Using a Bayesian approach to improve and calibrate a dynamic model of polycyclic aromatic hydrocarbons degradation in an industrial contaminated soil[☆]

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ABSTRACT

A novel kinetics model that describes the dynamics of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils is presented. The model includes two typical biodegradation pathways: the co-metabolic pathway using pseudo first order kinetics and the specific biodegradation pathway modeled using Monod kinetics. The sorption of PAHs to the solid soil occurs through bi-phasic first order kinetics, and two types of non-extractible bounded residues are considered: the biogenic and the physically sequestered into soil matrix. The PAH model was developed in Matlab, parameterized and tested successfully on batch experimental data using a Bayesian approach (DREAM). Preliminary results led to significant model simplifications. They also highlighted that the specific biodegradation pathway was the most efficient at explaining experimental data, as would be expected for an old industrial contaminated soil. Global analysis of sensitivity showed that the amount of PAHs ultimately degraded was mostly governed by physicochemical interactions rather than by biological activity.

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1. Introduction

The wide exploitation and use of fossil energy and its by-products have caused the dispersion of original and transformed fossil organic compounds in the environment. These pollutants accumulate in soils causing acute or more diffuse contamination. Among them, polycyclic aromatic hydrocarbons (PAHs) pose a serious threat to the human health and the environment owing to their carcinogenicity, bioaccumulation and persistence (Iarc, 2010). Their general behavior and impact on all environmental

compartments, e.g. transfer from soil to water resources or into the food chain, need to be addressed in the general context of contaminated soil risk assessment and safe land-reuse. Thus, models predicting the dissipation rate of PAHs over a wide range of environmental conditions with sufficient accuracy are necessary for environmental risk assessment and decision support.

Models dedicated to the description and prediction of organic pollutants behavior in soils remain scarce. Most existing tools have been developed and applied for pesticides in the context of cultivated lands (Beulke et al., 2000; Köhne et al., 2009). Only very few models deal with other organic pollutants such as PAHs (Geng et al., 2015) or pharmaceutical products (Moenickes et al., 2011; Zarfl et al., 2009). These models display a great variety of assumptions and mathematical formalisms and for most of them they have not been validated or tested in the field (except those developed for

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pesticides).

We develop a new modeling tool to predict the general behavior of PAHs in soil that might be applicable in a wide range of situations from agricultural land, with low concentration values, to highly contaminated soils from industrial sites. To achieve this goal, a specific module describing PAHs reactivity in soil systems including physical and biological processes has been developed and calibrated with laboratory data corresponding to extreme situations of contamination.

First, we propose a new dynamic model accounting for the different biological and chemical processes governing general PAHs behavior in contaminated soils. The model is then calibrated using previously published data from a laboratory incubation experiment, with a global optimization algorithm called DREAM based on the Bayesian approach. This method helps identifying the controlling processes governing PAHs behavior under several hypotheses of degradation pathways of PAHs. Finally we present a sensitivity analysis of model parameters that strengthen the ranking of controlling processes.

2. Modeling

2.1. Model description and assumptions

2.1.1. PAHs reactivity in soils

PAHs dissipation in soil is mostly driven by two processes: adsorption and biodegradation (White et al., 1999; Wilcke, 2000). When PAHs enter the soil, they rapidly sorb on minerals and organic matters in soil aggregates. Due to their hydrophobicity and strong interaction with soil organic matters, only a minor part moves into soil solution where PAHs can associate to colloids or remain. The fixed fraction can diffuse into small pores where it remains being scarcely accessible for microorganisms, forming what is called physical non-extractible residues (NER). Kinetics of adsorption and desorption of pollutant depends on different many factors such as soil properties (e.g. texture, structure, organic matter content) (Chung and Alexander, 2002; Nam et al., 2003), pollutant hydrophobicity, initial loading level (Johnson et al., 2001; Pignatello, 1990), climate (Dagois et al., 2015) and the biological activity (Gevao et al., 2005). Moreover, results from both lab-scale and field experiments show that the potential rate of desorption decreases with increasing contact time. This phenomenon also referred to “aging” actually encompasses multiple processes including the diffusion and sorption of PAHs into the soil organic and inorganic fractions. It highlights the fact that (bio)availability decreases with increasing contact time (Hatzinger and Alexander, 1995; White et al., 1999).

The biodegradation of PAHs occurs through two main pathways corresponding to two different biological strategies for microorganisms. The adapted microorganisms use the target compound as the sole carbon and energy sources; they are referred as specific biomass (B_{SPE}). The non-growing microorganisms rely on another substrate for their growth and maintenance; they are referred to as co-metabolic biomass (Janke and Fritsche, 1985; Pomiès et al., 2013). Recent works have highlighted the importance of microbial activity in increasing the amount of NER of PAHs in soil, suggesting the need of distinguishing between NER by physical processes (aging), and the biogenic NER resulting from microorganisms transformation of pollutants and further incorporation in soil organic matters (SOM) (Barriuso et al., 2008; Kästner et al., 2013; Richnow et al., 2000).

