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Fate of polycyclic aromatic hydrocarbons during composting of lagooning sewage sludge

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Abstract

The fate of 16 polycyclic aromatic hydrocarbons (PAHs), targeted by the USEPA agency, has been investigated during composting of lagooning sludge. Composting shows efficient decrease of the content and the bioavailability of each PAH. Biodegradation and sorption are suggested as the main mechanisms contributing to this decrease. During the stabilization phase of composting, extensive microbial degradation of PAHs, mainly those with a low number of aromatic rings, was achieved following development of intense thermophilic communities. However, partial sorption of PAH to non-accessible sites temporarily limits the mobility mainly of PAHs with a high number of aromatic rings plus acenaphthene and acenaphthylene, and allows them to escape microbial attack. During the maturation phase, the development of a mesophilic population could play an important role in the degradation of the remaining PAH. During this phase of composting, PAH sequestration and binding of their oxidative metabolites within new-formed humic substances might also explain PAH decrease at the end of composting. The tendency of change of content or bioavailability of various PAH compounds during composting is found to be strongly related to the number of their aromatic rings, their molecular weight and structure.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important group of organic contaminants present in sewage sludge. Due to their low water solubility and their resistance to biodegradation, they are removed during the wastewater biological treatment from the water phase by adsorption onto suspended solids and they are hence accumulated in the sludge. PAHs constitute a group of hydrophobic organic contaminants composed of two or more aromatic rings. They originate from industrial and domestic waste. Atmospheric rainfall drains airborne pollutants and road surface dirt contributing to organic water pollution. PAHs can also be produced naturally in smaller amounts by forest fires (Pérez et al., 2001). Considering their persistence and carcinogenic potential, determination of their content in sewage sludge is necessary to assess the safety and the possibility for agricultural recycling of these organic

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wastes (IARC, 1983; Lega et al., 1997). Other limiting factors such as content of heavy metals and pathogenic organisms must be also considered. Among the many PAH compounds, 16 have been identified as "priority pollutants" by the United States Environmental Protection Agency (USEPA) and seven of them are considered as probably carcinogenic (USEPA, 1997).

There are numerous legislations and regulations laid down by various organizations for sludge disposal. In the final regulations of USEPA, only metallic compounds are taken into account, since the levels of some organic compounds were not detectable and therefore had no significant effect on health and environment (Pérez et al., 2001). A new draft directive of the Council of the European Community has been issued (CEC, 2000) and provides the allowable content for some organic pollutants including PAHs for agricultural recycling of sewage sludge. The cut-off value of total PAHs is set to 6 mg kg^{-1}.

Prior to agricultural recycling of sludges, a treatment is needed to ensure their stability and increase their beneficial effect for soil. Composting is recognized to be the most useful treatment suppressing most pathogenic organisms, decreasing the bioavailability of heavy metals and stabilising the organic material in sludge before spreading on the land (Echab et al., 1998; Amir et al., 2004). Numerous studies have shown that composted material has an enormous potential for bioremediation through sustaining populations of a wide range of presumed microorganisms, which are able to degrade a variety of organic contaminants (Crawford et al., 1993; Kästner and Mahro, 1996; Semples et al., 2001; Reid et al., 2002; Lau et al., 2003). However, the knowledge of the effect of the composting process on the fate of PAHs is lacking. Composting is defined basically as biological processes occurring in favorable conditions (good aeration, moisture, etc.) and allowed to transform the raw initial material probably unsanitary or with phytotoxic properties to stable and mature end product. According to numerous previous studies, a wide variety of microorganisms demonstrated contribute in these processes classified among Bacteria, Actinomycetes, fungus, Protozoons, Algae, others. The identification of all microorganisms selecting those responsible of biodegradation is operationally difficult at the moment and consume much time, and with very expensive cost if followed at different periods of composting. Indeed, in the researchs in field of composting, the monitoring of some physico-chemical properties during composting has been considered as indirect indices whose their variations are resulted from the activities of the sets of microorganisms within compost pile. Among numerous methologies published for PAH analysis, Lega et al. (1997) has proposed a procedure permitting simultaneous determination of all classes of organic pollutants on sludge matrix. These authors has discussed the validity of methodology and reported the sufficient recoveries for all PAH compounds with average varied from 65% to 127%; habitually a recovery ranged from 70% to 115% is valid. Besides, The method detection limit (MDLs) demonstrates low level detection values for PAH ranging from 0.09 to 0.5 mg/kg.

