Fate of contaminants in Baltic Sea sediments: role of bioturbation and settling organic matter

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ABSTRACT: This experimental study examined the interactive effects of bioturbation and settling organic matter (OM) on the fate (burial and remobilisation) of 2 surface-deposited contaminants in Baltic Sea sediment: the metal Cd and a hydrophobic organic pollutant, the flame retardant BDE-99. Three macrofaunal species with diverse feeding and bioturbation strategies were used: the amphipod *Monoporeia affinis*, the clam *Macoma balthica* and the polychaete *Marenzelleria* spp. Radio-labelled contaminants were added to the sediment surface in association with 3 different OM types: (1) phytoplankton, (2) terrestrial lignin and (3) Baltic sediment. Bioturbation by all species increased the retention of both contaminants in the sediment, most effectively *M. affinis* and *M. balthica*. A decoupled transport of Cd and BDE-99 by *Marenzelleria* was observed. Generally, *Marenzelleria* buried the highest amount of Cd into the sediment but also caused the highest remobilisation to the water, indicating an effective transport of (soluble) Cd over the sediment–water interface via bio-irrigation. Lack of the highly hydrophobic and mainly particle-associated BDE-99 below the sediment surface suggests that *Marenzelleria* caused no significant particle mixing. The addition of various OM types significantly affected the distribution of Cd, but not of BDE-99. There was an interactive effect between bioturbation (species) and OM type, generally showing an increased burial and release of Cd when associated with phytoplankton in the presence of *Marenzelleria*. Our results emphasise the importance of understanding the complex interactions between ecological (e.g. infaunal feeding and bioturbation activities) and physiochemical processes (contaminant speciation and sorption kinetics) when assessing the fate of contaminants in aquatic ecosystems.

KEY WORDS: Cadmium · BDE-99 · HOC · POP · Flame retardant · *Marenzelleria* spp. · *Macoma balthica* · *Monoporeia affinis* · Remobilisation

INTRODUCTION

A key process for the fate of many persistent organic pollutants (e.g. PCBs, dioxins) and metals (e.g. Cd, Pb) in aquatic ecosystems is their sorption to settling organic matter (OM) and subsequent deposition on and burial in sediments. Contaminants can be effectively incorporated into the sediment as a result of active bioturbation (i.e. sediment reworking) by benthic infauna (Gilbert et al. 1996, Magnusson et al. 2003). This can increase the retention of contaminants in the sediment and reduce their bioavailability, mak-

ing the sediment an important sink. However, bioturbation can also lead to an increased mobilisation of sediment-associated contaminants (Ciarelli et al. 1999, Ciutat & Boudou 2003).

The specific effect of macrofaunal bioturbation on contaminant fate in sediments has been attributed to the organisms' mode of bioturbation, i.e. their feeding and burrowing strategies and intensity (Schaffner et al. 1997, Petersen et al. 1998, Christensen et al. 2002, Banta & Andersen 2003). Random mixing (biodiffusion) and advective transport of particles within the sediment by infauna is especially important for the

cycling of sediment-associated organic contaminants and metals (Ferro et al. 2003, Caradec et al. 2004). Bioirrigation, on the other hand, increases the flux of solutes, i.e. dissolved compounds in the pore water and over the sediment–water interface (Aller & Aller 1998). The partitioning of a contaminant between the solid and water phase in sediments depends on the contaminant's inherent properties and the biogeochemical state of the sediment. Hydrophobic organic contaminants (HOCs) preferentially adsorb to particulate OM in sediments, and their distribution between phases generally can be calculated based on the physiochemical properties of the compound, such as water solubility and lipophilicity, and the amount of OM in the sediment (Schwarzenbach et al. 2003). The partitioning of metals is strongly affected by the sediment chemical environment, such as pH, redox conditions and the presence of other chemical species (Chapman et al. 1998). Under oxic conditions, many metal contaminants, e.g. Cd, Cu and Zn, partition to OM or inorganic fractions, such as clay particles and oxides/hydroxides, while the formation of less soluble metal sulphides dominates in anoxic sediments (Di Toro et al. 1990, Audry et al. 2006). Bioturbation can significantly affect the biogeochemical properties of the sediment, e.g. oxygenation, OM degradation and microbial activities (Aller 1988, Kristensen et al. 1992), and thereby also change the partitioning of contaminants.

Settling OM is the main food source for deposit-feeding infauna (Graf 1992). Typically, the supply of OM to benthic communities varies spatially and temporally, both in terms of quantity and quality. The 'quality' of OM can be defined in different ways and relates here to its nutritional value to benthic organisms and susceptibility to biodegradation (Gunnarsson et al. 1999a). Labile OM, e.g. phytoplankton, is highly nutritious and readily biodegraded, whereas refractory OM usually contains more low-quality structural elements, such as lignins and cellulose, and is more resistant to degradation. A positive relationship between bioturbation intensity and food availability has been found in several studies (Jumars & Wheatcroft 1989, Maire et al. 2006), and a more rapid burial of fresh particulate OM compared to older, more refractory OM has been suggested as a theory of 'age-dependent' mixing (Smith et al. 1993). Another aspect of OM 'quality' is the importance of its chemical composition in relation to contaminant sorption capacity. Generally, it is suggested that contaminants are more strongly associated with older refractory OM than with fresh labile OM (Lueking et al. 2000). OM composition may therefore influence the partitioning and distribution of contaminants in sediments directly due to their various sorption capacities, and indirectly by acting on the feeding and bioturbation activities of animals.

We investigated how the fate of surface-deposited contaminants was affected by: (1) bioturbation by benthic invertebrates with diverse feeding and bioturbation strategies, and (2) settling OM from different sources and of different nutritional qualities. Three common infaunal Baltic Sea species were used: the amphipod *Monoporeia affinis*, the clam *Macoma balthica* and the spionid polychaete *Marenzelleria* spp. The amphipod and the clam are mainly biodiffusors, mixing particles in the upper 5 cm of the sediment, while the polychaete creates semi-permanent burrows down to about 30 cm. We used 2 model compounds with different chemical characteristics: the metal cadmium (Cd) and a hydrophobic organic contaminant, the flame-retardant BDE-99. Cd is a common contaminant in aquatic environments, including the Baltic Sea (HELCOM 2003). During oxidising conditions, Cd can be mobilised to the sediment interstitial water due to the formation of free metal ions and complexation with soluble organic and inorganic ligands, while in reduced sediment, Cd forms insoluble sulphide precipitates (Di Toro et al. 1990). Polybrominated diphenyl ethers (PBDEs) are a group of persistent organic pollutants with high hydrophobicity (log K_{OW} values 4 to 10), high sorption affinity to particles and a tendency to accumulate in sediments and biota (de Wit 2002). Chemically, PBDEs resemble other HOCs, e.g. PCBs, but our knowledge of their environmental fate and effects is in comparison very limited. BDE-99 is one of the most commonly encountered PBDE congeners in environmental samples (de Wit 2002).

