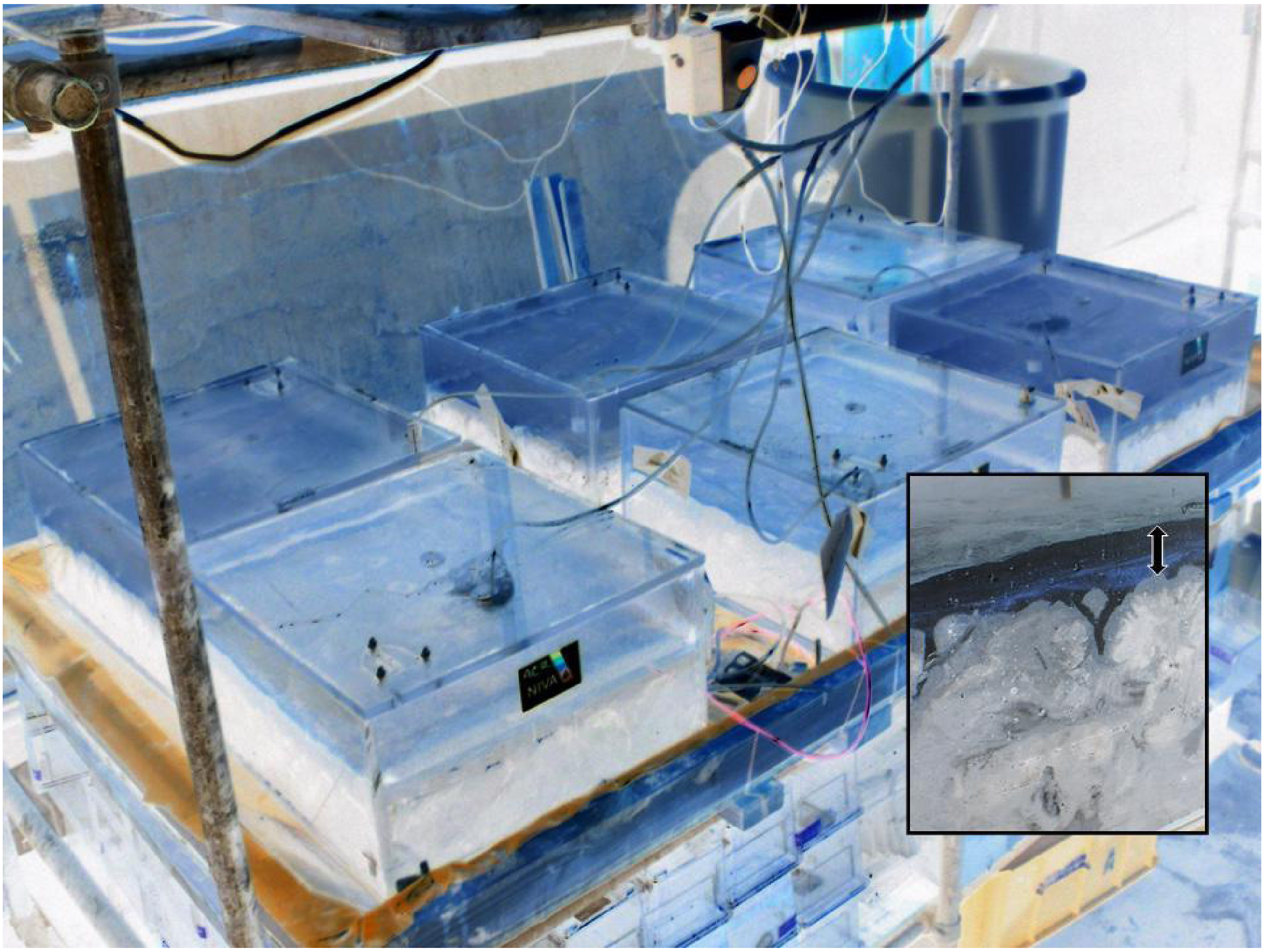
REPORT SNO 5728-2009

OLICAP

A mesocosm-scale evaluation of the relative effectiveness of contaminated sediment capping using a thin layer of fine-grained olivine or coarse-grained sand material



Norwegian Institute for Water Research
– an institute in the Environmental Research Alliance of Norway

REPORT

Main Office	**Regional Office, Sørlandet**	**Regional Office, Østlandet**	**Regional Office, Vestlandet**	**Regional Office, Central**
Gaustadalléen 21 NO-0349 Oslo, Norway Phone (47) 22 18 51 00 Telefax (47) 22 18 52 00 Internet: www.niva.no	Televeien 3 NO-4879 Grimstad, Norway Phone (47) 22 18 51 00 Telefax (47) 37 04 45 13	Sandvikaveien 41 NO-2312 Ottestad, Norway Phone (47) 22 18 51 00 Telefax (47) 62 57 66 53	P.O.Box 2026 NO-5817 Bergen, Norway Phone (47) 22 18 51 00 Telefax (47) 55 23 24 95	P.O.Box 1266 NO-7462 Trondheim Phone (47) 22 18 51 00 Telefax (47) 73 54 63 87

Title OLICAP – A mesocosm-scale evaluation of the relative effectiveness of contaminated sediment capping using a thin layer of fine-grained olivine or coarser-grained sand material	Serial No. 5728-2009	Date 01.02.2009
	Report No. Sub-No. O-28150	Pages Price 45
Author(s) Ian J. Allan, Jens Skei & Kristoffer Næs	Topic group Marine contaminants	Distribution
	Geographical area Solbergstrand	Printed NIVA

Client(s) North Cape Minerals AS	Client ref.