The objective of this work is to apply this methology for determining the fate of 16 PAHs during composting. For this purpose, PAH contents were determined at different steps of composting of lagooning sludges.

2. Material and methods

2.1. Composting

Lagooning sewage sludge (LS) was taken from an experimental wastewater treatment plant in Marrakech city. A composting trial was conducted on the mixture of sludge (165 kg) and straw (20 kg) in a heap on a purpose-built platform for 180 days. The mixture was turned every 15 days to provide aerobic conditions for the treatment. To monitor the progress of composting, the microbial activity was followed by the daily measurement of the temperature inside the heap of compost (Fig. 1) (Amir and Hafidi, 2001).

2.2. Sampling

For analysis purposes, sub-samples were taken from 10 various points of the compost pile goodly homogenized (bottom, surface, side, centre). These sub-samples are pooled at each time of composting: initial mixture; end of stabilization phase after 30 d (days); 60; 90 d (times representative of the beginning of the maturation phase) and 180 d (end of maturation phase). The samples were deep frozen until analysis.
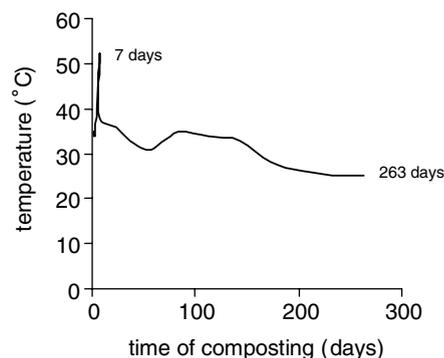

Fig. 1. Temperature change during composting of lagooning sludge.

2.3. Physico-chemical analysis

The following physico-chemical analyses were made on aliquots of the samples: the pH was determined on a suspension of sample in water (10 g in 15 ml), the Total Organic Carbon (C.org) was measured with the potassium bichromate method, the total nitrogen using the Kjeldahl method, the humic carbon extracted by 0.1 M NaOH solution was measured after oxidation by $KMnO_4$. After ignition of the dry sample at 550 °C (16 h), the percentage of decomposition was calculated by following formula:

$$DEC\% = [100 \times (a_t - a_0)/((100 - a_0) \times a_t)] \times 100$$

where a_0 is the level of ash in the initial sample; a_t is the level of ash in sample at each selected time of composting (30, 60, 90 and 180 d) (Amir and Hafidi, 2001).

2.4. PAH extraction

For each selected time of composting, a homogenized, dry (air) sample of about 10 g was used. PAH extraction was performed twice on this amount of matter with a mixture of: 10 ml of dichloromethane and 20 ml of diethylether (Lega et al., 1997). Analytical solvents obtained from Panreac grade E-08110 Martcada i Reixac, Spain.

The mixture: solvents + sample was poured in a centrifugation tube, shaken for 30 min and then centrifuged for 15 min at 2500 rpm. The procedure was repeated twice and the two extracts, collected for each sample, were pooled and dried by filtration through anhydrous Na_2SO_4. The extracts were sufficiently clean to be directly analyzed after a reconcentration step.

2.5. GC–MS Analysis

GC–MS analysis was performed with a Hewlett-Packard gas chromatograph HP-5890 series II, equipped with a mass detector MSD HP-5971 (ISO 9000) and a data analysis station HP Chem. The column used for analysis was a 25 m HP-5 MS type (crosslinked 5% phenylmethylsilicone; 0.2 mm I.D., 0.33 μm film thickness). As carrier gas, high grade helium N55 was used at a flow rate of 0.89 ml min^{-1}. Injection was made in splitless mode. The head column pressure was 62 hPa. Injector temperature was 280 °C and the purge time was set to 1 min.

The GC–MS oven temperature was maintained at 60 °C for 1.5 min and then increased at a rate of 30 °C min^{-1} up to 160 °C. The increase rate was then set to 5 °C min^{-1} until the temperature reached 195 °C. The next increase rate was then lowered to 3 °C min^{-1} until 280 °C. This final temperature was held for 18 min to eliminate all co-extracts. The detector temperature was 300 °C, and the Electron multipicator voltage (EMV) sensitivity was set to 2600 V.

