benzoylpyridine and all-trans-retinal and mediates superoxide formation through its redox cycling in pig heart. *Chem. Res. Toxicol.* 17, 1145-1150.
71. Zhu, H., Li, Y.B. and Trush, M.A. 1995. Characterization of benzo[a]pyrene quinone-induced toxicity to primary cultured bone-marrow stromal cells from Dba/2 mice: potential role of mitochondrial dysfunction. *Toxicol. Appl. Pharmacol.* 130, 108-120.
72. Chesis, P.L., Levin, D.E., Smith, M.T., Ernster, L. and Ames, B.N. 1984. Mutagenicity of quinones: pathways of metabolic activation and detoxification. *Proc. Natl. Acad. Sci. USA* 81, 1696-1700.
73. Durant, J.L., Busby, W.F., Lafleur, A.L., Penman, B.W. and Crespi, C.L. 1996. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutat. Res. Genet. Toxicol.* 371, 123-157.
74. Leary, J.A., Lafleur, A.L., Liber, H.L. and Blemann, K. 1983. Chemical and toxicologic characterization of fossil fuel combustion product Phenalen-1-one. *Anal. Chem.* 55, 758-761.
75. Lynes, K. 2006. *Mutagenicity of an Old Gasworks Site During Bioremediation*. MSc Thesis. Department of Biology, Carleton University, Ottawa, Canada.
76. Moller, M., Hagen, I. and Ramdahl, T. 1985. Mutagenicity of polycyclic aromatic compounds (PAC) identified in source emissions and ambient air. *Mutat. Res.* 157, 149-156.
77. Pitts, J.N., Lokensgard, D.M., Harger, W., Fisher, T.S., Mejia, V., Schuler, J.J., Scorziell, G.M. and Katzenstein, Y.A. 1982. Mutagens in diesel exhaust particulate identification and direct activities of 6-nitrobenzo[a]pyrene, 9-nitroanthracene, 1-nitropyrene and 5H-phenanthro[4,5-bcd]pyran-5-one. *Mutat. Res.* 103, 241-249.

78. Sakai, M., Yoshida, D. and Mizusaki, S. 1985. Mutagenicity of polycyclic aromatic hydrocarbons and quinones on *Salmonella typhimurium* TA97. *Mutat. Res.* 156, 61–67.
79. Bolton, J.L., Trush, M.A., Penning, T.M., Dryhurst, G. and Monks, T.J. 2000. Role of quinones in toxicology. *Chem. Res. Toxicol.* 13, 135–160.
80. Huang, X.D., Dixon, D.G. and Greenberg, B.M. 1993. Impacts of UV radiation and photomodification on the toxicity of PAHs to the higher plant *Lemna gibba* (duckweed). *Environ. Toxicol. Chem.* 12, 1067–1077.
81. Huang, X.D., Dixon, D.G. and Greenberg, B.M. 1995. Increased polycyclic aromatic hydrocarbon toxicity following their photomodification in natural sunlight: impacts on the duckweed *Lemna gibba* 1 G-3. *Ecotoxicol. Environ. Saf.* 32, 194–200.
82. Lemieux, C.L., Lambert, I.B., Lundstedt, S., Tysklind, M. and White, P.A. 2007. The mutagenic hazard of complex PAH mixtures in contaminated soil. *Environ. Toxicol. Chem.* (In press).
83. Alexander, R.R., Tang, J.X. and Alexander, M. 2002. Genotoxicity is unrelated to total concentration of priority carcinogenic polycyclic aromatic hydrocarbons in soils undergoing biological treatment. *J. Environ. Qual.* 31, 150–154.
84. Belkin, S., Stieber, M., Tiehm, A., Frimmel, F.H., Abeliovich, A., Werner, P. and Ulitzur, S. 1994. Toxicity and genotoxicity enhancement during polycyclic aromatic hydrocarbons biodegradation. *Environ. Toxicol. Water Qual.* 9, 303–309.
85. Morelli, I.S., Vecchioli, G.I., Del Panno, M.T. and Paineira, M.T. 2001. Effect of petrochemical sludge concentrations on changes in mutagenic activity during soil bioremediation process. *Environ. Toxicol. Chem.* 20, 2179–2183.
86. Sasek, V., Bhatt, M., Cajthaml, T., Malachova, K. and Lednicka, D. 2003. Compost-mediated removal of polycyclic aromatic hydrocarbons from contaminated soil. *Arch. Environ. Contam. Toxicol.* 44, 336–342.
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