Formation of non-extractable residues as a potentially dominant process in the fate of PAHs in soil: Insights from a combined field and modeling study on the eastern Tibetan Plateau☆

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ABSTRACT

Whereas non-extractable residue (NER) formation is recognized as an important process affecting the ecological risk of organic contaminants in soils, it is commonly neglected in regional-scale multi-media models assessing chemical environmental fate and risk. We used a combined field and modeling study to elucidate the relative importance of NER formation to the reduction in available organic contaminants compared with fate processes commonly considered in risk assessment models (volatilization, leaching, and biodegradation). Specifically, four polycyclic aromatic hydrocarbons (PAHs), i.e., phenanthrene (Phe), pyrene (Pyr), benzo[a]pyrene (BaP), and benzo[ghi]perylene (BghiP), were spiked and measured in a one-year field pot experiment at four sites with diverse environmental conditions on the eastern Tibetan Plateau. The rate of NER formation was derived as the difference between the overall rate of decline in total-extractable PAH concentrations, obtained by fitting a biphasic first-order model to the measured concentrations, and the sum of the calculated rates of volatilization, leaching, and biodegradation. Our work shows that the total-extractable PAH concentration undergoes a rapid decline and a slow decline, with shorter overall half-lives (especially for BaP and BghiP) than those observed in earlier studies. Generally, NER formation was assessed to be the dominant contributor (64 ± 33%) to the overall decline of PAHs, followed by biodegradation (35 ± 32%); volatilization and leaching were the smallest contributors. In particular, heavier PAHs (i.e. BaP and BghiP) tend to have shorter half-lives in the rapid and the overall decline phase, indicating that the erroneous estimation of environmental fate and risks might be more pronounced for organic contaminants with a large molecular size. The trend of overall decline rates of PAHs displayed a combined effect of NER formation and biodegradation. This work indicates the need to consider NER formation as a process in multi-media models of chemical fate and risk.

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1. Introduction

Soil is a major terrestrial reservoir for many organic contaminants generated by human activities, e.g., polycyclic aromatic hydrocarbons (PAHs), due to the large sorption capacity of soil constituents like minerals and organic matters (Cousins et al., 1999a). Organic contaminants can directly harm microbial communities (Sverdrup et al., 2002), plants (Sverdrup et al., 2003), and invertebrates (Van Brummelen et al., 1996) living in soil and can pose risk to higher organisms, including humans, via the food chain (Phillips, 1999). Soils can also act as a secondary source of accumulated organic contaminants to other environmental compartments (e.g. air and groundwater) through intercompartmental transport (Kobližková et al., 2009). Considering continual emissions of diverse organic contaminants and their long accumulation

history, the fate of organic contaminants in soil is of global concern (Jones and De Voogt, 1999; Ockenden et al., 2003).

Generally, after organic contaminants enter the soil, only a fraction is freely available, i.e., can undergo various transport (e.g. volatilization (Glotfelty et al., 1984) and leaching (Flury, 1996)) and/or transformation (e.g. biodegradation (Wilson and Jones, 1993)) processes. Another fraction becomes tightly bound to soil constituents, with the soil-contaminant interactions increasing with time. Even exhaustive extractions with solvents such as dichloromethane (DCM) cannot recover this fraction, which is therefore called non-extractable residue (NER) (Barriuso et al., 2008; Gevao et al., 2000; Mordaunt et al., 2005; Roberts, 1984). Steinberg et al. (1987) observed that even for organic contaminants with high volatility and short persistence (e.g. 1,2-dibromoethane, an agricultural fumigant), a "residual component" (i.e. NER) exceeding analytical detection limits can remain in the soil for a long time. This challenged the consensus of earlier studies, which had commonly presumed that the fate of organic contaminants in soil is only controlled by volatilization, leaching, and biodegradation (Beck et al., 1995). Later the application of labeled isotope technologies (Efroymson and Alexander, 1995; Goodin and Webber, 1995) confirmed NER formation as a crucial environmental fate process. For pesticides, it has been estimated that on average a third of the amount applied to agricultural soils eventually becomes NERs (Barriuso et al., 2008; Boesten, 2016; Kästner et al., 2014).

To date, Kästner et al. (2014) and the European Chemicals Agency (ECHA, 2019) proposed to categorize the NER formation of contaminants in soil into three types, depending on whether it is a result of strong sorption or physical entrapment (type I), chemical covalent bonding (type II), and biogenic transformation (type III). NER formation has long been subject to debate within the domain of risk assessment (Claßen et al., 2019). NER formation is often deemed a detoxification pathway or "degradation" process as it leads to a decline in residue availability (Bollag et al., 1992; Northcott and Jones, 2000). From a more recent regulatory viewpoint, NERs should by default be counted as undegraded parent compounds (ECHA, 2019; Kästner et al., 2018). Specifically, type I or sequestered NERs could potentially be released, posing a potentially unacceptable risk that should be considered in the risk assessment; Type II or strongly bound NERs (regarded as irreversibly bound) and type III or biogenic NERs (from the anabolic formation of biomolecules), posing less risk, could be regarded as being removed from soil for risk assessment purposes (ECHA, 2019; Kästner et al., 2018). Besides its relevance to risk assessment, the possibility of NER formation affecting other environmental processes of organic contaminants in soil also needs attention. For example, type I NER formation could be seen as being approximately equivalent to "sequestration" or "aging" (Kästner et al., 2014); this process can significantly decrease the rate of volatilization (Wong and Bidleman, 2011) and mineralization (Hatzinger and Alexander, 1995) of organic contaminants in soil, by competitively reducing the freely available fractions.

