

# Biological Responses to Activated Carbon Amendments in Sediment Remediation

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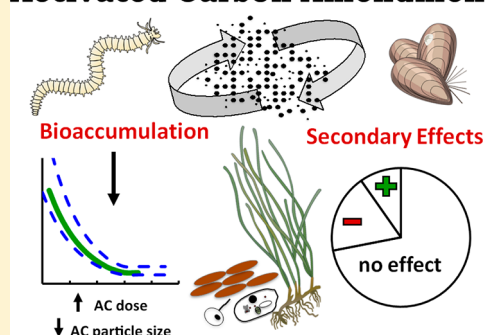
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**S** Supporting Information

**ABSTRACT:** Sorbent amendment with activated carbon (AC) is a novel in situ management strategy for addressing human and ecological health risks posed by hydrophobic organic chemicals (HOCs) in sediments and soils. A large body of literature shows that AC amendments can reduce bioavailability of sediment-associated HOCs by more than 60–90%. Empirically derived biodynamic models can predict bioaccumulation in benthic invertebrates within a factor of 2, allowing for future scenarios under AC amendment to be estimated. Higher AC dose and smaller AC particle size further reduce bioaccumulation of HOCs but may induce stress in some organisms. Adverse ecotoxicity response to AC exposure was observed in one-fifth of 82 tests, including changes in growth, lipid content, behavior, and survival. Negative effects on individual species and benthic communities appear to depend on the characteristics of the sedimentary environment and the AC amendment strategy (e.g., dose and particle size). More research is needed to evaluate reproductive end points, bacterial communities, and plants, and to link species- and community-level responses to amendment. In general, the ability of AC to effectively limit the mobility of HOCs in aquatic environments may outshine potential negative secondary effects, and these outcomes must be held in comparison to traditional remediation approaches.

## Activated Carbon Amendment



## INTRODUCTION

Sediments are often sinks and long-term reservoirs for hydrophobic organic chemicals (HOCs) released into the environment. Organisms can accumulate HOCs predominantly in lipid-rich tissues, and the tendency to concentrate through dietary transference in the food web, biomagnification, can result in critical body burdens in higher trophic species such as birds, fish, and humans. The risks posed by persistent, bioaccumulative, and toxic chemicals in sediments frequently need to be addressed through remediation activities to restore ecological vitality and protect human health.

The cleanup process of sediment sites is complex and creates unique challenges due to expensive cleanup strategies, large and diverse sediment sites, and presence of ecologically valuable resources or legislatively protected species or habitats.<sup>1,2</sup> In addition to risk reduction, limiting impacts to the existing benthic community or restoration of an improved ecological status may be included as a remediation goal. Traditional approaches for remediation of contaminated sediments include dredging (e.g., sediment excavation), conventional capping (e.g., cover by clean material), and monitored natural recovery. While these different approaches have and will continue to prove useful, there are also associated limitations to their use, as data limitations, and physical and political obstacles can challenge successful risk reduction.<sup>3–5</sup> New developments in remediation approaches are needed that either supplement or

provide alternatives to existing methods, are less energy-intensive, less expensive, and less disruptive to the environment, are able to reduce human and ecosystem exposure, and are defensible through well-grounded scientific understanding of contaminant fate processes. A combination of strategies including in situ approaches is likely to provide the most efficient long-term solution for dealing with contaminated sediments.

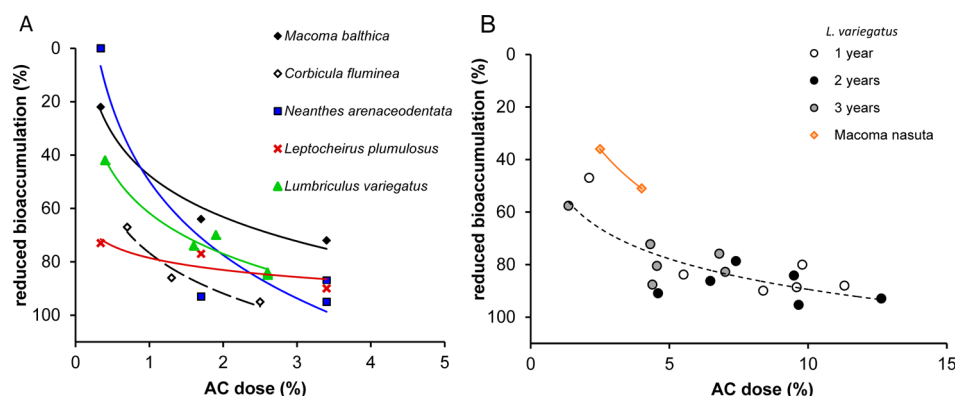
One emerging in situ strategy to reduce exposure to HOCs is the application of sorbent amendments. Condensed, carbonaceous “geosorbents” or “black carbons”, natural or anthropogenic, present in sediment are observed to strongly sorb HOCs and often control chemical availability.<sup>6–13</sup> The use of engineered black carbons, that is, activated carbon (AC), to augment sequestration and reduce bioavailability in situ has therefore been pursued as a sediment remediation strategy. Rather than resulting in removal and relocation or physical isolation of contaminated material, strong adsorption and slow kinetics of contaminant desorption from amendments reduces exposure and limits contaminant redistribution in the environment.<sup>8,14–22</sup> Capital costs are likely to be lower for sorbent

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**Figure 1.** Reduction of polychlorinated biphenyl bioaccumulation upon exposure to activated carbon (75–300  $\mu\text{m}$ , type TOG, Calgon Corp.) at different doses (% by dry weight of sediment) relative to exposure to untreated sediment for five benthic invertebrates, shown for (A) laboratory-amended sediment with *Macoma balthica*,<sup>41</sup> *Neanthes arenaceodentata*,<sup>26,42</sup> *Leptocheirus plumulosus*,<sup>26</sup> *Lumbriculus variegatus*,<sup>22,43</sup> and *Corbicula fluminea* and (B) field-amended sediment with *L. variegatus* shown temporally (1–3 years) after a mixed application<sup>30</sup> and *Macoma nasuta*<sup>14,45</sup> at 7 and 18 months after application (2.5% and 4% AC, respectively) with reductions compared to untreated reference sites. Lines indicate logarithmic fits.

amendment than conventional strategies,<sup>23</sup> and preliminary life cycle assessment has shown that through use of biomass-derived AC, the ecological footprint of AC amendments may be comparable to natural attenuation.<sup>24</sup>

Activated carbon is particularly effective at reducing bioavailability of sediment-associated HOCs due to a large surface area resulting from its extensive porous network. Sorption to AC is several orders of magnitude stronger than to organic matter occurring in sediments.<sup>8,25,26</sup> Adsorption to AC is a process that has been taken advantage of in drinking water treatment, poison control, and contaminant spill response for decades.<sup>27,28</sup> Five in situ pilot-scale projects have employed AC amendments in sediments and one in soil between 2004 and 2010.<sup>14,23,29–31</sup> Thus far, three of these pilot studies have published results demonstrating deployment techniques and their effectiveness by (1) achieving intended AC dose and stability of the amendment in relatively depositional sediment sites, and (2) reducing in situ bioavailability and mobility of contaminants.<sup>14,20,23,29–31</sup>

While other geosorbents may also strongly sequester HOCs and reduce bioavailability, the difference in origin or production methods result in varying physical and chemical properties. For example, charcoals or chars produced at lower temperatures than AC have lower surface area, porosity and C/H ratio in addition to higher ash content, and may contain some amount of bioavailable contaminants.<sup>32–35</sup> These properties could influence both primary (i.e., bioavailability) and secondary (i.e., toxicity) effects. Biochar as an amendment to sequester organic and inorganic pollutants in concert with carbon sequestration and the potential effects on soil biota have been previously reviewed.<sup>36,37</sup> Since AC has been the geosorbent of choice for the majority of pilot-scale demonstrations of in situ sediment amendments addressing HOCs,<sup>23</sup> the discussion is limited to AC in the present review.

Over the past decade, different aspects of sorbent amendments have been reviewed including mechanisms of contaminant sequestration, overview of end points to evaluate effectiveness, amendment technologies, sorption theory, and ecotoxicological effects on benthic species and communities.<sup>13,23,29,38,39</sup> The review by Luthy et al. (1997) focused on sequestration and distribution of HOCs within different geosorbent domains.<sup>38</sup> Their review concluded that a limited

understanding of microscale distribution processes presents an obstacle to assessing exposure and toxicity. Advanced knowledge of microscale processes gained during the following decade was reviewed in 2005 by Cornelissen et al.<sup>13</sup> The authors also pointed to implications of sequestration on bioaccumulation and biodegradation. Ghosh et al. recently featured application technologies for AC addition to field sediments.<sup>23</sup> Rakowska et al. (2012) presented an analysis of current amendment technologies and sorption theory as well as a summary of ecotoxicological effects on benthic species and communities.<sup>29</sup>

In the present review we focus explicitly on biological responses to AC amendments. First, we review the dependence of measured HOC bioaccumulation in benthic invertebrates on AC dose and particle size and extend this to predictive biodynamic modeling. Then, we further evaluate potential negative effects of AC amendment on individual benthic invertebrate species and communities in the context of AC dose, AC particle size, and sediment type. For individual species, we quantitatively evaluate the occurrence of adverse effects, that is, changes in survival, growth, lipid content, and behavior. For benthic communities, we review the outcome of field tests with AC amendments describing species abundance, diversity, and recruitment. Even though much progress has been made over the past decade toward a better understanding of the effects of AC amendments on biota, we conclude this review with some recommendations for future research that may be needed to gain wider regulatory acceptance of this novel remediation technology.