Both contaminants were added to the sediment surface associated with the different OM types. Our main hypotheses were that the redistribution of Cd and BDE-99 would be species-specific, and that the input of settling OM with a high nutritional quality would stimulate infaunal feeding and bioturbation activities, thereby increasing the overall redistribution of the associated contaminants.

MATERIALS AND METHODS

Experimental design. The experiment was performed using a 2-factorial design with animal and OM as fixed factors. The animal factor had 4 levels (3 different animal species and a control without animals). The OM factor had 3 levels (3 types of OM). Each treatment had 3 replicate sediment cores. Dependent variables were the measured activities of the 2 contaminants Cd and BDE-99. The distributions of the 2 contaminants within the same core were analysed in 2 separate 2-way analyses of variance (ANOVA), i.e. no statistical comparisons were done between Cd and BDE-99.

Field sampling and preparation of microcosm systems. Surface sediment (top 5 cm) was collected in

December from a depth of 45 m using a benthic sledge at Asenskallen (58° 46.5′ N, 17° 41.4′ E) near the Askö Marine Laboratory, NW Baltic Proper. The fresh sediment was sieved immediately, without the addition of extra water, through a 1 mm sieve into 30 l buckets and was then left with overlying aerated brackish water in a thermoconstant room at 4°C for 2 mo to settle and re-establish a natural sediment geochemical profile. All brackish water (6.4 to 6.7 psu) used in the experiment was collected at the Askö Marine Laboratory at 15 m depth and filtered through a 0.8 mm sand filter.

Three infaunal species were collected in January. The bivalve *Macoma balthica* and the amphipod *Monoporeia affinis* were collected in Hållsviken (58° 49.7′ N, 17° 32.3′ E) at 33 m depth. Polychaete *Marenzelleria* spp. were sieved out of sandy sediment collected at 1 m water depth off the island of Mörkö (59° 2.29′ N, 17° 41.45′ E). Recent genetic studies have suggested that there are at least 3 different species of the genus *Marenzelleria* in the Baltic Sea (Bastrop & Blank 2006). They are morphologically similar, and the individuals used in this experiment were not identified to species and are therefore hereafter referred to only by the genus name. All species were held for several weeks at field temperature (4°C) in separate 30 l aquaria containing sediment and water from the field area. The overlying water was continuously aerated and changed approximately every other week until the start of the experiment.

Kajak tube cores (inner diameter 8 cm, height 50 cm) were pushed by hand into the collected sediment, with care taken to avoid the formation of air bubbles, and then filled to the top with brackish water. They were sealed with a rubber stopper at the top and pulled out of the bucket, retaining the sediment by vacuum in the tube core. Another cork stopper was placed at the bottom of the cores, which were subsequently placed in a thermoconstant room at 4°C. The cores had a sediment column of ca. 30 cm height (1500 ml) and a water column of ca. 17 cm (850 ml). Aeration was provided by gently bubbling air through glass tubes inserted through the top stoppers. The stoppers had another hole to let air out and a third hole connected to silicone tubing for the collection of water samples. The cores were kept in a thermoconstant room for 5 wk before the addition of animals and the start of the experiment.

The number of animals added to the cores corresponded to average field densities common in the Baltic Sea (Table 1); therefore, all results in this experiment relate to the natural field density of each species. After addition to the core tubes, most of the animals buried into the sediment within 5 min. Animals that had not burrowed after 24 h (2 *Marenzelleria* and 4 *Macoma balthica*) were replaced by new animals. The cores were placed randomly in the thermoconstant room, which was held at a constant temperature of 4°C

Table 1. Number of animals and biomass added to the sediment cores

| | No. of animals | | Average total biomass per core | |
	Per core	Per m²	(g wet wt)	(g dry wt)
Monoporeia affinis[a]	15	3000	0.1	0.011
Macoma balthica[b]	5	1000	4.7	0.236[b]
Marenzelleria spp.[c]	7	1400	1.0	0.072
Control	–	–	–	–

[a]Individuals >1 mm long, no gravid females
[b]Shell size ca. 20 mm. Shell-free dry weight
[c]Individuals ca. 5 cm long with visible feeding palps

and a dark:light cycle with green light to mimic field conditions. The animals were allowed to acclimatise to the experimental conditions for 1 wk before the addition of spiked OM (see below).

Contaminants and organic material. Two radio-labelled contaminants were used in the experiment. ^{14}C-labelled BDE-99 (2, 2′, 4, 4′, 5-pentabromodiphenyl ether) dissolved in acetone (synthesised by the Department of Environmental Chemistry, Stockholm University, Sweden) with a specific activity of 3.2 kBq µg⁻¹ and log K_{OW} of 7.13 (Tittlemier et al. 2002). [109]CdCl$_2$ in 0.1 M HCl (Amersham) with a specific activity of 24 MBq µg⁻¹ Cd. This activity and all following [109]Cd activities were corrected for radioactive decay to 1 March 2004.

Three different types of OM were used: (1) microalgae, i.e. green flagellate algae *Tetraselmis* spp. (Reed Mariculture, San Jose, CA, USA); (2) terrestrial wood fibres of lignin (Curan 100, Holmen paper AB, Sweden); and (3) surface sediment (i.e. same as the sediment used in the cores). The different types represented a high (*Tetraselmis* spp.), low (lignin) and medium (sediment) quality OM source to the benthic invertebrates. The quality is here referred to as the nutritious value of the OM source, defined as the relative amount of total nitrogen (TN) to total carbon (TC) in the OM (Gunnarsson et al. 1999a,b). Chemical characteristics used to define the quality of the 3 OM sources are presented in Table 2. *Tetraselmis* spp. have a high content of fatty acids and

Table 2. Properties of the OM additions and the amount of TOC added to each core

| | Nutritional quality[a] | TN (%) | TC (%) | TOC (%) | TOC added (g dry wt) | |
					Per core	Per m²
Algae	High	5.02	40.2	32.2	0.0486	9.7
Lignin	Low	0.11	66.4	62.8	0.0481	9.6
Sediment[b]	Medium	0.27	1.77	1.37	0.0483	9.7

[a]From Gunnarsson et al. (1999a,b)
[b]Same as the sediment in the cores

amino acids and are therefore considered a labile OM source and palatable food source to marine detrivores, while lignins consist of unpalatable refractory aromatic polymers (Gunnarsson et al. 1999a).

