Novel, Activated Carbon-Based Material for in-Situ Remediation of Contaminated Sediments

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ABSTRACT: Applying activated carbon (AC) to contaminated sediments is an in-situ approach to remediation with great potential. The bioavailability of persistent organic pollutants can be rapidly reduced and kept low over long periods of time. However, there are limitations to the method. The high buoyancy of AC particles makes their application difficult in the field, and AC retention on the amended site can be low in turbulent waters. Furthermore, the fine particles of powdered AC (PAC) can have adverse effects on organisms, but their remediation potential is superior to coarser, granular ACs (GAC). To tackle these shortcomings, a novel sorbent material was developed, consisting of PAC embedded into a stable, granular clay–matrix, significantly reducing buoyancy. These AC–clay granules (ACC-G) were tested for remediation potential (PCB-bioaccumulation reduction) and adverse effects on the benthic invertebrates Chironomus riparius and Lumbriculus variegatus. The novel ACC-G material was compared to GAC of the same particle size, the clay–matrix, and PAC. The findings show that ACC-G has a significantly higher remediation potential than GAC, allowing for reductions in PCB-bioaccumulation of up to 89%. Adverse effects could not be totally eliminated with ACC-G, but they were less severe than with PAC, likely due to the increased particle size.

1. INTRODUCTION

Using traditional methods for the remediation of contaminated sediments, such as dredging or capping with inert materials, can be highly laborious and expensive. As a more cost-efficient alternative, the in-situ amendment of sorbents has been developed and tested. For this approach to sediment remediation, the contaminant does not have to be physically removed or separated, but its mobility and bioavailability are significantly lowered by binding to the applied sorbent material.1

The type of sorbent used depends on the contaminants that are present at the target site. For the remediation of sediments contaminated with hydrophobic organic contaminants (HOCs), activated carbon has been identified as a highly effective sorbent. Both the bioaccumulation and the release into the water phase of a wide variety of HOCs have been reduced by up to 98% with AC amendments.2–6 The AC doses necessary to achieve results of this magnitude generally lie under 5% of sediment dry weight (dw) when the sorbents are mixed directly into the sediment.7 When applied as a thin-layer cap, required AC amounts may be higher, as a gapless coverage of the treated site is desired. AC cap thicknesses of 2–5 mm have been found to be effective under both laboratory and field conditions.6,8,9

There are indications that the promising remediation potential of AC can be accompanied by strong adverse effects. In highly contaminated sediments, these adverse effects may be offset by a lowered contaminant bioavailability.10 However, in sediments with moderate, sublethal contaminant levels, the adverse effects of AC can be more problematic. Although some species, such as Neanthes arenaceaodentata,11 show comparably low or no adverse effects, other benthic invertebrates are highly sensitive to AC amendments. Commonly observed effects in sensitive organisms include a loss in organism biomass and inhibited reproduction.10–13 There are indications that the adverse effects are also less pronounced in field studies than in laboratory bioassays,14,15 but their occurrence cannot be excluded in any remediation scenario.16 A detailed review on these potential AC-induced adverse effects was conducted by Janssen and Beckingham.17

Both the adverse effects and the remediation potential of AC are strongly linked to the sorbent material’s particle size. Fine and powdered ACs with particle sizes below 300 μm are generally more efficient in binding contaminants due to their higher relative surface area but may also cause stronger adverse effects on biota.7 The stronger adverse effects have been suggested to be caused by ingestion of the fine particles.12,13,18

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Conversely, AC particles above 400 μm diameter, which few benthic organisms can ingest, can have little to no adverse effects in environmentally relevant doses. However, Zimmerman et al. found that these materials can have an insufficient contaminant binding potential to yield a satisfactory remediation result.

