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Modelling the fate of PAH added with composts in amended soil according to the origin of the exogenous organic matter

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HIGHLIGHTS

- The model simulates the release of PAH from compost in soil according to organic carbon degradation.
- Processes that occur before compost application to the soil influenced the fate of PAHs in the soil.
- The PAH dissipation was higher in incubations of mature composts.
- The PAH dissipation was higher in incubations of soil amended with non-mature composts.
- The model calculates the proportion of biogenic and physically bound residues of PAHs.

GRAPHICAL ABSTRACT

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ABSTRACT

A new model that was able to simulate the behaviours of polycyclic aromatic hydrocarbons (PAH) during composting and after the addition of the composts to agricultural soil is presented here. This model associates modules that describe the physical, biological and biochemical processes involved in PAH dynamics in soils, along with a module describing the compost degradation resulting in PAH release. The model was calibrated from laboratory incubations using three ¹⁴C-PAHs, phenanthrene, fluoranthene and benzo(a)pyrene, and three different composts consisting of two mature and one non-mature composts. First, the labelled PAHs were added to the compost over 28 days, and spiked composts were then added to the soil over 55 days. The model calculates the proportion of biogenic and physically bound residues in the non-extractable compartment of PAHs at the end of the compost incubation to feed the initial conditions of the model for soil amended with composts. For most of the treatments, a single parameter set enabled to simulate the observed dynamics of PAHs adequately for all the amended soil treatments using a Bayesian approach. However, for fluoranthene, different parameters that were able to simulate the growth of a specific microbial biomass had to be considered for mature compost. Processes that occurred before the compost application to the soil strongly influenced the fate of PAHs in the soil. Our results showed that the PAH dissipation during compost incubation was higher in mature composts because of the higher specific microbial activity, while the PAH dissipation in amended soil was higher in the non-mature compost because of the higher availability of PAHs and the higher co-metabolic microbial activity.

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1. Introduction

The recycling of composted organic residues in soils is a practice that is increasingly used in agriculture. It helps to prevent the loss of soil fertility by restoring soil organic matter contents as well as improving soil physical properties (Annabi et al., 2011; Goss et al., 2013; Mohammed et al., 2016; Tejada et al., 2009). However, certain organic pollutants, among them polycyclic aromatic hydrocarbons (PAH), may be present in the feedstock materials of these composts, leading to a soil contamination risk when they are recycled in agricultural areas (Brändli et al., 2005; Wilcke, 2000; Wild et al., 1991). It is of special importance to understand the dissipation of PAH that is added to soils with composted organic residues.

A number of studies have addressed the impact of compost applications on PAH-contaminated soils (as Puglisi et al., 2007; Zhang et al., 2012). They reported that compost application promotes both the formation of sequestered fractions of PAHs and its biodegradation, leading to the reduction of its concentration in contaminated soils. However only a few studies have addressed the fate of PAH when added to agricultural soils in composts (Haudin et al., 2013; Kästner et al., 1999). Haudin et al. (2013) studied the application of green waste and sludge compost containing different spiked ^{14}C -organic pollutants (and among them one PAH molecule, fluoranthene) on their fates in soil. They found that their dynamic in soil depended on the pollutant properties but also on its distribution between the available and non-available fractions in the composts that enter the soil. Little is known about the impact of the composting process and the final quality of composts on the fate of PAHs in soil according to their physico-chemical properties.

A number of models have been developed to explore the fates of organic pollutants in amended soils (e.g., Morais et al., 2013; Wu et al., 2013; Zarfl et al., 2009), but models that consider the impacts of organic matter decomposition on the sorption and degradation of the pollutants explicitly are very scarce. Lashermes et al. (2013) simulated the mineralization of four organic pollutants during the composting of green waste and sludge. Geng et al. (2015) simulated the mineralization of these four organic pollutants after their incorporation with compost into the soil. Both studies show the broad interest in simulating the explicit interactions between pollutants and organic matter in models. The impact of the composting process and the type of composted organic matter on the organic pollutant's fate after its addition to the soil has never been simulated.

The aims of the present work were threefold: (i) use an experimental approach to study the impact of the compost quality (for three composts consisting of green waste and sludge compost, biowaste compost, and municipal solid waste compost) on the fate of PAHs in composts and after compost applications to soil for three different ^{14}C -labeled PAHs (phenanthrene, PHE, fluoranthene, FLT and benzo(a)pyrene, BAP), (ii) propose a new coupled model to study the dynamics of PAHs in soil-compost mixture systems that explicitly accounts for the type of organic amendments on the fate of the PAHs during the decomposition of compost in the soil and (iii) calibrate the model with the experimental data and compare the kinetics of mineralization and dissipation for each PAH according to the compost quality.

2. Modelling

2.1. Model description

2.1.1. General structure

The PAH model is made of the following 3 modules: a PAH biodegradation/adsorption module, an OC (organic carbon) module and a PAH release module (Fig. 1 and Table A1). The structure of the PAH biodegradation/adsorption module is based on the model described by Brimo et al. (2016). The specific module of the OC dynamic and its interaction with the PAH module were added according to the models developed in

Lashermes et al. (2013) and Geng et al. (2015) that simulate the interactions between organic matter and organic pollutant (such as PAHs) dynamics during composting and after compost application to the soil. The novelty of our model here is that we add a PAH release module to simulate the release of PAHs from compost into soil during the decomposition of the compost.

The PAH biodegradation/adsorption module associated with the OC module is able to simulate the fate of PAH dynamics during compost incubation. The PAH biodegradation/adsorption module alone is able to simulate the PAH dynamic in soil without compost, and the 3 modules together are built to simulate the PAH dynamic in soils amended with compost.