In such a soil ecosystem, plants only represent a minor sink term but their indirect effect may however have a significant impact through water uptake, microbial activity enhancement and fresh carbon input.

2.1.2. Model modules

The different processes described in the previous section were modeled using 2 submodules: the sorption module and the biodegradation module (Fig. 1). The model equations including kinetics and stoichiometry for PAHs transformations are presented in the form of a Petersen matrix in Table 1, whereby the rate equations are read both down and across (Russell, 2006). The model includes 7 compartments and 12 parameters. For all compartments the concentration unit is $\text{mg } ^{13}\text{C}/\text{kg}_{\text{ds}}$, where the subscript “ds” refers to dry soil.

The PAHs adsorption mechanism is described by a bi-phasic first order kinetics module, which was commonly used in the literature (Johnson et al., 2001). We thus assume that the adsorption occurs in two compartments with two adsorption rates: the first one is characterized by a fast rate and weak stability (PAH_{WS} , where “ws” stands for weak sorption) (Processes I and II) followed by a second one characterized by a slower reactivity exchange but strong stability (PAH_{SS} , where “ss” stands for strong sorption) (Processes III and IV). Based on these assumptions, the formation of PAH_{SS} directly via the aqueous fraction is neglected.

The biodegradation module is built on the basis of four assumptions. Compounds in the aqueous phase (PAH_{AV} , where “av” stands for available) are the only substrates available for microbial biomass (Ogram et al., 1985; Thomas et al., 1986; Wodzinski and Coyle, 1974). The available fraction may contain both free dissolved PAHs and those complexed with colloids. Having no information about different compound speciation in solution we decided to merge two forms in a common compartment assuming that microorganisms use them at the same rate (Delgadillo-Mirquez et al., 2011; Laor et al., 1996).

Biodegradation occurs according to two pathways. The first one is driven by the specific biomass (B_{SPE}) whose growth and maintenance is described by the Monod equation (Monod, 1949; Wick et al., 2001) (Process VI, plotted in pointed line Fig. 1). The second pathway is the biodegradation by the co-metabolic microorganisms (plotted in dashed line Fig. 1). We chose herein to exclude modeling the growth of co-metabolic microorganisms because they have different and more complex growth and maintenance rates than B_{SPE} . Instead, the biodegradation rate is calculated using the pseudo first order kinetic formalism whereby the available substrate (PAH_{AV}) is the only rate limiting factor for PAHs biodegradation in soil (Govind et al., 1991) (Process V) i.e. the amount of co-metabolic microorganisms is not a limiting factor.

The metabolism of substrate by microorganisms by the two aforementioned pathways leads to mixed products of metabolites and biological wastes, in addition to CO_2 production (PAH_{CO_2}). For simplifications, all biological products are later described by one model compartment and referred to as “metabolites” (PAH_{MET}).

According to Kästner et al. (2013), biogenic NER are obtained by incorporating dead microbial cells in SOM, whereas the metabolites resulting from co-metabolic degradation lead to the formation of physical NER. To avoid confusion, we defined PAH_{BS} (where “Bs” stands for biogenics) corresponding to biogenic NER that include both dead specific biomass (Process VIII) and irreversible PAH_{MET} in soil (Process VII).

Soil biodegradation rates are related to temperature and water content using the correction factors f_T , f_W following equations proposed by Recous (1995) and Andréon et al. (1992) respectively:

$$f_T = e^{0.085(T - T_{\text{ref}})} \quad (1)$$

where T is the actual soil temperature in $^{\circ}\text{C}$ and T_{ref} is the reference temperature (15°C).

Fig. 1. Structure of the PAHs model. Cometabolism pathway is plotted by dashed lines whereas the pathway driven by specific biomass is marked by points, with k_{ij} : first order kinetic constant with the first subscript denoting the source and the second the sink of the corresponding process (A: PAH_{AV} ; B: PAH_{BS} ; M: PAH_{MET} ; S: PAH_{SS} and W: PAH_{WS}) (d^{-1}); $\mu_{S_{max}}$: maximum specific growth rate (d^{-1}); $k_{S_{spe}}$: half saturation of growth substrate for the specific biomass ($mg^{13}C/kg_{ds}$); Y_{spe} : yield of specific biomass (–); k_M : mortality rate constant (d^{-1}); α : magnitude of metabolites production by biodegradation for specific biomass (between 0 and 1); k_{deg} : pseudo first order kinetic constant of biodegradation for co-metabolism (d^{-1}); β : magnitude of metabolites production by biodegradation for co-metabolism (between 0 and 1).

