Ecotoxicology and Environmental Safety 130 (2016) 171–176

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

The mode of bioturbation triggers pesticide remobilization from aquatic sediments

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ARTICLE INFO

Article history:
Received 7 January 2016
Received in revised form
1 April 2016
Accepted 7 April 2016
Available online 22 April 2016

Keywords:
Mode of bioturbation
Pesticide remobilisation
Radioactively labeled pesticides
Monoporeia affinis
Chironomus riparius
Lumbriculus variegatus

ABSTRACT

After their release into the aquatic environment, contaminants may – depending on the physicochemical properties – adsorb to sediments. From there these contaminants can either be buried or remobilised by abiotic factors (e.g., resuspension) as well as by the bioturbating activity of sediment dwelling invertebrates. Little is, however, know about the effects of bioturbation on the fate of pesticides. Therefore, the present study quantified the impact of the bioturbation mode of benthic invertebrate species (biodiffusor vs. bio-irrigation), the invertebrate density (i.e. 0–8 individuals per replicate), and the substance-inherent properties (i.e. hydrophobicity, water solubility) on the remobilization of sediment-associated pesticides in a laboratory-based set-up over 13 days. We found that both the bioturbation mode (i.e., species identity) and species density, as well as pesticide properties (i.e., hydrophobicity) affected the direction and magnitude of remobilisation of sediment-bound pesticides. The oligochaeta *Lumbriculus variegatus* showed a density-dependent effect on the remobilization of lindane to the water phase, whereas those with the amphipod *Monoporeia affinis* and larvae of the midge *Chironomus riparius* did not. Although these findings show that sediments not per definition are a sink for pesticides, the rates of pesticide remobilization are limited. This observation, thus, suggests that the risk for aquatic communities posed by the remobilization of pesticides from the sediment due to bioturbation is low.

1. Introduction

Pesticides (i.e., insecticides, herbicides and fungicides) are essential components of the current agricultural practice that contribute to securing food production for a growing human population (sensu Verger and Boobis, 2013). Following their application pesticides, either dissolved or associated with soil particles, frequently enter aquatic ecosystems through diffuse sources such as drainage, spray drift and/or surface run-off (Schulz, 2004). Depending on their properties, pesticides dissolved in water are either transported further downstream (Schäfer et al., 2011) or absorbed to sediments (Cooper et al., 2003) and other submerged surfaces such as macrophytes (Stehle et al., 2011). In contrast, pesticides that enter aquatic ecosystems adsorbed to soil particles will, to a large extent, be removed from the water column during low-flow conditions and deposited in sediments (Bereswill et al., 2012). Sediment-associated pesticides can be remobilised by resuspension during high discharge events or by bioturbation (Ciarelli et al., 1999). Bioturbation, defined as the disturbance or sediment-mixing caused by the burrowing and feeding activity of sediment-dwelling organisms (Roberts, 2012), provides important ecosystem processes, such as preventing phosphate leakage from sediments by oxidizing surficial sediment layer (Palmer et al., 1997). Bioturbation by a sediment-feeding carp, for example, increased the cadmium water concentration as well as the total suspended solids in the water phase (Wall et al., 1996). Similar effects on the remobilization of cadmium (Ciutat et al., 2007), copper (Remaili et al., 2016), polychlorinated biphenyls (Hedman et al., 2009; Josefsson et al., 2010) and flame-retardants (Hedman et al., 2008) have been observed for polychaetes and amphipods.

The remobilisation potential of most sediment-associated organic contaminants largely depends on their hydrophobicity, but also on their burial depth, as the depth of bioturbation varies among invertebrate species. For example, while bio-irrigators such as the polychaete *Marenzelleria* spp. are capable of remobilizing contaminants buried in deep sediment layers (up to 10 cm) (Håkanson and Jansson, 1983), bio-diffusors such as *Monoporeia affinis* rework only the upper few centimetres of the sediment omni-directionally (Håkanson and Jansson, 1983). While these processes are relatively well described for metals and some organic contaminants, the role of bioturbation for pesticide remobilisation from sediments is largely unknown. To our

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http://dx.doi.org/10.1016/j.ecoenv.2016.04.013
0147-6513/

knowledge only a single study has assessed the remobilisation of pesticides through bioturbation by benthic invertebrates. In this study, the lindane concentrations in the water overlying experimental sediments increased across a gradient in densities of the bio-irrigator midge *Chironomus riparius,* whereas sediment concentrations declined (Goedkoop and Peterson, 2003).

In the present study we assessed the effects of (i) the bioturbation mode of benthic invertebrate species (i.e., bio-diffusor, bio-irrigation) (ii) invertebrate densities, and (iii) the substance-inherent properties (i.e. hydrophobicity, water solubility) on the remobilization of sediment-associated pesticides. In our experimental design we assessed the fate of ^{14}C-labeled pesticides with common freshwater invertebrate species that differ in their mode of bioturbation, that is the amphipod *Monoporeia affinis* (Crustacea), the midge *C. riparius* (Diptera) and the oligochaete *Lumbriculus variegatus* (Annelida). The amphipod is thoroughly mixing the surface layer of sediment (Van de Bund et al., 1994) and exclusively burrows and feeds in the top 1-cm of the sediment (Lopez and Elmgren, 1989) and thus acts as a bio-diffusor. Bio-irrigating larvae of *C. riparius* instead feed on the sediment surface and build distinct tubes into the sediment which they ventilate by undulating body movements. Their tube ventilation and feeding activity should result in a net downward transport of materials (Håkanson and Jansson, 1983). Similarly, oligochaetes such as *L. variegatus* are"conveyor belt-feeders" that forage in deep sediment and defecate at the sediment surface (Robbins et al., 1979). In contrast to amphipods, oligochaetes mix sediments in a highly ordered manner, bringing deep sediments back to the surface (Håkanson and Jansson, 1983). The insecticides lindane and chlorpyrifos were used as model pesticides at concentrations that would not directly affecting the organisms (i.e., no effects could be detect during the present study). We hypothesized that the mode of bioturbation would affect the reflux of the pesticides from the sediment to the water. More specifically, we assumed that bio-diffusors would remobilize higher pesticide loads from contaminated sediment relative to bio-irrigators.