In our previous model described in Brimo et al. (2016) the biological and chemical mechanisms controlling PAH behaviours in soil are modelled using two sub-modules as shown in Fig. 1: the adsorption module and the biodegradation module. The adsorption module is based on a bi-phasic first-order kinetic model with an initial fast kinetics characterized by weak sorption (PAH_{WS} , where “ws” refers to weakly sorbed), and a slower kinetics with strong sorption (PAH_{SS} , where “ss” refers to strongly sorbed). The biodegradation module assumes that biodegradation uses only the soluble PAH (PAH_{AV} , where “av” refers to available) with specific degradation pathways from a specific microbial biomass (B_{SPE}) whose growth and maintenance is described by the Monod equation (as indicated by dotted lines in Fig. 1) and co-metabolic degradation pathways modelled using second-order kinetics from the microbial biomass that degraded the compost (X_{CP}) (dashed lines in Fig. 1). The degradation of PAH produces CO_2 emissions (PAH_{CO_2}), metabolites (PAH_{MET}), and biogenic non-extractable residues (PAH_{BS}). The influences of the temperature and the water content on the biological processes are taken into account using the correction factors f_T and f_W for the temperature and the water content, respectively (see Table A1 in SI).

The OC dynamic module was based on the modules proposed by Lashermes et al. (2013) and Geng et al. (2015), which describe organic matter transformations during composting and during compost decomposition in soil, respectively. The organic carbon in the compost was divided into several pools that were measured using the Van Soest fractionation method and characterized by their specific degradability. All the organic pools are hydrolysed into available substrates (DOC) for the growth of the compost-degrading microbial biomass (X_{CP}) according to their specific hydrolysis constants. The microorganisms die at a specific death rate and the dead cells are recycled into either the compost organic compartment SND_{slow} (with slow degradation rate) or directly into the DOC compartment. Humified organic C (HOC) was assumed to be derived from dead microbial biomass to simulate the “Soil” condition, while for the “compost” condition, this part of the model is not activated and all the dead biomass is recycled. The PAHs available in the PAH_{AV} solution (as calculated in the PAH module) can be degraded through co-metabolism by microorganisms X_{CP} that use the compost organic matter as their primary energy source (as calculated in the OC module). We assumed that the contribution of PAH_{AV} to X_{CP} growth and maintenance can be neglected because PAH_{AV} has low concentrations of PAH compared to the total quantity of organic carbon substrates in the compost. The evolution of the microbial biomass in a soil-compost mixture system is essentially driven by the decomposition of the fresh organic matter that is added with the compost (see explanations in SI 1).

A new PAH Release module was developed in this study to describe the release of the PAHs contained in compost during the decomposition of the compost that was applied to the soil. This module is used only for amended soil incubations and not for composting incubations. The PAH_{CPWS} (where “cpws” refers to PAHs that are weakly sorbed onto organic carbon pools of compost) is subject to dual processes (Fig. 1). We assumed that the PAH is distributed among the OC fractions proportionally to the relative mass of each fraction. One fraction of PAH moves into the soil solution (PAH_{AV}), with the hydrolysis of organic pools of

Fig. 1. Diagram of coupling between the OC model (in the upper left corner) and the different modules of the PAH model (including the PAH release module in the upper right corner and the biodegradation/adsorption modules placed on the left lower and right lower corners, respectively). Dashed bold arrows indicate the interaction points between the modules. k_{ij} : first-order kinetic constant with the first subscript denoting the source and the second indicating the sink of the corresponding process (A: PAH_{AV}; B: PAH_{BS}; C: PAH_{CPWS}; M: PAH_{MET}; S: PAH_{SS}; and W: PAH_{WS}) (d^{-1}); k_{deg} : kinetic constant of biodegradation for co-metabolism ($mg\ C/kg_{dw} \cdot d$), considering that the concentration of the co-metabolism biomass is given by ($mg\ C/kg_{dw}$); β : magnitude of metabolite production by biodegradation for co-metabolism (between 0 and 1); μ_{smax} : maximum specific growth rate (d^{-1}); ks_{spe} : half saturation of the growth substrate for the specific biomass ($mg\ C/kg_{dw}$); Y_{spe} : yield of specific biomass (—); and k_M : mortality rate constant (d^{-1}).

compost set to become an available substrate for the microorganisms (Processes XI, XII, XIII, XIV, and XV in Table A1). We assume that the PAH release rates into the solution are proportional to the hydrolysis of the compost pool to which they belong because PAHs are closely associated with the organic carbon pools of compost. For simplicity, we assume the irreversibility of this process. The other fraction of PAH becomes much more strongly sorbed onto the surface of the soil-compost mixture (process IV in Table A1) and goes directly from the PAH_{CPWS} of the compost compartment into the PAH_{SS} soil compartment. This process was simulated because the experimental results described below show high bound residue formation in some treatments in spite of the low organic matter decomposition and then the low PAH release by hydrolysis.

The release rate of PAH_{CPWS} ($\mu g/kg_{ds}$) that was added with compost as a function of the organic pool hydrolysis kinetics is calculated using Eq. (1) as follows:

$$\frac{dPAH_{CPWS}}{dt} = -\sum_{i=1}^{i=5} \left[\frac{(k_{Ci} \cdot C_{i,t} - fr_{i,t}) \cdot f_{Ci}}{\sum_{i=1}^{i=5} C_{i,t}} \cdot PAH_{CPWS} \right] - k_{CS} \cdot PAH_{CPWS} \quad (1)$$

$C_{i,t}$ is the carbon mass concentration of organic pool i of the applied compost at time t as defined in Table A3 in SI with ($C_1 = SDN_{SLOW}$, $C_2 = SDN_{FAST}$, $C_3 = HCEL$, $C_4 = CEL$ and $C_5 = LIG$) [$kg\ C/kg_{cp}\ C$]; k_{Ci} is the hydrolysis constant of pool C_i in [d^{-1}] (see Table A3 in SI); k_{CS} is the first-order kinetic constant from PAH_{CPWS} to the PAH_{SS} compartment [d^{-1}];

f_{Ci} is the lignin content dependence factor proposed by Corbeels et al. (1999) (see also Iqbal et al., 2014) and $fr_{i,t}$ is a correction factor defined by Eq. (2) as follows:

$$fr_{i,t} = \begin{cases} 0 & \text{when } i \neq 1 \\ w_{CP} \cdot (1 - Y_{SWCP}) \cdot m_{cp} \cdot X_{cp,t} & \text{when } i = 1 \end{cases} \quad (2)$$

For $i = 1$ (SDN_{SLOW}), the flux of the dead co-metabolic microorganisms that might be recycled into organic pool C_1 does not contain any PAH anymore.