Table 1
PAHs model equations described by Petersen matrix (Russell, 2006).^a

Process	Variable							
	PAH_{AV}	PAH_{CO2}	PAH_{MET}	PAH_{WS}	PAH_{SS}	PAH_{BS}	B_{SPE}	Rate ($mg^{13}C/kg_{ds}/d$)
I Weak sorption	–1			1				$k_{AW} \cdot PAH_{AV}$
II sorption desorption	1			–1				$k_{WA} \cdot PAH_{AV}$
III Strong sorption				–1	1			$k_{WS} \cdot PAH_{SS}$
IV sorption desorption				1	–1			$k_{SW} \cdot PAH_{SS}$
V Substrate uptake by co-metabolism	–1	$(1-\beta)$	β					$k_{deg} \cdot PAH_{AV} \cdot f_T \cdot f_W$
VI Growth of specific biomass	$-1/Y_{spe}$	$(1-\alpha) \cdot \frac{(1-Y_{spe})}{Y_{spe}}$	$\alpha \cdot \frac{(1-Y_{spe})}{Y_{spe}}$				1	$\frac{\mu_{S_{max}} \cdot PAH_{AV}}{k_{S_{spe}} + PAH_{AV}} \cdot B_{SPE} \cdot f_T \cdot f_W$
VII Biogenic Metabolites production transformation			–1			1		$k_{MB} \cdot PAH_{MET}$
VIII Specific biomass mortality						1	–1	$k_M \cdot B_{SPE}$
	PAHs available $mg^{13}C/kg_{ds}$	PAHs mineralized into CO_2 $mg^{13}C/kg_{ds}$	Metabolites $mg^{13}C/kg_{ds}$	Weakly sorbed $mg^{13}C/kg_{ds}$	Strongly sorbed $mg^{13}C/kg_{ds}$	Biogenic residues $mg^{13}C/kg_{ds}$	Specific biomass $mg^{13}C/kg_{ds}$	

^a f_T : Temperature dependence factor (–); f_W : water content dependence factor (–); additional notations are defined in Fig. 1.

$$f_W = \frac{\log(-\Phi) - \log(-\Phi_{min})}{\log(-\Phi_{opt}) - \log(-\Phi_{min})} \quad (2)$$

where Φ is the water potential in cm H_2O , Φ_{min} is the minimum water potential (–75800 cm H_2O) at which the microbial activity ceases and Φ_{opt} is the optimum water potential (100 cm H_2O).

2.2. Experimental data

Data used for model calibration were taken from the experimental study of Cébron et al. (2011). It was an incubation experiment of freshly added fully ^{13}C labelled phenanthrene (PHE) in an aged PAH contaminated soil from a former coking plant site.

All incubation experiments were performed in triplicates at a controlled temperature of 24 °C. The moisture level of homogenized soil samples was adjusted to 80% of the soil water holding capacity. The concentration of ^{13}C -PHE spiked in soil was

250 $mg^{13}C/kg_{ds}$. The distribution of ^{13}C -PHE among the extractable, non-extractable and the mineralized fractions was assessed on days 0, 4, 8 and 12. Mass balances of the total ^{13}C recovery were within 80–106% of the initial ^{13}C -PHE added to the soil. We therefore applied a weight on the three aforementioned fractions at each time step to reach 100% recovery.

The amount of ^{13}C recovered by dichloromethane (DCM) using accelerated solvent extraction was considered as the extractable fraction, including the labelled phenanthrene present in soil/solution interface as well as its metabolites. No significant ^{13}C -labelled intermediate compounds were found in this DCM extract, we therefore considered the metabolites concentration (PAH_{MET}) to be zero. The amount of soluble ^{13}C -PHE (PAH_{AV} in the model) was calculated from the total ^{13}C -PHE in DCM extracts considering that the total ^{13}C -PHE recovered by DCM was sorbed on soil (*i.e.* neglecting contribution of soluble PHE, being 1/1000 to 1/960 of the total) using the sorption distribution coefficient K_d (L/kg_{ds}) as following:

$$K_d = \frac{\text{Sorbed labelled phenanthrene recovered by DCM (mg}^{13}\text{C/kg}_{\text{ds}})}{\text{PAH}_{\text{AV}}} \quad (3)$$

The K_d value was obtained using:

$$K_d = K_{\text{OC}} \cdot f_{\text{oc}} \quad (4)$$

where f_{oc} is the organic carbon content in soil (here 63 g C/kg_{ds}) and K_{OC} is the sorption distribution coefficient normalized to f_{oc} , which can be calculated using the correlation taken from [Nguyen et al. \(2005\)](#):

$$\log K_{\text{OC}} = 1.14 \log K_{\text{OW}} - 1.02 \quad (5)$$

where K_{OW} is the octanol-water partition coefficient equal to 4.57 for phenanthrene ([Mackay et al., 2006](#)).

The amount of ^{13}C remaining in the soil after DCM extraction was considered as the NER, from both physical and biogenic origins. This fraction, PAH_{NER} , corresponded to the three model compartments pooled together: PAH_{SS} , PAH_{BS} and B_{SPE} . Indeed, due to its polarity the specific microbial biomass B_{SPE} was supposed to remain in the soil after DCM extraction and to contribute to the NER. The concentrations of B_{SPE} on days 4, 8 and 12 were estimated from the measured bacterial population densities assimilating carbon derived from ^{13}C labelled phenanthrene using the hypothesis that a microbial cell is equivalent to 10^{10} carbon atoms ([Troussellier et al., 1997](#)).

Finally, the mineralized fraction was estimated from the difference between CO_2 released in incubations with and without labelled phenanthrene addition, and was considered corresponding to PAH_{CO_2} values.