Preparation of the organic material, spiking and addition to the cores. A concentrate of thawed *Tetraselmis* algae was washed and centrifuged 5 times for 20 min at $2700 \times g$ in brackish water to remove as much dissolved OM as possible, leaving a suspension of intact non-living algal cells. Dry powdered lignin was made into a suspension by adding brackish water and shaking vigorously. The suspension was then centrifuged for 15 min at $2700 \times g$ and the dissolved OM and very fine particles removed with the supernatant. The sediment was thoroughly mixed before being used as the third OM source. An amount corresponding to a final nominal enrichment of 0.05 g dry weight (dry wt) organic carbon (OC) per core, or ca. 10 g dry wt OC m^{-2}, was prepared from each OM source, based on their total OC (TOC) content (Table 2). The amount of OC (10 g OC m^{-2}) was chosen to provide an organic enrichment equivalent to the settling of OM during a spring bloom in the Baltic Sea (Larsson et al. 1986).

Radiolabelled BDE (^{14}C-BDE-99) and the radioisotope ^{109}Cd were combined with each of the OM sources to produce a spiked stock. The amounts of ^{14}C-BDE and ^{109}Cd were calculated to give a final nominal activity of 27 kBq and 118 kBq core^{-1}, respectively. Nominal activities were chosen to be detectable at the end of the experiment following bioturbation and mixing into the sediment, uptake by the animals and radioactive decay. These concentrations (equivalent to 8.44 µg BDE core^{-1} and 0.0049 µg Cd core^{-1}) were also below reported toxic concentrations for similar species. For example, LC50s for Cd are in the range of 31 µg l^{-1} (Voyer & Modica 1990) to 1.7 mg l^{-1} (DeWitt et al. 1999), and for various BDE congeners they are 108 µg l^{-1} to 2.4 mg l^{-1} (Wollenberger et al. 2005). First ^{14}C-BDE, then the OM source, and lastly the ^{109}CdCl$_2$ solution were added to Erlen flasks, which were then sealed with Parafilm and placed on magnetic stirrers at 4°C for 7 d to ensure a homogenous spiking of the organic material. The spiked OM was then divided into aliquots containing equal amounts of OC (and ^{109}Cd and ^{14}C-BDE) for addition to the cores.

The spiked organic materials were added to the overlying water of the cores through a glass funnel, with its tip held close to the sediment surface, and allowed to settle for 12 h without aeration. After this, the overlying water was siphoned off carefully to minimise resuspension and replaced with new brackish water. This was done to remove remaining spiked OM in the water, as the focus of the experiment was to examine contaminant redistribution from the sediment

surface, and to be able to measure the remobilisation of settled contaminants back into the water column. A 10 ml water sample was taken from the removed water to estimate the loss of ^{14}C-BDE and ^{109}Cd with the water change. The cores were then sealed with corks and aeration was switched on. Salinity was maintained between 6.4 and 6.7 psu throughout the experiment. The experiment was run for 34 d.

Sample collection and preparation. At the end of the experiment, the cores were processed in random order. First, a 20 ml sample from the overlying water column was taken. The remaining water was removed and mixed, and a volume of 20 to 120 ml of water was filtered through pre-combusted (550°C) and pre-weighed GF/F filters in order to measure suspended particles (>0.7 µm) and radioactivity associated with suspended particles. The filtered volume depended on the amount of suspended matter in the water and how fast the filters became clogged. The filters were dried for 24 h at 60°C and weighed again to obtain the dry weight of the suspended particles. Water samples were kept in 20 ml glass scintillation vials at 4°C until analysed.

The sediment in the cores were pushed up from the bottom using a plunger and a cork that was tightly fit within the core, and sliced into 1 cm slices from 0 to 5 cm, thereafter at 6–7, 8–9 and 14–15 cm, and in the *Marenzelleria* and control treatments also at 20–21 cm. Redox potential was first measured at the sediment surface and then immediately after slicing at the fresh sediment surface in each slice using a platinum electrode with a calomel reference electrode (Beckman Coulter) connected to a radiometer (Orion, pH meter) (Bogander 1976). In each slice, the most peripheral few mm of sediment were discarded to avoid edge effects, animals were gently picked out using forceps and detailed sediment samples from burrow linings were collected when possible. The remaining wet bulk sediment, approximately 40 ml, was thoroughly mixed and kept at 4°C until analysis. Ten ml of wet bulk sediment from each slice were put in 60 ml flat-bottomed containers for gamma analysis (Cd^{109}), and a subsample was taken for scintillation counting (^{14}C-BDE). The bulk sediment subsamples and detailed sediment samples of burrow linings were dried for 24 h at 60°C to obtain their dry wt.

Chemical analyses and radioactivity measurements. TC and TN content of the sediment and the OM sources were measured using oven-dried samples on a Leco CHNS 932 analyser. TOC was determined after acidification with HCl (Hedges & Stern 1983).

All samples were first analysed for ^{109}Cd using gamma spectrometry (Canberra GC2020 [GA1] and Ortec GEM HPGe-detectors), which detects only the gamma-emitting ^{109}Cd, and then for total radioactive

decay (combined ^{109}Cd and ^{14}C) using liquid scintillation counting (LKB Wallac Rackbeta 1214). The same samples were processed for gamma and scintillation counting, except for the bulk sediment samples, for which the sample sizes had to be different for the 2 machines. Radioactivity measurements were corrected for different efficiencies, background and decay (in the case of ^{109}Cd), and the ^{109}Cd activities were then subtracted from the total activities to provide ^{14}C-BDE activities as described below.

For gamma analysis, sample geometry, counting efficiency and background radiation were corrected for, using matching standards with a known ^{109}Cd activity. Samples were run until the error of the measurement was less than 10 % (between 10 min and 4 h depending on the activity). Counts were adjusted for radioactive decay to the date of subsequent scintillation counting and normalised to g dry wt (sediment) or ml (water samples).

Twenty-four hours before scintillation counting, 10 ml Hionic-Fluor (Perkin Elmer Life and Analytical Sciences) were added to all sediment samples and 10 ml Lumagel Safe (Lumac LSC) were added to all water samples. Detection efficiencies for both ^{109}Cd and ^{14}C-BDE were calculated from equations derived from a series of standards with known activity. These standards represented all sample types so that the resulting equations covered the range of sample colours and colour quenching was taken into account. The 2 isotopes did not affect each others' detection efficiencies.

The amount of ^{109}Cd present in the scintillation sample was calculated using the activity per g dry wt obtained from the gamma spectrometer, the efficiency equation for the scintillation machine and the weight of the sample. This was then subtracted from the total scintillation counts to obtain the amount of ^{14}C.

Calculations and statistics. Downward burial of ^{109}Cd and ^{14}C-BDE was quantified as follows. The measured activity per g dry wt in each cm-thick sediment slice was multiplied by the total dry wt of that slice. The total radioactivity in the bulk sediment of each core was calculated as the sum of the activities in the top 5 sediment slices (0 to 5 cm), since no activity was detected in the bulk sediment below 5 cm. Sediment profiles are thus based on the percentage of the total activity in the sediment at each 1 cm depth interval. The value '% buried' was also calculated as the percentage activity found below 1 cm sediment depth. Mean depth was calculated by multiplying the percentage in each slice by the median depth of that slice (i.e. 0.5, 1.5, 2.5, 3.5, 4.5 cm) and then adding together the products of all slices in each core. The percentage of particle-associated Cd and BDE-99 in the overlying water was calculated by dividing the activity measured on the filters, i.e. activity on the filter per volume filtrated water (Bq ml^{-1}), by the activity measured in the whole water sample, i.e. both dissolved and particle-associated (Bq ml^{-1}).