## ■ BENTHIC INVERTEBRATE SPECIES

**Effect of AC Dose, Particle Size, and Mass Transfer Kinetics on Bioaccumulation of HOCs.** Mass transfer of HOCs to AC in sediment has been demonstrated to follow a two-step process of initial fast release of a readily available chemical fraction from sediment and subsequent transfer to AC, with the result being a rapid initial reduction of aqueous concentration. This fast process is followed by a slower incremental release of the strongly sorbed sediment fraction.<sup>8,36,40</sup> The effectiveness of AC amendments to reduce bioaccumulation of HOCs in benthic invertebrates mainly depends on this process of desorption from the native sediment

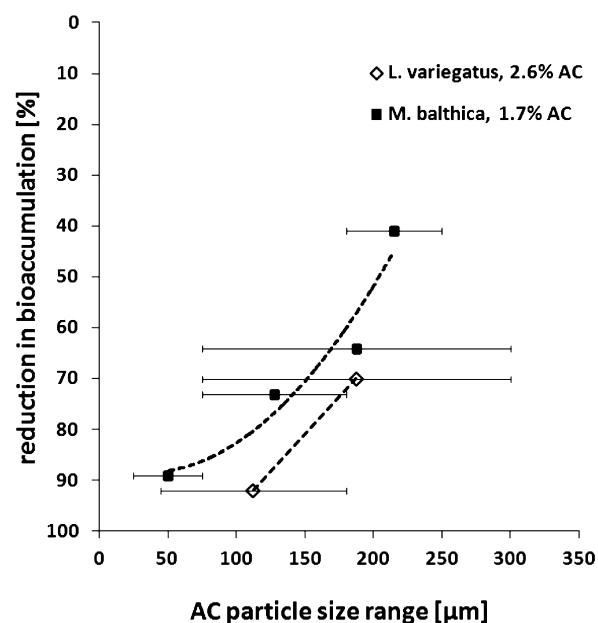
particles and subsequent sorption to AC. Consequently, besides sediment characteristics, the choice of AC dose and particle size affects sequestration of HOCs. For example, the effect of AC dose on bioaccumulation of PCBs for deposit and filter feeding invertebrates are presented in Figure 1. Here we present PCB data because analogous laboratory amendment and exposure setups allow direct comparison of several studies (Figure 1A). These studies employed the same AC type (TOG, Calgon Carbon Corp.), particle size distribution (75–300  $\mu\text{m}$ ) and amendment technique (28 days AC and sediment contact, on a roller) and report total PCB tissue concentrations (sum of 92 congeners and coeluting congeners). Data from two pilot-scale field trials using similar AC types (coal-based AC; Calgon Carbon Corp.) and size are also displayed (Figure 1B).

The employed AC doses range over 1 order of magnitude (0.34% to >3.4%) but are well within target values for in situ amendments. Low AC doses, < 1%, reduced PCB bioaccumulation significantly for *Leptocheirus plumulosus* (73%) and *Corbicula fluminea* (67%), while reductions were lower for *Lumbriculus variegatus* (42%) and *Macoma balthica* (22%). The polychaete *Neanthes arenaceodentata* did not respond to such low AC doses. This variation in response likely reflects differences in organism behavior, such as sediment contact, feeding, and respiration. However, AC doses of 3% or more resulted in effective reduction of bioaccumulation for all five species, in the range of 72% to 95% compared to untreated sediments.

Field exposure tests at Hunters Point (CA) and Grasse River (NY) have similarly reported decreasing bioavailability with increasing AC dose up to approximately 3.5–5% (Figure 1B).<sup>14,30</sup> The reduction of bioaccumulation of PCBs by *Macoma nasuta* deployed in the field at Hunters Point is less than for laboratory tests<sup>14,16</sup> and in comparison to observations for other invertebrates with similar dose (Figure 1A). At Hunters Point, sediment from surrounding, untreated areas deposited on top of the AC treated sediment layer<sup>14</sup> which resulted in higher pore water concentrations in the top 0.5 cm and masked the effect of the underlying AC amendment (0.5–3 cm).<sup>16</sup> At the Grasse River application site, doses above 5% AC did not further reduce bioaccumulation.<sup>30</sup> Most of the reduction of bioaccumulation for amended Grasse River sediments was observed after one year of the in situ amendment, yet some further improvement was reported over time for more highly chlorinated PCBs that undergo slower mass transfer kinetics.

Bioaccumulation also decreases with decreasing AC particle size at a constant AC dose (Figure 2). For a given dose of AC, a smaller grain size offers more surface area and shorter diffusional distances, which facilitate faster sorption kinetics.<sup>36</sup> The particle size dependency can also be observed in decreasing aqueous concentrations of HOCs with smaller particle size of applied AC.<sup>26,46</sup> Similar to the effect of AC dose, reduced kinetics of sequestration by coarser AC results in a significantly longer contact time required to reach final treatment efficiencies of months to several years.<sup>36</sup>

The general trends of decreasing bioaccumulation of HOCs with increasing AC dose and decreasing particle size parallel observations for aqueous phase concentrations (e.g., refs 14,26,40, and 48). In sediment, surface fouling or competitive sorption, for example, pore blocking by biofilms or humic substances, can reduce the capacity of AC to sorb target compounds and/or slow down kinetics.<sup>36,44,49–52</sup> Distribution coefficients established in sediment-free systems therefore



**Figure 2.** Reduced bioaccumulation of polychlorinated biphenyls relative to exposure to untreated sediment for *Lumbriculus variegatus* with 2.6% amendments<sup>47</sup> and *Macoma balthica* with 1.7% amendments<sup>41</sup> related to activated carbon particle sizes. Bars represent the size range of particles employed.

result in model overpredictions of aqueous phase concentration reductions following amendment.<sup>31,36,53</sup> Although diminished, the sorption capacity of AC can still be effective after contact in field sediments for several years,<sup>54</sup> or after simulated aging by physical (freeze–thaw cycles or heat), or biological (addition of nutrients, microorganisms) treatments.<sup>55</sup> Studies employing 2–4% AC amendments by dry weight of the sediment have consistently shown significant reduction of contaminant aqueous concentrations, for example, by 80–99% for PCBs,<sup>22,56,57</sup> by 60–94% for PAHs,<sup>49,50,56</sup> and by 67–83% for DDTs.<sup>58</sup> The extent of sorption attenuation will likely depend on characteristics of the AC, such as pore size distribution, and relative abundance of nontarget chemical species per available AC sorption site.<sup>54,59–61</sup>

Slower kinetics of sequestration result in longer times to reach the ultimate treatment efficiency at steady state and may partially be compensated for by reducing diffusional path-lengths with an increased AC dose,<sup>62,63</sup> finer AC particle size or more homogeneous distribution of the AC within the sediment. For example, reduction of PCB bioaccumulation by *L. variegatus* increased from 70% to 85% when the sediment and AC were mixed for 28 days instead of only 2 min.<sup>22,43</sup> Homogeneous distribution of AC in the field can be improved by enhanced mixing, multiple mixing periods, sequential reapplications, or use of smaller particle sizes. Mixing may be accomplished, for example, by mechanical tillers,<sup>30,45</sup> or the use of pressurized water jets.<sup>64</sup> Active bioturbation and hydrological site conditions, such as mechanical dispersion by tidal current or wave motion, or pore water flow can also enhance mixing of AC. Cho et al. demonstrated that the AC distribution determines the remedial duration using a numerical model.<sup>40</sup> The authors predicted that reduction in pore water concentration of PCB101 of 80% can be achieved within 1 year for a homogeneous deployment of AC, while this same decrease may take up to 6 years for heterogeneous deployments. Modeled time estimates to achieve optimal sequestra-



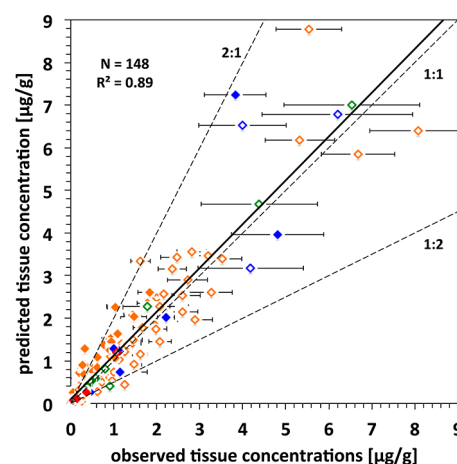
tion may help to guide sediment managers toward the minimal time required for postdeployment monitoring plans.

It can be concluded that organisms accumulate less HOCs at a higher dose, finer particle size, and more homogeneous distribution of AC after a sufficient AC–sediment contact time since mass transfer kinetics of sequestration are enhanced. Field observations suggest a threshold dose beyond which sequestration is controlled by mass transfer of the slowly released fraction of HOCs from sediment. AC dose, AC particle size, and mixing intensity must be considered within the context of potential toxicity and extent of the physical disturbance of the benthic community,<sup>65</sup> in addition to deployment practicability and capital costs.

**Biodynamic Modeling—Assessing Organism Exposure.** Direct measurements of bioaccumulation are key to evaluate the success of a remedial approach, like AC amendment, that limits exposure by altering the binding capacity of sediments. However, measuring bioaccumulation can be complex, for example, when field sites are not easily accessible, and tests are time-consuming and costly. Evaluating the effect of AC amendments on bioaccumulation was also challenging in the past in cases where only small pilot areas were remediated and the untreated, surrounding sediment influenced measurements.<sup>14,16,66,67</sup> Model prediction of chemical uptake by organisms in a given environment can provide a relatively quick and inexpensive estimate of bioaccumulation and can be used to simulate future scenarios, for example, the response to changes in contaminant bioavailability. These models can also be employed to estimate the extent to which bioavailability has to be decreased to reach target concentrations in organisms of interest.<sup>68</sup> In the context of sediment management, modeling bioaccumulation can be a practical complement to direct measurement of bioaccumulation during remedial planning as well as to describe outcomes during monitoring post remediation.

Biodynamic modeling, also known as bioenergetic or biokinetic modeling, quantifies chemical concentrations in the tissue of an organism by the balance of species- and matrix-specific uptake and loss mechanisms.<sup>69</sup> As described by Luoma et al., the biodynamic model first “deconstructs” bioaccumulation by quantifying each uptake and loss component mechanistically, and then using this information “reconstructs” bioaccumulation for specific exposure conditions.<sup>70</sup> Previous studies have derived empirical values for species-specific physiological parameters for exposure to sediment polluted with PCBs and sediment amended with AC. These parameters are presented in Supporting Information (SI) Table S1 for the facultative deposit feeding clam *M. balthica*,<sup>44</sup> the filter feeding clam *C. fluminea*,<sup>44</sup> the deposit feeding polychaete *N. arenaceodentata*,<sup>42</sup> and the deposit feeding oligochaete *Lumbriculus variegatus*.<sup>71</sup> A description of the parameters of the biodynamic model is detailed in the SI. Here, we summarize the use of biodynamic modeling to predict bioaccumulation before and after AC amendments.