The mathematical model uses a set of nonlinear ordinary differential equations that are solved numerically within a MATLAB code. All the model equations are presented in SI Table A1.

2.2. Experimental data (from Verge-Leviel, 2001)

The impact of the origin and characteristics of the compost on the PAH dynamics in soil was assessed experimentally by Verge-Leviel (2001). These data are used here to calibrate the PAH model. Three types of incubation containing the PAH have been analysed (Fig. 2a) as follows:

- 1 Incubations of composts spiked with PAH to stabilize the PAH in the compost before adding it to the soil and then to create conditions that were closer to reality.
- 2 Incubations of soil amended with PAH in compost to study the effect of the compost type on the PAH fate in soil.

③ Incubation of soil spiked directly with PAH as a control to observe the effect of the stabilization of PAHs in the compost compared to its direct addition to soil.

2.2.1. Soil and composts

A silt loam soil was collected from the upper horizon of an agricultural experimental farm located at Palaiseau, near Paris (91, France). Ten sub-samples were collected and mixed to obtain a homogeneous representative composite sample. The soil was sieved at 5 mm and stored fresh at 4 °C before use. Its primary characteristics were as follows (in g/kg_{dw}): clay, 187; silt, 756; sand, 57; and organic C content, 11.9. The soil pH in water was 5.5.

The experiments were performed with three composts that were sampled from Veolia composting plants in France during the maturation phase, and they consisted of green waste and sludge compost (GWS), biowaste compost (BioW) and municipal solid waste compost (MSW). The primary characteristics of these composts are detailed in Houot et al. (2012). The composts were sieved at 5 mm.

2.2.2. Incubation setup

The following ¹⁴C-PAHs were used: [9C-ring-14C] phenanthrene (PHE; 1459 MBq/mmol; >98% purity), [3C-ring-14C] fluoranthene (FLT; 1665 MBq/mmol; 98% purity) and [7C-ring-14C] benzo(a)pyrene (BAP; 984 MBq/mmol; >98% purity). ¹⁴C-labelled and non-labelled

Fig. 2. (a) Schematic design of the incubation experiments over 83 days. There were three incubation series as follows: ① pure compost, ② soil-compost mixtures, and ③ control unamended soil. For each of the first and second incubations, three different composts were incubated independently, and they were GWS, MSW and BioW. Each incubation was performed with each of the labelled pollutants (PHE, FLT and BAP). All the incubations were run in triplicates. (b) A schematic overview of the modelling methodology. There were 83 days of simulation for the data in series ① (3 treatments corresponding to 3 composts) to determine the mass ratio between the biogenic, PAH_{BS}, and physical PAH_{SS}, with non-extractable residues at the 28th incubation day, which was the initial day of the incubations for the compost-soil mixtures. The model was run simultaneously in calibration mode over 55 days and 83 days, using the data in series ② (3 treatments corresponding to 3 amended soils) and the data in series ③ (control unamended soil) to determine the parameter distribution set of the PAH model for each PAH.

PAHs were purchased from Sigma (St. Quentin Fallavier, France). Solutions of the labelled pollutants were first prepared in methanol. The radioactivity levels of the prepared solutions were 29.899, 34.481 and 47.709 MBq/L for PHE, FLT and BAP, respectively. The final concentrations were adjusted with non-labelled PAH at 13 mg/L for each PAH.

The incubation experiments were performed as follows. One hundred microliters of each ^{14}C -PAH solution was added to 1 g_{fw} of compost in 100 mL glass jars. The closed jars were then pre-incubated for 28 days at 28 °C. On the 28th day, 20 g_{fw} soil (water content equivalent to pF = 2.5) was added and the incubation of the soil-compost mixtures (20:1) was performed for 55 additional days at 28 °C (series 2 in Fig. 2a). Control incubations containing only ^{14}C -PAH solution with compost or soil were run simultaneously under the same conditions for 83 days (series 1 and 3 in Fig. 2a). All the experiments were run in triplicates.

2.2.3. Analysis (see SI 2 for details)

The C-CO_{2org} and ^{14}C -CO₂ from the mineralization of the total organic carbon and the ^{14}C -PAH, respectively, were periodically measured on days 3, 7, 10, 14, 21, 28, 31, 36, 41, 47, 54, 61, 67, 74 and 83. The distributions of ^{14}C -PAH among the metabolites, parent extractible pollutant and the non-extractible and mineralized fractions were assessed on days 28 and 83 for each incubation.

2.2.4. Experimental data handling

Assuming the mineralized fraction was precisely measured compared to the measured extractable and non-extractable fractions, the yields of the three fractions were adjusted to 100% recovery by applying a weight distribution error to the metabolites and the parent extractible and non-extractible fractions at each of the two extraction times. To assess the suitability of the raw data for the purpose of modelling, a two-factor analysis of variance (ANOVA) with replication was performed to verify whether a significant difference was present between the four treatments (i.e., the 3 different composts + soil, in addition to the control soil without amendment) across both days and the type of analysed fraction on the dissipation of labelled ^{14}C -PAH through the soil-compost mixture system.