Statistical comparisons between treatments were tested by using a 2-factor ANOVA (p < 0.05) followed by post-hoc multiple comparisons using the Student-Newman-Keuls (SNK) test to test for differences among treatments (within main effects). Data were log transformed, if necessary, to meet the assumptions of homogeneity of variances, evaluated using Cochran's *C*-test.

RESULTS

Animal activity and recovery

The cores were visually inspected on a daily basis. Amphipods were frequently observed swimming in the water column during the entire experimental period (34 d). Faecal pellets were continuously renewed at the sediment surface in cores with *Macoma balthica* and *Marenzelleria*, indicating continuous feeding and burrowing activity throughout the experiment. Polychaete burrows were observed from the side of the core down to 15 cm depth with a clear oxidised zone around the burrow linings.

All added individuals of *Macoma balthica* were recovered alive at the end of the experiment (100 % survival). Thirty-eight percent of the *Marenzelleria* were found whole and alive. Many of the worms were cut during the slicing of the cores, and when all pieces were included, close to 100 % of the *Marenzelleria* were recovered. The recovery of *Monoporeia affinis* was 42 % (52 % when including dead individuals). The low recovery of amphipods was at least partly due to the difficulty of finding them without sieving the sediment and not due to high mortality (the sediment could not be sieved as it was needed intact for radioactivity analyses).

Sediment characteristics and radioactivity measurements

Sediment geochemistry and radioactivity data measured in the sediment at the end of the experiment are summarised in Table 3. TOC content in the top 1 cm of sediment ranged between 1.5 and 1.9 % among treatments. Water content ranged between 66 % in the top sediment with *Monoporeia affinis* and 58 % in the control cores. The redox potential discontinuity (RPD) layer, here denoting a sharp gradient in redox potential, was generally observed deeper in the sediment

Table 3. Sediment geochemistry and radioactivity measured in the top 1 cm at the end of the experiment (34 d). The redox potential discontinuity (RPD) layer indicates the depth of a sharp gradient in the redox potential. TOC: total organic carbon, Control: no added macrofauna. Values are mean ± SD, n = 3

	TOC (%)	Water content[a] (%)	RPD (cm)	^{109}Cd (kBq g dry wt^{-1})	^{14}C-BDE
Monoporeia affinis					
Algae	1.90	66	2–3	2.8 ± 0.5	1.0 ± 0.1
Lignin	1.77	66	2–3	2.7 ± 0.4	0.7 ± 0.1
Sediment	1.77	66	3–4	4.8 ± 0.3	1.2 ± 0.0[b]
Macoma balthica					
Algae	1.67	61	4–6	1.7 ± 0.2	0.6 ± 0.2
Lignin	1.48	61	4–6	1.4 ± 0.7	0.4 ± 0.2
Sediment	1.48	61	4–6	2.6 ± 0.3	0.6 ± 0.3
Marenzelleria spp.					
Algae	1.50	59	4–6	1.1 ± 0.3	0.5 ± 0.2[b]
Lignin	1.74	59	6–8	2.0 ± 0.7	0.5 ± 0.2[b]
Sediment	1.59	59	4–6	2.9 ± 0.4	1.2 ± 0.4[b]
Control					
Algae	–	58	3–4	1.2 ± 0.1	1.0 ± 0.2
Lignin	–	58	3–4	0.8 ± 0.1	0.3 ± 0.1[b]
Sediment	–	58	4–6	2.3 ± 0.2	0.8 ± 0.0[b]

[a]Average per animal treatment
[b]n = 2

cores with *Marenzelleria* (between 4 and 8 cm depth) and *Macoma balthica* (4 to 6 cm) than in the control cores (3 to 6 cm). In cores with *Monoporeia affinis*, however, the RPD layer was closer to the sediment surface (2 to 4 cm) than in the controls. Despite the poor precision of the measured RPD layer, which was due to the crude scale of slicing, the results gave a good indication of relative differences between animal treatments. No differences in RPD depth between OM treatments were observed. In general, the activity of both ^{109}Cd and ^{14}C-BDE per g dry wt sediment in the top 1 cm was higher in the cores treated with sediment than those with algae or lignin. This was probably caused by a higher loss of Cd and BDE-99 in these treatments following the initial water change (estimated loss: 33 ± 8% and 43 ± 11% Cd and 39 ± 25% and 51 ± 25% BDE-99 for algae and lignin, respectively) compared to the sediment treatment (2 ± 2% for Cd and 3 ± 1% for BDE-99).

Burial of Cd and BDE-99 into the sediment

The 2 contaminants were affected differently by the presence of macrofauna and OM additions (Fig. 1). In general, a higher fraction of Cd than of BDE-99 was transported deeper into the sediment. No contami-

nants were detected below 1 cm depth in the control cores, i.e. those without macrofauna.

There was a significant interaction effect between animal and OM treatments on the mean burial depth of Cd (ANOVA; $F_{6,24}$ = 5.64, p < 0.001). In the algae and lignin treatments, the general pattern was *Marenzelleria* > *Macoma balthica* > *Monoporeia affinis* > control (Fig. 2A). A post-hoc SNK test showed that the mean burial depth of Cd was significantly higher in cores with *Marenzelleria* compared to all other animal treatments (SNK; p < 0.05). In addition, the mean burial depth in cores with *M. balthica* was significantly higher in the algae treatment than in the control. In the sediment treatment, however, only *M. balthica* had a higher mean burial depth of Cd than the control. Within animal treatments, there were no significant differences between OM additions with the exception of a higher mean burial depth of Cd by *Marenzelleria* in the algae treatment compared to sediment (SNK; p < 0.001; Fig. 2A).

No interaction was observed in the mean burial depth of BDE-99 between animal and OM treatments, and there was no significant effect of OM type. However, there was a significant animal effect (ANOVA; $F_{3,22}$ = 3.47, p < 0.05). The general pattern was *Macoma balthica* > *Monoporeia affinis* > *Marenzelleria* > control in all OM treatments (Fig. 2A). The mean burial depth of BDE-99 was significantly higher in cores with *M. balthica* than with *Marenzelleria* and controls (SNK; p < 0.05).

The amount (%) of Cd and BDE-99 buried below 1 cm had the same pattern as the mean burial depths, and showed the same significant differences between treatments except for the amount of Cd buried below 1 cm by *Macoma balthica* in the algae treatment (SNK; p = 0.058; Fig. 2B).