2.6. Quantification

Data acquisition was carried out in the selected ion monitoring mode (SIM). Quantification was based on the external standard technique utilizing integrated peak areas of each selected ion. The purity of all standards is superior to 99%. The standard range (100–1000 μg l^{-1}) was prepared from dilutions of certified solution containing the 16 PAH at 10 ng μl^{-1} in acetonitrile (Mix 9, Dr Ehrenstorter LS 209509, supplied by C.I.L.33220 Ste Foy la Grande, France). The values measured concern only the amount of solvent-extractible PAH for each point of measure.

To take into account the weight loss of the heap of sludge mixture during composting, due to release of carbon dioxide, water and mineralization processes; all measurements were corrected by referring to the amount of ash. The latter constitutes the most chemically stable parameter during the composting process. The corrected values at each step of composting are obtained from the following formula:

$$C_{ash} = C_m \times (a_0/a_t) \quad (\mu g\,kg^{-1*})$$

where C_m is the mean measured value expressed by μg of PAH per kg of dry compost (μg kg^{-1}); a_0 is the level of ash in the initial sample; a_t is the level of ash in sample at each selected time of composting (30, 60, 90 and 180 d).

3. Results and discussion

3.1. Physico-chemical properties of sewage sludge during composting

The results obtained from physico-chemical analysis show that two phases occurred during composting: a phase of stabilization (about 30 d of composting), where temperature peaked to 52 °C after 7 d of processing. The temperature then decreased to 30 °C and followed by a temperature plateau of about 35 °C after 60 d marking maturation phase, which is characterized by the development of mesophilic populations (Fig. 1). Indeed, temperature has been considered as good indicator of microbial activities (thermophilic, mesophilic). The reactions of organic matter biodegradation yielded by native microorganisms within material to composted produce a calorific energy which cause the rise of temperature (70 °C), and the grown so of wide class of microorganisms selectively with thermophilic character. With the decrease of temperature, mesophilic populations were set up in maturation phase. The grown of these varieties of microbial communities involving the numerous biological and biochemical reactions lead to change of the chemical composition of the starting organic material. These changes are presented by the reduction of organic carbon and of C/N ratio in course of 180 days of composting

Table 1
Various physico-chemical characteristics of sewage sludge during composting

Time of composting (days)	pH	C/N	C.org (%)[a]	M.O. (%)[a]	H.S. (mg g^{-1})[a]	Ash (%)[a]	DEC (%)
0	7.3	24.0	17.7	30.6	/	65.9	/
30	7.4	21.4	16.2	27.9	17.5	70.7	19.9
90	6.8	18.5	15.0	25.9	20.0	75.3	36.6
180	6.7	16.4	14.3	24.6	20.8	76.3	40.0

C.org: organic carbon; M.O.: organic matter; H.S.: humic substances; DEC: decomposition percentage.
[a] Result expressed in dry weight.

(Table 1). The percentage of decomposition reached 40% and an enrichment of compost in humic substances occurred (Amir et al., 2004). These physico-chemical properties show a good biotransformation of initial organic material and that the final compost is stable and mature (Amir and Hafidi, 2001).

3.2. Total PAH behaviour

The levels of 16 PAHs identified as "priority pollutants" (USEPA, 1997, Fig. 2) were measured during the composting of lagooning sludge. The level of total extractible PAH. (TE-PAH) was obtained by summation over all the extractible-solvent amounts of 15 PAH. The benzo(k)fluoranthene content was below the detection limit of GC/MS. Fig. 3 illustrates TE-PAH content behaviour during the lagooning sludge composting. The level of TE-PAH in the sludge was 0.24 mg kg^{-1}. This value is very far below the accepted Euro-

pean Union cut-off limits for sludge to be considered safe for agricultural application, which is 6 mg kg^{-1} (CEC, 2000). However, even though they were present in very low concentrations, during composting these pollutants can be concentrated or not, depending on their biodegradability and on losses of carbon oxide, water and volatile compounds in general (Genevini et al., 1987). After mixing the sludge with straw, the TE-PAH decreased to 0.21 mg kg^{-1}.

