Environmental Science & Technology

Article

pubs.acs.org/est

# Modeling Trade-off between PAH Toxicity Reduction and Negative Effects of Sorbent Amendments to Contaminated Sediments

D. Kupryianchyk,[†,*] M. I. Rakowska,[‡] J. T. C. Grotenhuis,[‡] and A. A. Koelmans[†,§]

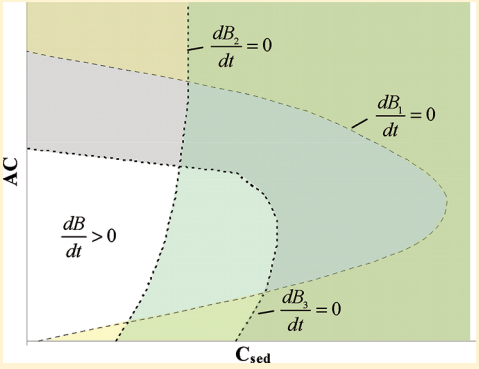
[†]Aquatic Ecology and Water Quality Management Group, Department of Environmental Sciences, Wageningen University, P.O. Box 47, 6700 AA Wageningen, The Netherlands

[‡]Subdepartment of Environmental Technology, Department of Agrotechnology and Food Science, Wageningen University, P.O. Box 17, 6700 AA Wageningen, The Netherlands

[§]IMARES − Institute for Marine Resources & Ecosystem Studies, Wageningen UR, P.O. Box 68, 1970 AB IJmuiden, The Netherlands

Supporting Information

**ABSTRACT:** Adding activated carbon (AC) to contaminated sediment has been suggested as an effective method for sediment remediation. AC binds chemicals such as polycyclic aromatic hydrocarbons (PAHs), thus reducing the toxicity of the sediment. Negative effects of AC on benthic organisms have also been reported. Here, we present a conceptual model to quantify the trade-off, in terms of biomass changes, between the advantageous PAH toxicity reduction and the negative effects of AC on populations of benthic species. The model describes population growth, incorporates concentration-effect relationships for PAHs in the pore water and for AC, and uses an equilibrium sorption model to estimate PAH pore water concentrations as a function of AC dosage. We calibrated the model using bioassay data and analyzed it by calculating isoclines of zero population growth for two species. For the sediment evaluated here, the results show that AC may safely protect the benthic habitat against considerable sediment PAH concentrations as long as the AC dosage remains below 4%.




## INTRODUCTION

Sediment contamination by hydrophobic organic compounds (HOCs) has been recognized as an environmental problem for decades.[1] Sediment-dwelling and pelagic organisms may be exposed to these compounds, either directly through their diet or through uptake from the water column or interstitial water, or indirectly through HOC release after resuspension or bioturbation. Dredging with subsequent disposal of the dredged material in sediment depot is the most common technique to remediate contaminated sediments. Dredging, however, is expensive, laborious, and can lead to resuspension of sediment material, increasing concentrations of HOCs in the overlying water. Moreover, dredging is also very invasive, which may be a problem in vulnerable ecosystems. Recently, amendment of contaminated sediments with activated carbon (AC) has been proposed as a less disruptive, less expensive, and more efficient remediation technique.[2] Several in situ and ex situ studies have demonstrated the advantageous effects of AC application, such as the reduction of bioavailable HOC pore water concentrations,[3−6] reduced HOC bioaccumulation,[3,5,7−9] and reduced toxicity of sediment-bound HOCs.[4,10−13] Despite these advantageous effects, it has also been hypothesized that AC itself may have negative impacts on the habitat quality for benthic organisms. It is important that these possible side-effects are properly addressed before AC amendments can be implemented as a safe and accepted method for sediment remediation. For several aquatic species, a variety of adverse effects of AC have been observed in laboratory settings, such as mortality,[4,7] growth inhibition,[4,9] and a decrease in lipid content.[3,14]

A major question is under what conditions the improvement of habitat quality due to HOC immobilization would compensate for the possible negative effects of AC itself on the habitat quality for benthic aquatic organisms. Additionally, there is a need for a framework allowing these counteracting effects to be generalized. Such a framework could be calibrated for different chemicals, ecosystems, and activated carbon types and then used for decision support in the management of contaminated sediments.

Here, we present a general approach to the conceptual modeling of the development of a population of benthic invertebrates in contaminated sediments amended with AC. The model calculates the direct effects of AC addition on the population, the secondary effects of AC on the reduction of pore water PAH concentrations, and the effects of these reduced PAH exposure concentrations on the population. As such, the model is also capable of quantifying the trade-off between the advantageous HOC toxicity reduction and the negative effects

Received: December 14, 2011
Revised: March 14, 2012
Accepted: March 15, 2012
Published: March 15, 2012

 © 2012 American Chemical Society 

of AC addition on macroinvertebrate populations. The scope of the model is to describe effects for the first weeks after AC amendment. We are not aware of earlier studies modeling the combined effects of AC amendment and HOCs on benthic population development.

The general model is implemented for a specific case using sediment- and species-specific toxicity data derived from our previously published 8- and 28-day whole sediment laboratory bioassays.[4] We briefly summarize the characteristics of these bioassays and introduce the modeling approach. The bioassays were used to test the effects of AC addition (0, 3, 6, 15, and 30% d.w.) to uncontaminated sediment and to sediment natively contaminated with PAHs, for two species: *Gammarus pulex* and *Asellus aquaticus*. The experimental results showed that AC addition (a) leads to lower survival and to growth inhibition of these species in uncontaminated sediment, and at the same time (b) facilitates survival of both species in the PAH-contaminated sediment.[4] *G. pulex* and *A. aquaticus* were selected as test organisms because they are common invertebrates in freshwater habitats and have been widely used in ecotoxicological studies.[15,16] They differ in their sensitivity to AC,[4] and have different species-specific properties, such as behavior, feeding strategies, and routes of HOC uptake,[17] and thus provide a good representation of benthic communities. Moreover, these are the two species that have been most frequently studied in Europe in regards to how they are affected by AC. The sediment was a highly contaminated hot spot sample from Petroleum Harbor (PH, Amsterdam, The Netherlands), with a total PAH concentration of 1100 mg/kg. Yield responses to the interrelated effects of PAH toxicity and activated carbon addition on *G. pulex* and *A. aquaticus* were analyzed using a general population growth model.[18] The effect of AC addition on PAH aqueous exposure concentrations was quantified using an AC-inclusive equilibrium sorption submodel.[19,20] The model was parametrized using literature data and the concentration-effect relationships and mortality rates derived from the laboratory experiments.[4]