Abstract

Olivine mineral produced in large quantities by North Cape Minerals AS is a good candidate to be used as part of capping procedures for the remediation of contaminated marine sediments. Mesocosms experiments were undertaken to evaluate the relative effectiveness of olivine material as a capping material for the containment of selected sediment contaminants, compared with that obtained with natural sand. Two different contaminated sediments impacted by a range of contaminants were used in this study. The primary objective was to compare sediment-overlying water fluxes of contaminants out of these sediments prior to and following capping with thin layers of olivine or natural sand. Additionally, populations of a selected benthic organism, ragworm, were added prior to cap placement in order to provide natural bioturbators to the sediments. Following cap placement two series of measurements of pore water and whole-sediment Hg concentration-depth profiles were made. Both capping materials did not appear to impact on ragworm activity. This work demonstrates some differences between contaminant fluxes observed following capping of contaminated sediments with olivine versus capping with sand. However, in many cases, these differences are limited. Based on these results and for these particular experimental conditions, no clear advantage of using olivine compared with sand for purposes such as thin layer capping. Alternative experimental designs may be implemented in to corroborate these findings. It is likely that increasing the thickness of the cap will result in an increase in the efficiency of olivine to reduce contaminant fluxes when the aim is isolation capping.

4 keywords, Norwegian	4 keywords, English
1. Olivin	1. Olivine
2. Sediment kappe	2. Sediment capping
3. Forurenset sedimenter	3. Contaminated sediment
4. Mesocosm	4. Mesocosms

	Kristoffer Næs	Jarl Nygard
Ian J. Allan Project manager	*Kristoffer Næs* Research manager	*Jarle Nygard* Strategy Director

ISBN 978-82-577-5463-1

O-28150

OLICAP –

A mesocosm-scale evaluation of the relative effectiveness of contaminated sediment capping using a thin layer of fine-grained olivine or coarser-grained sand material

Preface

North Cape Minerals AS contacted Jens Skei and subsequently contracted NIVA to undertake mesocosm-level experiments to evaluate the potential of olivine mineral to be used as sub-aqueous capping material for the remediation of contaminated marine sediments. The contract was agreed on the 4th March 2008 (J.No 299/08) and the contact person at North Cape Minerals AS throughout the project was Øystein Warnes.

Six-month long mesocosm experiments were conducted at NIVA's field/fjord marine research station Solbergstrand. The project was divided into two phases, prior to and following capping contaminated sediments with olivine or common sand. Measurements of sediment-water fluxes of a range of contaminants were undertaken using semipermeable membrane devices. Sampler extraction and analysis was undertaken at NIVA's laboratory. Hg concentration depth profiles were measured in sediment and pore waters using an atomic absorption spectrometer. Boxes and *Nereis virens* ragworm were looked after by Sigurd Arne Øxnevad and Nassir Hamdan El-Shaikh.
Following a request from North Cape Minerals AS, a late contribution by Joe Jersak (Biologge AS) involved commenting on drafts of this report.

Oslo, 1st February 2009

Ian Allan

Contents

Summary

Anthropogenic activity results in the release of many types of organic, metallic and other contaminants to the environment. Owing to their tendency to bind to sediment particles and organic matter, many of these contaminants are often found to accumulate in aquatic bottom sediments. In turn, such contaminated sediment deposits can represent a long-term source of contaminants to the overlying water and can pose a serious risk to aquatic organisms and human health.

Management and remediation of such contaminated deposits and the risks they pose may be achieved with the placement of a capping layer to isolate contaminated sediments. While relatively inert, natural (quartz-rich) sand is often used for the purpose of “conventional” sediment capping; recent investigations have focussed on the use of alternative materials to accomplish “innovative” sediment capping. Such materials are those that can be found in large quantities and at a relatively low cost and that demonstrate an improved sorption capacity for contaminants of interest, relative to the sorption capacity of natural sand. Relatively fine-grained olivine material, available from North Cape Minerals (NCM) in Norway, is one such capping material.

The present work was undertaken in the laboratory to evaluate, at a mesocosm scale (0.25 m^2 sediment boxes), the relative effectiveness of fine-grained olivine material as a capping material for the containment of selected sediment contaminants, compared with that obtained with natural sand. Two different contaminated sediments impacted by hexachlorobenzene (HCB), mercury (Hg), octachlorostyrene (OCS), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and tributyltin (TBT) were used in this study.

Specifically, the primary goal of this work was to compare sediment-overlying water fluxes of contaminants out of each of these sediments over a 6 months period for two different system conditions: (i) prior to capping and (ii) following capping with relatively thin (2-4 cm thick) layers of either fine-grained olivine or coarser-grained natural sand. Additionally, populations of a selected benthic organism, ragworm (*Nereis virens*), were added prior to cap placement in order to provide natural bioturbators to the sediment, and to evaluate their effect on contaminant fluxes into the overlying water column. Semipermeable membrane devices (SPMDs) were in the overlying water of the mesocosms and were used as an infinite sink to evaluate contaminant fluxes from uncapped and capped sediments. Comparisons between fluxes obtained following sediment capping with olivine or sand were made. Following cap placement two series of measurements of pore water and whole-sediment Hg concentration-depth profiles were made. This was used to investigate the profile distribution of Hg in the sediment and cap material following cap placement.

Key results from these experiments may be summarised:

- No differences in ragworm activity (decrease) could be observed following capping with either cap materials indicating that the olivine cap did not negatively influence biota activity
- No differences between PAH fluxes could be observed upon capping with sand and olivine
- Slightly lower fluxes of TBT could be observed when capping with olivine compared with sand
- Based on relative fluxes of PCBs, HCB and OCS, the use of a thin layer of olivine material, however, resulted in lower fluxes than when capping with natural sand.
- Capping layers of sand and olivine could be clearly identified through the measurements of Hg concentrations profiles with depth in whole sediment and in pore water.
- Generally lower Hg concentrations in pore water could be observed in the caps compared with the underlying sediment (1 month after capping). An increase in Hg concentration in both caps could be observed 11 weeks later.