During composting, after the stabilization phase (30 d of composting), TE-PAH showed a decrease of about 75%. This could be attributed to biodegradation due to the intense microbial activity during the thermophilic phase (Lazzari et al., 1999). The microorganisms capable of degrading organic matter could be responsible for cometabolic degradation of the PAHs (Kästner and Mahro, 1996; Gramss et al., 1999). The organic matter percentage is decreased from 30.6% to 27.9% and the calculated decomposition percentage (DEC%)
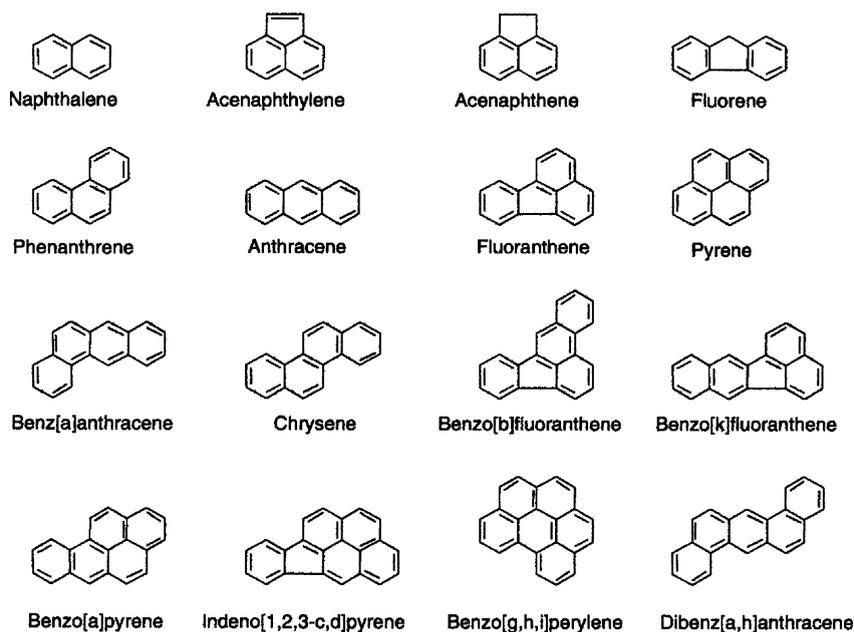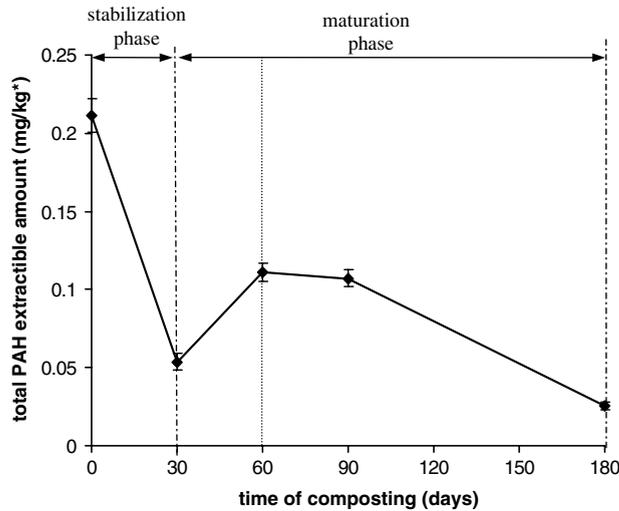

Fig. 2. Molecular structure of the 16 polycyclic aromatic hydrocarbons (PAHs) considered as priority pollutants by the American Environmental Protection Agency (EPA).

*mg of PAH per kg of dry compost (mean values corrected by referring to the amount of ash)

Fig. 3. Change of total extractible content of 16 polycyclic aromatic hydrocarbons (PAHs) during composting of lagooning sludge.

during this phase is about 20% (Table 1). However, at the beginning of the maturation phase, TE-PAH showed an increase. This was probably due to part of the PAHs that, at start of composting, were initially adsorbed to sites where they were temporarily less solvent extractible. Sorption of organic contaminants into non-accessible sites of organic material is estimated to be the most significant parameter decreasing the bioavailability of PAHs for microbial degradation (Weissenfels et al., 1992; Pignatello and Xing, 1996).

Therefore, the strong decrease occurring during the stabilization phase could be the combined result of both mechanisms: biodegradation by thermophilic populations and sorption by the compost matrix, for instance by lignin-cellulosic residues (Carlstrom and Tuovinen, 2003). The microbial population quickly attacks the sludge material, which is more readily bioavailable than straw material. The latter lignin-cellulosic structures temporarily resistant to microbial decomposition could have a high potential for PAH adsorption. After the stabilization phase or after 90 d of composting, the straw residues were observed completely disappeared in compost mixture. Therefore, their ultimate biodegradation could contribute to PAH release and hence an increase of TE-PAH in the beginning of the maturation phase.