NER formation is commonly studied experimentally with isotope-labeled (e.g. ^{13}C and ^{14}C labeled) tracers (Richnow et al., 1999; Umeh et al., 2017), which can be quantified against the background of soil constituents (Schäffer et al., 2018). Other studies attempted to use modified exhaustive extractions (Umeh et al., 2019) to recover NERs. Besides such "wet lab" approaches, several computational approaches have been developed to describe NER formation in soil (Brimo et al., 2016, 2018; Matthies et al., 2008; Zarfl et al., 2009), some of which focused on the formation of a specific type of NERs (e.g. biogenic NERs) (Brock et al., 2017, 2019; Trapp et al., 2018). While NER formation has been tentatively captured in these models describing contaminant fate in soils

alone, it has yet to be applied to many multi-media models seeking to evaluate the environmental fate and risks of chemicals on a larger scale (e.g., regional or global). For example, multi-media models considering only (i) volatilization, (ii) leaching, and (iii) biodegradation as elimination processes of organic contaminants in soil, such as EUSES (Vermeire et al., 1997), CalTox (McKone, 1993), ChemCAN (Woodfine et al., 2002), and USEtox (Rosenbaum et al., 2008), are still widely used in regulatory practice. Without considering NER formation, these approaches might give inappropriate estimates for these three processes and therefore also for the environmental risk of a contaminant. The relative importance of NER formation for the fate of organic contaminants in soil has yet to be investigated within the context of a multi-media modeling approach.

This article describes a combined field and theoretical study, based on observations from a field experiment and estimations with a model algorithm that describes contaminant fate in soil and is shared by most currently-used multi-media fate models. It is aimed at elucidating the relative importance of NER formation to the fate of 4 PAHs with diverse physico-chemical properties (phenanthrene or Phe, pyrene or Pyr, benzo[a]pyrene or BaP, and benzo[g,h,i]perylene or BghiP) in soil. We conducted a year-long field pot experiment with spiked soils at different elevations on the eastern Tibetan Plateau. We investigated how natural environmental conditions (ambient temperature, precipitation, etc.) influence NER formation, by relying on a diversity of study sites located along a transect ranging from the subtropical to the alpine zone. The overall rate of decline in PAHs was derived from measurements of total extractable concentrations, whereas the relative contribution of volatilization, leaching, biodegradation, and NER formation was estimated by modeling. This research seeks to quantify the importance of NER formation relative to volatilization, leaching, and biodegradation in the fate of a wide range of PAHs under a wide variety of environmental conditions. It indicates the need to take NER formation into account when evaluating contaminant fate in soil within the context of regional-scale multi-media modeling.

2. Materials and methods

2.1. Chemicals and soils

Crystalline solids of Phe, Pyr, BaP, and BghiP were obtained from Dr. Ehrenstorfer GmbH, Germany. Recovery surrogates (2-fluorobiphenyl and *p*-terphenyl-d$_{14}$) and internal standards (phenanthrene-d$_{10}$, chrysene-d$_{12}$, and perylene-d$_{12}$) were from o2si Smart Solutions, USA. All organic solvents including DCM, *n*-hexane, acetone, and isooctane were GC grade and purchased from Thermo Fisher Scientific, USA. Alumina (Al$_2$O$_3$) and anhydrous sodium sulfate (Na$_2$SO$_4$) were from Sinopharm Chemical Reagent Co., Ltd., China. Diatomite was from Anpel Laboratory Technologies Inc., China.

Substrate soil for the field experiments was collected by a stainless-steel spade, from surface soil layers (0−20 cm) at 38 sites across the eastern Tibetan Plateau in July 2015 during earlier fieldwork (Huang et al., 2019), and stored at −20 °C until PAH spiking. The substrate soils were air-dried at room temperature and, after removal of roots and stones, were passed through a 2 mm sieve for mixing and homogenization. The substrate from all sites was combined to form a composite soil. Total organic carbon (analyzed according to Huang et al. (2019)) and pH (soaked in deionized water) of the composite soil were 3.0 ± 0.1% and 8.03 ± 0.04, respectively. The composite soil prior to spiking contained 16.8 ± 0.8 ng/g dry weight (dw) of Phe, 4.3 ± 0.3 ng/g dw of Pyr, 1.0 ± 0.4 ng/g dw of BaP, and 0.8 ± 0.3 ng/g dw of BghiP,

respectively.

2.2. Spiking and field experiment

Each 1000 g of the composite soil, placed in a solvent rinsed glass jar with a volume of 5 L, was spiked with 5 mL of a stock solution (acetone:isooctane = 1:1, v:v) containing Phe, Pyr, BaP, and BghiP (with concentrations of 100−200 mg/L for each chemical). The soil was then sealed and shaken in the jar for 30 min to blend homogeneously, and air-dried for 2 h in a fume-hood to dissipate residual solvent. A total of 9000 g soil was spiked and thoroughly mixed. Finally, 100 g of spiked soil was placed above glass-fiber filters in polypropylene pots. Since PAHs have a much higher affinity with soil organic matter than polymers, the potential sorption of PAHs to the polypropylene pots would not significantly affect our observations (Text S1).