Enrichment of Cd and BDE-99 in macrofaunal burrows

There was a clear enrichment of both Cd and BDE-99 in the burrow linings of *Marenzelleria* and *Macoma balthica* compared to the surrounding bulk sediment down to 5 cm depth. Although highly variable between and within replicates, the factor of enrichment (burrow sediment / bulk sediment) for both Cd and BDE-99 in *Marenzelleria* and *M. balthica* burrows ranged from 2 to 4 in the surface sediment (0 to 1 cm) and from 10 to 60 in the 3 to 5 cm slices. There were no differences between animal or between OM treatments. Both Cd and BDE-99 were also detected in *Marenzelleria* burrows at all analysed depths down to 15 cm. No distinct *Monoporeia affinis* burrows were visible and hence no samples were taken.
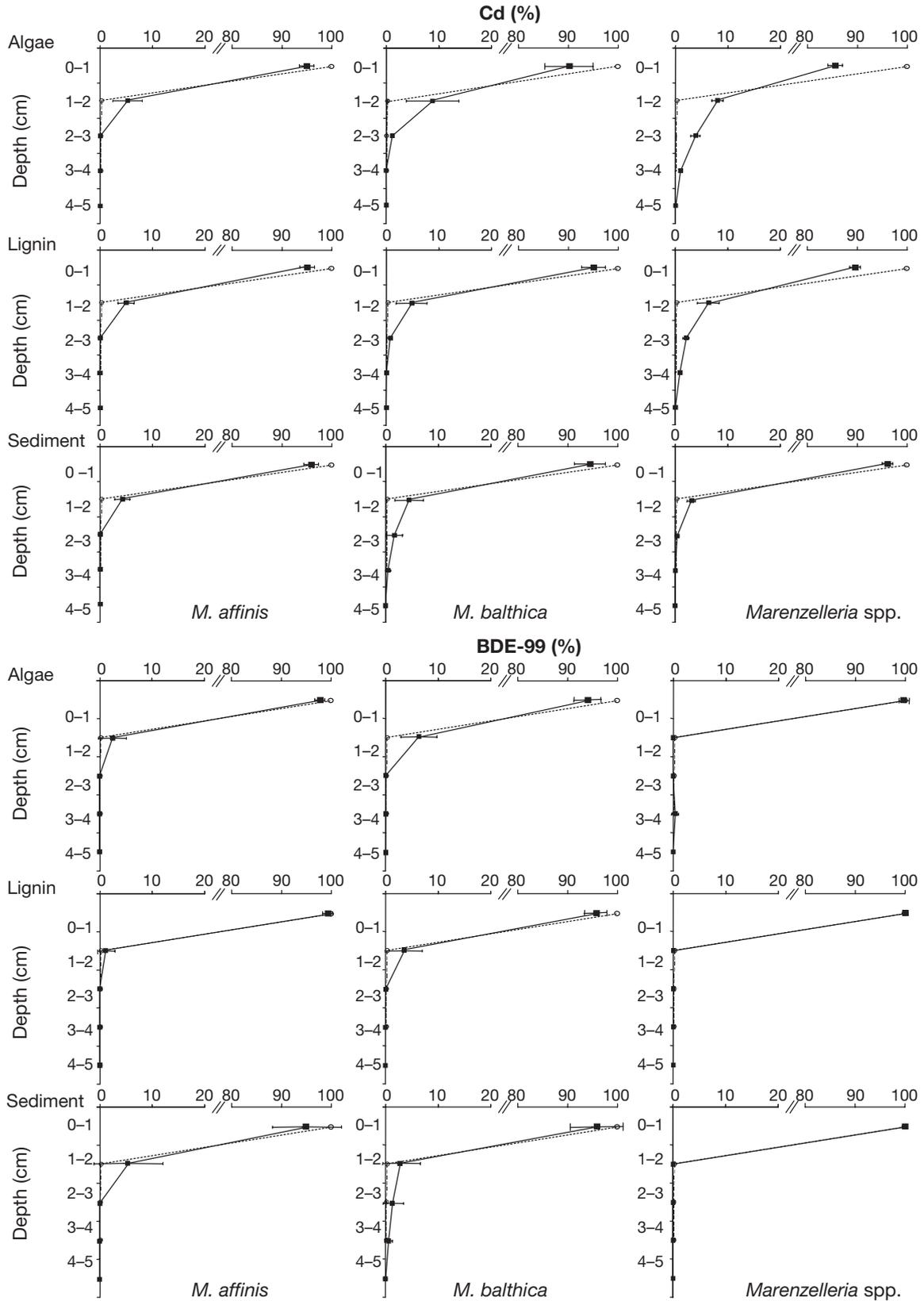
Fig. 1. *Monoporeia affinis*, *Macoma balthica* and *Marenzelleria* spp. Cd and BDE-99 depth profiles in sediment cores after 34 d of bioturbation (solid lines). Dashed lines are controls (no macrofauna). Cd or BDE-99 was added to the sediment surface associated with algae, lignin or sediment (rows)
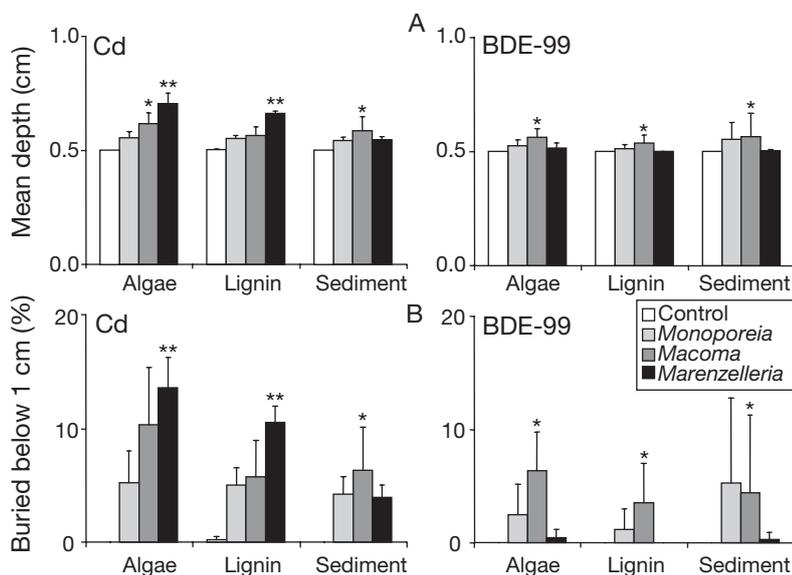
Fig. 2. *Monoporeia affinis*, *Macoma balthica* and *Marenzelleria* spp. (A) Mean burial depth and (B) percentage buried below 1 cm of Cd and BDE-99 in sediment microcosms with and without macrofauna (controls) after 34 d. Contaminants were added associated with algae (*Tetraselmis* spp.), lignin or sediment. Cd: Significant interaction between animal and OM (ANOVA; mean burial depth $F_{6,24}$ = 5.64, p < 0.001; % buried $F_{6,24}$ = 2.93, p < 0.05). *M. balthica* (*) was significantly different from controls and *Marenzelleria* spp. (**) from all other animals within each OM treatment (SNK; p < 0.05). BDE-99: No interaction effect. *M. balthica* (*) significantly different from controls and *Marenzelleria* (SNK; p < 0.05). Mean values, error bars denote SD, n = 3