At the end of composting, the TE-PAH content decreased again to reach 88% between the start and the end of composting (D.tot%). The decrease of TE-PAH at the end of maturation phase might originate from further decomposition by mesophilic microorganisms during this phase. The percentage organic matter decreased again from 27.9% to 24.6% and decomposition percentage was recorded at about 40% (Table 1). Martens (1982) found that when mature compost was

incubated with 14C-labelled anthracene, benzo[a]-anthracene, benzo[a]pyrene and dibenzo[a,h]anthracene, significantly higher amounts of mineralization were observed than when fresh (immature) compost was used. Therefore, mesophilic populations could play an important role in PAH degradation. During this phase of composting, PAH sequestration or binding of their oxidative metabolites within new-formed humic substances might be also suggested to explain PAH decrease at the end of composting (Laor et al., 1996; Kästner and Richnow, 2000; Richnow et al., 2000; Carlstrom and Tuovinen, 2003). The amount of humic substances increased from 17.5 to 20.8 $mg\,g^{-1}$ (Table 1) and the high degree of humification through aromaticity and oxidative polycondensation during the last step of composting has been described in previous studies (Amir et al., 2004).

The profile of change in TE-PAH level found during sludge composting in this study is similar to the total amount change of PAH during composting trials described in other studies. Lazzari et al. (1999) showed, during composting of mixtures of sewage sludge and ligneous waste, that PAHs decreased during the accelerated bioxidation or stabilization phase (20 d) and increased throughout the maturation phase (up to 90 d). These authors have similarly taken into account the possibility of incorrect values caused by a decrease in the weight of compost materials during treatment, also considering the ash content as a stable chemical parameter. Other authors, Ahtiainen et al. (2002), found that after 4 months of composting of a creosote-contaminated soil mixed with spruce bark chips, PAH concentrations temporarily increased, but at the end of composting (after 5 months) decreased by about 80%.

3.3. Behaviour of individual PAH compounds

The follow-up of changes of extractible-solvent amounts of the various 15 PAH during composting process shows that each PAH compound exhibits similar behaviour to the TE-PAH profile change observed previously (Figs. 4 and 5). During the stabilization phase, the levels of all PAHs decreased (D.st). This was less notable for PAH with three or fewer aromatic rings ($N \leqslant 3$) and more notable for PAH with a higher number of aromatic rings ($N \geqslant 4$) (Tables 2 and 3). The sharp decrease of extractible amounts of the latter PAHs could be explained by their strong adsorption to compost matrix such as ligno-cellulosic material, probably due to their greater hydrophobicity compared to the smaller ones ($N \leqslant 3$). Smith et al. (1997) show that in soil, adsorption is less reversible with increased numbers of fused aromatic rings or increased hydrophobicity. Other authors, Weissenfels et al. (1992) and Laor et al. (1996) suggest that the hydrophobicity of the PAH compounds results in their strong adsorption to soil organic matter and reduces their availability for the soil micro-organisms.