## METHODS

**Model Description.** *Population Dynamics in Sediment Amended with AC.* One of the most basic models of population growth is the logistic growth model.[18,21] A population with sufficient food and space to grow tends to grow at a rate that is proportional to the population size and is commonly described as

$$\frac{dB}{dt} = kB\left(1 - \frac{B}{K}\right) \tag{1}$$

where $B$ is biomass (mg), $k$ is a growth rate constant ($d^{-1}$), and population growth is limited by the carrying capacity $K$ (i.e., an upper limit of population size) (mg). We assume that in the first relatively short period, as in the 28 d toxicity tests from which the majority of the input parameters for the model were derived,[4] the population is unconstrained by resource limitations, that is, $B$ is small relative to $K$, and the population growth follows an exponential pattern[18]

$$\frac{dB}{dt} = kB \tag{2}$$

Whereas population growth occurs through production or assimilation, growth failure may occur through respiration, natural mortality, and mortality caused by toxic chemicals. These are the factors we included in the growth model. Respiration was described as a gross loss term and was not subdivided into costs for maintenance, growth, and reproduction. Population growth due to reproduction and recolonization is not relevant for our toxicity test systems and is therefore omitted. Similarly, the model does not consider biomass losses due to inter- and intraspecific competitions or predation. The resulting population growth equation follows previously published approaches,[18,22,23] and details the rate constant $k$ in eq 2 as follows

$$\frac{dB}{dt} = (k_a - k_r - k_{inh} - \mu_{nat} - \mu_{AC} - \sum_{i=1}^{m} \mu_{PAH_i})B \tag{3}$$

where $k_a$ is an assimilation rate constant ($d^{-1}$), $k_r$ is the respiration rate ($d^{-1}$), $k_{inh}$ is a growth inhibition rate ($d^{-1}$), and $\mu_{nat}$, $\mu_{AC}$, and $\mu_{PAHi}$ are rates constants for natural mortality, mortality due to AC, and mortality due to individual PAH $i$, respectively, ($d^{-1}$). The summation term adds up the mortality rates due to all $m$ individual $PAH_i$ to obtain one overall mortality rate ($\sum\mu_{PAHi}$) for the PAH mixture present in the sediment pore water. The use of these mortality rate constants implies that mortality is assumed to be a first-order process, proportional to population size. Following Traas et al.,[24] the mortality rate $\mu$ ($d^{-1}$) due to the stressors, that is either an individual PAH (or mixture of PAHs) or AC, is modeled to depend on their concentration $C$ ($\mu$g/L) in the water, according to

$$\mu = \frac{1}{D}\ln\left[1 + \left(\frac{C}{LC_{50}}\right)^b\right] \tag{4}$$

where $LC_{50}$ is the concentration at which 50% mortality is observed in a single-species toxicity test ($\mu$g/L), $b$ (>0) is a slope parameter of the concentration−response curve on a linear scale, and $D$ is the duration of the single species toxicity test ($d^{-1}$). Parameterization and calibration of the model eqs 3 and 4 is detailed below.

*Trade-off between Toxicity Reduction and Negative Effects of Activated Carbon.* The trade-off between the advantageous effect of PAH toxicity reduction and the direct negative effects of AC addition on the test species was addressed using the parametrized and calibrated model to calculate population equilibria. The population equilibrium for a species is the combination of model variables that results in a stable population with zero growth. In our case, these model variables are % AC and total PAH concentration. The equilibria can be visualized graphically by plotting the line of zero growth for each of the species. The lines of zero growth are called isoclines, and separate the regions in the state space where the population increases from the regions where the population decreases.

Because the population equilibrium occurs when the population density is not changing, we can calculate the isoclines by equating $dB/dt$ in eq 3 to zero, or

$$B(k_a - k_r - k_{inh} - \mu_{nat} - \mu_{AC} - \sum_{i=1}^{m} \mu_{PAH_i}) = 0 \tag{5}$$

Eq 5 has two solutions. The first solution, $B = 0$, is called a trivial equilibrium and effectively represents the absence of the

species, which therefore is not relevant from an ecological point of view. The second solution balances the assimilation rate constant, $k_a$, to all loss rate constants in the model, that is, the rate constants for respiration, growth inhibition, and mortality

$$\mu_{AC} = k_a - k_r - k_{inh} - \mu_{nat} - \sum_{i=1}^{m} \mu_{PAH_i} \quad (6)$$

Eq 6 shows that, if $k_a$, $k_r$, $k_{inh}$, and $\mu_{nat}$, are known, the mortality rate constant due to AC ($\mu_{AC}$) can be calculated for any value of the mortality rate due to PAH ($\sum\mu_{PAHi}$), and vice versa. It is more convenient, however, to express eq 6 in terms of the control variables $C_{AC}$ (as % AC) and the aqueous concentration for $PAH_i$: $C_W^i$, or even better, the total concentration of PAH in the solid phase. This can be achieved by substituting eq 4 parametrized for AC into $\mu_{AC}$, and substituting eq 4 parametrized for PAH toxicity into $\mu_{PAH,i}$, which yields

$$\frac{1}{D_{AC}}\ln\left[1 + \left(\frac{C_{AC}}{LC_{50}^{AC}}\right)^{b_{AC}}\right] = k_a - k_r - \mu_{nat} - \sum_{i=1}^{m} \frac{1}{D_{PAH_i}}\ln\left[1 + \left(\frac{C_W^i}{LC_{50}^i}\right)^{b_i}\right] \quad (7)$$

Eq 7 determines the isocline, linking $C_{AC}$ values (% AC) to those values of $C_W^i$ in the mixture of PAHs that result in zero growth of the population, so a $\sum\mu_{PAHi}$ can be calculated for each AC concentration. Note that numerous combinations of concentrations $C_W^i$ in the pore water mixture of PAHs may result in the same value for $\sum\mu_{PAHi}$ (the right-hand summation term in eq 7). However, the actual composition of the PAH mixture in the sediment pore water is fixed and sediment-specific and under equilibrium conditions has to relate to a fixed ratio of solid phase PAH concentrations in the sediment. Therefore, we first calculated the isocline-$\sum\mu_{PAHi}$ from eq 7 and then fitted the pore water concentrations $C_W^i$ of the four dominant PAHs constituting more than 95% of the aqueous $\sum$PAH concentration (phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), and pyrene (PYR)),[4] to fulfill two criteria: (a) the $\sum\mu_{PAHi}$ value calculated from the four fitted $C_W^i$ values equates to this required isocline-$\sum\mu_{PAHi}$, and (b) the solid phase PAH concentrations $C_{sed}^i$ for the four dominant PAHs as calculated from the fitted values for $C_W^i$ by equilibrium sorption modeling are in agreement with the corresponding PAH $C_{sed}^i$ ratios in the PH sediment (Table S1 of the Supporting Information). For this conversion of pore water concentrations of individual PAHs ($C_W^i$) to solid phase concentrations ($C_{sed}^i$), single or multiple domain sorption models may be selected that may or may not account for sorption nonlinearity to hard carbon phases[10,20,25−28] depending on the case considered. Here, we decided to keep the model general and to follow the approach that seems to be accepted most frequently in the recent literature, which is a multiple domain Freundlich sorption model.[10,19,20] The model accounts for the distribution of PAHs over the organic matter domains of organic carbon (OC) and black carbon (BC) and added AC

$$\sum_{i=1}^{m} C_{sed}^i = f_{OC}\sum_{i=1}^{m} K_{OC}^i C_W^i + f_{BC}\sum_{i=1}^{m} K_{BC}^i (C_W^i)^{n_{F,BC}} + f_{AC}\sum_{i=1}^{m} K_{AC}^i (C_W^i)^{n_{F,AC}} \quad (8)$$