The model parameters were fitted to the experimental fractions. The measured mineralized fraction was assigned to the simulated PAH_{CO2} and the extractible metabolite fraction corresponded to the simulated PAH_{MET}, whereas the non-extractible fraction (NER) corresponded to the two model compartments that were pooled together, namely the biogenic residue PAH_{BS} and the physical residue PAH_{SS}. The extractible fraction of the parent compound in the soil-compost mixtures system corresponded to the available soluble compartment PAH_{AV} and the two adsorbed compartments PAH_{WS} and PAH_{CPWS} (see SI 3). The initial soil microbial biomasses, X_{soil}, X_{cp} and B_{spe}, were taken as explained in SI 1.

2.3. Modelling methodology

Four groups of runs were performed sequentially as summarized in Table 1 and Fig. 2b. While the two first runs of models 1 and 2 were conducted with the OC model alone, the two other runs 3 and 4 were implemented with a PAH model coupled to an OC model. Runs 1 and 3 were performed to simulate the compost incubations to calculate the amount and distribution of non-extractable PAHs between biogenic and strongly sorbed fractions at 28 days (PAH_{BS} and PAH_{SS}, respectively) that were not available from the experimental data. Runs 2 and 4 were used to estimate a set of parameters that could simulate all the treatments in the soil-compost mixtures for each PAH. In run 3 (of soil amended with composts), the initial data for the PAH compartments were obtained from the experimental data obtained on the 28th day of the compost experiments.

During run 4, the DREAM algorithm (Vrugt, 2016) was inserted into the code of the coupled model and was used to estimate the probability density functions of the PAH model parameters in the soil (see more

Table 1
The calibration procedures.

# Run	Data set	Objectives
N° 1 OC Model In compost 3 composts	CO ₂ mineralized Fig. 2, series ①	Calibration of OC model parameters to be used by run N° 3 Table A3 and Fig. 3 (a, b)
N° 2 OC Model In soil-compost mixture 3 composts	CO ₂ mineralized from compost Fig. 2, series ②	Calibration of the OC model parameters to be used by run N° 4 Table A3 and Fig. 3 (c, d)
N° 3 Coupling model OC × PAH In compost 3 composts × 3 PAH	^{14}C -CO ₂ mineralized ^{14}C -PAH fractions Fig. 2, series ①	Determining the ratio between biogenic NER PAH _{BS} and strongly sorbed PAH _{SS} at the 28th day of compost incubations/initial time of soil-compost incubations run N° 4 Table A4 and Fig. 4
N° 4 Coupling model OC × PAH In soil-compost mixture In soil control 3 composts × 3 PAH 1 sol × 3 PAH	^{14}C -CO ₂ mineralized ^{14}C -PAH fractions Fig. 2, series ② ^{14}C -PAH fractions Fig. 2, series ③	Get 1 set of parameters to simulate each PAH for the 3 compost-soil mixtures and the soil control Table 2 and Figs. 6, A1, A2, A3

details in Brimo et al., 2016)). The parameter ranges required by DREAM as prior parameter distributions were chosen on the basis of the literature survey and further adjusted using a stepwise trial and error strategy. Each run included a maximum total of 5000 model simulations, and only the best 50% of the simulations were chosen (Brimo et al., 2016)) and used to build the histograms of the probability density functions in the model parameter values. A Nash Sutcliffe index (Nash and Sutcliffe, 1970) was calculated to perform a quantitative evaluation of the model accuracy.

3. Results and discussion

3.1. Calibration of the OC model for the control compost and amended soil

The OC model required a parameter calibration prior to use. We chose to optimize the hydrolysis rates of the cellulose (CEL) and hemicellulose (HCEL) pools so that k_{CEL} is equal to k_{HCEL} because Iqbal et al. (2014) found that the CEL and HCEL organic pools have similar decomposition rates. The OC calibration yielded an estimated value of 0.03 d⁻¹ for both the k_{CEL} and k_{HCEL} parameters in the model of pure composts and a very similar value of 0.02 d⁻¹ in the amended soil. The updated values of k_{CEL} and k_{HCEL} obtained through this study were very close to the 0.028 d⁻¹ reported by Iqbal et al. (2014) for crop residue decomposition in soil.

Zhang et al. (2012) reported that the soluble organic pool would have very different characteristics in the fast pool (SDN_{fast}) and the slow pool (SDN_{slow}) depending on the origin of the compost. Consequently, during the compost incubation, we also re-adjusted the parameter k_{fast} (hydrolysis rate of the fast soluble pool) and found an estimated value of 0.212 d⁻¹ for k_{fast} . In the amended soil, we also fit both the parameters linked to the microbial biomass, namely, the mortality rate and the proportion of recycling dead microbial biomass (m_{cp} and w_{cp} , respectively), because Zhang et al. (2012) found that the organic mineralized fraction (CO_{2org}) was very sensitive to the parameters linked to the microbial biomass. The calibration in amended soil yielded an estimated value of 0.085 d⁻¹ for m_{cp} and two different estimated

values for w_{cp} . Their values were 0.1% in GWS and BioW, which were also the same as that obtained by Geng et al. (2015) for a GWS treatment, whereas the estimated value with MSW was 99.9%. These results indicated that the microbial biomass was recycled in the immature compost MSW treatments while the more stable composts such as GWS and BioW were made directly into soil-humified organic matter. The updated sets of parameters for the OC model are summarized in Table A3 in SI. A single set of parameters was found to simulate the dynamics of OC adequately in all the composts for each type of incubation in the pure composts and amended soils.