At the beginning of the maturation phase of composting, levels of all the PAHs were increased. As suggested above, the microbial decomposition of ligno-cellulosic material leads to the release of adsorbed PAHs. However, this PAH desorption varies with the number of aromatic rings. Extractible amounts of PAHs with few aromatic rings ($N \leqslant 4$) except acenaphthene and acenaphthylene showed maximum desorption after 60 d of composting (Fig. 4). Furthermore, the percentages of their levels remaining (Rm%)—except for fluorene and phenanthrene—exhibited low values (Table 2). In contrast, for PAH with higher numbers of aromatic rings ($N \geqslant 5$), plus acenaphthene and acenaphthylene ($N = 3$; with a condensed ring of five carbons), maximum desorption was observed after 90 d of composting (Fig. 5). The percentage of their levels remaining (Rm%) were higher except for dibenzo(a,h)anthracene and benzeno(g,h,i)perylene (Table 3). This tendency could be explained by the fact that PAHs with low molecular weight are weakly adsorbed and so could be easily and rapidly desorbed from 60 d of composting. The lower amount of these PAH remaining suggests that they are subjected to a strong microbial decomposition.
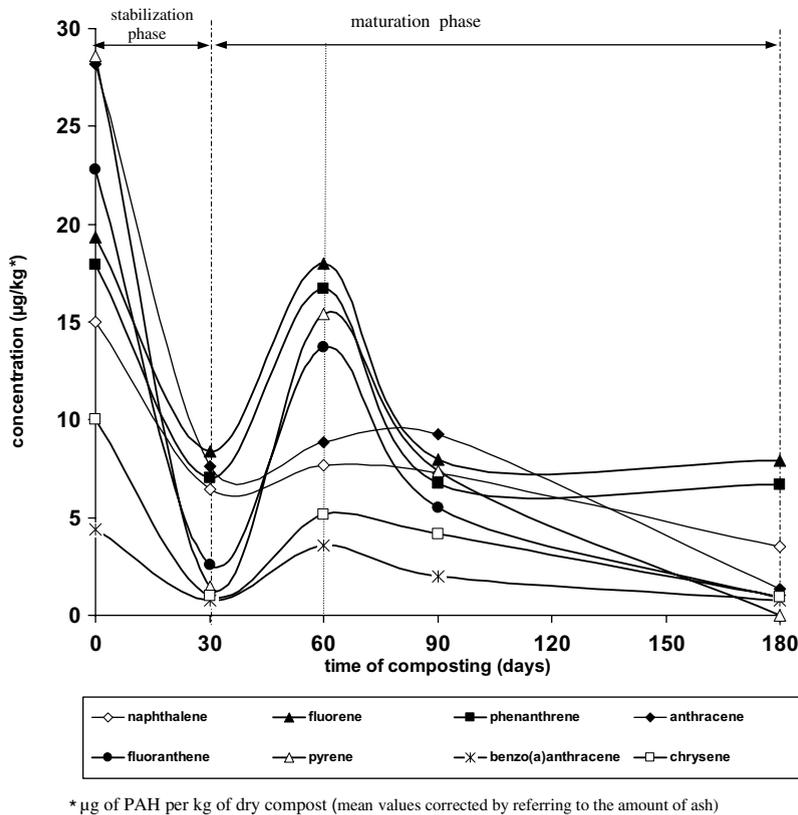

* μg of PAH per kg of dry compost (mean values corrected by referring to the amount of ash)

Fig. 4. Individual amount change of polycyclic aromatic hydrocarbons (PAHs) with $N \leqslant 4$ during composting of lagooning sludge.
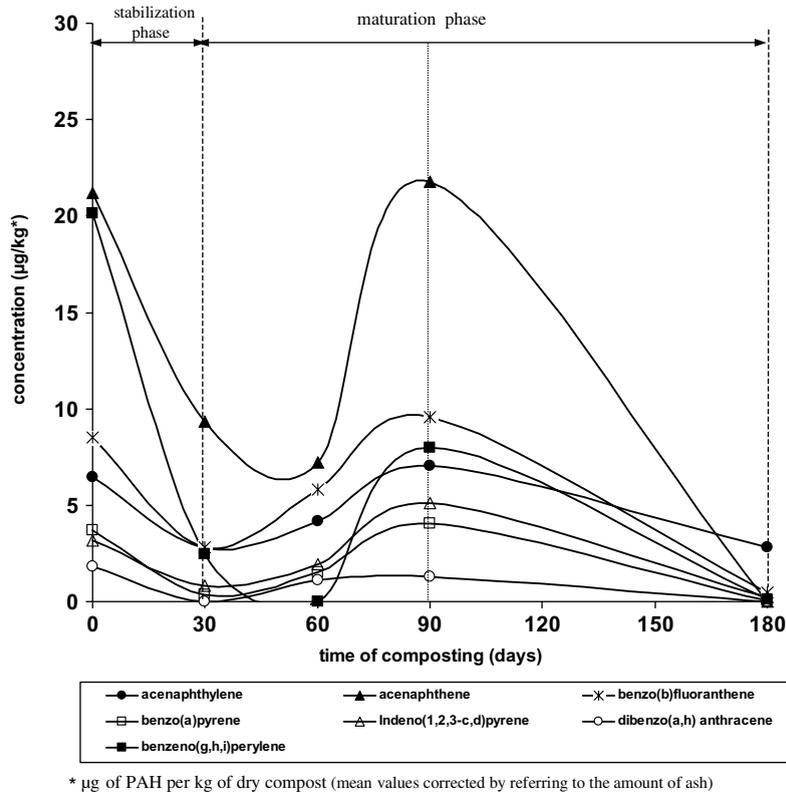
Fig. 5. Individual amount change of polycyclic aromatic hydrocarbons (PAHs) with $N \geqslant 5$ during composting of lagooning sludge.