The aim of this study was to find a solution for the above-mentioned trade-off by developing a novel remediation material that would combine the low environmental impact of granular AC (GAC) and high remediation potential of powdered ACs (PAC). An additional conceptual requirement for the novel material was its easy application in the field without the need for special equipment. As the material’s high buoyancy is one of the major issues that hampers the sinking of the AC particles to the desired location (especially in deeper waterbodies), the newly developed material was also optimized to be fast sinking. This allows it to be applied from the water surface in both shallow and deeper waters.

2. MATERIALS AND METHODS

2.1. AC Remediation Materials. The basic concept behind the newly developed AC material was to produce granules in particle sizes that would not be ingested by benthic organisms by coagulating PAC into a clay matrix. This would tackle a potential cause for the adverse effects of PAC while simultaneously retaining its high contaminant binding efficiency. The resulting AC–clay granules (ACC-G) are designed to retain their form after application to water or sediment. The PAC was obtained from KW-Filter (Mynämäki, Finland) and sieved to particle sizes < 100 μm. Clay was added (ratio 1:1) to serve as binding material and to add bulk to the granules, reducing the buoyancy of the final product. The constituents were mixed into a thick slurry and poured into aluminum trays. To increase the total surface area and porosity of the granules, NaHCO₃ was mixed into the slurry (at a dose of 5% of the other dry constituents). First, the slurry was dried at slowly increasing temperatures up to 200 °C. At this temperature the NaHCO₃ releases CO₂, forming pores in the drying AC–clay mixture. Thereafter, the trays were burned at temperatures up to 580 °C in muffle ovens to obtain a stable, solid material that retains its structure even when brought back into contact with water. Burning clay at the chosen temperatures ensures this desired stability by irreversible dehydration. To reduce the loss of AC due to oxidation from the material, a top layer of GAC was added to the trays before this high-temperature burning step. After cooling down the trays, the AC-depleted layer and retained GAC were removed and discarded. The remaining material was ground and sieved to a particle size of 400–1000 μm. The obtained granules were rinsed with deionized water to remove dust particles and dried at 105 °C.

The total organic carbon (TOC) content of the final product was tested and compared to its raw constituents to determine the retained AC content after burning. Dry samples of clay, PAC, and ACC-G granules were ground. Inorganic carbon was removed with 1 M H₂PO₄. The samples were measured using an Analytik Jena N/C 2100 analyzer.

The ACC-G were compared to conventional GAC (KW-Filter OY, Mynämäki, Finland) of the same 400–1000 μm particle size for their remediation efficiency and adverse effects. As with ACC-G, the GAC was sieved, rinsed with deionized water, and dried before application. TOC was determined as described above. To determine the particle size distribution within the range of 400–1000 μm for ACC-G and GAC, a sieve tower was used (wet sieving through 1000, 630, 500, and 400 μm sieves).

The buoyancy of the ACC-G granules and the GAC was tested as time required for a single grain to sink through a 1.40 m water column (tested in a 160 × 1 cm acrylic pipe filled with tap water). The GAC was included in the test as both untreated and preboiled for 10 min in hot tap water to remove air from the pore space. ACC-G and both GAC variants were added to the water column dry and soaked in tap water. The results were analyzed applying a one-way ANOVA followed by an all-pairwise posthoc test (Bonferroni p-value adjustment).

In addition, all tested materials were characterized for their specific surface area (SSA) by means of nitrogen adsorption using a FlowSorb II 2300 surface area analyzer (Micromeritics, Norcross, GA, USA). Tests were conducted on ground samples as well as with the particle sizes used in the experiments. The water holding capacity (WHC) of ACC-G and GAC was determined to assess their water permeability. The sorbents were soaked in room-temperature water for 60 min. For GAC, hot water was used as well for soaking (preboiling treatment). The samples were then transferred to a paper towel to remove excess water and weighed into triplicate samples. The WHC was then measured as the loss of mass after drying overnight at 105 °C.