The evolution of organic carbon mineralization into CO_2 , CO_{2org} , and microbial biomass are displayed in Fig. 3. According to Fig. 3 (a and c), there is very good consistency between the simulated and experimental data obtained for CO_{2org} as confirmed by the high Nash Sutcliffe efficiency indexes of 0.97, 0.84, and 0.89 for the MSW, BioW, and GWS treatments, respectively, in the pure composts, and of 0.99, 0.98, and 0.90 for MSW, BioW, and GWS, respectively, in the amended soils. During the initial step of the incubations of the control composts (Fig. 3a and b), a rapid mineralization and a significant increase in the microbial biomass are observed. At the end of the simulation period, the mineralized CO_{2org} levels in the treatment driven by MSW are 1.7 to 3.8 times higher than that observed in the BioW and GWS treatments, respectively. The maximum predicted peak for biomass growth is higher in the BioW treatment than in the MSW and GWS treatments. However, after reaching the maximum peak, the microbial biomass in the MSW treatment remains much higher than it was in the BioW and GWS (Fig. 3b). Following the compost applications to the soil (Fig. 3c and d), the dynamics of OC decomposition for the different treatments in amended soil followed the same order as those that were previously found in the pure compost incubations but with much higher mineralization and microbial growth in the MSW in comparison to the other treatments. This result showed that the MSW compost was not mature when it was sampled from the composting plants or after 28 days of incubation by itself, compared to the other one. These varying behaviours for the different composts during the incubations can be attributed to the origin and the degree of maturity of

the applied compost as reported by Chalhoub et al. (2013), Franco et al. (2008) and Zhang et al. (2012).

3.2. Simulation of PAH fractions in compost

As previously mentioned, we first predicted the dynamics of the ^{14}C -PAH during the 83 days of compost incubations, but we identified the initial conditions of the compost when it was added to the soil on the 28th day. All the simulations were performed using the PAH model coupled to the OC model. The model was calibrated for each compost and each PAH. Table A6 in the SI gives the Nash-Sutcliffe efficiencies for the extractable PAH, the metabolites, the total non-extractable and the mineralized fractions for each of the three ^{14}C -PAHs. The performance of the model in reproducing the experimental measurements was good, as confirmed by the Nash Sutcliffe efficiency index that was generally >0.60 , except for the metabolite fractions measured in the MSW treatment that registered negative Nash Sutcliffe index values. The discrepancy between the simulations and experiments in the MSW treatment was primarily due to the model overestimation of the data at the end of the incubation.

The simulated results for the non-extractable residues ($PAH_{SS} + PAH_{BS}$) and the mineralized fraction (PAH_{CO_2}) for each ^{14}C -PAH over all the treatments are presented in Fig. 4 using the estimated parameters of Fig. A4. The amount of mineralized CO_2 increased in the following order: BAP, FLT and PHE, because of the higher microbial degradation due to their lower number of benzene rings. We found that the highest mineralization intensity was obtained in the treatments containing BioW and GWS composts for all the PAHs. Lower mineralization was observed in the incubations with MSW compost. This finding suggests that the potential amounts of microorganisms that were degrading the organic pollutants should have been smaller in the treatment with MSW compost in comparison to the GWS and BioW, as already mentioned in Houot et al. (2012). These observations contrast with the results for the organic decomposition of the three composts, where the mineralization was significantly higher for the MSW than for the GWS and BioW composts (Fig. 3). To fit the data, the model

Fig. 3. Experimental and simulated results obtained using the OC model for the three treatments. The experimental data are indicated by $\square$. The figures in the first line are the results obtained during the 83 days of the compost incubations, whereas those in the second line are obtained from the incubation of the amended soil over 55 days. a) The carbon emission, CO_{2org} from the decomposition of compost during composting, b) microbial biomass, or X_{cp} , during composting, c) CO_{2org} emission from the decomposition of compost in the amended soil (CO_2 from soil is not included), and d) microbial biomass X_{cp} , during the decomposition of compost in the amended soil. Error bars indicate the standard deviation (3 replicates).

Fig. 4. Simulated and observed ^{14}C -PAH in control composts. The panes line up in a (3×6) matrix, in which the three rows define the three ^{14}C -PAHs, namely, PHE, FLT, and BaP. The simulation results are marked in lines, whereas the experimental data are represented by dots. The error bars indicate the standard deviation (3 replicates). The panels entitled " $\text{PAH}_{\text{SS}} + \text{PAH}_{\text{BS}}$ " include the total simulated non-extractable fraction (in a solid line, blue), the simulated strongly sorbed (in pointed line, brown) and the simulated biogenic NER (in pointed dashed line, violet). All the data are given in $\mu\text{g}/\text{kg}_{\text{cp}}$ (dry weight). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

therefore simulated that the biodegradation of the labelled pollutants into ^{14}C - CO_2 and PAH_{CO_2} occurred through the pathway that was driven by the specific biomass and not only by the co-metabolism pathway (Fig. 5). This assumption is supported by Cerniglia (1997), who reported that composts rich in lignin, including ligninolytic fungi, can be efficient at the bioremediation of PAH in contaminated wastes. Houot et al. (2012) found higher PAH mineralization in GWS and BioW than in

MSW, and they concluded that the maturation microflora was more efficient than the thermophilic microflora at mineralizing organic pollutants. The PAH mineralization was well simulated in the treatments with BioW and GWS composts when considering both biodegradation pathways. By contrast, regarding the treatment with MSW compost, the model predicted that the mineralized fraction was produced only through the specific biomasses pathway and not from the co-

Fig. 5. Dynamics of the specific biomass for all the treatments. The figures in the first column are the simulated results that were predicted during the 83 days of the compost incubations, whereas those in the second column are predicted for the incubation in the amended soil over 55 days. The figures in the first line are the simulated results predicted for phenanthrene, and those in the second line are predicted for fluoranthene, whereas those in the third line are predicted for benzo(a)pyrene (green dashed line for GWS, blue solid line for BioW and pink dashed line for MSW).

metabolic one. The model simulated a very low specific biomass (Fig. 5). This result was corroborated by the observed initial lag-phases in the mineralized fraction with this treatment.