where $\sum C_{sed}$ ($\mu$g/kg) is the sum concentration of $m$ PAHs sorbed to the total sediment, which is assumed to remain unchanged after AC addition, and $f_{OC}$, $f_{BC}$, and $f_{AC}$ are the fractions of OC, BC, and AC, respectively (kg/$kg_{sed}$), $K_{OC}$ is the organic carbon normalized sorption coefficient for OC (L/$kg_{OC}$), $K_{BC}$, and $K_{AC}$ are the Freundlich adsorption coefficients for BC and AC respectively ($\mu$g/kg)/($\mu$g/L)$^{nF}$ and $n_{F,BC}$ and $n_{F,AC}$ are the Freundlich exponents for BC and AC, respectively. The conversion of the PAH mortality rate ($\sum\mu_{PAHi}$) to pore water concentrations and then to PAH concentrations in the sediment solid phase that correspond to the actual composition of the sediment can be performed for any sediment using this procedure. For a given PAH mortality rate ($\sum\mu_{PAHi}$), however, sediments with a different PAH profile will yield a different $\sum C_{sed}$ based on eq 8. In summary, for a given level of PAH $\sum C_{sed}$, this model procedure provides the value of % AC for which a stable population of zero growth can be expected or vice versa. It is convenient to have the isocline expressed in terms of $\sum C_{sed}$ (solid phase) rather than pore water concentration because total contaminant concentrations are the common descriptors in sediment quality management. With respect to the application of eq 8, we formulate three disclaimers. First, nonequilibrium may cause pore water concentrations to be higher than predicted by this equilibrium model. Second, eq 8 may yield theoretical values for $\sum C_{sed}$ that are beyond the range of PAH concentrations for which the BC and AC sorption parameters were calibrated. Third, at high $C_W^i$, sorption behavior may not comply with the Freundlich model because of saturation of the AC and BC surfaces. To better address saturation of the surface of hard carbon materials such as BC and AC, Langmuir or Polanyi−Dubinin−Manes models have been suggested before.[29] Because of better data availability and the lesser number of parameters needed, we evaluated a Langmuir model scenario as an alternative to eq 8

$$\sum_{i=1}^{m} C_{sed}^i = f_{OC}\sum_{i=1}^{m} K_{OC}^i C_W^i + f_{BC}\sum_{i=1}^{m} \frac{K_d^{BC} C_W^i}{1 + \frac{K_d^{BC} C_W^i}{C_{max}^{BC}}} + f_{AC}\sum_{i=1}^{m} \frac{K_d^{AC} C_W^i}{1 + \frac{K_d^{AC} C_W^i}{C_{max}^{AC}}} \quad (9)$$

where $K_d$ is the initial slope of the isotherm equal to the sorbent-water distribution coefficient (L/kg) at low $C_W^i$, and $C_{max}$ is the maximum adsorption capacity ($\mu$g/kg) of the sorbent. A detailed explanation of eq 9 is provided as Supporting Information.

**Parameterization of the Model.** As explained in the introduction, the model was parametrized using data derived from 28 d and 8 d exposure experiment with uncontaminated and PAH-contaminated sediment respectively amended with different AC concentrations.[4] To our knowledge, this is the

only data set available that can be evaluated in the context of the proposed model framework.

*Biomass Estimation.* Biomass ($B$) was monitored by counting the number of individuals in a series of whole-sediment toxicity tests described previously.[4] The observed numbers were converted to biomass using length - dry weight relationships established by Graca et al.[35] (Table 1). For *G. pulex*, the relationship reads: Ln $DW$ = 3 Ln $L$ − 5.64, where $DW$ and $L$ are the dry weight (mg) and length (mm) of an individual organism, respectively. For *A. aquaticus*, the relationship is: Ln $DW$ = 2.7 Ln $L$ − 4.58. Assimilation and respiration rates, estimated from the balanced energy equation, were taken from the literature[36,37] (Table 1).

*Mortality and Growth Inhibition Rates.* Natural mortality of *G. pulex* and *A. aquaticus* was estimated from the observed mortality in the experimental controls[4] by fitting eq 3 to the dose−response curve with parameters $k_a$, $k_r$, $k_{inh}$, $\mu_{AC}$, and $\mu_{PAH}$ set to zero. $LC_{50}^{AC}$, $b_{AC}$, and $D_{AC}$ (eq 4) for *G. pulex* were derived from a series of AC toxicity tests (Table 1)[4] and $\mu_{AC}$ was calculated using eq 4. For *A. aquaticus*, no concentration-effect curve could be derived to calculate $LC_{50}^{AC}$ and $b_{AC}$, so $\mu_{AC}$ was estimated as total mortality observed in the sediment minus natural mortality.[4] For both species $k_{inh}$ was set to zero because no growth inhibition was observed in the AC toxicity tests.

Mortality due to PAHs in AC-amended sediments was calculated in two different ways. For the purpose of modeling the population dynamics during the bioassays, mortality due to PAHs was calculated as total mortality observed in our laboratory experiments minus natural mortality and mortality due to AC. This uses the assumption that mortalities due to multiple stressors (here PAHs and AC) can be assumed additive (eq 3).[18,38] Factors that might interfere with AC and PAH toxicity in the tests like oxygen, pH, un-ionized ammonia, metals, other HOCs) were irrelevant as was shown in our previous article.[4] For the purpose of modeling the isoclines, mortality due to PAHs in PH sediment was estimated using eq 4, as described above. To our knowledge, no $LC_{50}$ and $b$ values for *G. pulex* and *A. aquaticus* have been published for individual PAHs. However, it has been shown previously that the shape of the dose−response curve, which is determined by the median sensitivity of the exposed populations, is similar for compounds with the same mode of action.[39] Thus, $\beta$, the slope parameter of the log-transformed dose−response relationship ($\beta = 1/b$), was assumed to be the same for all individual PAHs, both for *G. pulex* and *A. aquaticus* (Table 1).[39] As for $LC_{50}$, the values for two closely related gammarids, *Gammarus aequicauda* and *Gammarus locusta* were taken to feed the model (Table 1)[40] because species with similar traits have similar sensitivity to stressors.[17] Using the previously published approach,[4] the $LC_{50}$ for ANT was assumed to be equal to that for PHE given the similarity between these chemicals (Log $K_{OW}$, molecular weight, and shape) and between their final chronic values.[41]

*Sediment Characteristics.* The total concentrations of PAHs in the system ($\sum C_{sed}$), $f_{OC}$, $f_{BC}$, and $f_{AC}$ were determined experimentally and are given in Table S1 of the Supporting Information.[4] The $K_{OC}$ values for amorphous carbon were calculated from compound class specific quantitative structure property relationships (QSPRs) taken from van Noort.[42] The QSPR for PAHs, is: log $K_{OC}$ = 1.11, log $K_{OW}$ − 1.14. log $K_{OW}$ values for PAHs were taken from Booij et al.[43] Following,[19] BC and AC Freundlich sorption affinity constants for all individual chemicals ($K_{BC}$ and $K_{AC}$) and their Freundlich exponents were estimated using previously published data.[10,25,28,44−47] Values for $K_d$ for BC and AC were taken from Jonker and Koelmans[30] and corrected for 1 order of magnitude organic matter fouling, as reported previously.[29,31] Adsorption capacities $C_{max}$ were taken from van Noort.[32−34]

*Uncertainty Analysis.* A robust uncertainty analysis was performed for the isocline calculations by varying the values of the input parameters within a range of plus or minus one SD (Table 1). If no SD was available, the input parameter value was varied within 20% of the values (Table 1). The resulting lowest and highest isocline estimates were plotted together with the isocline at the default parameter values.

## RESULTS AND DISCUSSION

**Modeling Population Dynamics in AC-amended Sediment.** *Mortality Rates Due to AC and PAHs.* The results of the whole-sediment 28 d toxicity tests with *G. pulex* and *A. aquaticus* in uncontaminated sediment[4] were used to calculate the mortality rates due to AC. For *G. pulex*, the mortality rate due to AC gradually increases with increasing AC concentration and appears to level off at higher AC concentrations, that is > 15% (part a of Figure S1 of the Supporting Information). This may suggest that addition of AC at these very high concentrations will probably cause 100% mortality of the population. In contrast to *G. pulex*, *A. aquaticus* survived at all AC concentration and its mortality rates due to different AC concentrations were very low and not statistically different from one another (one-way ANOVA, $F(5, 18) = 0.514$, $p = 0.763$) (Figure S1 of the Supporting Information). Therefore, the average value of 0.005 $d^{-1}$ for all AC concentrations was used to calculate the isoclines (as described in the next section).