- *In situ* K_d or distribution coefficients for Hg between solids and pore water were slightly lower for cap layers compared with the underlying sediment while those for layers of olivine appeared slightly higher than for capping layers of sand.

To conclude:

- This work demonstrates some differences between contaminant fluxes observed following capping of contaminated sediments with finer-grained olivine versus capping with relatively coarser sand. However, in many cases, these differences are limited.
- Based on these results and for these particular experimental conditions, no clear advantage of using finer grained olivine compared with relatively coarser sand for purposes such as thin layer capping (where for example, decreases in pore water concentrations may be expected in surficial sediment layers). Alternative experimental designs may be implemented in order to corroborate these findings.
- This work demonstrate that olivine material is as efficient as sand in reducing contaminant fluxes to the water column. Sand has been shown to be effective in reducing contaminant fluxes to the water column when applied in thick isolation capping layers. It is therefore likely that olivine will be of a similar efficiency when applied in thicker layers.
- It is likely that increasing the thickness of the cap will result in an increase in the efficiency of olivine to reduce sediment-water contaminant fluxes when it is used for isolation capping purposes.
- While the efficiency of olivine as a passive thin layer cap may be limited, it can be combined with other types of materials such as activated carbon for both active thin-layer and isolation capping purposes.

1. Introduction

Hydrophobic organic contaminants and heavy metals, released to the aquatic environment through a variety of processes, typically associate strongly to sediment particles and ultimately accumulate in bed sediments in lakes, rivers and harbour areas or in the marine environments. In many cases, such sediment deposits represent a source of contaminants to the overlying water, and can pose a serious risk to aquatic organisms and human health over extended periods of time.

Significant natural recovery can be achieved by natural deposition over time of cleaner sediment above contaminated sediments. However, this phenomenon can be accelerated through purposeful placement of a capping layer to isolate the contaminated layer from the overlying water or organisms that may be present in the sediment[1]. Coarse particulate material such as sand is commonly used as capping material as it is relatively inexpensive and can often be found in sufficiently large quantities. Factors such as particle type, size and density or the thickness of the cap may affect the deposition procedure and ultimately the cap efficiency in preventing release of contaminants from the sediment. It may also have an impact on the potential for resuspension of cap material.

More specifically, capping projects may be initiated to obtain:

- Physical isolation of bioturbating benthic organisms from contaminated sediments;
- Physical containment and stabilization of contaminated sediments, to prevent their erosion, transport and re-suspension; and
- Chemical isolation of contaminants, to reduce their long-term flux into the overlying water column (as well as into the bioturbation zone).

An additional consideration is the type and quality of benthic habitat created as a result of cap placement.

In most cases, contaminants are associated with the finest-sized sediment particles (possessing higher surface areas and more enriched in natural organic matter) and, as such, are generally found in areas of sediment deposition.

While under certain conditions, “conventional” sediment capping using relatively inert and natural granular material such as sand is able to achieve the objectives above (with sometimes an armoured layer added above the sand cap to minimise losses due to erosion), in other cases (e.g. when the aim is long-term flux reduction) where such conventional capping may not be adequate, “innovative” (i.e. reactive or sorptive) capping materials represents a viable alternative approach. Fine-grained olivine represents one such sorptive mineral material.

1.1 Olivine material

Olivine mineral material produced and commercialised by North Cap Minerals (NCM) in Norway has the potential to be used as capping material, and large volumes can be available for capping projects. Olivine is one of the most common rock-forming minerals on earth and is a magnesium iron silicate $(Mg,Fe)_2SiO_4$, with a high particle density (~ 3.3 g cm^{-3}) relative to that of typical, quartz-rich sand (~ 2.7 g cm^{-3}) Manganese and nickel are typically the only additional elements present in the mineral in elevated concentrations.

---

[1] RK Mohan, MP Brown, CR Barnes (2000) Design criteria and theoretical basis for capping contaminated marine sediments. *Applied Ocean Research.* Vol. 22 pp 85–93

1.2 Experimental testing

Based on results of preliminary laboratory sorption testing, a relatively high affinity of contaminants for fine-grained olivine material was observed for a range of contaminants commonly found in contaminated sediments (see Table 1).

Table 1. Preliminary results of contaminant sorption to olivine assessed in shake flask assays (data provided by NCM, February 2008)

Analyte	Fraction sorbed to olivine at equilibrium (%)
TBT	84.0 - 96.0
PCBs	94.8 - 99.3
PAHs (ANT, B*a*A, DB*ah*A)	60.0 - 99.0
PAHs (PYR, BiP, B*ghi*P, I*123cd*P, FLUO, B*b,k*F, CHRY)	80.0 - 99.6

A wide variety of tests (physical, chemical, biological) may be undertaken to evaluate the suitability of a candidate material for use in sediment capping. These can range from laboratory-scale up through to pilot- and field-scale.

Since the sorption capacity of a candidate capping material is a critical factor affecting the rate of contaminant diffusive/advective movement through a capping layer, a thorough characterisation of a material's ability to sorb to contaminants under controlled laboratory conditions and using standard/accepted procedures should be the focus of initial testing (see Table 1 for *preliminary* sorption data for olivine).

Column- or mesocosm-scale experiments, involving contaminated sediment and overlying water components, may then be conducted to investigate the efficiency of the candidate material for capping under more realistic or "field-relevant" conditions[2]. Selected biota (i.e. site-specific bioturbating benthic organisms) may also be incorporated into such experimental set-ups to assess not only habitat-related compatibility of the capping material with the organisms but to also assess the relative influence of bioturbation processes on contaminant fluxes into the overlying water column, both within uncapped and capped systems. Such benthic-related issues should also be considered during cap design and assessed at the field- and pilot-scale level, post-capping. Additionally, and prior to field- and pilot-scale study, placement characteristics of the candidate capping material – particularly graded materials enriched in reactive fines - should first be demonstrated and optimised at the laboratory (column) scale.