Data in Figure 3 present observed PCB tissue concentrations against the values predicted with the biodynamic model for these four, aforementioned benthic invertebrates. The predictions were within a factor of 1.6 on average (maximum 4.8) over a wide range of tissue concentrations (<0.1–10 µg/g) and only 14% of the predictions were off by a factor greater than 2. The model was capable of predicting high internal concentrations that are expected from polluted, untreated sediment exposure as well as very low concentrations that are

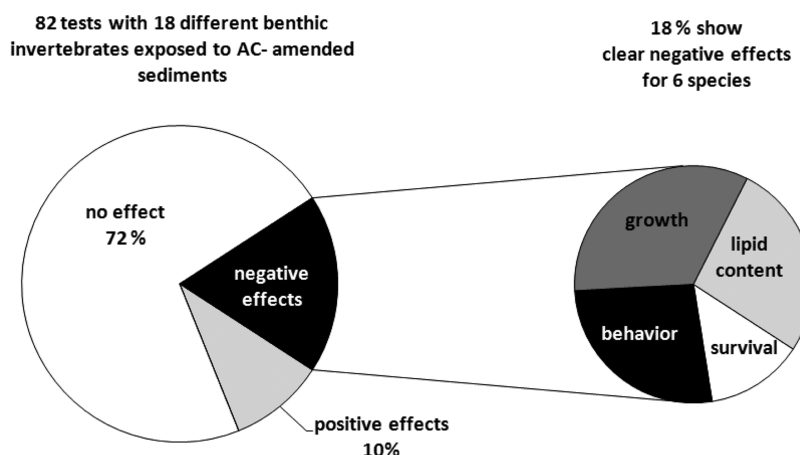


**Figure 3.** Measured tissue concentrations of polychlorinated biphenyls against predicted values employing the biodynamic model for *Macoma balthica* (blue),<sup>41</sup> *Nereis arenaceodentata* (green),<sup>42</sup> *Corbicula fluminea* (red),<sup>41</sup> *Lumbriculus variegatus* (orange)<sup>71</sup> exposed to untreated (open symbols) and activated carbon amended sediments (closed symbols). Error bars represent one standard deviation of the measured concentrations. Solid line represents the linear fit of all data ( $N = 148$ ), dashed lines represent the 1:1, 2:1, and 1:2 relationships.

present in organisms exposed to AC-amended sediments (see also SI Figure S1). Biological variability contributes mostly to the standard deviation on the measured data. The uncertainty of the model predictions does not simply depend on the propagation of errors of each parameter in the model because physiological parameters can be dependent on each other. For example, it has been observed that during polychaete growth, the assimilation efficiency can increase possibly as a result of increased gut residence times.<sup>42</sup> Because the investigation of possible correlation for all parameters is very complex, we decided to present the range of over- and under-estimation of the model by factor 2 for guidance instead.

When the bioavailability of pollutants is altered by an AC amendment, the uptake from water and sediment is changed. The biodynamic model allows illustrating how changes in assimilation efficiency of HOC from sediment, aqueous HOC concentrations, and physiological parameters affect bioaccumulation. The concentration of HOCs in sediment upon AC amendment stays constant but the assimilation efficiency from sediment will be significantly reduced because HOCs partition to the AC where they are sorbed strongly and become less available to water and extraction by digestive fluids in the organism's gut.<sup>26,42,72–74</sup> The aqueous concentration of HOCs will be significantly reduced upon AC amendment as the flux from the sediment is reduced, although the assimilation efficiency of HOCs from water remains unchanged. However, uptake rates from water and sediment may also change when organisms vary their filtration or feeding rate or if AC influences the balance of gut fluid chemistry. Reduced feeding can lower exposure and change growth dilution effects, which has been observed for one invertebrate.<sup>75</sup> Once parametrized, this model approach can be further extended to simulate how ecosystem exposure would change throughout a food web.<sup>76,77</sup>

**Secondary, Negative Effects on Individual Species.** Although significant reduction of bioaccumulation by AC amendment has been demonstrated and this may lead to reduced toxicity, the potential for inadvertent negative effects has been investigated more recently. Negative responses to AC



**Figure 4.** Incidence of response of 18 different benthic invertebrate to activated carbon amendments to various sediments comprising of reduced lipid, growth, survival, and behavioral changes.

are considered secondary effects relative to the main objective to reduce bioavailability. End points of survival, lipid content, and growth have been routinely measured along with bioaccumulation tests. Behavioral changes (i.e., egestion, burrowing, avoidance) have been included more recently. The current literature of 18 studies covers 82 tests employing 18 different benthic invertebrates tested for various AC amendment scenarios to polluted and unpolluted sediments. Among the benthic invertebrates were deposit feeders, facultative deposit feeders, filter feeders, shredder/detritivores, and carnivores of different taxa. The species and end points reviewed from these studies are listed in SI Tables S2–S5. This list of studies and effects has to be reevaluated as ongoing and future research will add new information. However, the coverage of 82 tests and 18 different invertebrates seems a fair representation for an overall ecotoxicological assessment at this time. We will provide a summary of secondary effect assessments followed by details for each end point. Overall, about 72% of all tests did not show an effect (neither positive nor negative) on the health of the organisms relative to exposure to untreated sediment (Figure 4).

Negative effects were most frequent for changes in growth (6%) followed by lipid content (5%), and behavior (5%), and were least frequent for survival (2%). In general, most negative effects appear species-specific and are more prominent for amendments to unpolluted sediment and with higher AC dose and finer AC particle size. For instance, AC amendment impacted the survival of three filter feeding species out of 17 species tested and affected the lipid content of two burrowing worms out of seven species tested. Fine-grain AC of less than 75  $\mu\text{m}$  affected lipid content and growth more strongly than coarser AC. An AC dose–response relationship was observed for some species regarding survival, growth, and lipid content, which can have implications not only for biomass development of individuals but also overall production at population and community levels. However, these links between responses of individuals to effects on communities remain to be established. Recent studies show that behavioral measures of feeding rates, avoidance, or burrowing activity can be valuable sublethal end points. However, biological variability and low reproducibility of the data can limit their use to evaluate AC amendments. AC amendments to polluted sediments benefited survival in some tests where bioavailable pollutants in the untreated sediment posed toxicity. We note that most negative effects were

observed when AC was amended to unpolluted sediments. However, the primary goal of AC amendments is to reduce pollutant availability where the alternative (exposure to polluted sediment) evokes adverse secondary effects of acute or chronic toxicity and bioaccumulation. Thus, results from unpolluted sediments have to be evaluated in the context of the net remedial benefit of AC to reduce pollutant bioavailability.

**Survival.** Of the tests that monitored survival, 28% observed different mortality rates (higher and lower) for exposure to AC amendments relative to exposure to untreated sediment. Increased survival in AC-amended sediment was observed in 22% of the tests and for four out of the 17 species tested possibly due to reduced toxicity caused by lower HOC bioavailability from the sediments.<sup>44,78,79</sup> A pronounced increase in survival from 8% to 100% was observed for the mussel *Mytilus edulis* when DDT-polluted sediment was amended with 3.2% of coal-based AC or reactivated AC.<sup>58</sup> *Corbicula fluminea* showed improved survival only at low AC dose and a negative AC dose–response relationship was observed beyond 0.7% AC.<sup>44</sup> The detritivore *Asellus aquaticus* low survival in PAH and PCB polluted sediments was improved (from approximately 5% to 20–35%) for amendments with fine as well as coarse AC (PAC 1–150  $\mu\text{m}$ ; GAC 425–1700  $\mu\text{m}$ ).<sup>80</sup> No negative effects on survival were observed for *Asellus aquaticus* by AC addition to unpolluted sediment.<sup>78</sup> The detritivore *Gammarus pulex* showed no survival after 8 days exposure to untreated, polluted (PAHs) sediment, but survival was improved (5–30% survival) with AC addition in the range of 5–30% AC. However, when AC was amended to unpolluted sediment, survival of *G. pulex* decreased after 28 days exposure from about 80% (untreated sediment) to 0–40% with AC doses of 3–15%, respectively. For untreated sediments, a sediment- and species-specific LC50 (50% lethal concentration) of 3.1% was estimated.<sup>78</sup> These observations show that AC, acting either as a detriment or a benefit to organism survival, can depend on the relative toxicity of the untreated sediment.

Most studies observed no effect on survival of AC doses of up to 30% for the mysid shrimp *Americamysis bahia*,<sup>81</sup> the filter feeding amphipods *Ampelisca abdita*<sup>81</sup> and *Corophium volutator*,<sup>75</sup> the deposit feeding oligochaete *Lumbriculus variegatus*,<sup>75,82</sup> and the deposit feeding polychaete *Neanthes arenaceodentata*.<sup>83</sup> Additional tests with AC doses below 5% also showed no effect on survival for the clams *Macoma*

*balthica*<sup>41</sup> and *M. nasuta*,<sup>14,45</sup> the deposit feeders *Nereis diversicolor* and *Hinia reticulata*,<sup>49</sup> as well as the filter feeder *Leptocheirus plumulosus*.<sup>84</sup> Amendment of AC as a thin layer cap (0.5 or 3 cm) to dioxin/furan contaminated sediment in a laboratory mesocosm study also did not affect the survival of several marine invertebrates (the clam *Abra nitida*; two polychaetes, *Nereis* (spp.); two echinoderms *Amphiura* spp.; and the gastropod, *Nassanus nitidus*) compared to uncapped controls.<sup>19</sup>

**Growth.** Negative effects on growth were observed for 29% of all studies that monitored for weight changes and for 4 out of the 10 species tested. *C. fluminea* showed a negative dose–response relationship at AC doses greater than 0.7%, similar to observations of survival for this species.<sup>44</sup> Kupryianchyk et al. observed no effect of AC in unpolluted sediment on the growth of *G. pulex*, but did find a negative dose–response relationship for *A. aquaticus* after 28 days exposure (1–30% AC by dry wt.) leading to an estimated sediment-specific EC50 (50% effect concentration) of 5.3% for *A. aquaticus*.<sup>78</sup> Growth rates of *N. arenaceodentata* and *L. variegatus* show dependency on the sediment and/or AC particle size. While 3.4% AC caused 50% reduction of growth in *N. arenaceodentata* in some tests,<sup>84</sup> no growth effects were observed upon exposure to 20% AC in different polluted and unpolluted sediments.<sup>83</sup> For *L. variegatus*, Nybom et al. found biomass was reduced at lower doses when finer AC (<63  $\mu\text{m}$ ) was amended to two unpolluted sediments and was likely the consequence of reduced feeding.<sup>82</sup> Furthermore, the authors noted a slight increase of biomass for lowest AC doses (<1%), which may be an observation of hormesis, a case in which low dose or stress can evoke a beneficial effect.