2.3. Procedure for parameters estimation

2.3.1. Numerical solution and optimization method

The model differential equations were solved numerically within a MATLAB code using Crank Nicolson finite different scheme with a varying time step to assure the computational stability ([Crank and Nicolson, 1996](#)).

The DREAM (DiffeRential Evolution Adaptive Metropolis) algorithm ([Vrugt et al., 2008; Vrugt, 2016](#)) based on the Markov Chain Monte Carlo method applied within Bayesian framework was used for estimating model parameters thanks to the dual advantage: (1) ensuring global optimum in the given searching range, instead of local optimum by a numerical nonlinear regression algorithms ([Aster et al., 2013](#)), and (2) determining uncertainty in parameters in the posterior probability density functions (pdfs) shown in Eq. (6) ([Sun and Bertrand-Krajewski, 2013](#)):

$$\rho(\theta/y, x) = \frac{\rho(y/\theta, x) \cdot \rho(\theta)}{\rho(y/x)} \quad (6)$$

where x and y are the observed values of model inputs and outputs, $\rho(\theta)$ is the probability density of prior distribution of parameters, $\rho(y/\theta, x)$ is the likelihood function returning the probability density for model results for given values of parameters and inputs, and $\rho(y/x)$ is the marginal likelihood.

For this work, the matrix of input variables (x) was composed of the 4 compartments: PAH_{WS} , B_{SPE} , PAH_{NER} and PAH_{CO_2} measured on

days 0, 4, 8 and 12. The model outputs matrix (y) was the corresponding values computed numerically by daily time step. Hence, the DREAM software written in MATLAB ([Vrugt et al., 2008](#)) was used to fit our model. The prior distribution of each parameter was assigned to follow a uniform distribution reflecting the limited prior information about parameters values. A maximum number of 200,000 model evolutions (based on an error-and-trial approach) was set. The likelihood function was chosen to have the form an exponential power density function as described by [Box and Tiao \(1992\)](#). After DREAM terminated, the last 50% of the evaluated parameter samples from all the chains were selected to generate histograms of probability density functions of the evaluated model parameters.

2.3.2. Setting up

The searching ranges of model parameters are listed in [Table 2](#). They were chosen based on available literature studies ([Delgadillo-Mirquez et al., 2011; Fragoulis et al., 2005; Geng et al., 2015; Johnson et al., 2001; Köhler et al., 1994; Tao et al., 2007; Weissenfels et al., 1990; Wick et al., 2001](#)) and further adjusted using a stepwise trial and error strategy. The model was run with the initial conditions observed a few minutes after the beginning of the experiment: PAH_{CO_2} , PAH_{BS} , PAH_{SS} and PAH_{MET} were null; all ^{13}C -PHE in soil was PAH_{WS} and PAH_{AV} as described in [section 2.2](#). The initial specific biomass concentration was 0.575 mg ^{13}C /kg_{ds} calculated from data reported by [Cebon et al. \(2009\)](#).

2.3.3. Goodness of fit criteria

Both the Nash Sutcliffe index (NS) ([Nash and Sutcliffe, 1970](#)) and the Akaike information criterion (AIC) ([Burnham and Anderson, 2004](#)) are used to quantitatively evaluate the model performance in reproducing the observations:

$$\text{NS}_{i \rightarrow m} = 1 - \frac{\sum_{t=1}^n (y_{\text{obs},t,i} - y_{\text{calc},t,i})^2}{\sum_{t=1}^n (\bar{y}_{\text{obs},i} - y_{\text{obs},t,i})^2} \quad (7)$$

$$\text{AIC} = n \cdot m \cdot \ln \left(\frac{\sum_{i=1}^m \sum_{t=1}^n (y_{\text{obs},t,i} - y_{\text{calc},t,i})^2}{n \cdot m} \right) + 2 \cdot p \quad (8)$$

where $y_{\text{obs}, t, i}$ and $y_{\text{calc}, t, i}$ are respectively the observed and predicted values at the t th observed time step for the i th model output, $\bar{y}_{\text{obs}, i}$ represents the mean observed value of the i th model output, p is the number of estimated parameters excluding constant parameters, n is the number of measured points, and m is the number of model outputs, as defined in paragraph 2.3.1. The effect of the model outputs PAH_{MET} and PAH_{AV} on the goodness of fit is neglected due to lack of observed data. The best fit is assessed by the closest to one NS value. AIC is used to compare models with different levels of complexity as it includes the number of parameters in addition to the information about the accuracy of the model outputs compared to experimental data. The smallest AIC value indicates the best compromise between model complexity and model accuracy.

Table 2

Prior ranges, optimal values and confidence intervals (CI) for PAHs model parameters as obtained with DREAM by running the model with the two different biodegradation pathways independently.