2.2. Test Organisms. Two different benthic invertebrate species were exposed to sediments treated with the sorbent materials. Lumbricillus variegatus, a sediment-dwelling oligochaete, and larvae of Chironomus riparius, a nonbiting midge. These organisms are present in many aquatic environments, where they play a key role as the basis of food webs and as primary vectors for the sediment–biota contaminant transfer. The organisms used in this study were reared at 20 ± 2 °C in artificial freshwater (0.5 mM Ca + Mg hardness) at a 16:8 h light:dark cycle. Culture substrates for the organisms were cut cellulose tissue papers (L. variegatus) and natural, clean sediment (C. riparius). Ground Tetramin was used as culture food source for both organisms.

2.3. Experimental Microcosms. The experimental microcosms were setup in glass beakers. The beaker sizes were chosen according to the amount of sediment necessary for the specific test run (Table S1). The beakers were filled with a layer of test sediment and topped with artificial freshwater (pH = 7; Ca + Mg hardness 1 mM for L. variegatus and 0.5 mM for C. riparius). The vessels were left to settle overnight, after which gentle aeration was started and the test organisms were introduced. All tests were carried out in a 16:8 h light:dark cycle. Throughout the organism exposure time the water quality was monitored. Acceptable ranges were set to pH 6–9, dissolved oxygen content > 40%, temperature 20 ± 1 °C, and NH₄⁺ concentration < 10 mg/L.

2.4. Remediation Efficiency of the AC Materials. The remediation efficiency of the sorbent materials was assessed as their capability to reduce the bioaccumulation of PCBs in L. variegatus and C. riparius. Natural, PCB-contaminated sediment (sieved to particle size < 1 mm) from Lake Kernaalanjärvi, southern Finland, was used in the tests and treated with GAC and ACC-G in doses of 0.75%, 2.0%, 4.0%, and 7.5% (of sediment dw; doses are based on the AC content of the sorbent materials, not their total weight). An unamended control group (0% AC) was set up using the same sediment. The sorbent materials were mixed into the sediment after shortly soaking in ultrapure water. Additional
water was added to obtain a sediment slurry that could be mixed thoroughly in a roller mixer over a period of 2 weeks. This agitation was conducted in intervals, reaching a total agitation time for each vessel of 232 h (9.7 days). The same mixing regime was used for the unamended control (with only water added to the sediment). The continuous, active mixing can simulate years of sediment–sorbert contact under field conditions, thus reducing the time required to reach an equilibrium in the partitioning of PCBs between sediment and sorbent particles.

After the sediment–water microcosms were set up as described above, the test organisms were added. For the L. variegatus tests about 0.4 g of worms was introduced to each replicate and exposed for 28 days. The C. riparius microcosms were stocked with 35 larvae (aged 1–3 days post hatching), which were exposed for 13 days. The larvae were fed with 0.4 mg (0.5 mg from day 7 onward) of ground Tertramin per day and larva. The experiments were finished by separating the organisms from the sediment using a 200 μm sieve. After a depuration time of 6 h in clean, artificial fresh water, the organisms’ fresh weight (fw) was determined with a fine scale (Analytic AC 210 P, Sartorius, Göttingen, Germany). The samples were frozen and stored at −20 °C until further handling.

For the determination of total PCB body burdens, the organisms were homogenized by ultrasonication and two times extracted with 8 mL of n-hexane. The extracts were concentrated to 2 mL and cleaned up using silica columns (Soxtec extraction unit 1043/1046, Tecator, Högnäs, Sweden), cleaned up with sulfuric acid, and quantified as described for the biota samples. Both PCB methods were validated with certified reference standards (SRM 1944 for sediments; SRM 1974c for organism tissue).

The organism lipid content was determined from a small subsample (20–60 mg fw) diverted from each replicate. A spectrophotometric method after van Handel28 was used. After homogenization with a spatula, the tissue samples were extracted with chloroform:methanol (1:1). The supernatant was digested with sulfuric acid, and a vanillin–phosphoric acid reagent was added prior to the absorbance measurement at 525 nm (Varian Cary 50 UV–vis spectrophotometer, Palo Alto, CA, USA). The method was calibrated with standards prepared from commercially available, refined canola oil.