1.3 Aims and objectives

Original aims as described in the proposal of work

"Assumption: North Cap Mineral would like to see experiments conducted at the mesocosm level to evaluate the capacity of olivine to act as a contaminant barrier

The aim of the work is to evaluate its capacity to reduce contaminant fluxes from contaminated marine sediments into overlying water when used as a sub-aqueous capping layer. Model contaminants

---

[2] M Schaanning, B Breyholtz, J Skei. Experimental results on effects of capping on fluxes of persistent organic pollutants (POPs) from historically contaminated sediments (2006) *Marine Chemistry.* Vol. 102 pp 46-59.

selected for this study are mercury (Hg) and hexachlorobenzene (HCB). Mesocosm experiments using naturally contaminated marine sediment will be conducted to:

- Evaluate the reduction in fluxes of contaminants following capping with a thin layer (1 cm) of olivine
- Compare these fluxes with those observed with a more commonly used capping material (e.g. sand)
- Include the impacts of bioturbation on these fluxes

In order to estimate the efficiency of olivine to act as a barrier to contaminant movement out of sediments, measurements may be undertaken:

- In the overlying water using passive sampling (e.g. SPMDs for non-polar organic contaminants). Passive sampling will be used for Hg.
- In the sediment phase by measuring profiles of contaminant concentration with depth at certain time points during the course of the experiment in order to assess contaminant movement into the cap."

The present work was undertaken in the laboratory to evaluate, at a mesocosm scale (0.25 m^2 sediment boxes), the relative effectiveness of fine-grained olivine material and coarser natural sand as capping materials for the containment of selected sediment contaminants. Two different contaminated sediments (contaminated with HCB, Hg, OCS, PAH, PCBs and TBT) were used in this study.

Specifically, the primary objective of this work was to compare contaminant fluxes out of each of these sediments and into the overlying water column, over a 6-month period and under two different system conditions: (i) prior to capping and (ii) following capping with relatively thin (several cm thick) layers of either fine-grained olivine or coarser-grained natural sand. Additionally, populations of a selected benthic organism, ragworm (*Nereis virens*), were added prior to cap placement in order to provide natural bioturbators to the sediment, and to evaluate their effect on contaminant fluxes into the overlying water column. Semi-permeable membrane devices (SPMDs) were placed in water columns and used as an infinite sink to evaluate contaminant fluxes from uncapped and capped sediment. Comparisons between fluxes obtained following thin-layer sediment capping with olivine or sand were made. Following cap placement and over time, two series of depth-discrete measurements were made of Hg concentrations in pore waters of the sediment and cap materials (total and dissolved Hg forms) to investigate the profile distribution of Hg in the sediment following cap placement.

2. Methods

The experiment was conducted from the 10/03/08 to the 12/09/08 at NIVA's field experiment station at Solbergstrand.
Experiments were designed to provide a comparison between fluxes obtained following capping with normal sand and with olivine material in 0.25 m^2 sediment boxes. To improve the representativeness of the set-up, *Nereis virens* (ragworms) were added to the boxes as they are common sediment bioturbators. Representative contaminants were selected for this study and included mercury (Hg), hexachlorobenzene, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), octachlorostyrene (OCS) and tributyltin (TBT). Fluxes of PAHs, PCBs, HCB, OCS and TBT from the sediment to the overlying water phase were measured using semipermeable membrane devices (SPMD passive samplers). Profiles of Hg concentrations in sediment were measured twice during the course of the experiment.

2.1 Experimental set-up and conditions

A total of 12 Plexiglas boxes (50 long × 50 wide × 30 cm high) were prepared with 2 distinct sediments and filled with Oslo fjord water collected at 60 m deep. Six boxes (Boxes 1-6) were filled with a 10 cm deep layer of sediment contaminated with polycyclic aromatic hydrocarbons and tributyltin. This sediment was prepared by mixing two sediment batches previously held and stored at Solbergstrand. These two batches were thoroughly mixed prior to adding to the boxes (porosity = 0.76 % vol/vol). The second sediment was already placed in 6 boxes prior to the start of the experiment (Boxes 7-12). This sediment originates from Gunnekleivfjord in the vicinity of chlor-alkali and magnesium plants with a long history of discharges of mercury and chlorinated compounds, respectively (porosity = 80 % vol/vol; 3-4 % TOC). The final placed thickness of sediment in each box set, as described above, was approximately 15 cm. According to a draft report[3] for previous work undertaken with these boxes, total mercury concentrations in the second sediment were in the range 5-25 mg kg^{-1} dry weight. Boxes were positioned in 2 basins as shown on diagram on Figures 1 and 2.

Nereis virens (ragworms) were purchased from Topsy bait (The Netherlands) and 30 worms were added to boxes 1-12 prior to capping (followed by another 10 worm per box 2 days later) to obtain a density of approximately 150 ind m^{-2}. Following worm addition, only a few individuals (1-3) died in boxes 1, 2, 4, 7, 9 and 11. Owing to the length of the experiment (i.e. ~ 6 months), ragworms were regularly fed twice a week with algal pellets until completion of the experiment. Water was aerated constantly throughout the experiment. Water temperature was regularly measured. The height of the water column in boxes containing the Hg-contaminated sediment (i.e. Boxes 7-12) was approximately 15 cm, while this was either 15 or 35 cm for boxes 1-6.