Table 4. Radioactivity measured in the overlying water (unfiltered; kBq l^{-1}), suspended particles (>0.7 µm; mg l^{-1}) and percentage particle-associated Cd and BDE-99 in the overlying water column at the end of the experiment (34 d). Control: no added macrofauna. All values are mean ± SD, n = 3

Treatment	^{109}Cd (kBq l^{-1})	^{14}C-BDE (kBq l^{-1})	Suspended particles (mg l^{-1})	Particle-associated Cd (%)	Particle-associated BDE-99 (%)
Monoporeia affinis					
Algae	1.0 ± 0.4	0.5 ± 0.2	158.3 ± 91.7	33 ± 31	63 ± 20
Lignin	0.6 ± 0.2	0.2 ± 0.1	121.1 ± 76.4	44 ± 39	91 ± 31
Sediment	0.6 ± 0.4	0.4 ± 0.2	137.5 ± 79.6	36 ± 63	57 ± 34
Macoma balthica					
Algae	0.7 ± 0.3	0.4 ± 0.1	19.3 ± 17.2	14 ± 4	13 ± 4
Lignin	0.8 ± 0.4	0.4 ± 0.1	17.5 ± 1.9	3 ± 5	10 ± 5
Sediment	1.1 ± 0.4	0.6 ± 0.1	14.3 ± 0.5	8 ± 4	9 ± 2
Marenzelleria spp.					
Algae	2.8 ± 0.5	1.0 ± 0.2	33.5 ± 8.9	6 ± 5	28 ± 9
Lignin	3.1 ± 1.4	1.4 ± 0.9	29.9 ± 3.3	3 ± 3	9 ± 5
Sediment	2.6 ± 0.4	1.1 ± 0.7	27.6 ± 9.8	11 ± 6	19 ± 18
Control					
Algae	5.5 ± 1.3	2.6 ± 0.2	–	10 ± 3	15 ± 3
Lignin	2.9 ± 1.3	1.7 ± 0.7	–	2 ± 2	3 ± 1
Sediment	4.0 ± 1.0	2.3 ± 0.3	–	5 ± 2	4 ± 1

Remobilisation of Cd and BDE-99 to the overlying water

The measured activity of Cd and BDE-99 (Bq ml^{-1}) in the overlying water at the end of the experiment is presented in Table 4. To obtain a comparable net release of contaminants from the sediment, the measured activity in the overlying water (Bq ml^{-1}) was normalised to the concentration in the top 1 cm of sediment (Bq g dry wt^{-1}). The general pattern of net release for both contaminants was control > *Marenzelleria* > *Macoma balthica* > *Monoporeia affinis* (Fig. 3).

The net release of Cd showed a significant interaction between animals and OM (ANOVA; $F_{6,24}$ = 5.48, p < 0.01). In the algae and lignin treatments, the net release of Cd in the control cores was significantly higher than when macrofauna were present (SNK; p < 0.05). In addition, in the algae treatment, the release of Cd caused by *Marenzelleria* was higher than that caused by *M. balthica* and *M. affinis* (SNK; p < 0.001). In the sediment treatment, there were no significant differences in the release of Cd to the water between any of the animal treatments. In the absence of macrofauna, the release of Cd to the water was significantly affected by the OM type (algae > lignin > sediment; Fig. 3). In cores with macrofauna, only the addition of algae to the cores with *Marenzelleria* increased the net release of Cd to the water compared to the sediment treatment (SNK; p < 0.01).

No interaction effects between animals and OM were observed for the release of BDE-99 to the water, and there were no differences between OM type. However, there was a significant difference between animals (ANOVA; $F_{3,22}$ = 9.76, p < 0.001), with a higher release in controls and *Marenzelleria* compared to *Macoma balthica* and *Monoporeia affnis* (SNK; p < 0.05).

The amount of suspended particles in the water at the end of the experiment was highest in cores with *Monoporeia affinis* (up to 158.3 ± 91.7 mg l^{-1}) followed by *Marenzelleria* (33.5 ±
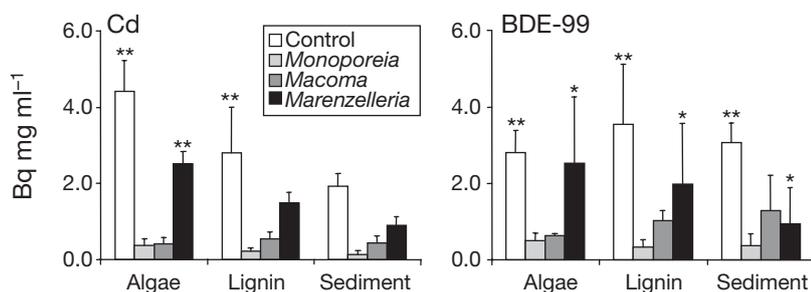
Fig. 3. *Monoporeia affinis*, *Macoma balthica* and *Marenzelleria* spp. Cd and BDE-99 in the overlying water (Bq ml^{-1}) normalised to sediment concentration (Bq g dw^{-1}) in cores with or without macrofauna (control) after 34 d. Contaminants were added associated with algae (*Tetraselmis* spp.), lignin or sediment. Cd: Significant interaction between animal and OM (ANOVA; $F_{6,24}$ = 5.48, p < 0.01). Controls and *Marenzelleria* spp. (**) were significantly different from all other animal treatments (SNK; p < 0.05). BDE-99: No interaction effect. Controls (**) significantly different from all other animal treatments and *Marenzelleria* (*) from *M. balthica* and *M. affinis* (SNK; p < 0.05). Mean values, error bars denote SD, n = 3

8.9 mg l^{-1}) and *Macoma balthica* (19.3 ± 17.2 mg l^{-1}; Table 4). There were no observed differences between OM treatments. The percentage of particle-associated Cd (ANOVA; $F_{3,24}$ = 3.82, p < 0.05) and BDE-99 (ANOVA; $F_{3,24}$ = 39.6, p < 0.001) in the overlying water differed significantly between animal treatments (Table 4). In cores with *Monoporeia affinis*, an average of 38 ± 41% of the Cd and 70 ± 30% of the BDE-99 in the overlying water was associated with suspended particles. This was a significantly higher ratio than in the other animal treatments for both Cd (average 6 to 8%; SNK; p < 0.05) and BDE-99 (7 to 19%; SNK; p < 0.001).