The data was analyzed in R using a standard one-way ANOVA method (Bonferroni posthoc) or a Kruskal–Wallis test (Dunn’s posthoc), depending on whether normality and equal variances assumptions were met (tested with QQ and residual plots).

2.5. Adverse Effects of the AC Materials. The adverse effects of the AC materials were tested in clean, artificial sediment, prepared in accordance to the OECD guideline 225, using Urtica powder as food source.22 As for the remediation efficiency tests, the ACC-G were compared to GAC. In addition to these two coarse-grained AC materials, the raw materials used to produce ACC-G were included. PAC (<100 μm) was used after sieving. The clay was burned at 580 °C and ground to 400–1000 μm, yielding inert granules. All tested materials were applied in doses of 0.75%, 2.0%, 4.0%, and 7.5% (based on sediment dw) and mixed into the sediment 1 week prior to the organism exposure. The shorter mixing period was chosen to reduce the overall storage time of the artificial sediment, as recommended in the OECD guideline.22 Due to the absence of contaminants, the main target of the sediment mixing was to achieve a homogeneous dispersion of the applied materials; for this purpose, the shortened mixing regime was considered still sufficient.

Each L. variegatus microcosm was set up with 10 individuals (n = 3, exposure time 28 days). Nine days prior to the exposure, the worms were taken from the culture and artificially fragmented to synchronize their reproductive cycle (only fully regenerated, posterior ends were used).22 A subsample of ca. 35 individuals not used for the experiments was weighed (Sartorius Micro M3P microscale, Sartorius GmbH, Göttingen, Germany) to determine the fw of the organisms at the start of the exposure. Additionally, organism dw was measured after drying overnight at 105 °C. Small organism counts per replicate were utilized to reliably monitor organism reproduction, survival, and growth. Single exposures of 10 days were carried out with C. riparius (n = 15, exposure time 10 days), and larvae were introduced to the microcosm within 3 days of hatching from the egg sacs.

At the end of the exposures the surviving organisms were sieved from the sediment with a 200 μm sieve and surviving individuals were counted for the determination of survival or reproduction. Both fw and dw were determined for L. variegatus after a 6 h depuration period. C. riparius larvae were killed and stored in ethanol immediately after sieving. Body and head capsule dimensions were measured with a Nikon SMS 800. Larval biomass (growth) was measured after drying the samples at 105 °C. The larval head capsule measurements were used as an indicator for their developmental stage (instar).

The high number of different treatments required the adverse effects tests to be split up. The experiments were hence designed as three, fully repeated runs, initiated on three consecutive days, and results were analyzed with a linear mixed effects model (R, lme4 package). Details on the setup and statistical analysis are given in the Supporting Information (SI).

2.6. AC Material Stability. ACC-G granules are intended to retain their form over an extended time to avoid their ingestion by benthic organisms and improve the long-term retention of AC to the amended site. The material’s stability was assessed as its recovery after the experiments were concluded. This period includes both the active mixing regime and the bioturbation caused by the test organisms. The C. riparius test vessels from the remediation tests with contaminated sediment (described in section 2.4) were used for this test. During the final sieving of the test organisms, the sediment with a particle size > 200 μm was collected and dried at 105 °C. Since the PAC used as raw material for ACC-G was <100 μm, sieving the sediment to 200 μm removes all of the AC particles that separated from the clay matrix. By measuring
Figure 1. Novel AC–clay granules (ACC-G, A), consisting of powdered activated carbon particles embedded in a stable clay matrix, and conventional granular activated carbon (GAC, B). Pictures taken with a Leica Z6 APO macroscope (Leica Microsystems, Wetzlar, Germany). An extended version of this figure showing the sorbent materials after use in the bioassays and subsequent recovery from the sediment is shown in the SI (Figure S1).