The results of the whole-sediment 8 d toxicity tests with *G. pulex* and *A. aquaticus* in heavily contaminated sediment were used to calculate the mortality rates due to PAHs. An increase in AC concentration in PAH-contaminated sediment leads to an exponential decrease in mortality rates for both species (part b of Figure S1 of the Supporting Information) suggesting that 1−3% AC efficiently removes PAHs from the sediment pore water and thus reduces risks associated with these chemicals.

*General Model Results.* Whereas Kupryianchyk et al.[4] evaluated the results of the bioassay using statistical tests, we here evaluate the modeling of the population dynamics in these laboratory tests. The agreement between modeled and measured values for the biomass increase in the bioassays is good for *G. pulex* and *A. aquaticus* in uncontaminated and heavily contaminated sediment (Figure 1). The agreement between modeled and measured data includes values for two different test durations, that is 8 and 28 days (Figure 1). Although the latter agreement does not demonstrate a full validation of the model, it provides some support for the assumed validity of the first-order approach as condensed in eqs 2 and 3.

*Population Dynamics in Uncontaminated AC-Amended Sediment.* The calculated mortality rates were used as input to model the population development of *G. pulex* and *A. aquaticus* in uncontaminated and heavily contaminated (PH) sediment. It appeared that amendment of uncontaminated sediment with 1% AC has no or only very mild effects on the modeled population dynamics of *G. pulex* (part a of Figure 2). Addition of 3% AC leads to an approximately 50% inhibition of biomass development compared to the control group. Amendment of sediment with AC > 3% has a significant effect on *G. pulex* and eventually leads to extinction of the population. As for *A. aquaticus*, addition of AC to clean sediment also affects the modeled biomass development of the species. However, the

**Table 1. Default Model Parameters (SD)**

| | | *G. pulex* | | | | | *A. aquaticus* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ***Biological parameters*** | | | | | | | | | |
| Assimilation rate | $k_a$[b], $d^{-1}$ | 0.052[36] | | | | | 0.051[d 37] | | | | |
| Respiration rate | $k_r$[b], $d^{-1}$ | 0.034[36] | | | | | 0.008[d 37] | | | | |
| Natural mortality | $\mu_{nat}$[a,c], $d^{-1}$ | 0.0069 (0.0021) | | | | | 0.0019 (0.0022) | | | | |
| | | ***Activated Carbon*** | | | | | | | | | |
| | | **1** | **3** | **6** | **15** | **30** | **1** | **3** | **6** | **15** | **30** |
| Mortality rate | $\mu_{AC}$[a,c], $d^{-1}$ | 0.0048 (0.0053) | 0.0260 (0.0165) | 0.1987 (0.0823) | 0.2398 (0.0021) | 0.2398 (0.0021) | 0.0050 (0.0030) | 0.0062 (0.0115) | 0.0041 (0.0045) | 0.0036 (0.0089) | 0.0064 (0.0056) |
| AC toxicity[4] | 28-d $LC_{50}$[a,c], % | 3.1 (0.64) | | | | | - | | | | |
| | $b$[b,c], - | 4.5 | | | | | - | | | | |
| | $D_{AC}$[c], d | 28 | | | | | 28 | | | | |
| | | ***Polyaromatic hydrocarbons*** | | | | | | | | | |
| | | **PHE** | **ANT** | **FLU** | **PYR** | | **PHE** | **ANT** | **FLU** | **PYR** | |
| PAH toxicity | 2- d $LC_{50}$[b], $\mu g/L$[40] | 150 | 150 | 50 | 60 | | 150 | 150 | 50 | 60 | |
| | $b$[bf],- | 2.36 | | | | | 2.36 | | | | |
| | $D_{PAH}$,[c] d | 2 | | | | | 2 | | | | |
| Sorption affinity parameters | Log $K_{BC}$[a,e] $(\mu g/kg_{BC})/(\mu g/L)^{nF,BC}$ | 7.5 (0.2) | 7.5 (0.2) | 7.7 (0.3) | 7.7 (0.3) | | 7.5 (0.2) | 7.5 (0.2) | 7.7 (0.3) | 7.7 (0.3) | |
| | Log$K_{AC}$[a,e], $(\mu g/kg_{AC})/(\mu g/L)^{nF,AC}$ | 7.7 (0.3) | 7.7 (0.3) | 8.6 (0.3) | 8.6 (0.3) | | 7.7 (0.3) | 7.7 (0.3) | 8.6 (0.3) | 8.6 (0.3) | |
| | Log $C_{max}^{BC}$[g], $\mu g/kg$ | 6.91 | 6.91 | 6.73 | 6.73 | | 6.91 | 6.91 | 6.73 | 6.73 | |
| | Log $C_{max}^{AC}$[g], $\mu g/kg$ | 7.45 | 7.45 | 6.97 | 6.97 | | 7.45 | 7.45 | 6.97 | 6.97 | |
| | Log $K_d^{BC}$[h], L/kg | 5.56 | 5.76 | 6.04 | 6.04 | | 5.56 | 5.76 | 6.04 | 6.04 | |
| | Log $K_d^{AC}$[h], L/kg | 7.76 | 7.96 | 8.06 | 8.06 | | 7.76 | 7.96 | 8.06 | 8.06 | |
| | $n_{F,BC}$[b,e],- | 0.7 | | | | | 0.7 | | | | |
| | $n_{F,AC}$[b,e],- | 0.7 | | | | | 0.7 | | | | |

[a]Uncertainty analysis used value ±SD. [b]Uncertainty analysis used value ±10%. [c]Calculated using data from [4]. [d]1 mg = 20.7 kJ [36]. [e]Estimated using data from [10,25,28,44−47] as summarized in [19]. [f]$b$ (=1/$\beta$) estimated using data from [39]. [g]Estimated using data from [32−34]. [h]Estimated using data from [30].



dx.doi.org/10.1021/es2044954 | Environ. Sci. Technol. 2012, 46, 4975−4984

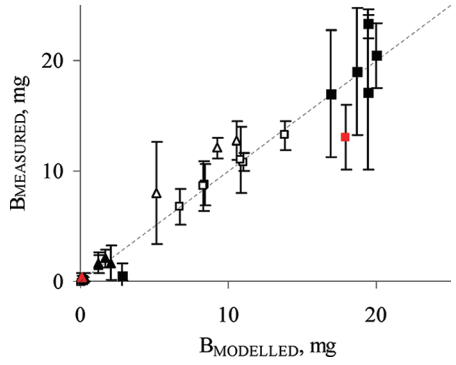



**Figure 1.** Modeled vs measured biomass (±SD) of *G. pulex* (triangles) and *A. aquaticus* (squares). Open symbols relate to 28 d toxicity tests in uncontaminated sediment, closed black, and closed red symbols relate to 8 and 28 d toxicity test in PAH-contaminated Petroleum Harbor sediment amended with AC, respectively. Dashed line is the 1:1 line.