However, for 71% of the tests reviewed no effect on growth was observed including tests with *M. balthica*,<sup>41</sup> *M. edulis*,<sup>79</sup> *L. plumulosus*,<sup>84</sup> and *G. pulex*<sup>78</sup> for AC doses below 5%, and for *N. nitidus* (also known as *H. reticulata*), *A. nitida*, and *Amphiura* spp. in mesocosms with AC applied as a thin layer cap (high localized dose).<sup>19</sup>

**Lipid Content.** Lipid content was the most common energetic biomarker monitored for exposure studies, mainly because bioaccumulation of HOCs is routinely normalized by lipid contents. Reduced lipid content was observed for one out of four of all lipid tests and these negative effects were limited to two out of seven species investigated, both deposit feeders. The lipid content of *L. variegatus* appears very sensitive even to low AC, with a negative dose response effect observed in two independent studies.<sup>75,82</sup> Both studies employed fine AC with particle diameter of less than 75  $\mu\text{m}$ . In contrast, Beckingham et al. showed no influence of AC on the lipid content of *L. variegatus* exposed to polluted (PCBs) sediments amended in situ with up to 17% AC but a coarser particle size (75–300  $\mu\text{m}$ ).<sup>85</sup> The particle size may play a critical role, with finer AC more likely to evoke adverse effects. Inconsistent results were observed for *N. arenaceodentata*. Amendment of the same AC (75–300  $\mu\text{m}$ ) at a dose of 3.4% in the same sediment both decreased lipid contents by 66% and increased lipid contents by 50% in different trials.<sup>16,42,85</sup> Yet another study employing a higher dose of 20% AC showed that the effects of slightly lower lipid and glycogen contents in *N. arenaceodentata* were sediment-specific while protein contents were not affected.<sup>83</sup>

No effects on lipid contents for amendments with less than 5% AC were observed for tests with *M. nasuta*,<sup>41,45</sup> *L. plumulosus*,<sup>84</sup> *H. reticulata*,<sup>49</sup> *N. diversicolor*,<sup>49</sup> and *L. variegatus*,<sup>85</sup>

nor for thin-layer capping with AC in mesocosms for *Nereis* spp., and *N. nitidus* (also known as *H. reticulata*).<sup>19</sup>

**Behavior.** Adverse effects on organisms' behavior were observed in 14% of all behavior tests. Most behavioral tests have tracked avoidance and feeding behavior end points. Sediment avoidance has been tested in the laboratory by providing untreated sediment in one-half of an exposure compartment and AC-amended sediment in the other, and monitoring the location preference of organisms. *A. aquaticus* and *C. volutator* partially showed avoidance of AC amended sediments after 3 days exposure with doses of 4–25% powdered AC in polluted (PAHs) sediment.<sup>75</sup> However, results were inconsistent and varied across different sediments tested. In one sediment tested, *A. aquaticus* showed no preference at any AC dose, in two other sediments the organisms avoided the AC-amended sediment at high AC doses (15% and 25%), and for a fourth sediment organisms avoided all AC amendments of 4%, 7%, and 25% but not with 15% AC. The same study showed inconsistent results for avoidance tests with *C. volutator* (avoidance was observed toward amendments with 4%, 7%, and 15% AC but not for the 25%). On the other hand, no avoidance was observed for *A. aquaticus* or *G. pulex* for two sediments (one unpolluted, one PAH-impacted) amended with up to 30% powdered AC.<sup>78</sup> These results are difficult to explain, and natural variability and sediment-specific responses to AC amendments and robustness of the testing procedure have to be considered. Sediment characteristics such as total organic carbon content, water content, and texture (i.e., grain size composition) influence habitat suitability, and influences of AC on local pH, color, smell or taste may also play a role in avoidance, and organism behavior in general.<sup>86</sup>

Studies on feeding behavior are limited. Severe effects on egestion were observed for the oligochaete *L. variegatus*,<sup>75</sup> which infers reduced ingestion rates. The deposit feeders reduced egestion by 92% independent of the powdered AC doses of 1% and up to 25% (particle size, 90% < 74  $\mu\text{m}$ ) but lipid contents did not correlate with these observations. Another study found that *L. variegatus* did not change burrowing behavior in AC amended sediment but did show reduced egestion in response to increased AC dose and finer grain size (<63  $\mu\text{m}$ ).<sup>82</sup> For coarser AC (>200  $\mu\text{m}$ ) the organisms' egestion rate declined only at high dose (10–15%). Reduced ingestion rates will simultaneously affect bioaccumulation due to lowered dietary uptake and has to be differentiated from the effectiveness of AC to reduce bioavailability.

**Sediment Nutrition.** Altered bioavailability of carbon and nutrients in sediment has been discussed as a potential mechanism for growth effects (both lipid and biomass). Activated carbon may either directly sorb nutritive substances or sorb enzymes and other solubilizing agents in the gut, which would be dependent on AC particle size and an organism's feeding behavior. Nitrogen content of AC can enrich greatly (by a factor of 32) after exposure to dissolved nutrients.<sup>31,83</sup> Decreased solubilization of PAHs in the gut of *Arenicola marina* was seen to likely be due to sorption of micellar moieties by organic matter in sediment,<sup>87</sup> which suggests that these processes may also affect uptake of nutritive compounds in the presence of strongly sorbing amendments. However, no effects of AC amendment were observed on enzyme activity or surfactancy of digestive fluid by *Arenicola brasilienses*,<sup>84</sup> yet the authors caution that the result could likely be sediment-specific.



In addition, preliminary tests have detected no changes in nutrient flux from amended sediment or soil.<sup>31,88</sup>

## ■ EFFECTS ON BENTHIC COMMUNITIES

Benthic community health is a widely used metric for hazard assessment and is a potential indicator of an overall ecosystem response.<sup>89</sup> Invertebrates play an important role in regulating sediment chemical profiles and water quality through bioturbation and filtration activities, and in supporting upper trophic levels as a food source.<sup>90</sup> Thus far, only a few studies have addressed the response of benthic communities to AC amendments. The analysis of effects on abundance, diversity and robustness of the local populations requires well-characterized community conditions prior to remediation and long-term monitoring studies afterward.

Overall, those studies conducted show that low dose AC amendments generally show no or only mild effects on the diversity and abundance of the benthic community. However, there are exceptions where significant changes were observed for individual species or deployments, indicating that the response may be site-, amendment-, and community-specific. Here, we briefly summarize four benthic community studies followed by a discussion on how the observations may be potentially influenced by AC application mode, timing, dose, and particle size.

**Benthic Community Field Studies. AC-Amendment, Hunters Point (CA).** Hunters Point (CA) is a PCB-impacted tidal mudflat where AC was amended in 2004 and 2006.<sup>45</sup> A fine-granular AC (75–300  $\mu\text{m}$ ) was applied in the range of 2–3.2% AC by dry wt. either mixed or injected into surficial sediments. The site was characterized as net-depositional with a deposition rate of about 1 cm per year.<sup>14</sup> No effects to the benthic community, taxa richness, composition or diversity were observed compared to control plots 6–18 months following the amendment.<sup>14,45</sup> Natural fluctuations, for instance driven by season and salinity, were found to have a greater influence on the benthic community than the amendment. Due to PCB contamination, the benthic assemblage at Hunters Point is noticeably degraded compared to reference locations within the greater San Francisco Bay and is expected to improve given the efficacy of AC to reduce contaminant exposure.<sup>88</sup>

**AC Amendment, Grasse River (NY).** At Grasse River (NY) fine-granular AC (75–300  $\mu\text{m}$ ) was applied either as a layer, or injected or mixed into PCB-impacted surficial sediments in September of 2006.<sup>30</sup> The target dose was 3.75% AC by dry wt., although levels measured after amendment ranged from 1 to 17%. The pilot site was in a net-depositional area and AC was observed to be mixed into deposited sediment layers, likely by bioturbation. No differences in the benthic community composition (diversity, tolerance or functional measures such as feeding mode or habit) or organism abundance were observed up to 3 years postapplication compared to unamended reference locations.<sup>85</sup> An increase in oligochaete biomass was observed following amendment at all monitoring sites. Thus like the Hunters Point trial, natural site fluctuations had a larger effect on the benthic community than the AC amendment itself.

**AC-Amendment Transplants, Veenkampen (NE).** A recent study of the effect of AC amendments on recolonization was conducted at the experimental research area “de Veenkampen” (Netherlands), in an unpolluted shallow ditch site.<sup>67,85</sup> Powdered AC (15  $\mu\text{m}$  median diameter) was homogeneously

mixed into field-collected sediment at doses between 2% and 10% dry wt. and placed in trays that were transplanted back into the field, and recolonization of benthic species was monitored after 3 months and 15 months. Full recovery of diversity and total abundance was observed for the AC-amended transplants, indicating that the sorbent amendment had no effect on short- or long-term recruitment. The taxa of *Lumbriculidae* (deposit-feeding oligochaetes) and *Pisidiidae* (clams) showed, however, significantly lower abundance in AC-amended transplants indicating that these species may be sensitive to sorbent amendments. The authors further showed that the AC dose and especially the duration of recolonization explained most of the variation in the benthic communities (2–5% and 44% of variation, respectively).