3. RESULTS AND DISCUSSION

3.1. Novel AC Sorbent Granules. The production method of ACC-G was considered successful, as the material retained its shape and did not disintegrate in water. The efficiency of the production process was relatively low. About 25–50% of the prepared AC–clay mixture was lost due to AC burnoff. However, the AC burnoff created a depleted clay layer, which, in combination with the applied GAC layer, prevented oxygen from reaching the material below. The structure of AC-depleted and usable material was great enough to allow for an easy, mechanical separation. Examining the final product under a stereomicroscope revealed the intended, sandstone-like structure of the granule; the single PAC grains are embedded within the clay matrix (Figure 1).

The TOC content of the PAC used for the ACC-G production was 409.6 ± 20.9 g/kg (Figure S3). The second raw constituent of the granules, the modeling clay, contained only traces of carbon (0.5 ± 0.1 g/kg). The finalized ACC-G granules, consisting of equal parts of both raw materials, had about one-half of the PAC’s TOC content (213.9 ± 2.9 g/kg). Therefore, it can be assumed that the final product reached the intended AC content of 50% and that the obtained material did not contain significant shares of AC-depleted material. The TOC content of the conventional GAC was 409.2 ± 10.2 g/kg and thus almost identical to the PAC.

The SSA of PAC and GAC was determined at 963 and 831 m²/g, respectively (Figure S3). Although in the lower range of most commercially available ACSs, sorbents with comparable SSAs were found to sufficiently bind organic contaminants. The SSA of the inert clay granules (14 m²/g) is insignificant compared to the sorbents. As for the TOC content, ACC-G showed approximately one-half the surface area (506 m²/g) of the raw PAC, confirming a 50% AC content. Furthermore, this indicates that no loss in the SSA of PAC occurs during the manufacturing process.

The WHC and thus water permeability of ACC-G is significantly increased over conventional GAC (1.74 vs. 1.19 g water/g sorbent; Figure S4). Although the WHC could be slightly increased by preboiling the GAC, this difference was not statistically significant. The greater water permeability of ACC-G is a result of its sandstone-like GAC. It increases the possibility for interaction of AC surfaces inside the particle with the surrounding medium and facilitates contaminant diffusion.

The buoyancy test of the sorbent materials showed that ACC-G granules sank significantly faster through the water column than GAC (0.03 vs. 0.02 m/s; Figure 2). The tests could not be conducted with the untreated, dry GAC, as a large fraction of particles adhered to the water surface and did not traverse through the whole column but instead drifted back up to the surface. This observation was made as well during the sediment preparation phase prior to the organism exposure.

Figure 2. Sinking speed of conventional granular activated carbon (GAC), newly developed AC–clay granules (ACC-G), and inert clay granules. Both AC materials were tested prewetted and dry. GAC was tested pristine and pretreated by boiling. Untreated, dry GAC could not be tested. Pretreatments had no significant effect on the buoyancy of materials. Statistically different groups marked a–c. Differences between groups are significant at p < 0.001 (log-transformed data to meet model assumptions). Lines and whiskers indicate mean and standard deviation.
had a dw content of 53.5 during the tests. GAC particles were hard to apply to the sediment due to their buoyancy. This indicates that GAC needs to be pretreated before being applied in the field to avoid unintentional spread to nontarget areas due to drift. Neither the materials’ pretreatment nor the presoaking in water had a significant impact on their sinking speed. Conforming to expectation, ACC-G buoyancy lied in between that of the GAC and that of the inert clay granules (sinking speed: 0.05 m/s) used during the adverse effects study. The faster travel through the water column of ACC-G and their lack of pretreatment requirements are clear advantages over conventional GAC.