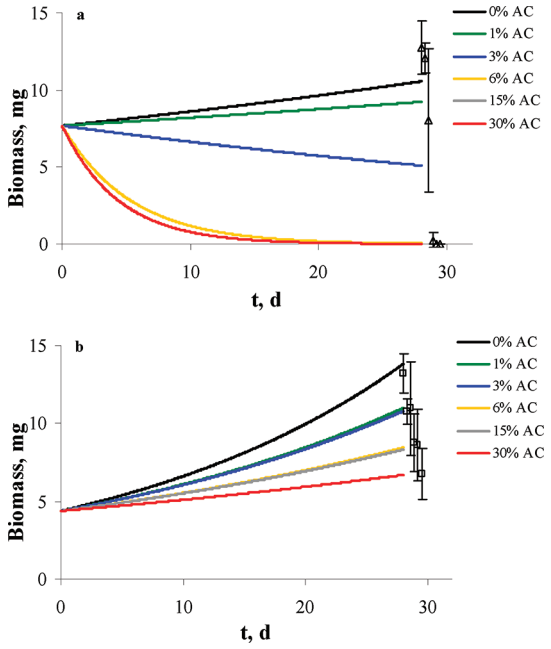



**Figure 2.** Population dynamics of *G. pulex* (a) and *A. aquaticus* (b) in uncontaminated sediment amended with 0, 1, 3, 6, 15, and 30% AC d.w. The markers correspond to a biomass (SD) measured in the 28 d toxicity test. The markers were deliberately set apart by ±1 d to avoid overlap of error bars (±SD).

predicted decrease in biomass can largely be explained by growth inhibition of *A. aquaticus* rather than mortality caused by AC addition (part b of Figure 2b). After all, the fitted growth inhibition constant is about three times higher than the mortality rate constant at sediment AC concentrations exceeding 3% (Table 1).

*Population Dynamics in PAH-Contaminated Sediment Amended with AC.* In contaminated PH sediment without AC, the modeled effect of PAHs on the *G. pulex* population is severe and leads to a rapid decline of the population density within several days (part a of Figure 3). AC addition is able to improve survival of the species. Even the highest doses of AC, however, do not completely mask the high levels of PAHs in the PH sediment, which results in a predicted extinction of the

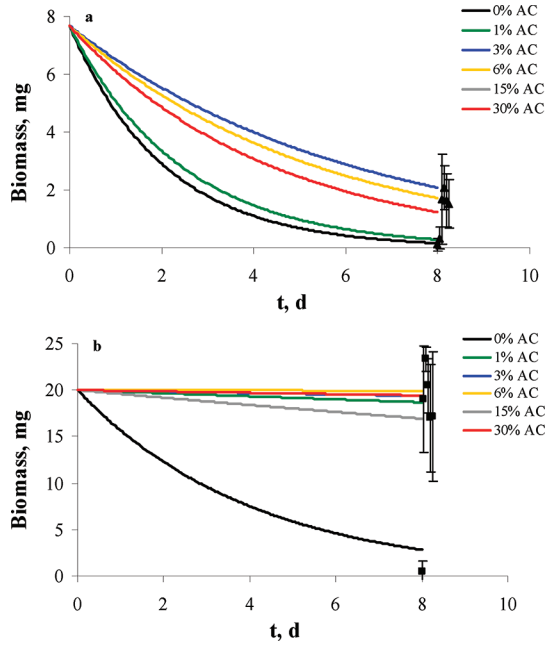



**Figure 3.** Population dynamics of *G. pulex* (a) and *A. aquaticus* (b) in PAH-contaminated sediment amended with 0, 1, 3, 6, 15, and 30% AC d.w. The markers correspond to biomass (±SD) measured in the 8 d toxicity test. The markers were deliberately set apart by ±0.5 d to avoid overlap of error bars (SD).

population of *G. pulex* (part a of Figure 3). Note that the 30% AC curve, which represents the condition with the highest reduction of PAH pore water concentrations, does not provide the best overall growth condition for *G. pulex*. This can be explained by the fact that at these high AC levels, the negative effects of AC are bigger than the positive effects of the reduction of pore water concentrations and associated toxicity of the PAHs. Instead, the curve for 3% AC appears to provide a better compromise for this species. Similarly, exposure of *A. aquaticus* to contaminated PH sediment without AC also leads to extinction within several days. Addition of AC to PH sediment again leads to survival, which for this AC-tolerant species requires only 1% AC, and does not show any decline at higher AC concentrations (part b of Figure 3).

The assimilation, growth, respiration, growth inhibition, and AC- and PAH-related mortality rate constants as specified in Table 1 and Figure S1 of the Supporting Information may be lumped into one overall value per AC concentration in the PH sediment, from which a population half-life can be calculated. If we define the time of extinction as four times the half-life, the calibrated model predicts that 3% AC extends the time to extinction from approximately 8 to 16 days for *G. pulex* and from 12 days to infinity for *A. aquaticus*.

**Modeling the Trade-off between Toxicity Reduction and Negative Activated Carbon Effects on Macroinvertebrate Populations.** The previous section evaluated model simulations for the conditions of our previously published bioassays. Here, we address the main aim of the paper, that is the exact trade-off between PAH toxicity reduction and negative AC effects on *G. pulex* and *A. aquaticus*, by simulating population equilibria for PH sediment. The equilibria are plotted as isoclines defining all combinations of AC dosage (% AC) and total PAH concentration in sediment ($\Sigma C_{sed}$) that yield zero growth of the population, and where the PAH ratios of the individual PAHs that make up $\Sigma C_{sed}$, agree with the ratios in


dx.doi.org/10.1021/es2044954 | *Environ. Sci. Technol.* 2012, 46, 4975–4984

the PH sediment (Figure 4). The PAH concentration matching that of PH sediment is marked in Figure 4. Lower concentrations

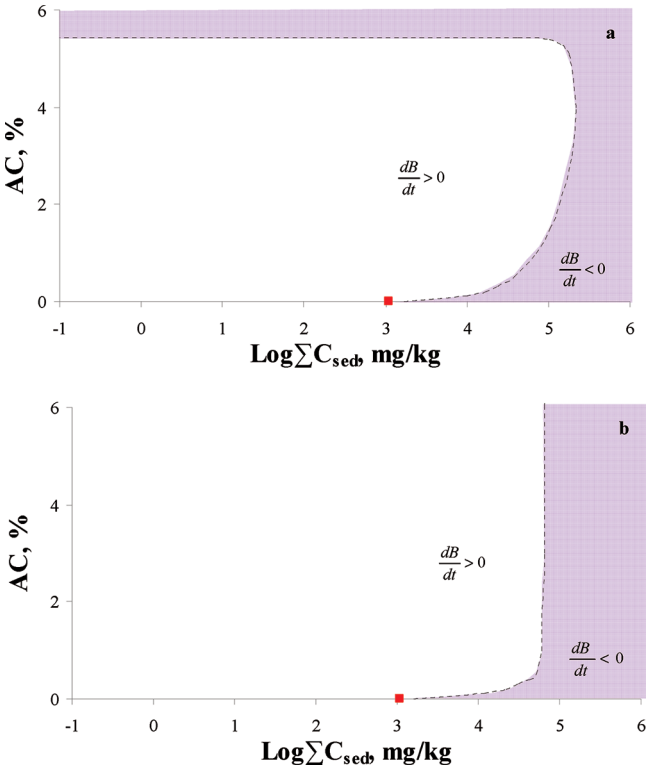



**Figure 4.** Isoclines, i.e. lines of zero growth, for *G. pulex* (a) and *A. aquaticus* (b). An isocline separates the part of the state space where the populations decrease (dashed area) from the state space where the populations increase (blank area). The red marker corresponds to the position of Petroleum Harbor sediment in the state space. To convert aqueous PAH exposure to sediment PAH concentrations, a Freundlich sorption model (eq 8) was used.

can be regarded as dilutions of PH sediment, whereas higher concentrations resemble hypothetical sediments with a higher loading of PAHs.