**Thin-Layer Capping, Trondheim (NO).** Thin-layer capping was tested in a marine harbor in Trondheim, Norway.<sup>20</sup> Capping represents a different deployment strategy than the other trials discussed above. Powdered AC (90% of the AC < 74  $\mu\text{m}$ ) was applied to the sediment surface (2–5 mm layer) in April of 2009. Caps consisted of either pure AC or mixtures of AC with clay or sand. A sand-only cap served as an inactive control and results of all capped tests were compared to an unamended reference location. Benthic community analysis showed that total abundance decreased by 60% or more in all capping tests, including sand-only, 5 and 11 months after amendment relative to the unamended reference location. Species richness was also reduced with the exception of the AC cap with clay. Overall, the largest effects were seen for caps with AC-only and AC overlaid by sand, and the least disturbance was created by the AC cap with clay. Mixing by bioturbation in the top 3–4 cm was evident for all caps after 12 months. There were no statistically significant differences among treatments in community composition in terms of dominant taxa or species tolerance, although it was noted that relatively sensitive *Corophium* crustaceans were only found at the reference site. Benthic Quality Index (BQI),<sup>91</sup> which combines species tolerance, abundance and diversity was found to be significantly decreased upon AC addition to the sediment. The benthic community at Trondheim harbor was sampled by sieving to >1 mm. Given the size class of organisms collected, it was concluded that reduced macrofauna richness was observed in the Trondheim harbor study. In a 137-day laboratory mesocosm study with thin layer capping to a clean marine sediment with the same powdered AC employed at Trondheim, Näslund et al. found no impact to benthic community composition and abundance, except in the case of macrofauna species richness (>1 mm).<sup>88</sup> In this study, a negative effect to the macrofauna richness was separated from a lack of effect to the meiofauna community (40–1000  $\mu\text{m}$  size), which matches the Trondheim benthic community assessment.

**Effects of AC Dose, Particle Size, and Amendment Timing on Benthic Communities.** No significant changes of the benthic communities were observed at Hunters Point and Grasse River where AC dose ranged from 1% to 17% (doses greater than 5% were due to heterogeneous application in Grasse River).<sup>14,30</sup> Also, the benthic community was robustly recolonized at Veenkampen where AC ranged from 2% to 10%, with the composition impacted only in terms of abundance of two relatively sensitive taxa. However, at Trondheim reduced abundance was observed for different AC caps. The caps applied consisted of a thin layer of material(s) translating to an AC dose of up to 40%, exceeding the conditions of the other studies.<sup>20</sup> The physical burial of the capping itself may not be

the reason for community changes because the layers were very thin (2–5 mm) compared to the 50% hazardous level for burial (HLS0) of 5.4 cm estimated for marine benthic species.<sup>92</sup>

Observations of changes in abundance of individual taxa, or total abundance and species richness upon AC addition were limited to Veenkampen and Trondheim, respectively. A difference between these two studies and the other AC-amendment tests is that fine-grained, powdered AC of 15–74  $\mu\text{m}$  was applied. At Hunters Point and Grasse River coarser AC particles sizes were used (75–300  $\mu\text{m}$ ). Due to a smaller particle diameter a greater number of organisms are capable of AC uptake either by filtration or ingestion. It was previously observed that powdered AC of <70  $\mu\text{m}$  can cause distress to polychaetes when the AC particles do not agglomerate within the amendment (e.g., in sand–AC amendments), possibly disrupting respiratory functions.<sup>83</sup> A study evaluating the sensitivity of some species toward changes in sediment texture further supports that finer AC amendment can evoke adverse effects. Smit et al. determined that species with a preferred median grain size of 90  $\mu\text{m}$  experience stress with median grain size EC50 values of 18 and 305  $\mu\text{m}$ .<sup>92</sup> The lower abundance of *Lumbriculidae* for tests at Veenkampen is in line with laboratory tests indicating higher sensitivity towards finer AC (<75  $\mu\text{m}$ ).<sup>75,82</sup> Thus, the negative effect observed in short-term laboratory tests for individuals seems to translate into changes in abundance of *Lumbriculidae* on the community level. Even though higher AC dose and small AC particle size prove to be more effective in reducing bioaccumulation of HOCs, secondary effects on individual species and benthic communities emphasize limits in regards to the net benefit to the ecosystem.

Recovery of the benthic community following a major disturbance, such as a remedial activity, is known to be site-specific and dependent upon a number of factors including the timing and spatial scale of the disturbance, and resilience of the ecosystem.<sup>1,2,93</sup> For instance, community recovery following navigational dredging in coastal areas may take up to a year in fine-grained deposits, 2–3 years in sands and gravels, and perhaps longer when communities are not subjected to recurring stresses and are thus at later successional stages.<sup>94</sup> Therefore, the monitoring period after the amendment activity (e.g., “the disturbance”) has to be coherent with the time needed for recruitment and recovery. Beckingham et al. suggest that an amendment during spring may conflict with an important season for organism recruitment.<sup>85</sup> Resilience is the ability of an ecosystem to resist damage and recover after a disturbance.<sup>2,93</sup> Differences in the resiliency of the ecosystems at the field amendment locations may partially account for the benthic community observations in these studies. For example, soft-bottomed freshwater river systems, such as Grasse River, are dominated by smaller, usually more mobile organisms than a marine system and thus may be more resilient, and communities at a tidal estuarine mudflat, like Hunters Point, are more likely to be accustomed to frequent hydrological disturbances. Negative changes of the benthic community were observed at Veenkampen and Trondheim, two studies that monitored the site for up to 15 and 11 months, respectively.<sup>20,67</sup> Thus, it may be that these defined monitoring periods captured only a transitory ecological state in these habitats.

In the case of direct toxic effects of the amendment material (AC) itself if applicable, the duration of exposure to this material in the bioactive zone is a function of the mode of

deployment, the deposition rate of clean sediment and the stability of the amendment layer. Repeated and longer periods of disturbance, for example staggered amendments or mechanical mixing, may lead to an extended recovery time for the benthic community. Since mass transfer of HOCs from sediment to AC and reduction of bioaccumulation is improved with homogeneous well-mixed amendments, this has to be accounted for in optimizing remediation. Depending on the benthic substrate and community structure, different amendment strategies and monitoring periods may be warranted.

## RESEARCH NEEDS

Notable progress has been made in understanding possible effects of AC amendments on the chemical exposure and biotic integrity of the aquatic benthos, both through laboratory and pilot-scale field studies. The benefit of reducing exposure to HOCs has to be balanced with minimizing possible adverse effects. Since it is the objective to ensure the utmost benefit of any environmental action, additional uncertainties remain as possible barriers to acceptance of this novel remediation strategy for full-scale applications. Areas for recommended future research are detailed below.

**Effects on Individual Benthic Invertebrates.** The efficiency of an AC amendment to reduce bioaccumulation with higher AC dose and finer AC particles size is well established. However, adverse secondary effects of AC amendments to benthic species were observed in some cases to also increase with AC dose and smaller AC particle size. Furthermore, secondary effects often appeared to be sediment- or amendment-specific. More research is needed to link observed adverse effects to specific pathways of exposure and stress, and to physical–chemical properties of the amendment and sediment. Adverse impacts linked to particular sorbent properties could then be avoided by selective screening or pretreatment (e.g., washing) of the materials.

A better understanding of whether AC amendments influence reproduction, for example, fecundity or oocyst development, is highly desirable to link sublethal effects (e.g., reduced growth, lipid content) with reduced abundance of these species on a population level. However, reproductive studies with invertebrates in AC amendments are not available to date. One study observed that reproduction of *L. variegatus* was absent in AC-amended sediment but present in untreated sediments.<sup>82</sup> However, the authors acknowledge that the tests were not designed to monitor reproduction with a relatively short exposure time of 28 days.

**Effects on Benthic Communities.** Field studies incorporate the dynamic environmental conditions of a site that may dominate over or alleviate AC-related effects, such as deposition of sediments, refreshment of food sources, or species recruitment, and thus they are important to augmenting laboratory ecotoxicity data. Benthic community surveys at pilot-scale application sites have provided essential insights into the potential ecological effects of AC amendment. These surveys also imply suggestions for future tests regarding strategies for amendment and monitoring. Future studies would benefit from specific consideration of the system dynamics and local recruitment pool when planning the amendment strategy (e.g., timing) and the monitoring frequency and duration. The timing of amendments should consider reproductive cycles to benefit faster recruitment upon AC deployment and should be long enough to allow for recovery of the benthic community.



Besides strategies of amendment and monitoring, the approach of sampling and sample analysis can be crucial to detect effects of the remediation. Size classes of benthic invertebrates may respond differently to AC amendment. For instance, two studies were able to separate negative effects on macrofauna richness (>0.5 or 1 mm) from a lack of effect to the meiofauna community (0.03 to 0.5–1 mm, size) by thin layer AC caps on sediments.<sup>20,88</sup> Furthermore, changes of benthic communities and their causation may not always be identified using traditional analysis based on abundance, diversity and taxonomic groups. Identification to the species level is complex and expensive, and assigning all functional groups is challenged by incomplete information for rare species. At the same time, this level of detail may be necessary to identify a community shift. Analysis based on functional traits can reveal underlying causes of sensitivity to AC amendments since these traits define exposure to the contaminated environment (e.g., feeding mode, protection of their soft tissue, niche within the habitat, or reproductive mode).<sup>16</sup> In addition, analysis of functional groups may allow potential changes in structure to be linked to ecosystem performance and ecosystem services.<sup>95</sup>

**Effects on Plants.** Plants are at an ecosystem's foundation, providing both energy and habitat. Currently, there is a limited understanding of the vitality and community succession of plants in a sediment amendment scenario. The vast majority of ecotoxicology studies with plants to date have considered the impacts of carbonaceous geosorbents, such as biochars and AC, in terrestrial systems. Studies with AC amendments to soils show reduced exposure to HOCs and only minor negative secondary effects on plant growth and germination rate and these effects appear specific to the species, and the AC–soil system.<sup>96–104</sup> Activated carbon is known to sorb biologically active compounds in root exudates that are responsible for many functions, such as chemical signaling for symbiotic partners and allelopathy.<sup>105,106</sup> In this manner, AC has been used to control invasive terrestrial plants,<sup>107</sup> but could have less beneficial implications on community dynamics. The only two studies of effects on plants by AC amendment to sediment have shown limited adverse effects on growth (likely caused by dilution effects or changes in sediment bulk density) and none on recolonization or macrophyte composition and density.<sup>67,85</sup> Effects of AC amendments on plants by changes of nutrient flux from sediment are discussed but not well understood. Reduction of plant available nutrients was observed for AC-amended sediments in the laboratory growth study (Morgan-extraction technique<sup>85</sup>). At the same time, AC amendments have been seen to increase available nitrogen through interactions with bacteria, for instance by increasing nitrification rates.<sup>100,108</sup> Therefore, there is a need to further study the influence of AC on aquatic vegetation, and nutrient availability and cycling in sediments, which extends to impacts on bacterial communities.