Parameter	Unit	Range	Calibrated parameters			
			Biodegradation via specific biomass		Biodegradation via co-metabolism	
			Optimum	95% CI	Optimum	95% CI
k_{AW}^a	d^{-1}	NA	55.725	[55.39, 56.70]	44.534	[44.18, 44.91]
k_{WA}	d^{-1}	[0, 0.2]	0.0567	[0.058, 0.059]	0.0453	[0.0449, 0.0456]
k_{WS}	d^{-1}	[0, 0.2]	0.0582	[0.058, 0.059]	0.0584	[0.0582, 0.0585]
k_{MB}	d^{-1}	[0, 0.5]	$60 \cdot 10^{-5}$	$[10 \cdot 10^{-5}, 440 \cdot 10^{-5}]$	$20 \cdot 10^{-5}$	$[3 \cdot 10^{-5}, 126 \cdot 10^{-5}]$
μS_{max}	d^{-1}	[0, 12]	4.89	[2.99, 9.50]	—	—
k_{spe}	$mg^{13}C/kg_{ds}$	[0.01, 0.15]	0.0024	[0.0012, 0.0384]	—	—
Y_{spe}	—	[0.05, 0.3]	0.127	[0.122, 0.131]	—	—
k_M	d^{-1}	NA	NA	NA	—	—
α	—	[0, 1]	0.0121	[0.0015, 0.150]	—	—
k_{deg}	d^{-1}	[0, 200]	—	—	133.05	[128.24, 137.83]
β	—	[0, 1]	—	—	0.016	[0.015, 0.018]

^a The parameter k_{AW} was calculated by k_{WA} using Eq. (9).

3. Model simplifications

Some simplifications were performed on the model structure by eliminating the appearing non-significant processes for our case study. The slow desorption of the phenanthrene from the strongly sorbed compartment (PAH_{SS}) to the weakly one (PAH_{WS}) was considered negligible (*i.e.* $k_{SW} = 0$), meaning that PAH_{SS} corresponded effectively to an irreversibly bound (*i.e.* NER) compartment of phenanthrene. This simplification was consistent with previous studies reporting that the effective time scale required for slow desorption process is in the order of magnitude of months or years (Johnson et al., 2001) instead of a few days as in our case study.

The first model runs using DREAM and all the parameters initially defined but with k_{SW} set to 0 showed that the histogram of the pdfs for the mortality rate constant (k_M) was concentrated to the lower bound around $10^{-5} d^{-1}$ (results not shown). When this lower bound was relaxed, the distribution was uniform meaning that this parameter was not sensitive to explain our experimental data. Thus the mortality phase for the specific biomass turnover was negligible during the few days experiment and the k_M value was set to 0. This simplification seems biologically realistic since a 12 days monitoring period might be insufficient for the microbial biomasses to reach their maximum growth, starving and then cellular death.

Independent optimization of k_{WA} and k_{AW} also led to inconsistent results. Correlation matrix between the two parameters showed that they were not linearly linked (linear correlation coefficient, $r = 0.04$) and that the most likely values for k_{WA} were generally much higher than those of k_{AW} , which is physically unrealistic. Such modeling discrepancies could be attributed to the lack of data on the compound fraction in solution. Thus, we decided to keep k_{AW} as a calibration parameter and to calculate k_{WA} using the K_d value and the dynamic definition of adsorption (Pomiès et al., 2013) giving:

$$K_d = \frac{k_{AW}}{k_{WA}} \quad (9)$$

4. Biodegradation pathways discrimination

The model based on the simplifications described in the previous section was then run using DREAM. However, the model including both pathways of biodegradation at the same time led to

ambiguous fits pertaining to the microbial rates. Indeed, experimental data did not give any indication on relative implications of both pathways and it was not possible to define constant or even narrow ranges for most of biodegradation kinetic values, such as μS_{max} and k_{deg} (see Supplementary Information (SI), Fig. S1). We thus chose to run the model alternatively with the separate pathways alone (2 scenarios) and to use the results to discriminate between both pathways to identify the most probable or most effective one. From a mathematical point of view, this approach also resulted in a model with less parameters to be calibrated. The scenario 1 driven by co-metabolic biomass led to a model with 5 parameters and the scenario 2 driven by specific biomass led to a model with 7 parameters. Three parameters are used in both scenarios k_{WA} , k_{WS} and k_{MB} .

4.1. Scenario 1: co-metabolic biodegradation pathway

The histograms representing the posterior probability density functions (pdfs) of model parameters against the parameters searching ranges, as well as the correlations among the parameters are presented in Fig. 2a. The parameter searching range and the most likely parameter estimated value together with the 95% confidence interval for each parameter are all summarized in Table 2. Results showed that most of the model parameters tended to display a Gaussian distribution with 95% confidence intervals covering only relatively small ranges within the uniform prior distributions. Only k_{MB} seems to be log-normally distributed. Thus experimental data contain sufficient information for model parameter estimation. The relatively small linear correlations between most of the parameters indicate that model parameters are rather independent each other, with the unique exception of the negative correlation between the parameters k_{deg} and k_{WA} ($r = -0.775$), which could be described by the following empirical formula:

$$k_{deg} = 587.18 - 10024 k_{WA} \quad (\text{with } R^2 = 0.78) \quad (10)$$

This correlation illustrates the close link interconnection between adsorption and biodegradation processes on the fate of the target compound. It also shows that k_{WA} with tolerance error might be used to calculate k_{deg} and thus Eq. (10) can be used to further reduce the number of model parameters necessary to describe the observations. Moreover, this result reveals that k_{WA} is a key parameter within scenario 1 being correlated to both k_{deg} (Eq. (10)) and k_{AW} (Eq. (9)). This raises the question of whether these three parameters actually represent an invariant mechanism of the