---

[3] N. Johnson. Summary of work for NIVA-UT-Austin collaboration (Draft report), 6 pages, 11 December 2007

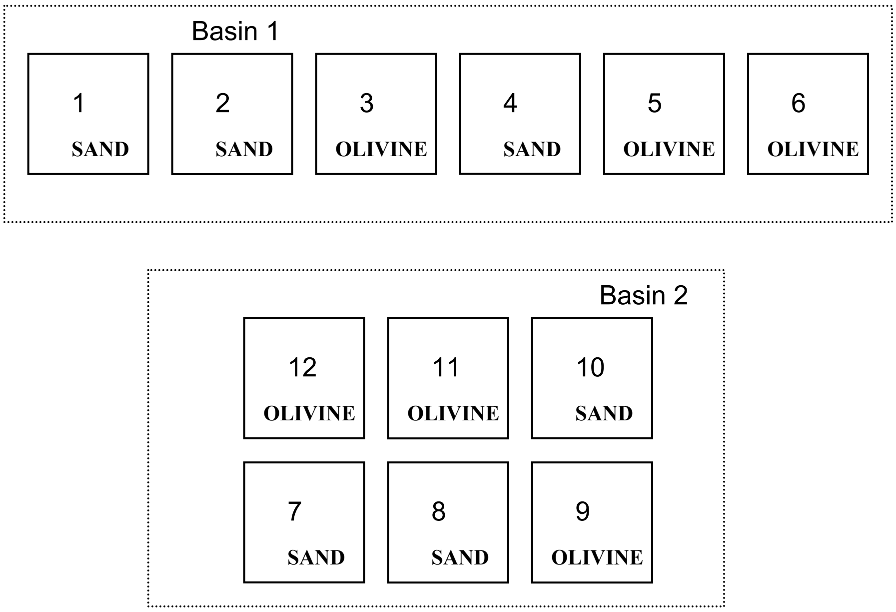


Figure 1. Position of boxes at Solbergstrand

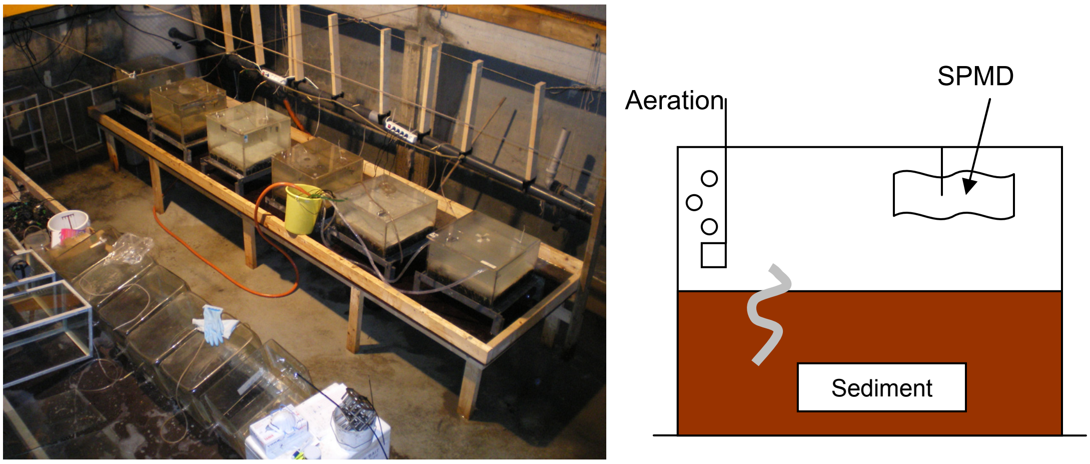


Figure 2. Boxes 1-6 containing mixed contaminated sediment. Picture taken following cap placement and replenishing overlying water

2.2 Technique for cap addition at mesocosm scale

Olivine and sand caps were placed above contaminated sediments contained in all 12 boxes. Randomly selected boxes containing either of the two types of contaminated sediments were capped with several cm of olivine or sand. The finest olivine material was used for this study while sand was provided by Storsand AS and sieved at 1 mm prior to be used in these capping experiments.

The achievement of an accurate cap depth was challenging since ragworms had significantly reworked previously flat sediments.

A similar procedure was used for the placement of both the olivine and the sand caps, although the materials were, by necessity, placed in different physical forms (wet sand versus an olivine slurry). The cap placement procedure involved the following steps:

1. Overlying water was first removed from boxes with tubing to leave only a few mm of water above the sediment bed
2. Sand was deposited carefully above the sediment layer while the fine olivine particles were prepared into a slurry (salt water) that was then carefully poured over the sediment layer. Caps were applied in 2 layers to ensure that a proportion of the cap was sediment-free
3. Addition of fresh saltwater from Oslo fjord to fill boxes upon cap placement.

Figure 3. Removal of overlying water (top left), addition of olivine material (top right), addition of water to boxes (bottom left) and example of deposited olivine cap (bottom right)

A sand cap was placed into Boxes 1, 2, 4, 7, 8 and 10 while an olivine capping layer positioned in Boxes 3, 5, 6, 9, 11 and 12.

2.3 Measurement of sediment-water fluxes of organic contaminants

Semipermeable membrane devices (SPMDs), which were suspended in the water column within each box (Figure 2), are made of 92 cm long and 2.5 cm wide low density polyethylene tubing filled with 1 mL of triolein lipid. While these passive sampling devices are most often used for environmental monitoring of contaminant concentrations in water, SPMD are used here as infinite sink for hydrophobic contaminants in the overlying water above the sediment layer. With high sampler-water partition coefficients (log $K_{\mathrm{SW}} > 3\text{-}4$) and a large surface area (460 cm^2), they are expected to create contaminant depletion in the water phase in their vicinity, thereby creating a concentration gradient between this water phase and the sediment bed. This results in a flux of contaminant out of the sediment. Since initial contaminant masses in SPMD are negligible, the contaminant mass accumulated in SPMD during exposure may be used to estimate fluxes out of the sediment:

$$F = \frac{m_t - m_0}{SA \times t} \qquad [1]$$

where F is the flux out of the sediment (pg m^{-2} d^{-1}), m_t and m_0 are contaminant masses at time = 0 and time = t, SA the sediment surface area (m^2) and t the exposure time (d).