2. Material and methods

2.1. Chemicals

Lindane (International Izotope, Munich, Germany) and Chlorpyrifos (American Radiolabeled Chemicals, St Louise, MO, USA) were purchased as ^{14}C-labeled standards with a purity of $>99\%$ and a specific activity of 1.099×10^{12} Bq/mol and 1.184×10^{12} Bq/mol, respectively. These compounds were selected as they differ in their hydrophobicity and water solubility. Lindane has a log K_{ow} of 3.5 and a water solubility of 8.52 mg/L at 20 °C, while the equivalent numbers for chlorpyrifos are 4.7 and 1.05 mg/L, respectively. Stock solutions with a concentration of 30.7 μg lindane/mL and 17.0 μg chlorpyrifos/mL – concentrations have been verified by scintillation counting – were prepared with acetone (analytical grade). Concentrations of both compounds in the water phase, in the sediment, and associated with suspended particles were quantified by liquid scintillation counting using Optisafe Hisafe2 scintillation cocktail and a Tri-Carb 2100TR liquid Scintillation counter (Beckman LS6000TA, Beckman Counter AB) and Optisafe Hisafe 2 scintillation fluid (Wallac, PerkinElmer, Turku, Finland). Each sample was counted for 10 min or a minimum of 10,000 CPM. Quench corrections were done using internal ^{14}C-standards (Wallac, PerkinElmer, Turku, Finland). Scintillation counts for samples were corrected for background values using blanks with no spiking of radioactive compounds. All other chemical were purchased from VWR if not otherwise specified.

2.2. Test organisms and sediment

The chironomid *C. riparius* and the oligochaete L. *variegatus* were obtained from the in-house cultures at the Department of Aquatic Sciences and Assessment and from ECT Oekotoxikologie GmbH, respectively. *Chironomus* were cultured at 20 ± 1 °C and fed with commercial fish-food (Tetraphyll®). Three days prior to the start of the experiments approximately 200 fourth instar *Chironomus* larvae were transferred to aerated lake water at 11 ± 1 °C. *M. affinis* were collected from in the Görväln basin of Lake Mälaren near Stockholm, Sweden, and stored at 11 ± 1 °C in lake water until further use (max 10 days). Also natural fine grained sediment was sampled in the Görväln basin from a depth of 40–44 m using an Ekman sampler. The sediment is characterized by a water content of approximately 90%, an ash-free dry weight of around 13% of the dry weight and exhibits an organic carbon content of 65 mg/g sediment dry weight (Goedkoop and Johnson, 1994). In the laboratory, the sediment was sieved (250 μm) to remove ambient fauna and stored at 11 ± 1 °C for 10 days to allow sediment particles to settle. After 10 days the overlying water was discarded and replaced with fresh lake water in the experimental units (see below).

2.3. Experimental design

Bioturbation effects on the fate of lindane and chlorpyrifos were investigated in a set-up with microcosms (170 mL cylindrical glass vessels, i.d. 5.5 cm) that contained a 1.5-cm sediment layer and 33 mL of overlying lake water. Either 0, 2, 4 or 8 individuals per replicate were added to quantify the effects of invertebrate density on the fate of these pesticides. These experimental densities correspond to 3360–13,400 ind/m^2, densities that well cover those found in natural sediments (see for chironomids Armitage et al., 1995). While the experiments with lindane run with all three species of invertebrates ($n=4$), those with chlorpyrifos were run only with *M. affinis* ($n=3$).

Spiking of the experimental sediment with pesticides was done in two steps, adopting the methodology described in OECD-guideline 218 (OECD, 2004). First 2.4 g quartz sand was added to each of the test microcosms and 500 μL of pesticide stock solution was amended to this sand. Over the subsequent 24 h the solvent acetone was completely evaporated under a stream of air. Second, 36.3 g of sieved (250 μm) Görväln basin sediment was added and thoroughly mixed with the spiked sand. Subsequently, 33 mL of lake water was carefully added to each replicate without re-suspending the sediment particles. Each microcosm was aerated for 15 min/h 2.0–3.0 cm above the sediment surface using capillary tubing (i.d. 0.76 mm). The test organisms were introduced after a seven-day equilibration phase (OECD, 2004).

All experiments were run for 13 days as the emergence of *C. riparius* was expected thereafter (OECD, 2004). During the study pesticide water concentrations were quantified at days 0, 1, 2, 4, 10 and 13 by subtracting 500-μL water samples 0.5 cm above the sediment-water interface. At the termination of the experiments (i.e. on day 13), pesticide concentrations in the sediment as well as those associated with suspended particles were quantified. Suspended particles were separated from the overlying water by filtering 20 mL of the overlying water (0.2 μm pore filters). All samples were mixed with 10 mL of scintillation cocktail and analyzed using liquid scintillation counting. Please note that the concentrations associated with the suspended particles contributed far less than 1% to the overall pesticide mass budget. Thus, these measurements are not further considered in this study.