The proportion of biogenic non-extractible residues, or the PAH_{BS} (referring to the total non-extractible residues fractions, PAH_{NER}) after the 28th day of composting (days during which the composts were amended into the soil) are given in Fig. 4 and Table A5. A very low percentage of biogenic non-extractible residues was predicted for the FLT and PHE in the MSW compost. The model estimated much higher PAH_{BS} for BAP at approximately 18.7%. We observed that the higher the mineralization rates of ¹⁴C-PAH were, the higher the model estimation of the biogenic contribution to the total non-extractible residues (Fig. 4 and Table A5). These findings are consistent with the results reported in the literature about the biogenic bounded residue formation. There are numerous references reporting that the microbial activity has a direct and significant effect on the formation of non-extractible residues for persistent organic pollutants (Barriuso et al., 2008; Gevaio et al., 2005; Kästner et al., 1999; Nowak et al., 2013). However, the biogenic rates of formation during the incubations remain unknown because no chemical analyses were performed and very few studies can be found in the literature about the quantification or the modelling of biogenic residue formation during compost incubations or in compost-amended soil. We found that the biogenic residues were systematically lower than the strongly sorbed residues (see Fig. 4). Richnow et al. (2000) found that the contribution of the biogenic fraction to the total non-extractible residues for PHE was at least 11% after 50 days of incubation in a batch bioreactor. Kästner et al. (2014) simulated the dynamics of anthracene (PAH with 3 cycles) in non-amended soil and predicted that 50% of the non-extractible residues were biogenic after 50 days of simulations.

3.3. Simulation of PAH fractions in amended soils

The PAH model coupled with the DREAM algorithm was run to determine the best set of model parameter values for soil-compost incubations for each PAH. The initial conditions were obtained from the ¹⁴C-PAH distribution at the 28th day of the pure compost incubations. The best set of model parameters was the one that simulated the observed data as accurately as possible, as recorded for the pollutant in the amended soil with the three different composts and the unamended soil.

3.3.1. Estimated parameters

A single set of parameters for all the compost types was found to simulate the dynamics of PHE and BAP independently (Table 2). However, this single parameter set could not be determined for the FLT where different values were found for the K_{CS} parameter (the rate of strongly sorbed compartment formation from compost PAH) and the $\mu_{\max}$ (the maximum growth rate of a specific biomass).

The 95% confidence intervals listed in Table 2 for each estimated parameter were obtained from DREAM by using the histograms of the probability density functions (PDF) in the parameter value range (Fig. A4). The results show that some parameters were very well-defined since their histograms of values display Gaussian distributions with 95% confidence intervals, occupying small ranges inside the uniform prior distributions. This was also the case for the parameters k_{SW}, k_{WS}, k_{CS} and k_{MB} for PHE. However, some other parameters had more uniform PDF and/or they concentrated most of their probability mass at their lower or higher limits. These parameters are linked to the biodegradation pathway driven by specific biomasses ($\mu_{\max}$, k_M, y_{spe}, and k_{spe}). This finding was probably due to the lack of data for measuring the specific degradation. Low correlations were found between the parameters except between the sorption parameters k_{SW} and k_{WS}, with a correlation coefficient of 0.75. A comparison of the parameter values obtained in this current study with their values published in the literature was difficult because of the differences between the models. The fitted parameter values of the co-metabolism biodegradation pathway k_{deg} were found to be in the following order: PHE > FLT > BAP, which was correlated to the bioavailability of the pollutant itself as linked to its chemical hydrophobicity. The fitted value for the $\mu_{\max}$ of FLT in the GWS of 0.54 d⁻¹ was close to the value obtained by Geng et al. (2015) for the same PAH in the same compost. The optimized values of y_{spe} for PHE and FLT (0.251 and 0.274 [–] respectively) were found to be close to that proposed by Weissenfels et al. (1990) (0.24 and 0.23 [–] for PHE and FLT respectively).

3.3.2. Performance of the model

Two Nash Sutcliffe efficiency index (NS) values were calculated for each ¹⁴C-PAH and each treatment (Table 3). While the first one, NS_{global}, was used to evaluate the goodness of fit for all the model variables together, the second one, the NS_{CO₂}, accounted for the goodness of fit for the mineralized variable PAH_{CO₂} alone. In general, the overall performance demonstrated the good ability of the model to describe the observed PAH transformation in soil, as confirmed by the relatively high

Table 2
Optimal values and confidence intervals (CI) of PAH model parameters obtained with DREAM for the three ¹⁴C-PAH in amended soils.

Par	Unit	Phenanthrene		Fluoranthene		Benzo(a)pyrene	
		Optimum	95% CI	Optimum	95% CI	Optimum	95% CI
k _{AW}	d ⁻¹	1.770	[0.484, 3.865]	26.428	[1.44, 28.06]	24.810	[15.04, 28.15]
k _{WA}	d ⁻¹	0.230	[0.079, 0.238]	0.932	[0.0124, 0.94]	0.218	[0.075, 0.354]
k _{WS}	d ⁻¹	0.065	[0.030, 0.10]	0.021	[0.021, 0.114]	0.029	[0.0274, 0.036]
k _{SW}	d ⁻¹	0.032	[0.027, 0.045]	0.042	[0.037, 0.199]	0.007	[0.005, 0.012]
k _{MB}	d ⁻¹	0.037	[0.037, 0.149]	0.065	[0.017, 0.096]	0.138	[0.079, 0.184]
k _{CS}	d ⁻¹	0.238	[0.10, 0.570]	0.002 ^a 0.016 ^b 0.06 ^c	[5 × 10 ⁻⁴ , 2 × 10 ⁻²]	6 × 10 ⁻⁴	[1 × 10 ⁻⁴ , 1 × 10 ⁻³]
k _{deg}	(mg C/kg _{dw} ·d)	2.7 × 10 ⁻³	[2 × 10 ⁻³ , 2 × 10 ⁻²]	2.2 × 10 ⁻⁴	[1 × 10 ⁻² , 2 × 10 ⁻³]	1.7 × 10 ⁻⁴	[6 × 10 ⁻⁵ , 3 × 10 ⁻⁴]
β	–	0.478	[0.385, 0.498]	0.59	[0.445, 0.597]	0.59	[0.356, 0.597]
μ _{Smax}	d ⁻¹	2.606	[1.786, 11.29]	8.423 ^d 0.54 ^e	[0.394, 11.237]	0.908	[0.227, 1.685]
k _{Sspe}	μg ¹⁴ C/kg _{dw}	36.627	[25.52, 71.26]	12.133	[3.82, 73.3]	46.256	[16.65, 58.56]
y _{spe}	–	0.251	[0.13, 0.275]	0.274	[0.112, 0.289]	0.166	[0.124, 0.246]
k _M	d ⁻¹	0.035	[0.005, 0.088]	0.043	[0.0044, 0.0897]	0.018	[0.015, 0.087]