DISCUSSION

Results from this experimental study show that the fate (i.e. sediment burial and remobilisation to water) of contaminants deposited on the sediment surface is strongly influenced by macrofaunal bioturbation, with clear differences between species, and that the association to settling OM of various origins was important. The simultaneous use of 2 contaminants with different chemical characteristics allowed a specific insight into the complex interactions between ecological (infaunal feeding and bioturbation activities) and physiochemical (contaminant speciation and sorption kinetics) processes affecting contaminant fate in a sediment ecosystem.

Influence of bioturbation on the burial of Cd and BDE-99

The polychaete *Marenzelleria* digs deep into the sediment, creating J-shaped un-branched burrows

lined with a mucus layer (Zettler et al. 1995). In our study, the worms were observed down to 15 cm, but they have been reported to create burrows down to 35 cm depth in natural environments (Zettler et al. 1995). They feed on detrital OM at the sediment–water interface and egest their faecal pellets at the sediment surface. Most burrowing polychaetes regularly ventilate their burrows with water from above the sediment surface to maintain a suitable living environment (Riisgård & Larsen 2005). These bio-irrigation activities have been suggested to enhance the transport of soluble rather than particle-associated contaminants in the sediment (Banta & Andersen 2003). There is little information available about bio-irrigation by *Marenzelleria*. However, results from this study suggest an important transport of dissolved and/or apparently dissolved (e.g. dissolved OM-associated) compounds in their burrow structures and over the sediment–water interface.

Besides a clear enrichment of Cd in the *Marenzelleria* burrow walls as deep as 15 cm, a relatively high amount of Cd was also detected in the bulk sediment to depths of 5 cm. However, BDE-99 was only detected in the burrow walls but not in the bulk sediment. Cd primarily adsorbs to OM and to Fe and Mn oxides in sediments during oxidising conditions, with a small fraction present in the sediment interstitial water (Chapman et al. 1998). In a reducing environment, however, Cd can form sulphide complexes of very low solubility, also known as acid-volatile sulphides (AVS; Di Toro et al. 1990). The micro-zones created by infaunal burrow structures usually have strong redox gradients and high OM content (Aller 1988). Dissolved Cd transported into the sediment via bio-irrigation by *Marenzelleria* could be re-adsorbed at depth by metal oxides and OM in the oxidised mucus layer of polychaete burrows, and transit into the bulk sediment through molecular diffusion, where it could be precipitated due to anoxic conditions. For example, dissolved Cd transported from the overlying water into the burrows of the polychaete *Nereis diversicolor* was mainly adsorbed in the first 0 to 3 mm oxic layer but could penetrate into the bulk sediment up to 9 mm from the centre of the burrow (Petersen et al. 1998). BDE-99, on the other hand, is highly hydrophobic (log K_{OW} 7.13) and generally sorbs strongly to particles and OM (de Wit 2002). The lack of BDE-99 below the sediment surface in the bulk sediment thus indicates that *Marenzelleria* did not cause any significant particle mixing in the upper sediment column. The local transport of par-

ticle- and/or DOM-associated BDE-99 within the burrows could be a result of movement, burrow maintenance and downward transport of contaminated food particles. Similarly, other marine benthic invertebrates enrich HOCs, e.g. PCBs and PAHs, in their burrows (Gunnarsson et al. 1999a,b, Selck et al. 2005). BDE-99 transported into the burrow would rapidly associate with the organic-rich mucus layer and, in contrast to Cd, not desorb and migrate into the bulk sediment.

The bivalve *Macoma balthica* lives a few centimetres down in the sediment, protruding its 2 siphons to the surface where it can switch between surface deposit- and suspension-feeding (Lin & Hines 1994, Karlson et al. 2005). The clams mix particles from the surface into the sediment when they feed and move around, causing particles to fall into the space created around their shells. The burial of Cd and BDE-99 by *M. balthica* was probably mainly due to this type of passive particle displacement, indicated by the similar vertical distribution of both contaminants. Many bivalve species seem to have a limited influence on sediment–porewater exchange processes, since they feed and respire directly through their siphons (Mermillod-Blondin et al. 2005). Like *Marenzelleria*, *M. balthica* had elevated concentrations of both contaminants in its burrow lining compared to the bulk sediment. Although the burrow is not actively irrigated, it is likely that there is increased water circulation and hence oxygenation around the clam shell (Mermillod-Blondin et al. 2005, Michaud et al. 2005), as well as organic enrichment, resulting in an increased retention of both Cd and BDE-99 in the clam burrow walls.

The amphipod *Monoporeia affinis* is an active particle bioturbator in the upper centimetres of the sediment, causing extensive particle resuspension to the overlying water. The intense burrowing and ventilation activity by *M. affinis* and other similar amphipod species increases the porewater circulation, resulting in a higher sediment oxygen content and enhanced benthic nutrient fluxes over the sediment–water surface (Karlson et al. 2005, Riisgård & Larsen 2005). The amphipods did not induce a transport of either Cd or BDE-99 below their depth of active burrowing (2 cm). It could have been expected that *M. affinis*, in addition to the downward mixing of particle-associated contaminants, would stimulate a transport of dissolved compounds, in this study primarily Cd, below the zone of bioturbation due to a generally increased porewater flux in the upper sediment. However, no such transport of Cd was observed here. This could be due to a physical barrier created by the dense network of amphipod burrows hindering the molecular diffusion of Cd deeper into the sediment, as suggested by Petersen et al. (1998) in a similar study with the amphipod *Corophium volutator*. In our study, the RPD layer

was measured just under the bioturbated layer, indicating no increase in porewater flux below the zone of bioturbation.

Remobilisation to water

Bioturbation by all species in this experiment significantly increased the retention of both Cd and BDE-99 in the sediment. The higher remobilisation of contaminants to the water in the control cores (no macrofauna present) was likely due to the fact that no Cd or BDE-99 had been buried in the sediment, i.e. all contaminants remained at the sediment surface and were available for desorption to the overlying water.

The same argument can be made for the relatively high release of BDE-99 in cores with *Marenzelleria* (no burial), but not for the remobilisation of Cd, which was more effectively buried into the sediment by the polychaete than by the other species. Schaffner et al. (1997) found a relationship between the hydrophobicity of PAHs and PCBs and their fate in bioturbated sediments. The most hydrophilic compounds had the highest mean burial depths but they also had the highest loss rates from the sediments, probably due to a more effective macrofaunal transport of solutes than of particles. This is in agreement with the decoupled transport of Cd and BDE-99 in this study considering that even a small increase in redox potential can result in enhanced levels of dissolved Cd in the porewater and flux to the overlying water (Peterson et al. 1996, Riedel et al. 1999). *Marenzelleria viridis* increases the transport of oxygen over the sediment–water interface (Karlson et al. 2005), and the RPD layer in our study was generally extended deeper in cores with *Marenzelleria* than in controls.