3.2. Sediment Characterization and Water Quality during the Tests. The natural, PCB-contaminated sediment had a dw content of 53.5 ± 0.1%, a TOC content of 52.5 ± 0.6 g/kg, and a ΣPCB concentration of 1.82 ± 0.06 mg/kg sediment dw (35.9 ± 1.1 g/kg TOC). The dw content of the artificial sediment was 67.7 ± 0.1% with a TOC content of 42.9 ± 0.9 g/kg. The water quality parameters did not exceed the acceptable values in any of the experiments. The oxygen saturation was generally above 60%. The pH values in the natural sediment stayed in between 6.4 and 8.4, and the highest measured ammonia concentrations were 1.4 mg/L, although in most vessels no significant ammonia production occurred. The water in microcosms filled with artificial sediment showed higher pH values between 8.0 and 8.8 and higher ammonia levels (up to 3.3 mg/L).

3.3. Remediation Efficiency. The PCB-bioaccumulation results showed a clearly higher performance of ACC-G compared to the conventional GAC with both test species. For L. variegatus, only the highest applied dose (7.5%) of GAC was capable of significantly lowering the bioaccumulation of PCBs by 43.44 ± 3.03% compared to the unamended control sediment (Figure 3A). This is in line with findings by Zimmerman et al.,19 who found GAC to be mostly ineffective in doses up to 3.4% (higher doses were not tested). ACC-G on the other hand were effective in doses of 2.0%, 4.0%, and 7.5%. Already 4.0% of ACC-G reached a significantly higher reduction of PCB uptake (75.85 ± 9.04%) than seen with 7.5% of GAC. With the highest dose, the contaminant accumulation could be almost completely prevented (reduction of 89.26 ± 0.33%).

For C. riparius the remediation efficiencies of both AC materials were slightly lower, an observation also made by Nybom et al. None of the GAC treatments showed a significant reduction in PCB bioaccumulation in the larvae, although a nonsignificant reduction of 34.85 ± 6.12% was observed at the highest dose (7.5%, Figure 3B). ACC-G showed a reduction of PCB body burdens starting at a dose of 2.0% (28.42 ± 10.74%, not significant). At 4.0% and 7.5%, the granules significantly reduced the contaminant uptake by 54.04 ± 23.48% and 79.04 ± 2.98%, respectively.

These findings show that ACC-G was capable of reaching similar remediation efficiencies as PAC in practically applicable doses; it has been reported that 1.0–3.5% of PAC is generally enough to reach contaminant bioaccumulation reductions of at least 85% and more in L. variegatus and 70% in C. riparius.6,32–35 However, a higher dose of AC is required to reach similar results when applied as ACC-G (4.0–7.5%).

Lebo et al.33 and Zimmerman et al.18 showed the importance of available external sorbent surface area available for its contaminant binding potential. In GAC, a large share of the surface area can be inaccessibly locked in the core of the particle, thus reducing its adsorbent capacity, as seen in this study. The lower measured water permeability of GAC supports this hypothesis. Furthermore, it was observed that fine sediment particles can deposit on the AC particles (Figure S1C and S1D). This can potentially clog existing pores, further reducing the accessible AC surface. The SSA of GAC was not substantially lower compared to PAC. However, the increased external surface area of ACC-G, combination with the higher permeability of ACC-G, this provides a greater amount of surface area accessible for contaminant sequestration. It furthermore reduces the effect of pore clogging and thus prevents the isolation of PAC in the core of the granule from the surrounding sediment pore water.

The lipid analysis showed no significant impact of any treatment on C. riparius (Figure S5B), but there was a high variability between and within most treatment groups. For L. variegatus the only significant impact was a lowered lipid content in organisms exposed to the highest (7.5%) dose of ACC-G (Figure SSA).

3.4. Adverse Effects. The slightly lowered L. variegatus lipid contents in the highest ACC-G dose indicated a potential for adverse effects to certain benthic organisms. Similar observations with ACs in particle sizes below 200 μm have been made for example by Jonker et al.12 and Nybom et al.13 Furthermore, it was noted that the final biomass sampled in
the PCB bioaccumulation tests was comparably low at the higher doses of ACC-G (4.0% and 7.5% for L. variegatus and 7.5% for C. riparius; Figure S6). These indications motivated the more thorough investigation of targeting the sorbent material’s adverse effects. To further investigate the origins of the adverse effects, the test run included the raw material constituents of ACC-G: PAC (as powder) and clay (as granules).