Flatlands within sparsely populated areas at four sites on the eastern Tibetan Plateau (Fig. S1) were selected for a year-long field experiment. From Sites A to D, altitude increases, and the environment correspondingly becomes colder and drier (Table 1). In July 2017, a total of 80 pots (20 pots at each site) were placed into holes in the ground to ensure they remained upright (Fig. S2). The pots were covered with a 0.4 mm Nylon mesh to prevent bioturbation, e.g. by digging plateau pikas. Four pots were retrieved from each site after 1, 2, 4, 8, and 12 months, covered by aluminum foil, sealed in zippered polyethylene bags, transported to the laboratory, and stored at −20 °C until analysis (within five days).

2.3. PAH analysis

In this work, NER formation was derived from the rate of decline in the total-extractable fractions of PAHs in soil (see also Section 2.5). The extractable fraction was determined by accelerated solvent extraction (ASE, Thermo Fisher Dionex 150, USA) using the exhaustive solvent DCM. The ASE working conditions and the purification procedure are described in Text S2. The purified extract was spiked with 1800 ng of each internal standard, and its volume was adjusted to ca. 1.5 mL before instrumental analysis with an Agilent 7890B/7000C gas chromatograph-triple quadrupole mass spectrometer. Instrumental operating conditions are listed in Text S3 and Table S1.

For each batch of 4 spiked samples retrieved from the field, a method blank was analyzed for quality control. One of the four moist spiked samples was randomly selected and split into two sub-samples as laboratory duplicates during analysis. A standard solution of Phe, Pyr, BaP, and BghiP was analyzed before and after every six samples for instrumental quality control, with relative standard deviations lower than 10% considered acceptable. Surrogate recoveries of 2-fluorobiphenyl and p-terphenyl-d_{14} were $78 \pm 10\%$ and $90 \pm 12\%$, respectively. The method detection limits, calculated as the average of all blanks plus three times the standard deviation (Ding et al., 2018), were 1.25, 0.35, 0.32, and 0.08 ng/g dw for Phe, Pyr, BaP, and BghiP, respectively. The relative percent differences between laboratory duplicates were below 9% for Phe, 16% for Pyr, 21% for BaP, and 22% for BghiP, respectively. All presented results are corrected for the corresponding blank levels and

recoveries.

2.4. Kinetics of total-extractable PAH decline

A biphasic first-order model with three fitting parameters was recommended for describing the dissipation of organic contaminants in soil (FOCUS, 2006; Motoki et al., 2016). Here we used this model, which attributes the observed decline of chemicals as the superposition of a rapid and a slow decline, to describe the decline of total-extractable Phe, Pyr, BaP, and BghiP over time:

$$C(t)/C(t_0) = f \times \exp(-k_{rapid} \times t) + (1-f) \times \exp(-k_{slow} \times t) \qquad (1)$$

Where $C(t)$ is the total-extractable concentration after t months; $C(t_0)$ is the initial total-extractable concentration after spiking; f and $(1-f)$ represent the fraction or relative importance of the rapid and slow phases of decline, respectively; k_{rapid} and k_{slow} are pseudo-first-order rate constants (month^{-1}) for the rapid and slow phases of decline, respectively.

The half-lives (HL) of decline in total-extractable PAH concentrations, which describe the time required for a 50% decrease in $C(t_0)$, during the rapid and slow phases were calculated using:

$$HL_{rapid} = \ln2/k_{rapid} \qquad (2)$$

$$HL_{slow} = \ln2/k_{slow} \qquad (3)$$

For each PAH, the overall half-life ($HL_{overall}$) during the entire experimental period (i.e. considering both the rapid and slow phases) was calculated by substituting f, k_{rapid}, and k_{slow} into Equation (1) with a forced $C(t)/C(t_0)$ value of 0.5, via a goal-seek function in Microsoft Excel (FOCUS, 2006). Details of initial conditions for the regression are included in Text S4.

2.5. Derivation of NER formation

The overall decline in the total extractable PAH concentrations can be approximately viewed as a combination of three dissipation pathways (i.e. volatilization, leaching, and biodegradation) and NER formation. The three dissipation processes can be described as approximately following first-order kinetics (Mackay, 2001). Matthies et al. (2008) suggested NER formation could be described by first-order kinetics for a wide range of organic contaminants. Johnson et al. (2001) recommended a biphasic first-order model as best-suited to describe sorption/desorption (sorption is one of the key abiotic mechanisms of NER formation (Kästner et al., 2014)) of PAHs to soils. Thus, it should be possible to estimate the rate of NER formation from the overall rate of decline and the individual rates of volatilization, leaching, and biodegradation, as follows:

$$k_{NER\ formation} = k_{total} - k_{volatilization} - k_{leaching} - k_{biodegradation} \qquad (4)$$

Where the ks are all (pseudo) first-order rate constants; k_{total} is the rate constant of decline in total-extractable PAHs, and specifically is either k_{rapid} or k_{slow} mentioned in Section 2.4; $k_{volatilization}$, $k_{leaching}$, and $k_{biodegradation}$ are the rate constants of volatilization, leaching,

Table 1
Environmental conditions at the four studied sites.