**Effects on Bacterial Communities and Biodegradation.** Activated carbon amendment may impact nutrient cycling and long-term decontamination processes in sediment by altering the availability of contaminants and other chemical substrates to bacteria. However, only a few studies have assessed the impacts of AC amendments on bacterial communities in sediments while more studies are available for soil systems. An AC amendment to both clean and PAH-contaminated sediment with up to 20% powdered AC by dry wt. in the laboratory has shown no effect on the bacterial community composition (Terminal Restriction Fragment

Length Polymorphism analyses).<sup>75</sup> With AC amendment, the abundance of PAH degraders in AC amended soil may be unchanged,<sup>109</sup> but mineralization rates of several HOCs can be slowed.<sup>110–112</sup> It has been shown that certain aerobic and anaerobic bacteria may still be able to access sorbed HOCs such as PCBs and PAHs, perhaps by direct contact of biofilms or via the assistance of extracellular exudates.<sup>113–116</sup> It is also speculated that AC amendment may detoxify soils to enable microbial degradation.<sup>117</sup> How AC amendment may impact a particular field site is difficult to ascertain at this point since biodegradation in the environment is dynamic and challenging to predict.<sup>113,118,119</sup> More extensive research on the effect of AC on bacteria in sediments is warranted given the complexity of bacterial community dynamics and interactions in the environment. Important topics for further research include how AC contact time, and the biomass or functional behavior of the degrading species (for instance, if a biofilm is formed or the species display chemotaxis) impacts accessibility of contaminant substrates and the bacterial assemblages.<sup>116</sup>

#### Harmonizing Remediation Strategies and Success.

Comparative analysis is needed to evaluate the strengths and weaknesses of AC amendment relative to other traditional remediation strategies such as capping, dredging, and natural attenuation. Specifically, potential secondary effect(s) attributed to AC amendment should be evaluated in comparison to other remediation treatments or the impact of pollutant exposures in the absence of remediation. Further, measuring success in terms of bioavailability or benthic community recovery in comparison to reference sites needs to be harmonized with traditional cleanup goals that are commonly based on bulk sediment concentrations. Clearly, a paradigm shift in sediment management is underway in this regard. This necessitates the use of monitoring tools to measure chemical availability, such as passive samplers, and the development of modeling tools to translate the effects of sorption to AC to changes in chemical uptake and deleterious effects in organisms and the food web on a whole, such as biodynamic food web modeling. The likelihood of reaching both primary (reduced risk) and secondary (impact to the benthos) goals with a given AC dose and particles size should be able to be estimated, and in this way, remediation with AC amendment shall be part of an overall plan for ensuring the long-term future health of a presently impacted site.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Details of biodynamic modeling, and listed studies of secondary effects by activated carbon amendments are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

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## REFERENCES

- (1) Borja, A.; Muxika, I.; Rodriguez, J. G. Paradigmatic responses of marine benthic communities to different anthropogenic pressures, using M-AMBI, within the European Water Framework Directive. *Mar. Ecol.* **2009**, *30*, 214–227.
- (2) Bolam, S. G.; Rees, H. L. Minimizing impacts of maintenance dredged material disposal in the coastal environment: A habitat approach. *Environ. Manage.* **2003**, *32* (2), 171–188.
- (3) Zeller, C.; Cushing, B. Panel discussion: Remedy effectiveness: What works, what doesn't? *Integr. Environ. Assess. Manage.* **2006**, *2* (1), 75–79.
- (4) Wenning, R. J.; M, S.; Magar, V. S. Importance of implementation and residual risk analyses in sediment remediation. *Integrated Environmental Assessment and Management* **2006**, *2* (1), 59–65.
- (5) NRC, *Sediment Dredging at Superfund Megsites: Assessing the Effectiveness*; The National Academies Press: Washington, DC, 2007.
- (6) Lohmann, R.; MacFarlane, J.; Gschwend, P. Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York harbor sediments. *Environ. Sci. Technol.* **2005**, *39*, 141–148.
- (7) Accardi-Dey, A.; Gschwend, P. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environ. Sci. Technol.* **2002**, *36*, 21–29.
- (8) Ghosh, U.; Talley, J.; Luthy, R. Particle-scale investigation of PAH desorption kinetics and thermodynamics from sediment. *Environ. Sci. Technol.* **2001**, *34*, 2542–2548.
- (9) Ghosh, U.; Zimmerman, J.; Luthy, R. PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. *Environ. Sci. Technol.* **2003**, *37*, 2209–2217.
- (10) McGroddy, S.; Farrington, J.; Gschwend, P. Comparison of the in situ and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Environ. Sci. Technol.* **1996**, *30*, 172–177.
- (11) Koelmans, A.; Jonker, M.; Cornelissen, G.; Bucheli, T.; Van Noort, P.; Gustafsson, O. Black carbon: The reverse of its dark side. *Chemosphere* **2006**, *63*, 365–377.
- (12) Allen-King, R. M.; Grathwohl, P.; Ball, W. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. *Adv. Water Resour.* **2002**, *25*, 985–1016.
- (13) Cornelissen, G.; Gustafsson, O.; Bucheli, T.; Jonker, M.; Koelmans, A.; Van Noort, P. 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*, 6881–6895.
- (14) 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.
- (15) Beckingham, B.; Ghosh, U. Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* **2013**, *91* (10), 1401–1407.
- (16) Janssen, E. M. L.; Oen, A. M. P.; Luoma, S. N.; Luthy, R. G. Assessment of field-related influences on polychlorinated biphenyl exposures and sorbent amendment using polychaete bioassays and passive sampler measurements. *Environ. Toxicol. Chem.* **2011**, *30* (1), 173–180.
- (17) Oen, A.; Janssen, E.; Cornelissen, G.; Breedveld, G.; Eek, E.; Luthy, R. In situ measurement of PCB pore water concentration profiles in activated carbon-amended sediment using passive samplers. *Environ. Sci. Technol.* **2011**, *45*, 4053–4059.
- (18) Gidley, P.; Kwon, S.; Yakirevich, A.; Magar, V.; Ghosh, U. Advection dominated transport of polycyclic aromatic hydrocarbons in amended sediment caps. *Environ. Sci. Technol.* **2012**, *46*, 5032–5039.
- (19) Josefsson, S.; Schaaning, M.; Samuelsson, G.; Gunnarsson, J.; Olofsson, I.; Eek, E.; Wiberg, K. Capping efficiency of various carbonaceous and mineral materials for in situ remediation of polychlorinated dibenzo-*p*-dioxin and dibenzofuran contaminated marine sediments: Sediment-to-water fluxes and bioaccumulation in boxcosm tests. *Environ. Sci. Technol.* **2012**, *46*, 3343–3351.
- (20) Cornelissen, G.; Krusa, M.; Breedveld, G.; Eek, E.; Oen, A.; Arp, H.; Raymond, C.; Samuelsson, G.; Hedman, J.; Stokland, O.; Gunnarsson, J. Remediation of contaminated marine sediment using thin-layer capping with activated carbon—A field experiment in Trondheim Harbor, Norway. *Environ. Sci. Technol.* **2011**, *45*, 6110–6116.
- (21) Murphy, P.; Marquette, A.; Reible, D.; Lowry, G. V. Predicting the performance of activated carbon-, coke-, and soil-amended thin layer sediment caps. *J. Environ. Eng.* **2006**, *132*, 787–794.
- (22) Sun, X.; 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.
- (23) 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.
- (24) Sparrevik, M.; Saloranta, T.; Cornelissen, G.; Eek, E.; Fet, A.; Breedveld, G.; Linkov, I. Use of life cycle assessments to evaluate the environmental footprint of contaminated sediment remediation. *Environ. Sci. Technol.* **2011**, *45*, 4235–4241.
- (25) Lamoureux, E. M.; Brownawell, B. J. Influence of soot on hydrophobic organic contaminant desorption and assimilation efficiency. *Environ. Toxicol. Chem.* **2004**, *23* (11), 2571–2577.
- (26) Zimmerman, J.; Werner, D.; Ghosh, U.; Milward, R.; Bridges, T.; Luthy, R. Effects of dose and particle size on activated carbon treatment to sequester polychlorinated biphenyls and polycyclic aromatic hydrocarbons in marine sediments. *Environ. Toxicol. Chem.* **2005**, *24*, 1594–1601.
- (27) Shea, P.; Strek, H.; Weber, J. Polychlorinated biphenyls: Absorption and bioaccumulation by goldfish (*Carassius auratus*) and inactivation by activated carbon. *Chemosphere* **1980**, *9*, 157–164.
- (28) Weber, W. J. Adsorption processes. *Pure Appl. Chem.* **1974**, *37*, 375–392.
- (29) Rakowska, M.; Kuppryanichy, D.; Harmsen, J.; Grotenhuis, T.; Koelmans, A. In situ remediation of contaminated sediments using carbonaceous materials. *Environ. Toxicol. Chem.* **2012**, *31* (4), 693–701.
- (30) Beckingham, B.; Ghosh, U. Field scale reduction of PCB bioavailability with activated carbon amendment to river sediments. *Environ. Sci. Technol.* **2011**, *45*, 10567–10574.
- (31) Hale, S.; Elmquist, M.; Brandli, R.; Hartnik, T.; Jakob, L.; Henriksen, T.; Werner, D.; Cornelissen, G. Activated carbon amendment to sequester PAHs in contaminated soil: A lysimeter field trial. *Chemosphere* **2012**, *87*, 177–184.
- (32) Wang, F.; Bu, Q.; Xia, X.; Shen, M. Contrasting effects of black carbon amendments on PAH bioaccumulation by Chironomus plumosus larvae in two distinct sediments: Role of water absorption and particle ingestion. *Environ. Pollut.* **2011**, *159*, 1905–1913.
- (33) Amonette, J.; Joseph, S., *Characteristics of Biochar Microchemical Properties*; Earthscan: London, 2009.
- (34) Pulido-Novicio, L.; Hata, T.; Kurimoto, Y.; Doi, S.; Ishihara, S.; Imamura, Y. Adsorption capacities and related characteristics of wood charcoals carbonized using a one-step or two-step process. *J. Wood Sci.* **2001**, *47*, 48–57.
- (35) Hale, S.; Lehmann, J.; Rutherford, B.; Zimmerman, A.; Bachmann, R.; Shitumbanuma, V.; O'Toole, A.; Sundqvist, K.; Arp, H.; Cornelissen, G. Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars. *Environ. Sci. Technol.* **2012**, *46*, 2830–2838.