Table 2
Chemical characteristics (N, MW) and quantification of content change of PAHs with $N \leqslant 4$ during lagooning sludge composting

PAHs	N	MW	C_i^a	C_f^b	D.st. (%)	Rm (%) (60 days)	D.tot (%)
Naphthalene	2	128	15.0 ± 0.7	3.5 ± 0.2	57	51	76
Fluorene	3	166	19.0 ± 1.0	7.9 ± 0.4	57	93	59
Phenanthrene	3	178	17.9 ± 0.9	6.7 ± 0.3	61	93	63
Anthracene	3	178	28.2 ± 0.4	1.3 ± 0.1	73	31	95
Fluoranthene	4	202	22.8 ± 1.1	0.9 ± 0.1	89	60	96
Pyrene	4	202	28.6 ± 1.4	nd	95	54	100
Benzo(a)anthracene	4	228	4.4 ± 0.2	0.8 ± 0.0	82	82	82
Chrysene	4	228	10.0 ± 0.5	0.9 ± 0.1	90	51	91

PAHs: polycyclic aromatic hydrocarbons; N: number of aromatic ring; MW: molecular weight; nd: not detectable; D.st: percentage of PAH content decrease at stabilization phase (C_i − PAH content at 30 days/C_i) * 100; Rm: percentage of amount of PAH remaining at 60 days of composting = (PAH content at 60 days/C_i) * 100; D.tot: percentage of total PAH content decrease during composting = [($C_f − C_i$)/C_i] * 100.
  [a] C_i: initial concentration at start of composting μg of PAH per kg of dry compost (mean values corrected by referring to the amount of ash).
  [b] C_f: final concentration at end of composting μg of PAH per kg of dry compost (mean values corrected by referring to the amount of ash).

In fact, their relatively higher solubility (lower hydrophobicity) could lead to greater availability for microbial decomposition (lower adsorption). While, for the larger PAH (number of aromatic rings $\geqslant$ 5), desorption is delayed to 90 d of composting and the amounts remaining are higher, which confirms their high adsorption (during the stabilization phase) to sites where they had escaped the microbial attack. It is possible that an increase of their extractability by solvent could explain that the amounts were greater than those measured at

Table 3
Chemical characteristics (N, MW) and quantification of content change during lagooning sludge composting of PAHs with $N \geqslant 5$, plus acenaphthylene and acenaphthene

PAHs	N	MW	C_i^a	C_f^b	D.st (%)	Rm (%) (90 days)	D.tot (%)
Acenaphthylene	3	154	6.5 ± 0.3	2.8 ± 0.2	57	109	57
Acenaphthene	3	156	21.2 ± 1.1	nd	66	103	100
Benzo(b)fluoranthene	5	252	8.5 ± 0.4	0.5 ± 0.0	67	112	95
Benzo(a)pyrene	5	252	3.7 ± 0.2	nd	91	109	99
Indeno(1,2,3-c,d)pyrene	6	278	3.2 ± 0.2	0.2 ± 0.0	74	160	93
Dibenzo(a,h)anthracene	6	276	1.9 ± 0.1	nd	100	69	100
Benzeno(g,h,i)perylene	6	276	20.1 ± 1.0	0.1 ± 0.0	100	40	99

PAHs: polycyclic aromatic hydrocarbons; N: number of aromatic ring; MW: molecular weight; D.st: percentage of PAH content decrease at stabilization phase (C_i – PAH content at 30 days/C_i) * 100; Rm: percentage of PAH remaining at 90 days of composting = (PAH content at 90 days/C_i) * 100; D.tot: percentage of total PAH content decrease during composting = [(C_f – C_i)/C_i] * 100; nd: not detectable.

[a] C_i: initial concentration at start of composting µg of PAH per kg of dry compost (mean values corrected by referring to the amount of ash).

[b] C_f: final concentration at end of composting µg of PAH per kg of dry compost (mean values corrected by referring to the amount of ash).

the start of composting (Rm > 100%) and might be attributed to the microbial release of some PAH previously tightly bound in the initial sludge matrix. In the literature, Lazzari et al. (1999) also showed, in the course of composting of mixtures of sewage sludge and ligneous wastes, an increase in the percentage presence of the heaviest PAHs during the maturation phase. Wilcock et al. (1996) reported that PAHs with low molecular weights are rapidly lost from sediments, whereas the high molecular weight molecules are more persistent. Carlstrom and Tuovinen (2003) suggested that sequestration occurred concurrently with biomineralization and that slow mineralization gives time for more hydrophobic substrates to be sequestered through adsorption and binding to become unavailable to microbial metabolism.