Field site	Location	Altitude (m)	Average annual air temperature (°C)	Average annual precipitation (mm/yr)
Site A	Dujiangyan City, Sichuan Province	700	15.5	1120
Site B	Lixian County, Sichuan Province	1890	11.4	619
Site C	Aba County, Sichuan Province	3280	4.0	711
Site D	Maduo County, Qinghai Province	4280	−3.3	332

and biodegradation, respectively, estimated via a single-compartmental soil model which builds on the fugacity approach (Cousins et al., 1999b; Mackay, 2001); $k_{\text{NER formation}}$ is the rate of NER formation, and specifically is $k_{\text{NER formation (rapid)}}$ in the rapid phase or $k_{\text{NER formation (slow)}}$ in the slow phase.

The fugacity approach (Cousins et al., 1999b; Mackay, 2001) calculates the rate constants using fugacity capacities (Z-values) representing the storage capacity of chemicals in four phases (i.e. air, water, organic matter, and mineral matter) and transport parameters (D-values) representing the three transport and transformation processes (i.e. volatilization, leaching, and biodegradation). The calculation is mechanistic because it builds on physico-chemical properties and parameters describing environmental conditions (e.g., rate of precipitation and temperature). For each PAH, model inputs include water solubility (S_{WL}), liquid phase vapor pressure (P_{L}), octanol-water partition coefficients (K_{OW}), and biodegradation half-lives ($HL_{\text{biodegradation}}$). To reflect actual environmental conditions, thermodynamically consistent S_{WL}, P_{L}, and K_{OW} at 25 °C (Table S2, obtained from Ma et al. (2009)) were adjusted to the average temperature at the four sites using internal energies of phase transfer of PAHs (Table S3) and the Clausius-Clapeyron equation (Li et al., 2003; Schwarzenbach and Gschwend, 2016). Environmental parameters (Table S4) included those reflecting our experimental set-up (e.g. pot volume) and empirical parameters that are not environment-specific (e.g. mass transfer coefficient). The empirical parameters are obtained from Mackay (2001) and a surface soil model program (The Canadian Centre for Environmental Modelling and Chemistry, 2005). Details of the calculation and parameter selection are included in Text S5.

Experimentally derived $HL_{\text{biodegradation}}$ in the literature vary by a factor of 10, depending on experimental or observation conditions (Table S5). The selected value is anticipated to strongly influence the estimate of $k_{\text{NER formation}}$ using Equation (4) (to be discussed in Section 3.2). In order to fully consider the variation in $HL_{\text{biodegradation}}$ (Table S5), we use the medians, and the 5th and 95th percentiles of $HL_{\text{biodegradation}}$ compiled from the literature (Table S5) to derive $k_{\text{NER formation}}$. All $HL_{\text{biodegradation}}$ were adjusted for temperature with the Arrhenius equation (Schwarzenbach and Gschwend, 2016) (Table S6).

3. Results and discussion

3.1. Biphasic decline of total-extractable PAHs

After one year, the total extractable concentrations of Phe, Pyr, BaP, and BghiP in field-potted soil at all experimental sites decreased by 90−96%, 84−94%, 70−90%, and 66−79%, respectively, as is shown in Fig. 1 and Table S7. At all sites, the decline is more pronounced for lighter (Phe) than heavier PAHs (Pyr > BaP > BghiP). For all PAHs, the decline is more notable at sites A and B than C and D, indicating a stronger decrease at lower altitudes with higher ambient temperature and precipitation. We obtained kinetic coefficients by fitting the measured decline with the biphasic first-order model of Equation (1), displayed as colored curves in Fig. 1. The fitting performance is generally satisfactory, with a coefficient of determination (R^2) ranging from 0.78 to 0.93. Extractable PAHs underwent a rapid decline (with half-lives ranging from 0.07 to 1.32 months) and a relatively slow decline (with half-lives ranging from 7 to 69 months) (Table S8). The rapid phase plays a more relevant role in the decline of lighter PAHs (Phe and Pyr at sites A and B), reflected by their higher f values in the biphasic first-order model (Fig. 1).

Table 2 shows that the overall half-lives of four PAHs determined in our study are generally close to, but slightly shorter than, those reported previously, especially for heavier PAHs (i.e. BaP and BghiP). The literature-reported half-lives vary by a factor of 10, which may be attributed to the variability in soil properties (Oleszczuk and Baran, 2005), environmental conditions (Maliszewska-Kordybach, 1993), the initial concentration of the spiked PAHs (Chung and Alexander, 1999), co-existing competitive compounds (White and Pignatello, 1999), and extraction solvents (Northcott and Jones, 2001) in earlier studies. The difference between half-lives of PAHs observed in ours and earlier studies may also be attributed to different rates of decline in indoor incubations and field experiments. For instance, sequestration (i.e. type I NER formation) could be strengthened by natural wetting and drying cycles (White et al., 1997), while the growth of microorganisms may be suppressed if environmental conditions are less favorable for microbial activities (Wild and Jones, 1993).