^{a,b,c} Optimum values for k_{CS} for the amended soil with GWS, BioW, MSW respectively.

^d Optimum value for μ_{Smax} for the amended soil with GWS and BioW.

^e Optimum value for μ_{Smax} for the amended soil with MSW.

Table 3

Nash Sutcliffe index values as calculated in soils for CO₂ alone and for all the compartments together.

Treatment	Phenanthrene		Fluoranthene		Benzo(a)pyrene	
	NS _{global}	NS _{CO2}	NS _{global}	NS _{CO2}	NS _{global}	NS _{CO2}
GWS	0.98	0.78	0.99	0.99	0.9	0.84
BioW	0.97	0.60	0.75	0.01	0.99	0.99
MSW	0.95	0.92	0.98	0.88	0.99	0.98
Unamended soil	0.98	0.95	0.99	0.96	0.99	0.28

NS_{global} values that were above 0.75 for most of the simulation situations. The performance of the model in simulating the mineralized fractions was generally good and the NS_{CO2} values were close to 1 for many simulations. Still, for some situations, a poor performance was achieved, as with the BAP for unamended soil (NS_{CO2} = 0.28) or with the FLT for biowaste (NS_{CO2} = 0.01). In fact, the simulated curves were obtained using a unique parameter set that corresponded to the best compromise over the entire treatments, thus resulting in high discrepancies for some cases.

3.3.3. Comparison between the experimental and simulated results

The observed and simulated dynamics of the three PAHs in the soils that were amended with the three composts and in the unamended soil are presented in Figs. 6, A1, A2, and A3. These results could be explained by i) the physicochemical properties of the PAH, ii) the initial amount and distribution of PAHs in compost fractions and iii) the degradability of the composts.

As already observed in the compost (section 3.2), the amount of ¹⁴CO₂ that was mineralized for the BAP and FLT was much lower than the ¹⁴CO₂ mineralized for the PHE (Fig. 6) because their higher number of benzene rings compared to PHE was more difficult to degrade by microorganisms. For the PHE, a decrease in the mineralization was observed in the following order: unamended soil > MSW > BioW = GWS. Similar orders were obtained for BAP, but for FLT, a higher mineralization was obtained with the BioW treatment in comparison to the three others but with no significant differences. For the BAP and PHE,

the total amount of PAH brought by the MSW was higher than what was brought with GWS and BioW because of the low PAH mineralization observed in the MSW during the composting process. The higher microbial growth stimulated by the high decomposition of the MSW compared to the BioW/GWS (Fig. 3) may enhance the degradation by co-metabolism in this compost. PHE was localized in adsorbed fractions for unamended soil and MSW (Fig. 6, A1, A2, A3) and thus was available for microorganisms, while it was initially present primarily in NER fractions of BioW and GWS and thus was less available for microorganisms. For these two PAHs, the mineralization in unamended soils was higher than it was in amended soils because the bioavailability of PAH_{AV} in the soil alone was much higher than that of the PAH_{AV} coming from the release of PAHs from the compost PAH_{CPWS} in amended soil. For the FLT, we observed a higher mineralization for the BioW compared to the other treatments, although a lower amount was added with BioW. The BioW compost was also the treatment that mineralized the FLT more during composting, as shown in section 3.2. The degradation by a specific biomass from BioW (Fig. 5) may explain this higher mineralization in this treatment, as explained below.

Figs. 3 and 5 and Figs. A1, A2, and A3 (in the last columns) show the simulated total and specific biomass evolution during the incubation. For PHE and BAP, the simulated results highlighted that the biodegradation of PAH was primarily driven by co-metabolic microbial biomasses in amended soils, because the specific biomass decreased during the incubations. In unamended soil for PHE, the growth of the specific microbial biomass indicated that a specific biomass was also involved in the degradation of the PAH. For FLT, the model predicted a growth of specific biomass for GWS and BioW, indicating that a part of the mineralization fraction was formed through the specific biodegradation pathway (Fig. 5). For the FLT, we could not use the same parameters for all the treatments and we had to estimate the growth rate of specific microorganisms (μS_{max}) for each treatment, as shown in Table 2. In fact, Geng et al. (2015) also found the degradation of FLT by a specific biomass pathway, and Brimo et al. (2016) found that the model output is very sensitive to this parameter. We found a higher growth rate of specific microorganisms for BioW and GWS compared to MSW. Houot et al. (2012) showed that specific microflora were higher in mature composts

Fig. 6. Simulated and observed ¹⁴C-PAH concentrations over time in amended and control soils. Each row shows one treatment, and each pair of columns shows one ¹⁴C-PAH. The simulation results are marked in lines, whereas the experimental data are represented by red dots. The error bars indicate the standard deviation (3 replicates). The column entitled "PAH_{SS} + PAH_{BS}" includes the total simulated non-extractable fraction as a solid blue line, with the simulated strongly sorbed PAH in a pointed brown line and the simulated biogenic NER shown as a pink pointed dashed line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and affected FLT mineralization. Haudin et al. (2013) also noted the possible involvement of specific biomasses during FLT mineralization in GWS-soil mixtures, with a latency period (lag phase) being observed in the mineralization curves.