At the end of the maturation phase, all PAHs showed decreased amounts whatever the number of aromatic rings or molecular weight (Figs. 4 and 5). PAH with ($N \geqslant 4$) always showed a strong total decrease (D.tot%), which could be attributed to their high sequestration by humic substances (Tables 2 and 3) (Nieman et al., 1998; Karl et al., 1999; Richnow et al., 2000). Guthrie and Pfaender (1998) showed that when 14C is added to soil as 14C-pyrene, a major proportion of the recovered 14C (43–80%) was found in humic/fulvic acid extracts (6.6–26%) or in the residual humin (29–73%).

3.4. Molecular tendency of PAHs

Comparing the behaviour of all PAH compounds during composting showed that the 15 PAH could be classified into groups (Gi) that present the same patterns of change during composting: G1 (naphthalene, anthracene); G2 (fluorene, phenanthrene); G3 (pyrene, fluoranthene, benzo(a)anthracene, chrysene) (Fig. 4); G4 (benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene) (Fig. 5). Each group appears to be made up of PAH with a similar or the same number of aromatic rings or molecular structure (Fig. 2). G1, naphthalene and anthracene characterized by small number of aromatic rings ($N \leqslant 3$) and linear molecular structure, showed a low adsorption during the stabilization phase (Fig. 4). Fluorene and phenanthrene (3 aromatic rings) showed high adsorption during stabilization phase which explains theirs high amounts remaining (Rm%) and the percentages of their total decrease (D.tot%) are lower (Fig. 4; Table 2). Pyrene, fluoranthene, benzo(a)anthracene, chrysene (4 aromatic rings) show almost the same percentages of changes (Table 2). For groups G4 (5 or 6 aromatic ring), high adsorption could be—as described above—(Table 3; Fig. 5). This suggests that both the mechanisms of biodegradation and adsorption of PAH that occurred during composting are closely related to the number of aromatic rings and the PAH molecular structure.

4. Conclusion

The 16 PAH targeted by the USEPA agency, were investigated during composting of a lagooning sludge. Although, the amounts of total 16 PAH determined in the initial sludge were very far below the recommended limits for sludge to be spread on agricultural land. The fate of the extractible amounts of the PAHs during sewage sludge composting was unknown. The present study targeted the behaviour of PAHs during composting process. The results show the efficient reduction of extractible PAH amounts during composting. The decreases could result from both biodegradation by thermophilic and mesophilic populations and adsorption

to compost matrix. During the stabilization phase, the development of an intense thermophilic activity contributes to extensive decomposition mainly of PAH with small number of aromatic rings or low molecular weight. However, microbial biodegradation was limited for PAHs with a large number of aromatic rings or high molecular weight due to their strong adsorption, which can probably be attributed to their high hydrophobicity. At the beginning of the maturation phase, the decomposition of adsorbing material such as ligno-cellulosic structures, allows the release of the retained PAHs, but with different rates according to the number of aromatic rings and their molecular structure. PAHs with few aromatic rings or low molecular weight are weakly adsorbed and so could be easily and rapidly desorbed. For the PAHs with a large number of aromatic rings or high molecular weight, which were strongly adsorbed during the stabilization phase, desorption was delayed. During the maturation phase, the presence of mesophilic populations could play an important role in the final decrease of total extractible amounts of remaining PAH either by biodegradation or by humification. The high content of humic matter during this phase could contribute to the sequestration mainly of PAH with a large number of aromatic rings or high molecular weight, because of their strong hydrophobicity.

During composting, a similar behaviour pattern was recorded between PAH with a similar number of aromatic rings or molecular structure. This suggests that both the mechanisms of biodegradation and adsorption of PAH are strongly related to the number of aromatic rings and PAH molecular structure.

Information on the exact contribution of the mechanisms suggested "biodegradation or sequestration (adsorption)"—proposed in numerous research works—to the removal and decrease of PAH bioavailability is still not conclusive. But, a composting trial using radiolabeled 14C-PAH has been programmed to determine which mechanisms lead to the PAH decrease: ultimate biodegradation, sorption of parent PAH or binding of their oxidative metabolites to the compost matrix.

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