The artificial sediment provided a good substrate for both test organisms. L. variegatus showed a more than 2-fold increase in numbers of individuals (Figure S7A) and biomass (Figure 4A) over the 28 days exposure time in the untreated sediment. All C. riparius larvae survived in the control sediment (Figure S7B), and most individuals had reached the third or fourth (final) instar (Figure S8). However, larval growth in the control was lower during the first experiment repetition (Figure S9). This lowered growth could be seen throughout the treatment groups during the same run, which resulted in a higher relative contribution (ca. 50%) of the random factor to the overall variance in the statistical linear mixed effects model. The cause for this variation is likely a difference in the initial condition of the freshly hatched larvae used to stock the microcosms. This highlights the benefit of a repeated experiment setup in bioassays with this organism, as it allows one to obtain a more robust and reliable data set. For L. variegatus, the random effect of experiment repetition was lower (ca. 18% of the total variance).

The bioassays with the amended sediments showed that AC can pose a significant risk to benthic organisms. In particular, L. variegatus showed a strong adverse reaction to PAC. Already at the lowest applied dose of 0.75%, the organism’s growth was inhibited almost completely, and with 2.0% and more PAC in the sediment, the test organisms even lost biomass (Figure 4A). The most severe effect of any AC treatment was observed with 7.5% PAC, where the organisms lost 29.0 ± 5.0% biomass after 28 days in the sediment. The adverse effects of ACC-G were less severe. No significant impact on organism growth was detected with the 0.75% amendment. At 2.0% and higher doses, the growth started to be significantly lower than in the unamended control sediment. A significant loss in biomass, as observed with PAC, was not observed with ACC-G. However, at 4.0% and 7.5%, almost no growth was measured. Neither the clay nor the GAC in any of the applied doses showed a significant adverse effect on L. variegatus. Effects on reproduction (Figure S7A) followed the observed effect on growth. Mortality was not observed in any treatment, despite the loss in biomass in some PAC treatments, indicating that the effects of the presently tested AC concentrations are sublethal rather than lethal. Adverse effects of fine AC particles to L. variegatus have also been observed in previous studies. Using artificial sediment, losses of biomass in similar magnitudes have been observed by Nybom et al. The authors furthermore found a significant adverse impact of GAC to the test organism. However, GAC doses that caused a drastic reduction in growth were 10–15% and thus outside of the range of applied doses in this study. Studies conducted in natural sediment, which often provides less suitable conditions for L. variegatus, find even higher losses in biomass.

C. riparius showed similar adverse reactions to the applied AC materials, although at a much lower magnitude, suggesting a lower sensitivity in comparison to L. variegatus. Survival was above 80% in most treatment groups. Significant mortality occurred only in PAC treatments of 2.0%, 4.0%, and 7.5% (Figure S7B). Survival in these groups was 40.0 ± 32.7%, 46.7 ± 37.7%, and 26.7 ± 18.9%, respectively. Correspondingly, the final biomass and body length of the surviving larvae were significantly lowered at these PAC doses (Figure 4B and 4C). At the highest PAC dose, the larvae grew only 12.6 ± 5.9% of the larva in the control sediment. A weakly significant (*) negative impact on the biomass, but not on body length, was detected for ACC-G at 4.0% and 7.5% as well as for the inert clay granules at 7.5%. Unlike for L. variegatus, the growth of the larvae was still relatively high for both clay ACC-G, reaching more than 60% of that of the control group. The adverse effects of ACC-G thus did not reach severe levels for C. riparius. The development of larvae was strongly delayed by PAC in doses of 2.0%, 4.0%, and 7.5%, where a large share of larvae was still at the second instar after 10 days (Figure S8). In all other treatments, the larvae were at the third or fourth instar.