For *G. pulex*, the population equilibrium in untreated sediment is observed at $\log\sum C_{sed}$ = 3.23 (1700 mg/kg) (part a of Figure 4 intersects of isocline with 0% AC line). This means that the population grows if the PAH concentration in untreated PH sediment is lower than this value. An increase in $\sum C_{sed}$ increases the toxicant-related mortality and therefore requires an increased concentration of AC to keep the population at equilibrium. Increasing $\log\sum C_{sed}$ from 3.23 to a theoretical value of 5.34 (i.e., 220 000 mg/kg) requires an AC dose of 0% increasing to 4%, that is, about 1% AC per 70 000 mg/kg of extra $\sum C_{sed}$. This agrees to an unrealistically high AC binding capacity of 7 g PAH per g of AC, which illustrates the limitation of the Freundlich model to correctly describe sorption behavior at the highest concentration levels in Figure 4. A further increase in the PAH concentration becomes lethal and causes growth inhibition of the population. Besides the limit in $\sum C_{sed}$ there is a similar upper limit in the AC dose, which is indicated by the higher bound of the isocline. When $\log\sum C_{sed}$ gradually varies from −1.00 to 5.34 (i.e., from 0 to 220 000 mg/kg), the tolerance to AC gradually varies from 4.0 to 5.5% AC (part a of Figure 4). The maximum tolerance for PAHs is reached at an AC dose of about 4% and as indicated, is unrealistically high (220 g/kg PAH). This is explained by the Freundlich sorption model used (eq 8), which assumes equilibrium sorption to high affinity materials such as black carbon and activated carbon without a sorption maximum.

For *A. aquaticus*, the population equilibrium for untreated sediment is observed at $\log\sum C_{sed}$ = 3.02 (1600 mg/kg) (part b of Figure 4, intersect of isocline with 0% AC line). Because the mortality of *A. aquaticus* due to AC is constant in the range of 1−30% AC (i.e., 0.005 $d^{-1}$ on average), the isocline is constrained mainly by the toxicity of the PAHs in the sediment pore water. This implies a limit to the tolerance to PAHs, which in this case is calculated as $\log\sum C_{sed} \approx 4.82$ (65 000 mg/kg), and no limit to the tolerance (no upper bound) for AC (part b of Figure 4).

Once the isocline of zero growth has been estimated, one can predict what range of AC additions may be considered safe for a species, if safe is defined as sustaining a habitat quality sufficient for population growth. For instance, for a sediment with $\log\sum C_{sed}$ = 4.30 (20 000 mg/kg), population growth is expected to occur between AC concentrations of 0.5 and 5.5% (Figure 4). We emphasize that this result is conditional, that is it depends on the model formulations, the species used, the conditions in the test, and the specific sediment employed in the tests. However, individual PAH profiles in aquatic sediments may show limited variation. For instance, the PAH contamination in the PH sediment we studied was identified to be of pyrogenic origin.[4] Consequently, we assume that the isoclines for *G. pulex* and *A. aquaticus* may look very similar for other sediments of pyrogenic origin, because PAH concentration ratios for this type of sediments show a narrow range.[48]

The results of the uncertainty analysis show that the uncertainties in model parameters at both ends of their uncertainty ranges (either ± SD or ±10%) yield considerable uncertainty in the exact position of the isoclines (Figure S2 of the Suppoting Information). It is still possible, however, to define safe ranges of AC application, albeit by taking the conservative estimates of the isoclines that define the state space in which populations of *G. pulex* and *A. aquaticus* increase over time (Figure S2 of the Suppoting Information).

Using the same approach, isoclines were also calculated using a Langmuir sorption approach (eq 9). In this scenario the isoclines show the same general shape as the ones calculated with the Freundlich model, with almost identical values for AC% (Figure S3 of the Suppoting Information). However, the isocline values for $\log\sum C_{sed}$ are 1.3 to 1.8 unit lower than calculated using the Freundlich model (Figure 4 vs Figure S3 of the Suppoting Information). This is explained by the fact that, at equal values of $C_W$, the Langmuir model (eq 9) calculates lower values for $\sum C_{sed}$ than the Freundlich model (eq 8) does, due to inclusion of sorption saturation. At equal values of $\sum C_{sed}$ the Langmuir model thus calculates higher aqueous phase concentrations resulting in higher toxicity and to a smaller area in the state space where biomass development is positive ($dB/dt > 0$). In untreated sediment (AC % = 0), the population equilibrium is calculated at $\log\sum C_{sed} \approx 2.72$ (530 mg/kg) for both species (Figure S3 of the Supporting Information), which is three times lower than predicted with the Freundlich isotherms (Figure 4). This result agrees better to the experimental observation that both species did not survive in bioassays with untreated PH sediment but did survive when an AC dose of 1% was added.[4] Increasing $\log\sum C_{sed}$ from 2.72 to a theoretical value of 3.34 (i.e., 2200 mg/kg) now requires an AC dose of 0% increasing to 4%, that is, about 1%


dx.doi.org/10.1021/es2044954 | *Environ. Sci. Technol.* 2012, 46, 4975−4984

AC per 900 mg/kg of extra $\sum C_{sed}$ (Figure S3 of the Suppoting Information). This agrees to an AC binding capacity of 0.090 g PAH per 1 g of AC, which complies to the maximum adsorption capacities ($\sum C_{max}$) provided by van Noort,[32] which were used as input in the model. On the basis of the Langmuir scenario (Figure S3 of the Suppoting Information), a maximum of about 1 g/kg PAH with AC lower than 4% would be a conservative estimate of the limits for population growth.

In conclusion, a Langmuir modeling approach showed better agreement with experimental observations than a Freundlich approach. Although higher AC concentrations might have an effect on the biomass development of sensitive species such as *G. pulex*, the overall effects of AC addition to PAH contaminated sites are expected to be advantageous as long as AC is added at optimum concentrations (1−4%). At these AC concentrations, the positive effects of AC in terms of reducing PAH toxicity outweigh direct negative effects of AC.

**Implications.** The previous sections have shown how concepts from population ecology, environmental chemistry, and ecotoxicology may be unified in a simple framework to evaluate the interaction between multiple stressors, where one of the stressors has an advantageous (antagonistic) effect on the other. Once sufficient geochemical characteristics of sediments are known, like in a typical site-specific risk assessment, the state space where these characteristics support population growth of benthic communities can be simulated, taking into account the uncertainty in input parameters. If necessary, equations for population growth (eq 3), dose−response (eq 4), or exposure modeling (eq 8 and 9) may be adapted. This may include more detail in modeling for increased realism in higher tier assessments. For instance, better parametrization of Langmuir type sorption models (eq 9), which also may account for sorption competition, may further increase realism at the high concentration ranges for $\sum C_{sed}$, such as they may occur at hot spot locations. Because higher realism implies increased uncertainty, one might also choose for simplification of the sorption or effect submodels (e.g., refs 26 and 27). If accurate pore water concentration data are available, it may be preferred to use eq 7 directly, thereby omitting relatively complex sorption submodels. Furthermore, the validity of current assumptions such as additivity of AC and toxicant mortality, and translatability of AC effects across sediments may be studied in more detail.