3.2. NER formation: a potentially dominant process in the fate of PAHs in soil

Estimated rate constants of volatilization, leaching, and biodegradation (using median half-life values; Table S6) are given in Table S9. Based on these rate constants, we derived the pseudo-first-order rate constants of NER formation (fast and slow phases; Table S9), and the corresponding half-lives (Table S10). Volatilization, leaching, biodegradation, and NER formation contributed 0.02 ± 0.04%, 0.03 ± 0.06%, 7 ± 14%, and 92 ± 14%, respectively, to the overall decline of PAHs in the rapid phase (Fig. 2a), and 0.1 ± 0.1%, 0.2 ± 0.3%, 50 ± 36%, and 49 ± 37%, respectively, to that in the slow phase (Fig. 2b). That is, NER formation is the dominant process responsible for the reduced bioavailability of total-extractable PAHs during the rapid phase, whereas biodegradation is more relevant during the slow phase. In general, the overall contribution (considering both the rapid and slow phases) of the four processes to the decline of PAHs (Fig. 2c) shows that behavior of PAHs in soil is governed by both NER formation (with a contribution of 64 ± 33%) and biodegradation (with a contribution of 35 ± 32%; ranging from 12 ± 8% for BghiP to 85 ± 18% for Phe, presented in Table S11). Our result echoes an earlier finding which suggested a combined effect of sequestration (regarded as type I NER formation) and biodegradation on the availability reduction of PAHs in soil (Tang et al., 1998). It is interesting to note that some earlier studies (Sims and Overcash, 1983; Weissenfels et al., 1992) presumed biodegradation to be the only primary fate process of PAHs in soil, which, however, has been challenged by labeled isotope approaches which reveal the significance of NER formation (Richnow et al., 1999; Umeh et al., 2017).

We acknowledge that the derived rate constants of NER formation are uncertain because they were derived from the difference between the fitted overall rates of decline in PAH concentration and the modeled rate constants for volatilization, leaching, and biodegradation, instead of by directly measuring the rates of NER formation. Nevertheless, we believe that our fitted overall rates of decline in PAH concentration are reliable, given that our biphasic first-order model can explain 78%−93% of the observed variability (as indicated by R^2). In addition, our results show that volatilization and leaching had a marginal effect on the fate of PAHs, which also agrees with an earlier finding that these processes only contribute notably to the loss of PAHs with less than three rings (e.g. naphthalene) (Park et al., 1990). The variability associated with $HL_{\text{biodegradation}}$ can be important because biodegradation is much faster than volatilization and leaching, whose rate, therefore, strongly affects the estimation of NER formation. We use the 5th and 95th percentiles of the distribution of collected $HL_{\text{biodegradation}}$ (Table S6) to reflect the variability of this parameter. Table S12 give the rate constants of NER formation (corresponding
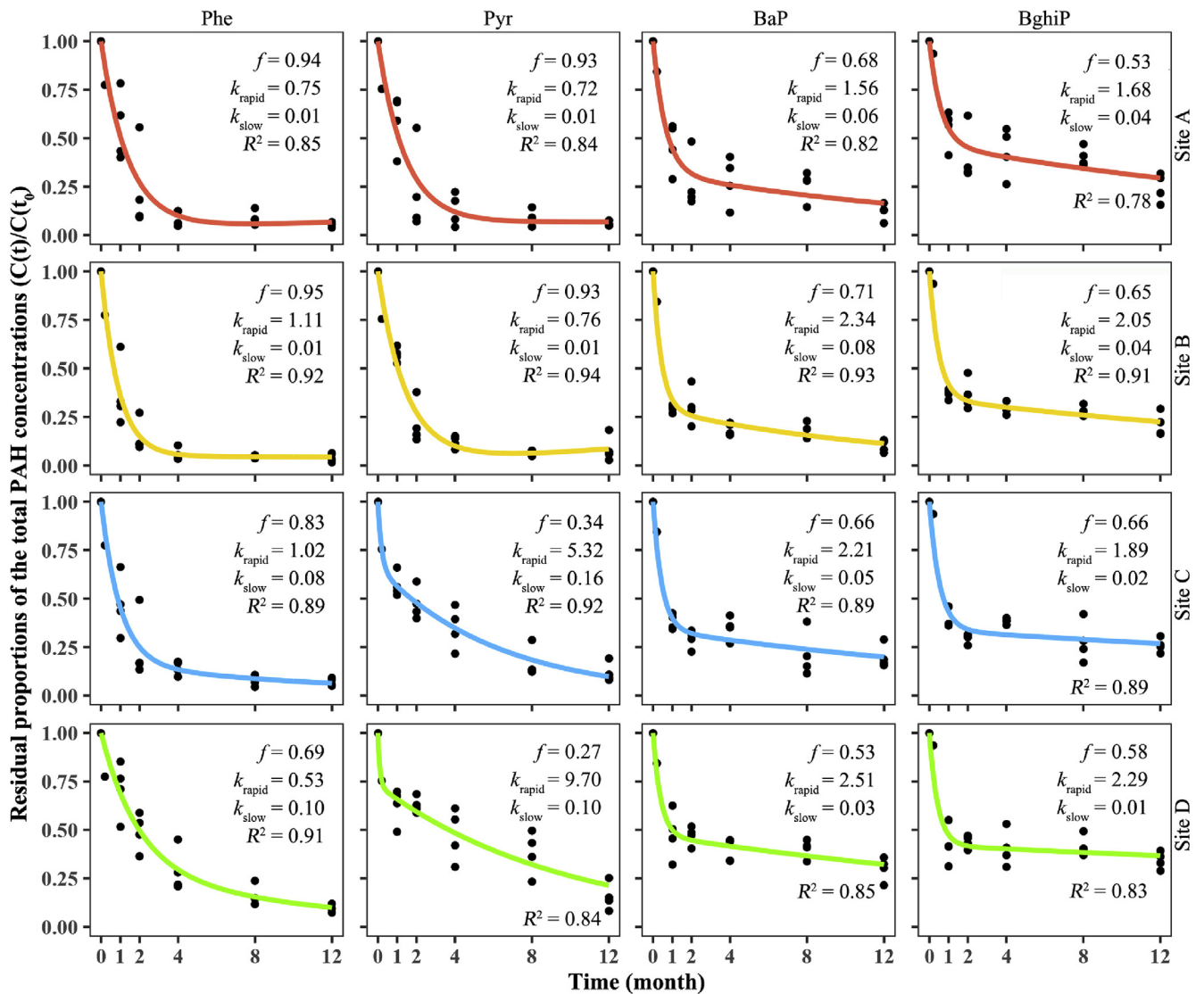
Fig. 1. Time-dependent decline in concentrations of four PAHs (in columns) in soil at four experimental sites (in rows) over the one-year field experiment. Also given are the rate constants of decline in the fast (k_{rapid}) and slow (k_{slow}) periods, the relative importance of the fast period (*f*), as well as the coefficient of determination for fitting.