Fig. 2. Histograms of the evaluated model parameters (diagonal panels) and correlations between parameters (off-diagonal panels) for the PAH model, supposing biodegradation by (a) co-metabolism biomass and (b) specific biomass. The y-axis refers to the probability distribution value in diagonal panels and to the parameter searching range in off-diagonal panels while x-axis indicates the parameter searching range. The panels plotted with a solid line denote a high linear correlation between the parameters. Dashed lines indicate the most likely parameter values.

underlying physiochemical and biological processes, or whether they correlate due to structural defaults in the model proposed within this scenario.

Using calibration results in Table 2, predicted model outputs along with their 95% confidence intervals were calculated and are presented in Fig. 3. These curves were obtained by stochastic simulation through running the model in the direct way using the 95% confidence intervals previously estimated for the five calibrated parameters. At the simulation starting time, the uncertainty in the measured PAH_{WS} was assumed to apply to a uniform distribution and the no uncertainty was considered for other model compartments with the values given in section 2.3.2.

For the mineralized fraction of labelled phenanthrene in soil, the model underestimates the observations as confirmed by a low value of the Nash Sutcliff index ($\text{NS} = 0.56$) (Fig. 3b). The weakly sorbed fraction matches well the observed values with NS values close to 0.85 (Fig. 3c). For the total non-extractable fraction (PAH_{NER}) in soil simulation is also satisfactory with NS equal to 0.69 (Fig. 3e). However, at the end of incubation time, the model tends to over estimate the NER value, predicting a still increasing amount with time whereas experimental data displayed a plateau. The model prediction for solution concentrations (Fig. 3a) and metabolites (Fig. 3d) are both within the range of experimental error tolerance.

The recorded Akaike information criterion value for this scenario is 79.84.

4.2. Scenario 2: specific biodegradation pathway

Following the same approach as used for the previous scenario, the model was run using the specific biodegradation pathway alone (i.e. 7 fitting parameters, see Table 2). For most parameters, 95% confidence intervals cover narrow ranges of their prior distributions with the exception of μ_{max} (Table 2), moreover most histograms appeared approximately Gaussian with the exception of k_{spe} which tends to concentrate near its lower bound (Fig. 2b). Such a behavior can be at least partially ascribed to the positive correlation between μ_{max} and k_{spe} ($r = 0.84$). No significant correlations among parameters are otherwise detected. We thus propose an empirical relationship between μ_{max} and k_{spe} that can be used to further simplify the model:

$$k_{\text{spe}} = 0.0099 - 0.0048 \cdot \mu_{\text{max}} + 0.0007 \mu_{\text{max}}^2 \quad \left(\text{with } R^2 = 0.91 \right) \quad (11)$$

It indicates that the half saturation substrate concentration in

Fig. 3. Comparison between simulated (—) and observed δ phenanthrene concentration over time using the first scenario with co-metabolism biomass. From top left: a) available PAH in solution, b) mineralized PAH into CO_2 , c) weakly sorbed on soil, d) metabolites, e) non-extractable residues as the sum of two fractions: strongly sorbed (— $\times$ —), biogenic (—■—). 95% confidence intervals for simulated concentrations are plotted with broken lines. Error bars indicate minimum and maximum values ($n = 3$).

solution (k_{spe}) could be a suitable monitoring parameter for deriving the growth rate (μ_{smax}).

The 95% confidence intervals of simulation evolutions of the labelled phenanthrene compartments together with the measured ones are shown in Fig. 4. With this scenario, the simulation of the mineralized fraction (Fig. 4b) is improved compared to scenario 1 and an almost perfect fit is obtained, with a high Nash Sutcliffe of 0.92. Minor improvements are obtained for other model compartments with NS values equal to 0.86, 0.70, and 0.72 for PAH_{WS} , PAH_{NER} and PAH_{BS} respectively. A sharp decrease of the initial concentration of labelled phenanthrene in solution is predicted (Fig. 4a), illustrating that a fast sorption equilibrium state for phenanthrene in solution is achieved at the end of the first incubation day. The model also predicts that less than $0.6 \text{ mg } ^{13}\text{C/kg}_{ds}$ metabolites production is obtained at the end of incubation. For this scenario, the Akaike information criterion value is 82.61. This is a little bit higher than for scenario 1, which means that the increase in accuracy (higher NS values) is partly obtained thanks to a higher level of model complexity with seven parameters instead of five in the previous scenario. In addition, Fig. 4f shows that B_{SPE} is not very well simulated (NS = 0.72).