The current framework was evaluated for a specific case but may be generally applicable to cases where sorbents are added to soils or sediments as amendments. Several recent approaches in sediment or soil treatment use the concept of sorbent addition, using, for example, biochars, nanoparticles, or clays.[2,49] As such, the conceptual modeling approach presented here may be used as a supporting tool in risk assessment or when designing sediment remediation scenarios. Obviously, for field applications more factors and processes need to be considered. For instance, the current model implementation addressed the potential effects of sorbents shortly after amendment of sediment, which is a relevant time frame for recolonization of benthic habitats. However, although this was realistic in terms of test species, environmental conditions and use of natively contaminated natural sediments, effects may be different at longer time scales and for other types of AC. Reported effects of AC from laboratory experiments may be less pronounced in ecologically realistic field settings. After all, deposition of fresh organic matter and dispersion of AC will form a new habitat for benthic species and may decrease or even eliminate effects observed in laboratory studies.[50] Furthermore, effects of AC could originate from reduction in the availability of trace nutrients,[3] which may be replenished more easily in an open system. Consequently, future work has to address the model's potential for field validation and application, including more accurate constraining of parameters where necessary and understanding their variability under natural conditions.[27,28] This includes accounting for other variables that are important for biomass growth, like nutrient loads, dissolved oxygen content, presence of macrophytes or carrying capacity.[51,52] Also, the use of other indicators of improved environmental quality than biomass, like biodiversity or species abundance, may be explored. Field-relevant processes such as colonization, competition and predation are available already in ecological models[52] and can easily be linked to the model constructs proposed and evaluated in this paper. Future work should also include validation of parameters using field data from demonstration sites.

## ■ ASSOCIATED CONTENT

### Supporting Information

Derivation of a dual domain Langmuir equation in terms of distribution coefficients $K_d$. Geochemical characteristic of the sediment. Additional figures on mortality rates, uncertainty analysis and Langmuir model - based isoclines. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: darya.kupryianchyk@wur.nl, tel: +31 317 482665, fax: +31 317 419000.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This study was funded by the Dutch Technology Foundation STW, project nr 10030. We acknowledge additional support from Alterra, RIVM, Deltares, Boskalis Dolman, Norit, Oostwaardhoeve VOF and De Vries & Van de Wiel.

## ■ REFERENCES

(1) Larsson, P. Contaminated sediments of lakes and oceans act as sources of chlorinated hydrocarbons for release to water and atmosphere. *Nature* **1985**, *317* (6035), 347−349.

(2) Ghosh, U.; Luthy, R. G.; Cornelissen, G.; Werner, D.; Menzie, C. A. In situ sorbent amendments: A new direction in contaminated sediment management. *Environ. Sci. Technol.* **2011**, *45* (4), 1163−1168.

(3) Jonker, M. T. O.; Hoenderboom, A. M.; Koelmans, A. A. Effects of sedimentary sootlike materials on bioaccumulation and sorption of polychlorinated biphenyls. *Environ. Toxicol. Chem.* **2004**, *23*, 2563−2570.

(4) Kupryianchyk, D.; Reichman, E. P.; Rakowska, M. I.; Peeters, E. T. H. M.; Grotenhuis, J. T. C.; Koelmans, A. A. Ecotoxicological effects of activated carbon amendments on macroinvertebrates in nonpolluted and polluted sediments. *Environ. Sci. Technol.* **2011**, *45* (19), 8567−8574.

(5) Sun, X. L.; Ghosh, U. The effect of activated carbon on partitioning, desorption, and biouptake of native polychlorinated biphenyls in four freshwater sediments. *Environ. Toxicol. Chem.* **2008**, *27* (11), 2287−2295.

(6) Werner, D.; Higgins, C. P.; Luthy, R. G. The sequestration of PCBs in Lake Hartwell sediment with activated carbon. *Water Res.* **2005**, *39* (10), 2105−2113.