Table 2
Half-lives of the four PAHs in soils observed in our and other studies, along with experimental conditions.

References	Days	Condition	Temperature (°C)	Extraction solvent	Initial concentration (ng/g)	Half-lives (month)			
						Phe	Pyr	BaP	BghiP
Our study	365	Field	−16−25	DCM	<1000	0.67−1.97[a]	1.02−2.58[a]	0.50−1.00[a]	0.68−1.36[a]
Doick et al., (2005)	4620	Field	Unknown	DCM	10800	N.R.[b]	N.R.	38.5	N.R.
Northcott and Jones, 2001)	525	Indoor	18−22	DCM	10000	59.6	8.47	8.47	N.R.
Northcott and Jones, (2001)	525	Indoor	18−22	Methanol and KOH	10000	4.67	3.2	6.93	N.R.
Wild and Jones, (1993)	205	Indoor	20−30	DCM	2910−7890	4.13	7.50	7.03	15.2
Park et al., (1990)	196	Indoor	25	DCM	33000−902000	0.53	8.67	10.3	N.R.
Maliszewska-Kordybach, (2005)	180	Indoor	20	Cyclohexane	20000	N.R.	1.13−2.7	N.R.	N.R.
Park et al., (1990)	105	Indoor	25	DCM	33000−893000	1.17	6.63	7.63	N.R.

[a] $HL_{overall}$.
[b] N.R. = Not reported.

half-lives are given in Table S13) derived using either the 5th or the 95th percentile of $HL_{biodegradation}$. Biodegradation and NER formation contributed 51 ± 37% and 49 ± 38%, respectively, to the overall decline using the 5th percentile, and 13 ± 14% and 86 ± 15%, respectively, using the 95th percentiles (Fig. S3). These derivations

indicate, that NER formation plays a role of similar or higher importance than biodegradation in the overall decline in total-extractable PAHs in soil, despite the difference in specific numbers. Likewise, Matthies et al. (2008) found in a ^{14}C-labeled experiment that median rate constants of NER formation (based on
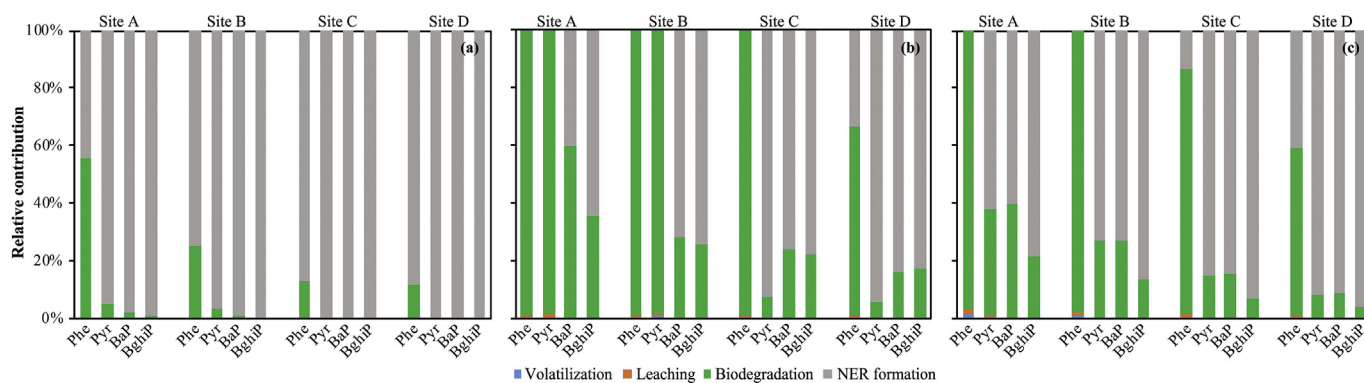
Fig. 2. Relative contribution[a] of four processes to the total decline of PAHs in the rapid phase (a) and slow phase (b) as well as the overall contributions[b] of the four processes over the one-year experiment (c), using median values of collected biodegradation half-lives. [a] Relative contributions in the rapid phase and slow phase were calculated by the quotient of rate constant between individual process and the total PAH decline. [b] Overall contributions were calculated by the quotient of declining amounts after 12 aging months between individual process (derived from rates of volatilization, leaching, and biodegradation via a first-order equation) and the total PAH decline via equation (1).