The NER fraction decreased or stayed constant in most treatments with GWS and BioW and highly increased for the MSW and soil treatments (Fig. 6). The simulated PAH_{SS} decrease was always accompanied by an increase in the PAH_{BS} . The increased NER in the MSW was due to the increase in biogenic NER that was stimulated by the higher microbial biomass growth in this treatment (see Table A5). In fact, in the model, the microbial activity controls both mineralization and biogenic NER production (Eq. IX and X in Table A1). The biogenic productions of NER estimated by the model for PHE were in the following order: unamended soil > MSW > BioW > GWS. This order was comparable to the order obtained for the mineralization of PHE. Similar results were also obtained for FLT, but for BAP, very little biogenic NER production was simulated because the rate of biogenic NER formation from PAH_{MET} (k_{MB}) was much lower for this PAH. The difference between PAHs indicated that the biogenic NER production rates were lower for PAHs with a high number of benzene rings. However, this result of the simulations could not be confirmed with this experiment. Additional measurements for the biogenic NER fraction using the methods proposed by Nowak et al. (2013) could be used in the future.

The decrease in the adsorbed compartments ($PAH_{CPWS} + PAH_{WS}$ as shown in Figs. 6, A1, A2, and A3) with time was more pronounced in the following order: PHE > FLT > BAP due to the increase in the PAH hydrophobicity, which increased the adsorption onto soil and composts. On the final day, much less PAH was adsorbed for PHE than for FLT and BAP. For each PAH, the decrease in the adsorbed fractions was more marked in the following order: Soil > MSW > BioW-GWS. For the BAP, we even noted an increase in the adsorbed compartments in the BioW and GWS compartments. The adsorption of hydrophobic contaminants is higher on mature organic matter as shown by Aslam et al. (2013) and was much more marked on amended than on unamended soil. We obtained the inverse order relative to mineralization curves in which the soil and MSW treatments displayed more carbon mineralization. In all

the treatments, the simulated PAH_{WS} compartment increased at the expense of the simulated “compost” compartment (PAH_{CPWS}) that diminished. This effect was more marked for less hydrophobic PAHs such as PHE. These results were very well simulated with the model.

3.4. Model sensitivity to the composition of non-extractable residues

The impact of the initial conditions of the biogenic fraction for the total non-extractable residues on the model PAH_{CO2} output was evaluated. The initial values of the percentage of biogenic contribution to the total non-extractable residues could vary between 0 and 100%. The CO_2 mineralization at the end of the incubations is presented for PHE and BAP for both the GWS and MSW treatments in Fig. 7.

The results show that the simulated PAH_{CO2} at the end of the simulation periods is highly impacted by the initial values of the biogenic fraction. We found that the PAH_{CO2} emission increased when decreasing the initial contribution of biogenic NER for all the treatments. This result was related to the model hypothesis, which assumed that the amount of PAH strongly sorbed onto the soil matrix PAH_{SS} , (the NER physical fraction), which might become bio-accessible for the microorganisms following a desorption process (because $k_{sw} \neq 0$) in contrast to the NER biogenic fraction, or PAH_{BS} , that could not be remobilized (Kästner et al., 2014). The relative decrease of PAH_{CO2} between 0% and 100% of the biogenic residue showed the following order: BAP $\times$ GWS > PHE $\times$ GWS > BAP $\times$ MSW > PHE $\times$ MSW. The impact of the biogenic NER initial fraction on the CO_2 emissions was higher for the GWS treatment than for the MSW, suggesting that the model was less sensitive for the initial biogenic NER fraction with the MSW treatment. The compost GWS created more initial non-extractable residues ($PAH_{BS} + PAH_{SS}$) than MSW for both PAHs (see Fig. A1) and thus, changes in the initial composition of PAH NER led to higher differences in the final PAH mineralization for the GWS. This result underlined the assumption about the significant role of the compost quality in the dissipation of PAH in the amended soil. The reliability of our assumption about the non-extractable residue distribution has not yet been fully assessed, and further validation is still needed in the future.

Fig. 7. Mineralized fraction of PAH_{CO2} as simulated at the end of the soil incubation period (blue line) as a function of the initial percentage of biogenic non-extractable residues. The (●) represents the mean value of the measured mineralized fraction of PAH_{CO2} with its error bars ($\pm$ standard deviation) versus the default biogenic residue percentage value simulated from the compost incubation and reported in Table A5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

The PAH-OC model was appropriate for describing the interactions between the primary physical, biological and biochemical processes that influenced the dissipation of PAHs included in the compost and after the compost application to soil under laboratory conditions. The most significant features of this model were to account for the organic matter characteristics of the applied compost, the production of non-extractable residues and the biodegradation pathway. A single parameter set for all the compost types was found to simulate the dynamics of PHE and BAP in the amended and non-amended soils to an adequate extent. For the FLT, this unique set of parameters could not be established, and a specific biomass biodegradation pathway had to be considered for mature composts. The modelling study confirmed that the processes occurring during composting, such as the non-extractable residue formation or the growth of a specific microbial biomass, had a strong impact on the fate of PAHs entering the soils through composts. During the compost incubations, the PAH dissipation was higher with mature composts because of the higher specific microbial activity, while in the incubations of soil amended with composts, the PAH dissipation was higher with the non-mature compost, partly because of the higher amount of available PAHs and the higher co-metabolic microbial activity. An experimental investigation to quantify the biogenic and physical proportion of the total non-extractable residues using recent methods reported in the literature is one of perspectives of this work. Further work should also be devoted to the application of the model in fields under long-term studies.

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Appendix. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2017.10.269>.

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