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Effects of activated carbon ageing in three PCB contaminated sediments: Sorption efficiency and secondary effects on *Lumbriculus variegatus*

Inna Nybom [a, *], Greta Waissi-Leinonen [a], Kimmo Mäenpää [a], Matti T. Leppänen [b], Jussi V.K. Kukkonen [c], David Werner [d], Jarkko Akkanen [a]

[a] *Department of Biology, University of Eastern Finland (UEF), P.O. Box 111, FI-80101, Joensuu, Finland*
[b] *Finnish Environment Institute (SYKE), Ecotoxicology and Risk Assessment Group, P.O. Box 35, FI-40014, University of Jyväskylä, Finland*
[c] *University of Jyväskylä, Department of Biological and Environmental Science, P.O. Box 35, FI-40014, University of Jyväskylä, Finland*
[d] *School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne, NE1 7RU, England, United Kingdom*

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A B S T R A C T

The sorption efficiency and possible secondary effects of activated carbon (AC) (ø 63–200 μm) was studied with *Lumbriculus variegatus* in three PCB contaminated sediments applying long AC-sediment contact time (3 years). AC amendment efficiently reduced PCB bioavailability as determined with both, *L. variegatus* bioaccumulation test and passive samplers. However, dose related secondary effects of AC on egestion rate and biomass were observed (applied doses 0.25% and 2.5% sediment dry weight). The sorption capacity and secondary effects remained similar when the experiments were repeated after three years of AC-sediment contact time. Further, transmission electron microscopy (TEM) samples revealed morphological changes in the *L. variegatus* gut wall microvilli layer. Sediment properties affected both sorption efficiency and secondary effects, but 2.5% AC addition had significant effects regardless of the sediment. In conclusion, AC is an efficient and stable sorbent to decrease the bioavailability of PCBs. However, sediment dwelling organisms, such as Oligochaete worms in this study, may be sensitive to the carbon amendments. The secondary effects and possible morphological changes in benthic organisms should not be overlooked as in many cases they form the basis of the aquatic food webs.

1. Introduction

Light density black carbonaceous particles in the sediment (e.g. soot carbon, coal, coke and charcoal) are efficient sorbents for hydrophobic organic compounds (HOCs) and capable of reducing contaminant aqueous concentrations and bioavailability (Jonker and Koelmans, 2002; Ghosh et al., 2003). Consequently synthetic black carbon amendments, such as activated carbon (AC), have been studied as an in situ remediation technique for stabilizing contaminated sediments. AC amendments have been shown to reduce biological and aqueous concentrations of a wide variety of HOCs e.g. polychlorinated biphenyls (PCBs) (Zimmerman et al., 2005; Sun and Ghosh, 2008; Cho et al., 2009; Janssen et al., 2010; Kupryianchyk et al., 2013b), polycyclic aromatic hydrocarbons (PAHs) (Zimmerman et al., 2005; Cornelissen et al., 2006; Rakowska et al., 2013), dichlorodiphenyltrichloroethanes (DDTs) (Tomaszewski et al., 2008; Hale et al., 2009; Lin et al., 2014), and organotins such as tributyltin (TBT) (Brändli et al., 2009).

Along with the remediation benefits, secondary effects of AC have also been investigated. Reduced weight or inhibition in growth (Millward et al., 2005; Kupryianchyk et al., 2011; Janssen et al., 2012; Nybom et al., 2012; Kupryianchyk et al., 2013b) and decreased lipid content (Jonker et al., 2009; Janssen et al., 2011; Nybom et al., 2012) have been reported for several organisms with AC doses of 4% sediment dry weight (dw) or lower, and with higher doses (15–20% sediment dw) avoidance behaviour has been observed (Jonker et al., 2009). Adverse effects have been seen especially on sediment-dwelling organisms exposed to AC amendments both externally through sediment and internally through ingested AC particles (Jonker et al., 2009; Nybom et al.,

* Corresponding author.
E-mail address: inna.nybom@uef.fi (I. Nybom).

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2012). Contrarily other studies have reported no effects on growth (Millward et al., 2005; Janssen et al., 2011; Kupryianchyk et al., 2011; Janssen et al., 2012; Josefsson et al., 2012), lipid content (Millward et al., 2005; Janssen et al., 2011, 2012; Josefsson et al., 2012; Kupryianchyk et al., 2013b) or avoidance behaviour (Kupryianchyk et al., 2011; Janssen et al., 2012) and through reduced sediment toxicity even some positive effects on survival in short term experiments has been observed (Kupryianchyk et al., 2011). The ecological responses were recently reviewed by Janssen and Beckingham (2013) and Kupryianchyk et al. (2015).

Despite of interest toward ecological responses the majority of the research has focused on assessing contaminant bioaccumulation. The mechanisms behind the AC induced ecological effects remain unclear. AC has been shown to bind nitrogen from the water (Janssen et al., 2012), but the observed avoidance behaviour and reduction in feeding (Jonker et al., 2009; Nybom et al., 2012) indicates that AC may also affect sediment dwelling organisms through some other mechanisms. Sediment-dwelling organisms are relevant test species since they form the base of many aquatic food webs acting as an important food source for predatory invertebrates and fishes. Changes at the bottom of the food webs may alter not only the food web structure but also food chain transfer of HOCs (Figueiredo et al., 2014).