- (36) Lehmann, J.; Rillig, M.; Thies, J.; Masiello, C.; Hackaday, W.; Crowley, D. Biochar effects on soil biota—A review. *Soil Biol. Biochem.* **2011**, *43*, 1812–1836.
- (37) Beesley, L.; Moreno-Jimenez, E.; Gomez-Eyles, J.; Harris, E.; Robinson, B.; Sizmur, T. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environ. Pollut.* **2011**, *159*, 3269–3282.
- (38) Luthy, R. G.; Aiken, G. R.; Bruseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Traina, S. J.; Weber, W. J.; Westall, J. C. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* **1997**, *31* (12), 3341–3347.
- (39) Hilber, I.; Bucheli, T. D. Activated carbon amendment to remediate contaminated sediments and soils: A review. *Global Nest J.* **2012**, *12* (3), 305–317.
- (40) Cho, Y.; Werner, D.; Choi, Y.; Luthy, R. Long-term monitoring and modeling of the mass transfer of polychlorinated biphenyls in sediment following pilot-scale in-situ amendment with activated carbon. *J. Contam. Hydrol.* **2012**, *129–130*, 25–37.
- (41) 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.
- (42) Janssen, E. M. L.; Croteau, M. N.; Luoma, S. N.; Luthy, R. G. Measurement and modeling of polychlorinated biphenyl bioaccumulation from sediment for the marine polychaete *Neanthes arenaceodentata* and response to sorbent amendment. *Environ. Sci. Technol.* **2010**, *44*, 2857–2863.
- (43) Sun, X. L.; Ghosh, U. PCB bioavailability control in *Lumbricus variegatus* through different modes of activated carbon addition to sediments. *Environ. Sci. Technol.* **2007**, *41* (13), 4774–4780.
- (44) 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.
- (45) Cho, Y. M.; Smithenry, D. W.; Ghosh, U.; Kennedy, A. J.; Millward, R. N.; Bridges, T. S.; Luthy, R. G. Field methods for amending marine sediment with activated carbon and assessing treatment effectiveness. *Mar. Environ. Res.* **2007**, *64* (5), 541–555.
- (46) Tomaszewski, J. E.; Werner, D.; Luthy, R. G. Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. *Environ. Toxicol. Chem.* **2007**, *26* (10), 2143–2150.
- (47) Sun, X. L.; Ghosh, U. PCB bioavailability control in *Lumbricus variegatus* through different modes of activated carbon addition to sediments. *Environ. Sci. Technol.* **2007**, *41* (13), 4774–4780.
- (48) Kupryianchyk, D.; Rakowska, M. I.; Grotenhuis, J. T.; Koelmans, A. A. In situ sorption of hydrophobic organic compounds to sediment amended with activated carbon. *Environ. Pollut.* **2012**, *161*, 23–9.
- (49) Cornelissen, G.; Breedveld, G. D.; Kalaitzidis, S.; Christanis, K.; Kibsgaard, A.; Oen, A. M. P. Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. *Environ. Sci. Technol.* **2006**, *40*, 1197–1203.
- (50) Brandli, R. C.; Hartnik, T.; Henriksen, T.; Cornelissen, G. Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. *Chemosphere* **2008**, *73* (11), 1805–10.
- (51) McDonough, K.; Fairey, J.; Lowry, G. Adsorption of polychlorinated biphenyls to activated carbon: Equilibrium isotherms and a preliminary assessment of the effect of dissolved organic matter and biofilm loadings. *Water Res.* **2008**, *42*, 575–584.
- (52) Rakowska, M. I.; Kupryianchyk, D.; Grotenhuis, T.; Rijnaarts, H.; Koelmans, A. A. Extraction of sediment-associated polycyclic aromatic hydrocarbons with granular activated carbon. *Environ. Toxicol. Chem.* **2013**, *32* (2), 304–311.
- (53) Jonker, M. T.; 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), 3725–34.
- (54) Oen, A. M.; Beckingham, B.; Ghosh, U.; Krusa, M. E.; Luthy, R. G.; Hartnik, T.; Henriksen, T.; Cornelissen, G. Sorption of organic compounds to fresh and field-aged activated carbons in soils and sediments. *Environ. Sci. Technol.* **2012**, *46* (2), 810–7.
- (55) Hale, S. E.; Hanley, K.; Lehmann, J.; Zimmerman, A. R.; Cornelissen, G. Effects of Chemical, Biological, and Physical Aging As Well As Soil Addition on the Sorption of Pyrene to Activated Carbon and Biochar. *Environ. Sci. Technol.* **2011**, *45* (24), 10445–10453.
- (56) Zimmerman, J. R.; Ghosh, U.; Millward, R. N.; Bridges, T. S.; Luthy, R. G. Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments: Physicochemical tests. *Environ. Sci. Technol.* **2004**, *38* (20), 5458–5464.
- (57) Werner, D.; Higgins, C. P.; Luthy, R. G. The sequestration of PCBs in Lake Hartwell sediment with activated carbon. *Water Res.* **2005**, *39*, 2105–2113.
- (58) Tomaszewski, J. E.; Werner, D.; Luthy, R. G. Activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. *Environ. Toxicol. Chem.* **2007**, *26* (10), 2143–50.
- (59) Amstaetter, K.; Eek, E.; Cornelissen, G. Sorption of PAHs and PCBs to activated carbon: Coal versus biomass-based quality. *Chemosphere* **2012**, *87*, 573–578.
- (60) Guo, Y.; Yadav, A.; Karanfil, T. Approaches to mitigate the impact of dissolved organic matter on the adsorption of synthetic organic contaminants by porous carbonaceous sorbents. *Environ. Sci. Technol.* **2007**, *41*, 7888–7894.
- (61) Ebbe, K.; Li, F.; Azuma, Y.; Yuasa, A.; Hagishita, T. Pore distribution effect of activated carbon in adsorbing organic micro-pollutants from natural water. *Water Res.* **2001**, *35*, 167–179.
- (62) Hale, S.; Kwon, S.; Ghosh, U.; Werner, D. Polychlorinated biphenyl sorption to activated carbon and the attenuation caused by sediment. *Global Nest J.* **2010**, *12*, 318–326.
- (63) Hale, S.; Tomaszewski, J.; Luthy, R.; Werner, D. Sorption of dichlorodiphenyltrichloroethane (DDT) and its metabolites by activated carbon in clean water and sediment slurries. *Water Res.* **2009**, *43*, 4336–4346.
- (64) Redell, C.; Elmore, A.; Burken, J.; Stringer, R. Waterjet injection of powdered activated carbon for sediment remediation. *J. Soils Sed.* **2011**, *11*, 1115–1124.
- (65) Kupryianchyk, D.; Rakowska, M.; Grotenhuis, T.; Koelmans, A. A. Modeling trade-off between PAH toxicity reduction and negative effects of sorbent amendments to contaminated sediments. *Environ. Sci. Technol.* **2012**, *46* (9), 4975–4984.
- (66) Cornelissen, G.; Amstaetter, K.; Hauge, A.; Schaanning, M.; Beylich, B.; Gunnarsson, J.; Breedveld, G. D.; Oen, A. M.; Eek, E. Large-scale field study on thin-layer capping of marine PCDD/F-contaminated sediments on Grenlandfjords, Norway: Physicochemical effects. *Environ. Sci. Technol.* **2012**, *46* (21), 12030–12037.
- (67) Kupryianchyk, D.; Peters, E. T. H. M.; Rakowska, M. I.; Reichman, E. P.; Grotenhuis, J. T. C.; Koelmans, A. A. Long-term recovery of benthic communities in sediments amended with activated carbon. *Environ. Sci. Technol.* **2012**, *46*, 10735–10742.
- (68) Janssen, E. M. L.; Thompson, J. K.; Luoma, S. N.; Luthy, R. G. PCB-induced changes of a benthic community and expected ecosystem recovery following in-situ sorbent amendment. *Environ. Chem. Toxicol.* **2011**, *30* (8), 1819–1826.
- (69) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2 ed.; John Wiley & Sons, Inc.: New York, 2002.
- (70) Luoma, S.; Rainbow, P. Why is metal bioaccumulation so variable? Biodynamics as a unifying concept. *Environ. Sci. Technol.* **2005**, *39*, 1921–1931.
- (71) Sun, X.; Werner, D.; Ghosh, U. Modeling PCB mass transfer and bioaccumulation in a freshwater oligochaete before and after amendment of sediment with activated carbon. *Environ. Sci. Technol.* **2009**, *43* (4), 1115–1121.