Contaminant mass transfer from the sediment ultimately up to the SPMD device is likely dependent on the following series of processes: (i) contaminant desorption from sediment particles and transfer into sediment pore water, (ii) transfer from pore waters to the overlying water across the diffusive boundary layer at the surface of the sediment bed, (iii) and across the diffusive boundary layer at the surface of the SPMD, and (iv) transport across the LDPE membrane of the SPMD sampler. Previous use of this experimental set-up demonstrated that for compounds with log $K_{\mathrm{OW}} > 4\text{-}4.5$, mass transfer in the LDPE membrane was not rate-limiting.

SPMD devices were transported from the laboratory to Solbergstrand in cold boxes on ice and field control SPMD were used to assess possible contamination during deployment and retrieval procedures (since these samplers are efficient air sampling devices, such blanks are opened to the air to ensure that contaminants accumulated in the samplers was solely due to accumulation from the water phase). SPMD were fitted onto spider holders fixed to the Plexiglas lid of each box. Initial (post-worm addition but pre-cap) flux measurements were undertaken in Boxes 2, 3, 4, 5, 8, 9, 11 and 12 for a period of 35 days. Flux measurement following cap placement were undertaken in all 12 boxes for a period of 35 days. At the ends of the initial and post-cap time periods, SPMD devices were retrieved from boxes and stored in tins, and transported back to the laboratory for analysis. Samplers from Boxes 1-6 were extracted and extracts split to allow for analysis of PAHs and TBT, while extracts from those from Boxes 7-12 were sent for analysis of PCBs, OCS and HCB.

Table 2. Deployment and retrieval dates for SPMD samplers

Event	Boxes	Deployment date	Retrieval date	Mean temperature (°C)
Flux measurement prior to capping	2,3,4,5,8,9,11,12	03/04/08	08/05/08	9.2
Flux measurement post-capping	1-12	25/06/08	30/07/08	19.4

2.4 Measurement of Hg depth-concentration profiles in sediment

The initial plan was to measure Hg depth-concentration profiles in pore waters of capped sediment using Diffusive Gradient in Thin film device (DGT)[4]. DGT sampling devices were purchased from Exposmeter AB (Sweden). The device is made of an agarose diffusing layer placed in front of a spheron thiol resin gel, which is supposed to efficiently bind a variety of Hg species. The probe may be inserted into sediment and dissolved Hg present in pore water diffuses through the agarose and bind to the receiving phase. With knowledge of Hg diffusion coefficient in the agarose gel, it is possible to estimate pore water concentrations from the mass of Hg accumulated in the receiving phase[5]. Probes were deployed for 48 hrs in all 6 Hg-contaminated sediment boxes following cap placement. Probes may then be sliced to the appropriate resolution for the determination of profiles. Blank probes were

---

[4] DGT Research handbook, 58 pages, www.dgtresearch.com

[5] P Divis, M Leermakers, H Docekalova, Y Gao (2005) Mercury depth profiles in river and marine sediments measured by the diffusive gradients in thin films technique with two different specific resins. Analytical & Bioanalytical Chemistry. Vol 382 pp 1715-1719

analysed and approximately 0.15 ng Hg cm^{-1} was measured repetitively, which was unacceptably high. As a note, spheron thiol resin is notoriously difficult to clean free from Hg contamination since thorough cleaning may result in irreversible damage of binding sites for Hg. Deployed probes were sliced and analysed. Levels measured in slices were not significantly different from blank values. This could be explained by (i) low Hg concentration in pore water resulting in low accumulation in the probes (in comparison with amounts already present in blank probes) and/or (ii) damaged binding sites preventing accumulation of Hg in the receiving phase.

As an alternative to the initial plan described above, a sediment coring and centrifuging procedure was developed and implemented in order to produce total and dissolved Hg depth-concentration profiles in sediments. Plastic coring tubes (5-6 cm diameter) were used to collect cores. Collected cores were then horizontally sliced into approximately 3 mm-thick layers. One core was collected per box and slices for sand and olivine capped sediment boxes respectively were joined. Supra-pure acid rinsed centrifuge tubes were used for centrifuging conducted on-site as soon after core slicing as possible. A Biofuge centrifuge with a rotation speed of 13,500 rpm was used for obtaining pore water samples. 1-5 mL pore water samples were collected in acid rinsed 10 mL plastic tubes. Supra pure nitric acid (HNO_3, 0.5 mL) and sulphuric acid (H_2SO_4, 0.5 mL) were added and samples were diluted to 10 mL. Standard solutions of Hg were prepared using the same volume ratios of HNO_3 and H_2SO_4. Standards and samples were analysed using the Lumex atomic absorption spectrometer with the cold vapour attachment specific to the analysis of water samples. Briefly, the sample is mixed with a strongly oxidising solution ($SnCl_2$) that allows volatilisation of all mercury species present in the sample. The sample is then pumped through a NaOH solution (10%) preventing damages to the Lumex analyser, and then through the analyser for analysis of the amount of Hg in the air sample. This sediment coring procedure was repeated for Boxes 9 and 10 at the end of August 2008. Slicing was undertaken with a resolution of 5 mm.

Total mercury concentrations in sediment were also measured using the Lumex atomic absorption spectrometer but using an oven system able to burn the sample. A sample (50-200 mg) placed in a sample boat is heated to > 500 °C and all mercury present in the sample (irrespective of speciation) volatilises and is measured through atomic absorption spectrometry. Accurate weighing of the sample was undertaken after burning the sample, so that dry weight data was obtained. Data obtained here could be normalised to the amount of organic matter that was burnt though is likely to be under 5 %.

2.5 Work plan and schedule

Below is a summary of the work plan and schedule of events for the experimental work conducted for the Olicap project.