The present study investigates the effects of AC amendments on bioavailability of PCBs in three different sediments by applying *Lumbriculus variegatus* bioaccumulation tests, and passive sampling with silicone coated glass method. The secondary effects of the amendments on *L. variegatus* were studied by determining egestion rate, reproduction, biomass and lipid content of the worms when exposed to AC, and by preparing transmission electron microscopic (TEM) samples to study internal structure changes.

2. Materials and methods

2.1. Organisms

L. variegatus used as a test organism were reared at the University of Eastern Finland in the Department of Biology. The rearing method has been described earlier (Leppänen and Kukkonen, 1998a). Prior to the experiments the worms were acclimated in artificial fresh water for 24 h. Small and actively swimming worms were chosen by visual observation (Leppänen and Kukkonen, 1998b). The weight of the worms at the beginning was evaluated by weighting a set of individuals (minimum 23 worms) with the representative size 5–9 mg ww (Leppänen and Kukkonen, 1998b) prior to experiment.

2.2. Sediments

Three natural sediments from PCB contaminated areas in Southern Finland were chosen in the experiment. The sediments were collected from the River Tervajoki (N 60° 82′ 34″ E 24° 63′ 52″, TJ) and from Lake Kernaalanjärvi (N 60° 85′ 44″ E 24° 64′ 21″, KJ) located downstream of the same water body. Some studies of the KJ water district have been previously published (Koponen et al., 2003; Mäenpää et al., 2011; Figueiredo et al., 2014). A third sediment for the experiments was collected from Viinikanlahti bay (N 61° 48′ 97″ E 23° 76′ 70″, VL) which is unrelated to the previously mentioned water body. The PCB contamination in KJ and TJ relates to discharges of PCB oils from a paper mill from 1956 to 1984 (Figueiredo et al., 2014). In VL a single source of contamination cannot be named, but the contamination is a result of an extensive use and production of PCB compounds prior to the 1970s. The sediments were sieved to a particle size smaller than 1 mm and stored at 5 °C prior to the experiments. Total organic carbon (TOC) and black carbon (BC) content of the sediments was analysed with an Analytik Jena TOC analyser with a solid sample module (Analytik Jena N/C 2100, Jena, Germany). Phosphoric acid (1 M) was used to remove the inorganic carbon from the sediment samples. BC content was determined according to the chemical oxidation pretreatment method (BC-chemox) described by Grossman and Ghosh (2009).

Sediment samples were extracted for PCBs with acetone:hexane (1:1). The fresh sediment was dried by applying Na_2SO_4, weighted in extraction thimbles and extracted with a Soxtec system (1043 Extraction unit, Tecator AB, Höganäs Sweden) and analysed by using an internal standard method. The procedure is described in detail in the Supplementary content. PCB 30 was used as internal standard and PCB 159 as an injection standard. Overall 20 PCB congeners were analysed; 18, 28, 31, 44, 49, 52, 70, 101, 105, 110, 114, 118, 138, 149, 151, 153, 156, 157, 167 and 180. The extracted samples were analysed for PCB congeners with a gas chromatograph (Hewlett–Packard series 6890) coupled with a mass selective detector (MSD) (Hewlett–Packard, Avondale, PA, USA). The methods of analysis and quality assurance are the same as in Figueiredo et al. (2014) and are described therein.

2.3. Activated carbon

Bituminous coal-based AC, Carbsorb® 40 (Chemviron Carbon, England) was used in the experiments. Prior to use the AC was ground and sieved to match the particle size range ø 63–200 μm. Based on the selected particle size fraction both internal and external exposure was expected, since particles smaller than 100 μm are ingestible for *L. variegatus* (Nybom et al., 2012). The particle size fraction of AC was verified by Nybom et al. (2012), stating that based on organic petrography analysis most of the particles were in the nominal size range, although some smaller particles were also detected. The mixing procedure may also cause some abrasion of AC particles, but the effect is expected to be for a minor fraction of the total mass of AC applied (Nybom et al., 2012). The AC was amended to the sediment by presoaking it into the water over night followed by mixing into the sediments with a stainless steel paddle driven by an overhead motor for 2 h. AC was added to the test sediments on a dw basis on dosages of 0.25% and 2.5%. Dosages were selected to represent low and average level of AC addition generally recommended for remedial purposes (1–5%) (Ghosh et al., 2011). Amended sediments were allowed to settle in closed glass vials for two weeks (12–18 days), in darkness at 5 °C prior to the first experiments. Experiments were repeated three year later, when the AC-sediment contact time (CT) was 1093–1171 days. Correspondingly the sediments were kept in dark, at 5 °C prior to the second experiment set. The control sediments without AC amendment were processed accordingly.

2.4. Experimental design and ecological responses

2.4.1. Experimental setup

Both experimental sets, with the settling time of two weeks and three years were performed according to the same methods. Experiments were conducted in standard conditions 20 ± 1 °C, 16:8 light:dark, (OECD, 2007). Sediment was weighted into a glass experimental vessel and artificial fresh water, 1 mM, pH 6.5–7.5 (OECD, 1992) was placed on top of the sediment, after which the experimental units were allowed to settle for two days under aeration prior to the experiments. Experimental units were aerated during the experiments. Oxygen content, water and sediment pH and temperature was monitored weekly (MultiLine P4, Weilheim Germany). Part of the overlying water in experimental units was changed when required with an objective to keep the water pH in