4.3. Final choice for model and behavior analysis

Results obtained for both scenarios show that the model using the specific biomass degradation pathway (scenario 2) gives the best fit according to the NS values, with a small increase of the AIC

criterion. Our selection of the specific biodegradation pathway is corroborated by the values of the calibrated microbial rates. The obtained value of 133 d^{-1} for k_{deg} in scenario 1, corresponding to a half degradation time of 1 h, is not biologically realistic. In contrast, kinetic values obtained with scenario 2 approach those found in the literature and increase thereby the confidence in the model predictions. Indeed, the model predicts that the specific biomass doubles within 5 h, which is in accordance with the values published by Tao et al. (2007) for a microbial biomass using the phenanthrene as the sole source of carbon and energy in PAHs contaminated soil. The most likely biomass yield, Y_{spe} , is equal to 0.127, which is about half of the value found by Weissenfels et al. (1990) for phenanthrene within a pure bacterial culture, but was close to the value of 0.158 proposed by Kästner et al. (2013) for the anthracene (knowing that anthracene is 3-cycles PAHs close to phenanthrene). Similarly, the value of K_{spe} measured for anthracene by Wick et al. (2001) lies within the 95% confidence interval obtained for phenanthrene in this study.

Furthermore, simulation results showed that the fitting of empirical values of PAH_{CO_2} is not improved when both biodegradation pathways are run simultaneously, meaning that the specific biodegradation pathway is most likely the main biodegradation mechanism for the labelled phenanthrene in our case study (see SI, Fig. S2 and Table S1). This result is further supported by the fact that a modification of the diversity of phenanthrene degrading bacterial population does not increase phenanthrene mineralization rate in this same contaminated soil (Cébron et al., 2011).

Fig. 4. Comparison between simulated (—) and observed $\diamond$ phenanthrene concentration evolutions over time using the second scenario with specific biomass. From top left: a) available PAH in solution, b) mineralized PAH into CO_2 , c) weakly sorbed on soil, d) metabolites, e) non-extractable residues as the sum of 3 fractions: strongly sorbed (— $\times$ —), biogenic (— $\blacksquare$ —) and specific biomass, f) phenanthrene assimilated by specific biomass. 95% confidence intervals for simulated concentrations are plotted with broken lines. Error bars indicate minimum and maximum values ($n = 3$).

Consequently, based on above discussion and for further *in situ* experiments, we suggest to use the model only with the biodegradation pathway driven by specific biomass (i.e. scenario 2 with 7 parameters). The specific pathway might, with a reasonable compromise between model complexity and model accuracy to represent processes in the soil, be used alone for further simulations at different time scales, especially with lack of information about the microbial biomass uptake rates which might never be measured in reality. It is important to underline that our findings do not mean by itself that the co-metabolic biomass is a negligible contribution to the overall labelled phenanthrene mineralization: it only indicates that the pathway driven by the specific biomass and modeled within the Monod kinetic is the best way to predict the degradation of PAHs in the studied soil.

For scenario 2, the highest efficiency of biodegradation is associated with the prediction of an exponential growth for the specific biomass (Fig. 4f). Such a prediction might appear in contradiction to the typical observations made for the growth of specific biomass, usually preceded by an initial lag period. A biological explanation of this finding could be related to the preliminary presence of phenanthrene degrading microbial biomasses in the aged contaminated soil but with limited accessibility for the PAHs due to the aging process. Once the labelled phenanthrene was added to the soil, an immediate use of the added compound by the specific biomass occurred, which was reflected by intense release of CO_2 with simultaneous sharp decrease of the concentration of labelled

phenanthrene during the first two days of incubation.

Another important result is that the calibrated parameters for the adsorption module are all within the ranges reported by Johnson et al. (2001) with only slight differences for both scenarios (Table 1). Finally, the model predicts that the metabolites production would be less than 1%, and that the contribution of the biogenic non-extractable residues to the total extractable residues could be neglected at such short time scale. This finding would be in agreement with results indicating that sorption occurs more rapidly than the biodegradation in the soil (Adam et al., 2014).

5. Sensitivity analysis

One objective of this work was to identify the main factors controlling the biodegradation of PAHs in the studied soil. A global sensitivity analysis was therefore carried out to identify the sensitivity of three of the model outputs to the model parameters for the selected model (scenario 2). The selected outputs were PAH_{CO_2} , PAH_{AV} and $\Gamma_{\text{PAH}_{\text{AV}}/\text{PAH}_{\text{WS}}}$, representing the kinetics of sorption and desorption of the labelled phenanthrene between the available compartment (PAH_{AV}) and the weakly sorbed one (PAH_{WS}):

$$\Gamma_{\text{PAH}_{\text{AV}}/\text{PAH}_{\text{WS}}} = k_{\text{AW}} \cdot \text{PAH}_{\text{AV}} - k_{\text{WA}} \cdot \text{PAH}_{\text{WS}} \quad (12)$$

The sensitivity analysis performed using the FAST 99 function (Saltelli et al., 1999) of the R package “sensitivity” (Pujol et al., 2015)