Date	Item
26/03-01/09/08	Feeding of worms twice a week Overlying water flushed with fresh fjord water regularly except during SPMD measurements
01-10/03/08	Preparation of Boxes 1-6
10-17/03/08	Fixing leaks in Boxes 2 and 3
26/03/08	Addition of 30 *Nereis virens* ragworms per box
28/03/08	Addition of another 10 ragworms per box
03/04/08	Removal of dead worms SPMD deployed in Boxes 2,3,4,5 (time 14:30) SPMD deployed in Boxes 8, 9, 11, 12 (time 15:30)
08/05/08	Retrieval of the first batch of SPMDs (time 15:00) Overlying water
13/05/08	Registration of SPMD for analysis in the lab
14/05/08	Application of a 2-3 cm sand or olivine capping layer to all boxes 48 h Deployment of DGT probes in Boxes 7-12
16/05/08	Retrieval of DGT probes and slicing of probes
15/06/08	Coring in Boxes 7-12, slicing of cores, centrifugation and collection of pore water samples
15-30/06/08	Analysis of sediment and pore water samples
24-25/06/08	2nd DGT probe exposure for 24 h
25/06/08	SPMD deployment in Boxes 1-12 (time 12:00)
30/07/08	SPMD retrieval from all boxes (time 12:00)
31/07/08	SPMD sample registration in laboratory
02/09/08	Sediment core collection, slicing and centrifugation for Boxes 9 and 10
05-10/09/08	Measurement of Hg concentrations in sediment and pore water samples
15-28/09/08	Data analysis and reporting

3. Results and discussion

3.1 Effect of capping on fluxes of polycyclic aromatic hydrocarbons and TBT

3.1.1 Contaminant fluxes prior to capping with a thin layer of olivine or sand

Fluxes of polycyclic aromatic hydrocarbons (PAHs) and TBT from sediment into the overlying water column were measured using SPMD passive sampling devices. Samplers were used as infinite sink for contaminants. Owing to the high affinity of PAHs and TBT for the low density polyethylene membrane and the triolein, a concentration gradient is created between the sediment pore water and the water at LDPE/water interface. This gradient drives the accumulation into the samplers and allows the calculation of contaminant fluxes out of the sediment. Mean masses accumulated in SPMD devices range from below respective limits of detection (<5 ng/SPMD) to, on average, 210 ng/SPMD for pyrene. Percent relative standard deviation (% RSD) values based on the measurement undertaken in 4 boxes are excellent, ranging between 6.9 and 30.7 %, with one higher value of approximately 60 % for benzo[a]pyrene. The high value for benzo[a]pyrene could be explained by the mean mass accumulated close to the limit of detection. Such relatively low % RSD values (for the most part) are encouraging, considering the numerous factors (processes) that can affect such flux measurements (as described in Section 2.2). Relatively low % RSD values would also tend to indicate that the contaminated sediment masses added to the replicate boxes were relatively well mixed, and thus provided a reasonably consistent flux of contaminants under these specific box conditions.

Table 3. Masses of PAHs and tin species accumulated in SPMDs exposed in Boxes 2, 3, 4 and 5 for 35 days prior to capping.

Analyte ID	Mass accumulated in SPMDs (ng) Mean[a]	Standard Deviation[a]	% RSD
Acenaphthylene	7.5	2.0	26.6
Acenaphtene	66.7	10.5	15.8
Fluorene	49.3	10.7	21.7
Dibenzothiophene	18.3	2.1	11.4
Phenanthrene	130.0	10.0	7.7
Anthracene	29.3	9.0	30.7
Fluoranthene	85.5	7.2	8.5
Pyrene	210.0	25.8	12.3
Benzo[*a*]Anthracene	23.3	4.2	18.0
Benzo[*k*]fluoranthene	28.0		
Benzo[*e*]pyrene	23.0		
Benzo[*a*]pyrene	9.6	5.8	60.3
Perylene	<5		
Indeno[123 cd]pyrene	<5		
Dibenzo[a,h]anthracene	<5		
Benzo[ghi]perylene	6.5		
Dibutyltin	2.5		
Tributyltin	2.5	0.2	6.9
Triphenyltin	<1		

[a] n=4

Sediment-to-water fluxes were calculated using Equation [1] with t = 35 days, and a sediment surface area, SA = 0.25 m^2. Fluxes range from just under 1 ng m^{-2} d^{-1} for acenaphthylene to 24 ng m^{-2} s^{-1} for pyrene. However, as may be expected due to their higher binding to sediment solids, fluxes were below level of detection (LOD) for the 3 largest PAHs. Fluxes measured for TBT were close to 0.3 ng m^{-2} d^{-1}.

The magnitude of the fluxes obtained for the various PAHs is consistent with the contamination levels in the sediment. Highest PAH concentrations were observed for phenanthrene and pyrene, with concentrations of 790 and 950 µg kg^{-1} dry weight, respectively.

Table 4. Calculated sediment-water fluxes of PAHs and tin species (pg m^{-2} d^{-1}) measured with SPMD prior to capping.

Analyte ID	Sediment-water flux (pg m^{-2} day^{-1}) Mean[a]	Standard Deviation[a]
Acenaphthylene	857	228
Acenaphtene	7619	1200
Fluorene	5638	1222
Dibenzothiophene	2095	238
Phenanthrene	14857	1143
Anthracene	3352	1031
Fluoranthene	9771	827
Pyrene	24000	2951
Benzo[*a*]Anthracene	2657	479
Benzo[*k*]fluoranthene	3200	
Benzo[*e*]pyrene	2629	
Benzo[*a*]pyrene	1100	664
Perylene	<570	
Indeno[*123 cd*]pyrene	<570	
Dibenzo[*a,h*]anthracene	<570	
Benzo[*ghi*]perylene	743	
Dibutyltin	286	
Tributyltin	286	20
Triphenyltin	<114	

[a]n=4

Other researchers have recently conducted similar experiments using smaller mesocosm experimental set-ups, and using contaminated sediment from Bjørvika in Oslo Harbour[6]. The sediment used in our work was slightly less contaminated than the sediment used in that particular study. However in that case, fluxes in the range 10-1000 ng m^{-2} d^{-1} were observed, which are one to two orders of magnitude higher than those observed here. This could be the result of differences (i) in sediment contamination, (ii) in contaminant desorption rates if mass transfer of contaminants into pore water is the limiting factor or (iii) in the experimental set-up used. In addition, that particular study did not involve the use of benthic organisms and fluxes did not incorporate a bioturbation factor.