Concentrations of both Cd and BDE-99 were very low in the overlying water in *Macoma balthica* and *Monoporeia affinis* cores. The clams caused little particle resuspension. This and the lack of active bioirrigation are the most likely reasons for the low release of contaminants to the water. However, the clams' constant pumping of water over the gills for respiration could also effectively filter out both suspended particles and contaminants present in the water. In the field, bivalves can significantly influence contaminant dynamics by transporting contaminants from the water column to the sediment through biodeposition of faeces and pseudofaeces (Gilek et al. 1997). In contrast, a continuous supply of particles, and thus new adsorption sites, due to particle resuspension may extract dissolved contaminants from the water phase and deposit them on the sediment surface. Thirty-eight percent of the Cd and 70% of the BDE-99 in the overlying water in the *M. affinis* cores was associated with suspended

particles. The relatively low contaminant release to the water in cores with *M. affinis* could thus be a result of contaminant scavenging by the continuous supply of particles and new adsorption sites, particularly in a closed microcosm system like the one used in this experiment.

Effects of OM quality

In the presence of macrofauna, the addition of various OM forms only had an effect on the redistribution of Cd, and only in the cores with *Marenzelleria*, where the burial and release of Cd increased when it was associated with algae compared to sediment or lignin. It was hypothesised that the input of OM with a high nutritional quality (i.e. the algae) would stimulate infaunal feeding and bioturbation activities, thereby increasing the overall redistribution of the associated contaminants. An immediate response of all 3 species to the addition of algae was observed, clearing the deposited green algal layer on the sediment surface within 1 or 2 d. The increased burial and release of Cd in the algae treatment by *Marenzelleria* could therefore, in part, be explained by increased feeding activity, burrow ventilation and mobility of these polychaetes, increasing water movement and hence physical transport of Cd in the sediment and over the sediment–water interface. Enhanced bio-irrigation rates after organic enrichment have previously been reported for the polychaete *Nereis diversicolor* (Banta et al. 1999, Heilskov et al. 2006), as well as for *Macoma balthica* (Heilskov et al. 2006) and *Monoporeia affinis* (Karlson et al. 2007). The lack of measurable effect of OM types on the redistribution of Cd by *M. balthica* and *M. affinis* could perhaps be due to the experimental design, with a single sampling occasion at the end of the experiment. Karlson et al. (2007) recently showed that the initial increase in activity of *M. affinis* following a simulated spring bloom only lasted for 5 d.

Several trace metals (e.g. Cu, Cd, V) are readily remobilised from freshly deposited OM due to aerobic mineralisation of the OM in the oxidised sediment surface layer (Riedel et al. 1999, Audry et al. 2006). In addition to the release of free metal ions to the interstitial water during OM degradation, an increase in DOM may add to the solubilisation of metals due to DOM-complexation (Hoss et al. 2001). Moreover, the sorption capacity is generally suggested to be lower for labile OM than for older more refractory OM. Lignins, for example, strongly adsorb many metal ions and are being developed for use as biosorbents for removing toxic metals from waste water (Mohan et al. 2006). They have a complex aromatic molecular structure, low water solubility and resistance to degradation. The higher

redistribution of Cd in the algae treatment by *Marenzelleria* is thus probably the result of several co-occurring factors: a higher diagenetic release of soluble Cd from the labile algae than from lignin or sediment, a higher bioturbation activity, and the mode of bioturbation displayed by *Marenzelleria* (bio-irrigation).

No effect of the various types of OM on the redistribution of BDE-99 was observed. This was probably due to the highly hydrophobic and particle reactive properties of BDE-99, resulting in a very low soluble fraction and thus limited transport by *Marenzelleria*. An organic contaminant with a more moderate K_{OW} and higher water solubility may have been more affected by the OM additions. For example, Dewitt et al. (1992) found increased porewater concentrations of the PAH fluoranthene in sediments amended with ground macroalgae compared to other OM types (e.g. mud), and Gunnarsson et al. (1999b) reported an increased release rate of PCB from unbioturbated sediments enriched with algae compared to non-enriched sediment.

Implications for contaminant fate in the field

The semi-enclosed brackish Baltic Sea is dominated by few macrofaunal species, mainly small-sized surface-deposit feeders (Bonsdorff & Pearson 1999). Although well studied in marine and freshwater environments (Schaffner et al. 1997, Christensen et al. 2002, Thibodeaux & Bierman 2003), few and inconclusive experimental studies have addressed the role of bioturbation on contaminant distribution in the Baltic Sea. For example, the remobilisation of metals from historically contaminated sediments by *Monoporeia affinis* was unexpectedly small (Sundelin & Eriksson 2001), while the release of organic contaminants from sediments bioturbated by *Marenzelleria neglecta* was significant (Granberg et al. 2008). Results presented here generally suggest that bioturbation by some of the most common species in the Baltic Sea increases the retention of contaminants deposited on the sediment surface.

The spionid polychaete genus *Marenzelleria* was first discovered in the Baltic Sea in the 1980s. In some areas, *Marenzelleria* now dominates both in biomass and abundance, and there are indications of concurrent decreasing densities of several native species, among them *Monoporeia affinis* (Kotta & Olafsson 2003, Perus & Bonsdorff 2004). Despite a significant change in the community structure, ecological impacts of the invasion are still not well investigated or understood, although it has recently been suggested that the high abundance of *Marenzelleria* may change sediment processes in the Baltic (Kotta et al. 2006). Results presented in our study support such speculations. For

example, a shift in the community composition of a deep, soft-bottom habitat dominated by *M. affinis* to a community dominated by *Marenzelleria* could significantly change the contaminant dynamics in that area, increasing the mobility of contaminants. Normal field densities of each species were used in this experiment, i.e. the density and biomass varied between treatments, for more ecologically realistic comparisons on their effect on contaminant fate in the field. However, large variations in population densities are common between areas (Perus & Bonsdorff 2004). This variation should be taken into consideration when interpreting the results, since bioturbation intensity has been positively correlated with both size and abundance of infauna (Reible et al. 1996, Sandnes et al. 2000).

Input of labile OM can increase the mobilisation of contaminants from the sediment surface. This may be the result of a combined effect of increased animal feeding and bioturbation activity, and a high diagenetic release due to OM degradation. In the presence of bioturbators similar to the ones used in this experiment, this effect is probably strongest for metals that are predominantly mobile under oxidising conditions (e.g. Cd, Cu, Zn), and for organic contaminants with moderate K_{OW} and/or soluble metabolites (e.g. PAHs and lower chlorinated PCBs). However, a high load of OM to the sediment surface can also cause oxygen depletion and in extreme cases defaunation (Pearson & Rosenberg 1978), leading to an opposite effect on the fate of the above mentioned contaminants due to a slower OM mineralisation, slower contaminant degradation and precipitation of metals under reducing conditions. Under normal spring-bloom conditions, the risk of contaminant mobilisation may increase. This emphasises the importance of understanding how ecological and physiochemical processes interact when assessing the fate, and ultimately the effect, of contaminants in aquatic ecosystems.

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