their results for parent compounds) were slightly slower (0.3–0.8 fold) or faster (1.8–3.0 fold) than biodegradation for a range of pesticides with different physico-chemical properties. This indicates that NER formation and biodegradation are of similar magnitude for these pesticides, which mirrors our results for PAHs. In terms of individual PAH compounds (Table S11 and Fig. S3), NER formation could be either a negligible or a primary process for Phe and Pyr whereas it is always the dominant process for BaP and BghiP irrespective of the chosen $HL_{biodegradation}$ value. Although lighter PAHs are more biodegradable, these chemicals could be utilized by microorganisms with different rates under different environmental conditions and/or by different types of microorganisms. Mass-transfer of PAHs with more than four rings to microbial cells is extremely slow (Johnsen et al., 2005), leading to relatively stable and slow biodegradation rates under different environmental conditions.

Our findings suggested that NER formation generally contributes more than half to the overall PAH decline in soil. This derivation does not consider the suppression of other environmental processes by sequestration (deemed as type I NER formation) (Hatzinger and Alexander, 1995). This implies that the contribution of NER formation could be even higher than what we derived here. Classic multi-media modeling approaches disregarding this important process might overestimate the rates of volatilization and leaching of organic contaminants in soil. Notably, biodegradation and NER formation were treated as two independent parallel processes in our derivation, which implies that estimated rates of NER formation in our study only account for the contribution of NERs originating from the parent compounds. Biogenic NERs, formed from metabolites (Nowak et al., 2013), were not included in our derivation. Thus, our derivation could refer to type I and type II NERs as classified by Kästner et al. (2014). Generally, the contribution of NER to the over PAH decline is of great importance and should not be neglected in most situations. However, this conclusion may not necessarily be applicable to other organic contaminants, especially if they are lighter in molecular weight or more readily biodegradable.

3.3. Effects of physico-chemical properties and environmental conditions

The decline in the total-extractable PAH concentrations is governed by multiple factors, including physico-chemical properties (e.g. log K_{OW} and the $HL_{biodegradation}$), ambient environmental conditions (e.g. temperature and precipitation), and soil properties

(Beck et al., 1993, 1995). We did not investigate the impact of soil properties on NER formation here, even though we acknowledge that soil properties can be an important factor affecting NER formation (Kästner et al., 2014). Instead, the same soil was used, and total organic carbon and pH values measured in the soil during the field experiment were indeed almost constant (Table S14) between the sites.

With respect to physico-chemical properties (comparing columns; Fig. 3), heavier PAHs (i.e. BaP and BghiP) tend to have shorter half-lives in the rapid phase (Fig. 3a) and longer half-lives in the slow phase (Fig. 3b, except for Phe and Pyr at sites A and B). Given that the rapid phase is predominantly governed by NER formation (which involves diverse mechanisms including sorption) (Fig. 2a), this result may be ascribed to the fact that heavier PAHs having stronger irreversible sorption to soil constituents. For instance, Hafidi et al. (2008) found that the bioavailability of PAHs with higher molecular weight decreased faster than those with lower molecular weight, which serves as evidence of strong or irreversible sorption between heavier PAHs and soil constituents. Our finding is also consistent with higher activation energies of desorption for heavier PAHs (Enell et al., 2005). Additionally, heavier PAHs can compete with and even displace lighter PAHs already adsorbed on sorption sites (White et al., 1999; White and Pignatello, 1999), although such competition may not be apparent in our study considering that concentrations of spiked PAHs were unlikely to be sufficiently high. During the slow phase, heavier PAHs tend to have longer half-lives, which could be related to biodegradation, a notable loss process in this phase (Fig. 2b). Heavier PAHs are mineralized or transformed by organisms with more difficulty than lighter PAHs (Haritash and Kaushik, 2009). The decline of Phe and Pyr at sites A and B in the slow phase should be ignored considering the negligible role (lower $(1 - f)$ values; Fig. 1) in the decline of concentrations in soils during this phase.