Fig. 5. Sensitivity indices for the parameters of the selected PAH model with respect to the variables: a) PAH_{av} , b) PAH_{CO_2} and c) $r_{\text{PAH}_{\text{av}}/\text{PAH}_{\text{ws}}}$

with 400 model runs per parameter (i.e. $400 \times 5 = 2000$ model runs in total). This method, also called the “extended-FAST” method, estimates the first order and total Sobol’ indices for all the factors. In other words, it evaluates the sensitivity to the chosen parameters when acting alone (first order) or when combined with the other parameters (total orders). We chose to keep the parameter α set to its value to avoid any compensation with the two Monod kinetic constants (i.e. μ_{Smax} , Y_{spe}). A uniform distribution was used for the tested parameters in the following ranges: $k_{\text{WA}} = k_{\text{WS}} = [0.00086, 0.086]$, $\mu_{\text{Smax}} = [0.0, 8.6]$, $Y_{\text{spe}} = [0.1, 0.3]$, $k_{\text{spe}} = [0.001, 0.1]$.

Fig. 5 shows the first orders and the total orders characterizing the relative importance of those parameters on the three outputs. The first and the total orders of ads/desorption rates k_{WA} , k_{AW} are very high for both PAH_{av} and $r_{\text{PAH}_{\text{av}}/\text{PAH}_{\text{ws}}}$, indicating that those two parameters have the major effects on the mass of hydrophobic compound in solution, while Y_{spe} , μ_{Smax} and k_{SW} are the second most important ones with interactions with other parameters. The maximum growth rate μ_{Smax} is the critical factor during mineralization, while the parameters k_{WA} and k_{AW} have the main effect with interactions with other parameters (Fig. 5b). The parameters k_{spe} and k_{MB} have negligible impacts on the three outputs and can thus be set to their calibrated values. These results illustrate that for longer time periods, the amount of ultimately degraded PAHs depends more on adsorption rates than on the Monod kinetics and that more generally in such systems physical interactions dominate the biological mechanisms in controlling the fate of PAHs.

6. Conclusion

The kinetic model proposed for simulating the dynamics of PAHs in soil is appropriate for describing the underlying biological and physical transformation of PAHs in soil for a few days laboratory incubation experiment. Model calibration was achieved by coupling the model to the Bayesian method (DREAM) that allowed us to estimate the probability density functions for all the model kinetic values. Results appear in good agreement with literature studies. The calibration procedure led to model simplifications retaining the specific biodegradation pathway as the predominant

biological process. A global sensitivity analysis of the model parameters shows that the amount of PAHs ultimately degraded is mostly governed by the adsorption/desorption kinetics rather than biological kinetics. In future work, this module will be included in a global modeling framework including dynamic water transfer, heat transfer and solute transport under climatic conditions in the Vsoil modeling platform to be applied on long term *in situ* experimental plots of agricultural soils or industrial soils.

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Nomenclature

AIC	Akaike information criterion
B_{SPE}	specific microbial biomass
DCM	dichloromethane
DREAM	differential evolution adaptive metropolis
ds	dry soil
f_{oc}	organic carbon content
f_{T}	temperature dependence factor
f_{W}	water content dependence factor
K_{d}	sorption distribution coefficient
k_{deg}	pseudo first order kinetic constant of biodegradation for co-metabolism
k_{AW}	first order kinetic constant that goes from PAH_{av} into PAH_{ws} compartment
k_{MB}	first order kinetic constant that goes from PAH_{MET} into PAH_{BS} compartment
k_{SW}	first order kinetic constant that goes from PAH_{SS} into PAH_{ws} compartment
k_{WA}	first order kinetic constant that goes from PAH_{ws} into PAH_{av} compartment

k_{WS}	first order kinetic constant that goes from PAH _{WS} into PAH _{SS} compartment
k_M	mortality rate constant
K_{oc}	sorption distribution coefficient normalized to organic carbon content
K_{ow}	octanol-water partition coefficient
$k_{S_{spe}}$	half saturation of growth substrate for the specific biomass
m	number of model outputs
n	number of measured points
NER	non-extractible residues
NS	Nash Sutcliffe index
p	number of estimated parameters excluding fixed parameters
PAH	polycyclic aromatic hydrocarbons
PAH _{AV}	available PAH in soil solution
PAH _{BS}	biogenic non-extractible residues fraction of PAH
PAH _{CO2}	carbon dioxide gas produced from the mineralization of PAH
PAH _{MET}	metabolites PAH fraction
PAH _{SS}	strongly sorbed PAH fraction
PAH _{WS}	weakly sorbed PAH fraction
pdfs	probability density functions
r	linear correlation coefficient
SOM	soil organic matter
x	model inputs
y	model outputs
$y_{calc,t,i}$	predicted values at the t th observed time for the i th model output
$y_{obs,t,i}$	observed values at the t th observed time for the i th model output
$\bar{y}_{obs,i}$	mean observed values for the i th model output
Y_{spe}	yield of specific biomass
α	magnitude of metabolites production by biodegradation for specific biodegradation
β	magnitude of metabolites production by biodegradation for co-metabolism
$\mu_{S_{max}}$	maximum specific growth rate
$\rho(y/x)$	marginal likelihood
$\rho(y/\theta, x)$	likelihood function
$\rho(\theta)$	probability density of prior distribution of parameters

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.04.094>.

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