Both the quality and the magnitude of effects reflect observations made by Nybom et al., who found PAC doses above 1.0% to reduce larval survival and growth but no significant impact of GAC. It remains unclear why the larvae reacted more sensitive to the clay-only granules. It cannot be ruled out that the growth-inhibiting impact of ACC-G is at least in part caused by the clay matrix. Whether this effect can be avoided by using different clay varieties should be tested in the future development of the material.

The cause of the adverse effects on small benthic organisms, such as L. variegatus and C. riparius, has been suggested to be the ingestion of AC particles, resulting in damage to the organism’s gut. This is supported by the lower impact of the noningestible GAC compared to the ingestible PAC, which
The adverse effects of the noningestible ACC-G granules are thus likely to be caused by PAC particles separating from the clay matrix. The adsorption of nutrients from the sediments has been suggested as an additional possible cause for the adverse effects observed with ACs. However, this would be expected to occur also with higher doses of GAC. The lack of adverse effects observed with GAC therefore indicate a smaller impact of nutrients becoming unavailable to benthic organisms after the amendment of AC. Another suggested source of the toxicity of AC is a local oxygen depletion due to hindered diffusion. This is mostly of concern where AC is applied as a thin-layer cap, leading to extremely high exposures of organisms at the sediment surface. The added space in between the coarser ACC-G granules, compared to a dense PAC layer, could thus provide another benefit of the newly developed material. However, further testing of the granules using a thin-layer capping application technique is required.

The small difference found for the particle size distribution of the granular sorbents GAC and ACC-G (Figure S10) cannot explain the observed differences in adverse effects or remediation efficiencies. As discussed above, both remediation efficiency and adverse effects rise with decreasing particle sizes. However, GAC was more skewed toward the medium and lower particle sizes within the 400–1000 μm range, while ACC-G was generally coarser (69% and 28% of particles < 630 μm, respectively). The reason for this is likely the large minimum particle size of both materials and a similarly low content of the finest particles (<20% particles < 500 μm).

3.5. AC Material Stability. The stability of the two granular AC materials (ACC-G and GAC) were assessed as their recovery from the sediment after the exposure experiments. The calculations for this are described in detail in the SI. Depending on the applied dose, approximately 56–90% of the initially applied GAC and 66–72% of ACC-G could be recovered (Figure S11). Although the maximum recoveries for ACC-G tended to be lower, the difference was not statistically significant. The random effect from the applied material doses accounted for ca. 17% of the total variance in the linear mixed effect model. This was mostly caused by the lower variation of recoveries in treatment groups treated with higher material doses.

Despite not being significant, a separation of PAC particles from the ACC-G granules cannot be ruled out. Given the high impact of PAC in small doses shown in this study, it cannot be ruled out that this had an impact on the results. In particular, the adverse effects might be further reduced if the production process of ACC-G could be optimized to further reduce losses of PAC.

4. IMPLICATIONS

Although ACC-G may not be cleared of the adverse effects caused by PAC, they show a tendency toward lower adverse effects in doses that are efficient for remediation. Compared to GAC, the novel granules showed a much greater remediation efficiency. These advantages are further combined with an easier application and potentially better on-site retention of the sorbent material due the higher density of the granule. Altogether, ACC-G can become a promising alternative to both conventional PAC and GAC. However, because of the early development stage of the material, further improvement of the manufacturing process is required before field-scale applications can be implemented. One of the top priorities in the current development process is to maximize the stability of the granules. This should prevent the unintentional loss of small amounts of PAC post amendment, thereby further lowering the adverse impact of the sorbent material to benthic organisms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b06471.

More detailed descriptions of experimental setups, additional photographs and characterization parameters (surface area, water holding capacity) of the sorbent materials, equation for material recovery (3.5), and graphs on minor end points (organism lipid contents, reproduction and C. riparius developmental stage) (PDF)

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Notes

The authors declare no competing financial interest.

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