- (72) Cook, R.; Wilson, K. Removal of pesticide residues from dairy cattle. *J. Dairy Sci.* **1971**, *54*, 712–718.
- (73) McLeod, P. B.; Van Den Heuvel-Greve, M. J.; Allen-King, R. M.; Luoma, S. N.; Luthy, R. G. Effects of particulate carbonaceous matter on the bioavailability of benzo(a)pyrene and 2,2',5,5'-tetrachlorobiphenyl to the clam *Macoma balthica*. *Environ. Toxicol. Chem.* **2004**, *38*, 4549–4556.
- (74) Poiger, H.; Schlatter, C. Influence of solvents and adsorbents on dermal and intestinal absorption of TCDD. *Food Cosmet. Toxicol.* **1980**, *18*, 477–481.
- (75) Jonker, M. T.; Suijkerbuijk, M. P.; Schmitt, H.; Sinnige, T. L. Ecotoxicological effects of activated carbon addition to sediments. *Environ. Sci. Technol.* **2009**, *43* (15), 5959–66.
- (76) Arnot, J. A.; Gobas, F. A. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environ. Toxicol. Chem.* **2004**, *23* (10), 2343–55.
- (77) Gobas, F.; Wilcockson, J. *San Francisco Bay PCB Food-Web Model*; San Francisco Estuary Institute: San Francisco, CA, 2003.
- (78) 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 non-polluted and polluted sediments. *Environ. Sci. Technol.* **2011**, *45* (19), 8567–8574.
- (79) Tomaszewski, J. E.; Luthy, R. G. Field deployment of polyethylene devices to measure PCB concentrations in pore water of contaminated sediment. *Environ. Sci. Technol.* **2008**, *42* (16), 6086–6091.
- (80) Kupryianchyk, D.; Noori, A.; Rakowska, M. I.; Grotenhuis, J. T. C.; Koelmans, A. A. Bioturbation and dissolved organic matter enhance contaminant fluxes from sediment treated with powdered and granular activated carbon. *Environ. Sci. Technol.* **2013**, DOI: 10.1021/es3040297.
- (81) Ho, K. T.; Burgess, R. M. 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.
- (82) Nybom, I.; Werner, D.; Leppanen, M.; Siavalas, G.; Christanis, K.; Karapanagioti, H.; Kukkonen, J.; Akkanen, J. Responses of *Lumbriculus variegatus* to activated carbon amendments in uncontaminated sediments. *Environ. Sci. Technol.* **2012**, *46* (23), 12895–12903.
- (83) Janssen, E. M.; Choi, Y.; Luthy, R. G. Assessment of nontoxic, secondary effects of sorbent amendment to sediments on the deposit-feeding organism *Neanthes arenaceodentata*. *Environ. Sci. Technol.* **2012**, *46* (7), 4134–41.
- (84) 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.
- (85) Beckingham, B.; Buys, D.; VanDerwalker, H.; Ghosh, U. Observations of limited secondary effects to benthic invertebrates and macrophytes with activated carbon amendment in river sediments. *Environ. Toxicol. Chem.* **2013**, DOI: 10.1002/etc.2231.
- (86) Hellou, J.; Cheeseman, K.; Jouvenelle, M.-L.; Robertson, S. Behavioral response of *Corophium volutator* relative to experimental conditions, physical and chemical disturbances. *Environ. Toxicol. Chem.* **2005**, *24* (12), 3061–3068.
- (87) Voparil, I. M.; Mayer, L. M. Dissolution of sedimentary polycyclic aromatic hydrocarbons into the lugworm's (*Arenicola marina*) digestive fluids. *Environ. Sci. Technol.* **2000**, *34*, 1221–1228.
- (88) Näslund, J.; Samuelsson, G.; Gunnarsson, J.; Nascimento, F.; Nilsson, H.; Cornelissen, G.; Schaanning, M. Ecosystem effects of materials proposed for thin-layer capping of contaminated sediments. *Mar. Ecol.: Prog. Ser.* **2012**, *449*, 27–39.
- (89) Apitz, S.; Davis, J.; Finkelstein, K.; Hohreiter, D.; Hoke, R.; Jensen, R.; Jersak, J.; Kirtay, V.; Mack, E.; Magar, V.; Moore, D.; Reible, D.; Stahl, R. J. Assessing and managing contaminated sediments: Part II, Evaluating risk and monitoring sediment remedy effectiveness. *Integr. Environ. Assess. Manag.* **2005**, *1* (1), 1–14.
- (90) Chapman, P. The sediment quality triad approach to determining pollution-induced degradation. *Sci. Total Environ.* **1990**, *97*, 815–825.
- (91) Rosenberg, R.; Blomqvist, M.; Nilsson, H. C.; Cederwall, H.; Dimming, A. Marine quality assessment by use of benthic species abundance distributions: A proposed new protocol within the European Union Water Framework Directive. *Mar. Pollut. Bull.* **2004**, *49*, 728–739.
- (92) Smit, M. G. D.; Holthaus, K. I. E.; Trannum, H. C.; Neff, J. M.; Kjeilen-Eilertsen, G.; Jak, R. G.; Singaas, I.; Huijbregts, M. A. J.; Hendriks, A. J. Species sensitivity distributions for suspended clays, sediment burial, and grain size change in the marine environment. *Environ. Toxicol. Chem.* **2008**, *27* (4), 1006–1012.
- (93) Lake, P. Disturbing hard and soft bottom communities: A comparison of marine and freshwater environments. *Aust. J. Ecol.* **1990**, *15*, 477–488.
- (94) Newell, R. C.; Seiderer, L. J.; Hitchcock, D. R. The impact of dredging works in coastal waters. In *A Review of the Sensitivity to Disturbance and Subsequent Recovery of Biological Resources on the Sea Bed*; UCL Press: London, 1998; Vol. 36.
- (95) Folke, C.; Carpenter, S.; Walker, B.; Scheffer, M.; Elmqvist, T.; Gunderson, L.; Holling, C. Regime shifts, resilience, and biodiversity in ecosystem management. *Annu. Rev. Ecol. Evol. Syst.* **2004**, *35*, 557–581.
- (96) Hilber, I.; Wyss, G.; Mäder, P.; Bucheli, T.; Meier, I.; Vogt, L.; Schulin, R. Influence of activated charcoal amendment to contaminated soil on dielrin and nutrient uptake by cucumbers. *Environ. Pollut.* **2009**, *157*, 2224–2230.
- (97) Jakob, L.; Hartnik, T.; Henriksen, T.; Elmquist, M.; Brändli, R.; Hale, S.; Cornelissen, G. PAH-sequestration capacity of granular and powder activated carbon amendments in soil, and their effects on earthworms and plants. *Chemosphere* **2012**, *88* (6), 699–705.
- (98) Kabouw, P.; Nab, M.; van Dam, N. Activated carbon addition affects substrate pH and germination of six plant species. *Soil Biol. Biochem.* **2010**, *42*, 1165–1167.
- (99) Langlois, V.; Rutter, A.; Zeeb, B. Activated carbon immobilizes residual polychlorinated biphenyls in weathered contaminated soil. *J. Environ. Qual.* **2011**, *40*, 1130–1134.
- (100) Lau, J.; Puliafico, K.; Kopshever, J.; Steltzer, H.; Jarvis, E.; Schwarzländer, M.; Strauss, S.; Hufbauer, R. Inference of allelopathy is complicated by effects of activated carbon on plant growth. *New Phytol.* **2008**, *178*, 412–423.
- (101) Murano, H.; Otani, T.; Makino, T.; Seike, N.; Sakai, M. Effects of the application of carbonaceous adsorbents on pumpkin (*Cucurbita maxima*) uptake of heptachlor epoxide in soil. *Soil Sci. Plant Nutr.* **2009**, *55*, 325–332.
- (102) Strek, H.; Weber, J.; Shea, P.; Mrozek, E.; Overcash, M. Reduction of polychlorinated biphenyl toxicity and uptake of carbon-14 activity by plants through the use of activated carbon. *J. Agric. Food Chem.* **1981**, *29*, 288–293.
- (103) Vasilyeva, G.; Strijakova, E.; Nikolaeva, S.; Lebedev, A.; Shea, P. Dynamics of PCB removal and detoxification in historically contaminated soils amended with activated carbon. *Environ. Pollut.* **2010**, *158*, 770–777.
- (104) Weber, J.; Mrozek, E. Polychlorinated biphenyls: Phytotoxicity, absorption and translocation by plants, and inactivation by activated carbon. *Bull. Environ. Contam. Toxicol.* **1979**, *23*, 412–417.
- (105) Callaway, R.; Aschehoug, E. Invasive plants versus their new and old neighbors: A mechanism for exotic invasion. *Science* **2000**, *290*, 521–523.
- (106) Wurst, S.; Vender, V.; Rillig, M. Testing for allelopathic effects in plant competition: Does activated carbon disrupt plant symbioses? *Plant Ecol.* **2010**, *211*, 19–26.
- (107) Kulmatiski, A. Changing soils to manage plant communities: Activated carbon as a restoration tool in ex-arable fields. *Restor. Ecol.* **2011**, *19*, 102–110.

- (108) Berglund, L.; DeLuca, T.; Zackrisson, O. Activated carbon amendments to soil alters nitrification rates in Scots pine forests. *Soil Biol. Biochem.* **2004**, *36*, 2067–2073.
- (109) Meynet, P.; Hale, S.; Davenport, R.; Cornelissen, G.; Breedveld, G.; Werner, D. Effect of activated carbon amendment on bacterial community structure and functions in a PAH impacted urban soil. *Environ. Sci. Technol.* **2012**, *46* (9), 5057–5066.
- (110) Bakhaeva, L.; Vasilyeva, G.; Surovtseva, E.; Mukhin, W. Microbial degradation of 3,4-Dichloroaniline sorbed by activated carbon. *Microbiology* **2001**, *70*, 277–284.
- (111) Yang, Y.; Hunter, W.; Tao, S.; Crowley, D.; Gan, J. Effect of activated carbon on microbial bioavailability of phenanthrene in soils. *Environ. Toxicol. Chem.* **2009**, *28* (11), 2283–2288.
- (112) Zhang, W.; Bouwer, E. J.; Ball, W. P. Bioavailability of hydrophobic organic contaminants: Effects and implications of sorption-related mass transfer on bioremediation. *Groundwater Monit. Rem.* **1998**, Winter, 126–138.
- (113) Payne, R.; May, H.; Sowers, K. Enhanced reductive dechlorination of polychlorinated biphenyl impacted sediment by bioaugmentation with a dehalorespiring bacterium. *Environ. Sci. Technol.* **2011**, *45*, 8772–8779.
- (114) Rhodes, A.; Riding, M.; McAllister, L.; Lee, K. S.; Semple, K. T. Influence of activated charcoal on desorption kinetics and biodegradation of phenanthrene in soil. *Environ. Sci. Technol.* **2012**, *46*, 12445–12451.
- (115) Leglize, P.; Alain, S.; Jacques, B.; Corinne, L. Adsorption of phenanthrene on activated carbon increases mineralization rate by specific bacteria. *J. Hazard. Mater.* **2008**, *151*, 339–347.
- (116) Marchal, G.; Smith, K.; Rein, A.; Winding, A.; Trapp, S.; Karlson, U. Comparing the desorption and biodegradation of low concentrations of phenanthrene sorbed to activated carbon, biochar and compost. *Chemosphere* **2013**, *90* (6), 1767–1778.
- (117) Vasilyeva, G.; Kreslavski, V.; Oh, B.-T.; Shea, P. Potential of activated carbon to decrease 2,4,6-trinitrotoluene toxicity and accelerate soil decontamination. *Environ. Toxicol. Chem.* **2001**, *20*, 965–971.
- (118) Aichberger, H.; Hasinger, M.; Braun, R.; Loibner, A. Potential of preliminary test methods to predict biodegradation performance of petroleum hydrocarbons in soil. *Biodegradation* **2005**, *16*, 115–125.
- (119) EPA, U. *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites*; Office of Solid Waste and Emergency Response: Washington, DC, 2005.