(7) McLeod, P. B.; Luoma, S. N.; Luthy, R. G. Biodynamic modeling of PCB uptake by Macoma balthica and Corbicula fluminea from sediment amended with activated carbon. *Environ. Sci. Technol.* **2008**, *42* (2), 484−490.
(8) McLeod, P. B.; van den Heuvel-Greve, M. J.; Luoma, S. N.; Luthy, R. G. Biological uptake of polychlorinated biphenyls by Macoma balthica from sediment amended with activated carbon. *Environ. Toxicol. Chem.* **2007**, *26* (5), 980−987.
(9) Millward, R. N.; Bridges, T. S.; Ghosh, U.; Zimmerman, J. R.; Luthy, R. G. Addition of activated carbon to sediments to reduce PCB bioaccumulation by a polychaete (*Neanthes arenaceodentata*) and an amphipod (*Leptocheirus plumulosus*). *Environ. Sci. Technol.* **2005**, *39* (8), 2880−2887.
(10) Koelmans, A. A.; Jonker, M. T. O.; Cornelissen, G.; Bucheli, T. D.; van Noort, P. C. M.; Gustafsson, O. Black carbon: The reverse of its dark side. *Chemosphere* **2006**, *63* (3), 365−377.
(11) Burgess, R. M.; et al. Evaluation of the effects of coal fly ash amendments on the toxicity of a contaminated marine sediment. *Environ. Toxicol. Chem.* **2009**, *28* (1), 26−35.
(12) Ho, K. T.; et al. Use of powdered coconut charcoal as a toxicity identification and evaluation manipulation for organic toxicants in marine sediments. *Environ. Toxicol. Chem.* **2004**, *23* (9), 2124−2131.
(13) Rakowska, M. I.; Kupryianchyk, D.; Harmsen, J.; Grotenhuis, T.; Koelmans, A. A. In situ remediation of contaminated sediments using carbonaceous materials: A critical review. *Environ. Toxicol. Chem.* **2012**, *31* (4), 693−704.
(14) Jonker, M. T. O.; Suijkerbuijk, M. P. W.; Schmitt, H.; Sinnige, T. L. Ecotoxicological effects of activated carbon addition to sediments. *Environ. Sci. Technol.* **2009**, *43* (15), 5959−5966.
(15) De Lange, H. J.; Sperber, V.; Peeters, E. T. H. M. Avoidance of polycyclic aromatic hydrocarbon-contaminated sediments by the freshwater invertebrates Gammarus pulex and Asellus aquaticus. *Environ. Toxicol. Chem.* **2006**, *25* (2), 452−457.
(16) Peeters, E. T. H. M.; de Lange, H. J.; Lurling, M. Variation in the behavior of the amphipod Gammarus pulex. *Hum. Ecol. Risk Assess.* **2009**, *15* (1), 41−52.
(17) Rubach, M. N.; Baird, D. J.; van den Brink, P. J. A new method for ranking mode-specific sensitivity of freshwater arthropods to insecticides and its relationship to biological traits. *Environ. Toxicol. Chem.* **2010**, *29* (2), 476−487.
(18) Traas, T. P.; Stab, J. A.; Kramer, P. R. G.; Cofino, W. P.; Aldenberg, T. Modeling and risk assessment of tributyltin accumulation in the food web of a shallow freshwater lake. *Environ. Sci. Technol.* **1996**, *30* (4), 1227−1237.
(19) Kupryianchyk, D.; Rakowska, M. I.; Grotenhuis, J. T. C.; Koelmans, A. A. In situ sorption of hydrophobic organic compounds to sediment amended with activated carbon. *Environ. Pollut.* **2012**, *161* (0), 23−29.
(20) Accardi-Dey, A.; Gschwend, P. M. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environ. Sci. Technol.* **2002**, *36* (1), 21−29.
(21) Verhulst, P. F. Notice sur la loi que la population poursuit dans son accroissement. *Correspondance mathématique et physique* **1838**, *10*, 113−121.
(22) Hallam, T. G.; Clark, C. E.; Lassiter, R. R. Effects of toxicants on populations: A qualitative approach I. Equilibrium environmental exposure. *Ecol. Model.* **1983**, *18* (3−4), 291−304.
(23) Hallam, T. G.; Clark, C. E.; Jordan, G. S. Effects of toxicants on populations: A qualitative approach II. first order kinetics. *J. Math. Biol.* **1983**, *18* (1), 25−37.
(24) Traas, T. P.; Janse, J. H.; Aldenberg, T.; Brock, T. C. M. A food web model for fate and direct and indirect effects of Dursban® 4E (active ingredient chlorpyrifos) in freshwater microcosms. *Aquat. Ecol.* **1998**, *32* (2), 179−190.
(25) Cornelissen, G.; Gustafsson, O.; Bucheli, T. D.; Jonker, M. T. O.; Koelmans, A. A.; van Noort, P. C. M. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* **2005**, *39* (18), 6881−6895.
(26) Arp, H. P. H.; Azzolina, N. A.; Cornelissen, G.; Hawthorne, S. B. Predicting pore water EPA-34 PAH concentrations and toxicity in pyrogenic-impacted sediments using pyrene content. *Environ. Sci. Technol.* **2011**, *45* (12), 5139−5146.
(27) Hawthorne, S. B.; Grabanski, C. B.; Miller, D. J. Measured partitioning coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: Part 1. Koc values. *Environ. Toxicol. Chem.* **2006**, *25* (11), 2901−2911.
(28) Hawthorne, S. B.; Grabanski, C. B.; Miller, D. J. Measured partition coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: part 2. Testing the KocKbc two carbon-type model. *Environ. Toxicol. Chem.* **2007**, *26* (12), 2505−2516.
(29) Koelmans, A. A.; Meulman, B.; Meijer, T.; Jonker, M. T. O. Attenuation of polychlorinated biphenyl sorption to charcoal by humic acids. *Environ. Sci. Technol.* **2009**, *43* (3), 736−742.
(30) Jonker, M. T. O.; Koelmans, A. A. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations. *Environ. Sci. Technol.* **2002**, *36* (17), 3725−3734.
(31) Hale, S. E.; Kwon, S.; Ghosh, U.; Werner, D. Polychlorinated biphenyl sorption to activated carbon and the attenuation caused by sediment. *Global Nest J.* **2010**, *12* (3), 318−326.
(32) Van Noort, P. C. M.; Jonker, M. T. O.; Koelmans, A. A. Modeling maximum adsorption capacities of soot and soot-like materials for PAHs and PCBs. *Environ. Sci. Technol.* **2004**, *38* (12), 3305−3309.
(33) Van Noort, P. C. M.; Jonker, M. T. O.; Koelmans, A. A. Response to comment on "Modeling maximum adsorption capacities of soot and soot-like materials for PAHs and PCBs". *Environ. Sci. Technol.* **2005**, *39* (1), 383−384.
(34) Werner, D.; Karapanagioti, H. K. Comment on "Modeling maximum adsorption capacities of soot and soot-like materials for PAHs and PCBs. *Environ. Sci. Technol.* **2004**, *39* (1), 381−382.
(35) Graca, M. A. S.; Maltby, L.; Calow, P. Importance of fungi in the diet of Gammarus pulex and Asellus aquaticus. 2. Effects on growth, reproduction and physiology. *Oecologia* **1993**, *96* (3), 304−309.
(36) Oertli, B. Leaf litter processing and energy flow through macroinvertebrates in a woodland pond (Switzerland). *Oecologia* **1993**, *96* (4), 466−477.
(37) Adcock, J. A. Energetics of a population of Asellus aquaticus (Crustacea, Isopoda): Respiration and energy budgets. *Freshwater Biol.* **1982**, *12* (3), 257−269.
(38) Park, R. A.; Clough, J. S.; Wellman, M. C. AQUATOX: Modeling environmental fate and ecological effects in aquatic ecosystems. *Ecol. Model.* **2008**, *213* (1), 1−15.
(39) Smit, M. G. D.; Hendriks, A. J.; Schobben, J. H. M.; Karman, C. C.; Schobben, H. P. M. The variation in slope of concentration-effect relationships. *Ecotoxicol. Environ. Safety* **2001**, *48* (1), 43−50.
(40) Sanz-Lázaro, C.; Marin, A.; Borredat, M. Toxicity studies of polynuclear aromatic hydrocarbons (PAHs) on European Amphipods. *Toxicol. Mech. Methods* **2008**, *18* (4), 323−327.
(41) *Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures*; EPA/600/R-02/013; U.S.E.P. Agency: Office of Research and Development Washington, DC 20460, 2003; http://www.epa.gov/nheerl/download_files/publications/PAHESB.pdf.
(42) Van Noort, P. C. M. Estimation of amorphous organic carbon/water partition coefficients, subcooled aqueous solubilities, and n-octanol/water distribution coefficients of alkylbenzenes and polycyclic aromatic hydrocarbons. *Chemosphere* **2009**, *76* (4), 578−578.
(43) Booij, K.; Sleiderink, H. M.; Smedes, F. Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. *Environ. Toxicol. Chem.* **1998**, *17* (7), 1236−1245.
(44) Accardi-Dey, A.; Gschwend, P. M. Reinterpreting literature sorption data considering both absorption into organic carbon and

adsorption onto black carbon. *Environ. Sci. Technol.* **2003**, *37* (1), 99−106.
(45) Hale, S. E.; Werner, D. Modeling the mass transfer of hydrophobic organic pollutants in briefly and continuously mixed sediment after amendment with activated carbon. *Environ. Sci. Technol.* **2010**, *44* (9), 3381−3387.
(46) Lohmann, R.; MacFarlane, J. K.; Gschwend, P. M. Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York, Harbor sediments. *Environ. Sci. Technol.* **2005**, *39* (1), 141−148.
(47) Moermond, C. T. A.; Zwolsman, J. J. G.; Koelmans, A. A. Black carbon and ecological factors affect in situ biota to sediment accumulation factors for hydrophobic organic compounds in flood plain lakes. *Environ. Sci. Technol.* **2005**, *39* (9), 3101−3109.
(48) Yunker, M. B.; Macdonald, R. W.; Vingarzan, R.; Mitchell, R. H.; Goyette, D.; Sylvestre, S. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* **2002**, *33* (4), 489−515.
(49) Karn, B.; Kuiken, T.; Otto, M. Nanotechnology and in situ remediation: A review of the benefits and potential risks. *Environ. Health Perspect.* **2009**, *117* (12), 1823−1831.
(50) Cho, Y. M.; Ghosh, U.; Kennedy, A. J.; Grossman, A.; Ray, G.; Tomaszewski, J. E.; Smithenry, D. W.; Bridges, T. S.; Luthy, R. G. Field application of activated carbon amendment for in-situ stabilization of polychlorinated biphenyls in marine sediment. *Environ. Sci. Technol.* **2009**, *43* (10), 3815−3823.
(51) Galic, N.; Hommen, U.; Baveco, J. M. H.; van den Brink, P. J. Potential application of population models in the European ecological risk assessment of chemicals. II. Review of models and their potential to address environmental protection aims. *Integr. Environ. Assess. Manag.* **2010**, *6* (3), 338−360.
(52) Koelmans, A. A.; van der Heijde, A.; Knijff, L. M.; Aalderink, R. H. Integrated modelling of eutrophication and organic contaminant fate and effects in aquatic ecosystems. A review. *Water Res.* **2001**, *35* (15), 3517−3536.