With respect to environmental conditions (comparing rows; Fig. 3), PAHs at lower-altitude sites (i.e. higher temperature and precipitation) tended to have longer half-lives in the rapid phase (Fig. 3a, except for Phe and Pyr at site D) but shorter half-lives in the slow phase (Fig. 3b, except for Phe and Pyr at sites A and B). Early work (Pignatello and Xing, 1995; ten Hulscher and Cornelissen, 1996) suggested that fast sorption of neutral organic contaminants is governed by the equilibrium sorption enthalpy (i.e. is thermodynamically controlled) whereas slow sorption is governed by the diffusive activation energy (i.e. is kinetically controlled). Since sorption enthalpies of PAHs are negative (Lamichhane et al., 2016), sorption occurring in the rapid phase becomes slower with
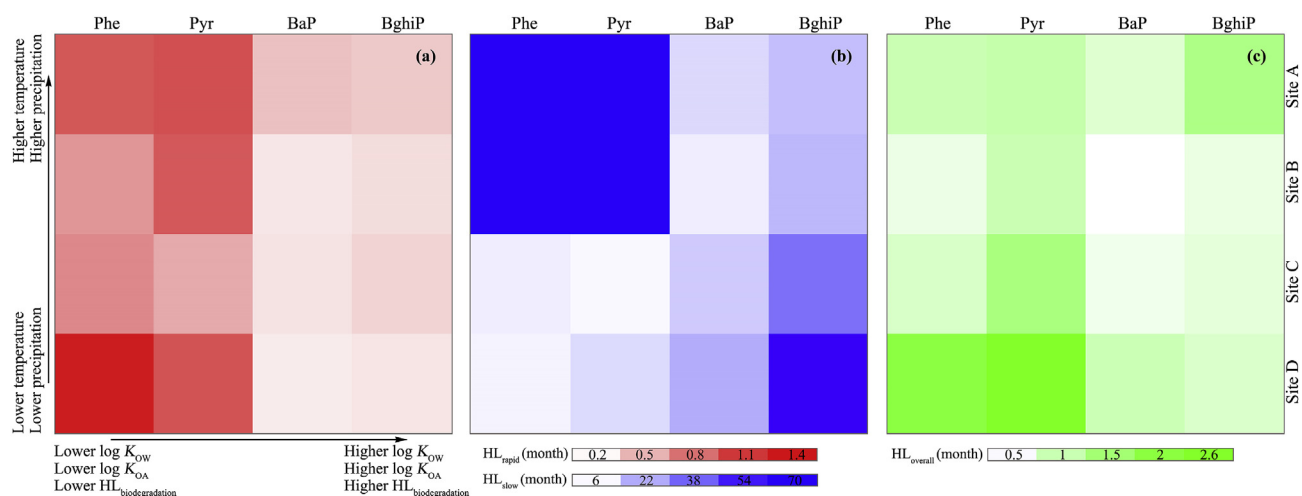
Fig. 3. Half-lives of PAHs in the rapid phase (HL$_{rapid}$, a) and the slow phase (HL$_{slow}$, b) as well as the overall half-lives of PAHs (HL$_{overall}$, c) at the experimental sites indicated by different color shading, whereby darker/lighter colors indicate longer/shorter half-lives. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

increasing temperature, which was also observed by Hiller et al. (2008). The activation energy of slow sorption is positive (ten Hulscher and Cornelissen, 1996); thus, sorption occurring in the slow phase should be faster at higher temperatures. This could be a plausible explanation for the opposite decline patterns of PAHs between the two phases. Higher water content can suppress the sorption of nonionic organic contaminants (Chiou et al., 1985), which would also support slower rates of sorption in the rapid phase at lower-altitude sites that receive more precipitation. The rate of biodegradation is lower at low temperatures (Schwarzenbach and Gschwend, 2016), which could be another reason for longer half-lives of PAHs at higher altitudes in the slow phase, considering the notable role of biodegradation in this phase.

Understanding the variability in the overall half-lives of PAHs (Fig. 3c) is complicated because of the divergent patterns of the contributions in the rapid and slow phases. For instance, heavier PAHs (i.e. BaP and BghiP) have shorter overall half-lives, similar to the trend in the rapid phase (Fig. 3a). However, the trend of effects of environmental conditions was more complex than when considered separately during the two phases, indicative of a combined effect of NER formation and biodegradation. In general, these observations suggest that the behavior of organic contaminants with a large molecular size is to a larger extent controlled by NER formation, whereas that of contaminants with a small molecular size is governed by both NER formation and biodegradation. The patterns of half-lives of PAHs (considering both physical-chemical properties and environmental conditions in Fig. 3) provides a very likely explanation that NER formation as derived in this field study is governed by sorption (the key mechanism in type I NER formation, with biphasic kinetics for PAHs (Johnson et al., 2001)). Given that partial type I NERs is not permanently irreversible (Barriuso et al., 2008; Schaeffer et al., 2018; Umeh et al., 2018), models not accounting for NER formation might underestimate the risks of PAHs in soil. Effects of physico-chemical properties and environmental conditions on biogenic NER formation, which were not included in this work, are worthy to be considered in future research.

4. Conclusion and implications

The total-extractable PAH concentration in soil underwent a rapid decline followed by a slow decline during a year-long field pot experiment. NER formation was identified as a dominant process in the fate of PAHs in soil, being as or more important than biodegradation. Heavier PAHs had a faster rate of decline than lighter PAHs in the rapid phase and during the entire experimental period, but a slower rate in the slow phase. PAHs at high altitudes demonstrated faster decline rates in the rapid phase and slower rates in the slow phase. The trend of the overall decline of PAHs under different environmental conditions displayed the joint influence of NER formation and biodegradation.

Although this is a case study of NER formation of PAHs in soil, it still reminds us to examine the role of NER formation in the fate of organic contaminants and the extent to which NER formation reduces the availability of a wider range of contaminants. Also, the importance of different types of NER formation is worthy of further investigation using direct measurement. Our work indicates that NER formation as an important process needs to be considered in future multi-media modeling studies assessing chemical fate and risk (especially of heavier PAHs and similar contaminants), to reduce the inconsistency between modeling and experimental studies.

Credit author statement

Yang Ding: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **Li Li**: Conceptualization, Methodology, Writing - review & editing. **Frank Wania**: Conceptualization, Methodology, Writing - review & editing. **Yuan Zhang**: Validation, Writing - review & editing. **Huanfang Huang**: Writing - review & editing. **Ting Liao**: Investigation. **Jinhong Liu**: Investigation. **Shihua Qi**: Resources, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.115383.

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