3.1.2 Contaminant fluxes following capping with a thin layer of olivine or sand

Fluxes were measured again approximately 6 weeks after cap placement, in order for the measurement to be undertaken when the capped systems had reached some sort of steady state.

Triplicate SPMDs were used in sand- and olivine-capped boxes. All analytes, apart from dibenzo[a,h]anthracene, were detected and quantified in all samplers deployed in both types of boxes. Relative standard deviation (n = 3) were also very good, and in the range 2 to 36.8 %.

---

[6] E. Eek *et al.* (2008) Diffusion of PAH and PCB from contaminated sediments with and without mineral capping; measurement and modelling. Chemosphere. Vol. 71 (9) pp 1629-1638

Table 5. Masses of PAHs and tin species (ng) accumulated in SPMDs during a 35 d exposure following application of 2-3 cm sand and olivine caps

Analyte ID	Sand cap			Olivine cap		
	Mean[a]	SD	% RSD	Mean[a]	SD	% RSD
Acenaphthylene	5.87	0.12	2.0	5.3[b]		
Acenaphtene	12.3	1.5	12.4	18.0	3.6	20.0
Fluorene	11.3	2.9	26.1	30.3	11.2	36.8
Dibenzothiophene	<5			6.2		
Phenanthrene	27.3	8.6	31.5	42.3	11.2	26.6
Anthracene	12.3	1.5	12.4	9.8	1.9	19.3
Fluoranthene	59.0	1.0	1.7	57.7	10.2	17.7
Pyrene	223.3	23.1	10.3	220.0	30.0	13.6
Benzo[*a*]Anthracene	17.13	6.7	39.1	25.3	6.5	25.7
Benzo[*k*]fluoranthene	14.3	1.2	8.1	24.7	4.2	16.9
Benzo[*e*]pyrene	29.7	1.5	5.2	44.0	7.0	15.9
Benzo[*a*]pyrene	13.3	1.2	8.7	19.0	3.0	15.8
Perylene	10.0	5.3	52.7	7.6	0.69	9.1
Indeno[*123 cd*]pyrene	5.8	0.9	15.8	8.7	1.3	15.0
Dibenzo[*a,h*]anthracene	<5			<5		
Benzo[*ghi*]perylene	8.53	0.35	4.1	12.0	1.0	8.3
Dibutyltin	3,70	0,14	3,8	11,3	10,1	89,5
Tributyltin	33,7	20,6	61,2	7,7	9,8	127,1
Triphenyltin	1,80	1,13	62,6	<1		

[a]n=3 for each capping material; [b]1 value > LOD only

SPMD exposure time, post-capping, was the same as that for the first, pre-capping, exposure (t = 35 days). Therefore, post-capping masses accumulated can be directly compared with those from the first set of pre-capping measurements.

Results indicate that mass values generally appear to be in a very similar range. When calculating observed fluxes following capping, these generally appear of a similar order of magnitude as those measured prior to capping, and differences between sand and olivine are not directly visible.

Table 6. Calculated sediment-water fluxes of PAHs and tin species (pg m^{-2} d^{-1}) measured with SPMD following capping with sand or olivine

Analyte ID	Sediment-water fluxes (pg m^{-2} d^{-1})			
	Sand cap		Olivine cap	
	Mean[a]	SD	Mean[a]	SD
Acenaphthylene	671	13	606[b]	
Acenaphtene	1410	175	2057	412
Fluorene	1291	337	3467	1274
Dibenzothiophene			709	
Phenanthrene	3124	985	4838	1285
Anthracene	1410	175	1124	216
Fluoranthene	6743	114	6591	1167
Pyrene	25524	2639	25143	3429
Benzo[*a*]Anthracene	1958	765	2895	744
Benzo[*k*]fluoranthene	1638	132	2819	476
Benzo[*e*]pyrene	3391	175	5029	800
Benzo[*a*]pyrene	1524	132	2171	343
Perylene	1139	600	869	79
Indeno[*123 cd*]pyrene	663	104	991	149
Dibenzo[*a,h*]anthracene				
Benzo[*ghi*]perylene	975	40	1371	114
Dibutyltin	423	16	1291	1160
Tributyltin	3848	2354	880	1120
Triphenyltin	206	129	<114	

[a]n=3 for each capping material; [b]1 value > LOD only

Following capping, it was possible to detect fluxes both of dibutyltin and tributyltin in all boxes, while only in sand-capped boxes was it possible to observe a flux of triphenyltin. Fluxes of TBT were significantly higher after capping than those measured prior to capping. Fluxes of TBT for olivine capped sediments appeared lower than those measured for sand capped while the opposite is observed for DBT.

3.1.3 Comparison of contaminant fluxes, pre- versus post-capping

Fluxes were calculated and the relative changes in flux resulting from capping with sand or olivine were calculated for each PAH compound. These are shown in the diagram below, where the flux changes are expressed in % and are plotted as a function of PAH hydrophobicity. For PAHs with log $K_{OW} < 5.5$, fluxes decreased by 25-75 % (except for pyrene, for which fluxes were similar). The analytical LOD for fluxes prior to capping were used for the estimation of increases in fluxes for PAH with log $K_{OW} > 5.5$. Increases in fluxes may have been larger. An increase in the range 5-100 % is observed for these compounds while, in a few cases, a decrease between 5-50 % can be observed. Some differences between the sand and olivine capping treatments can be observed.

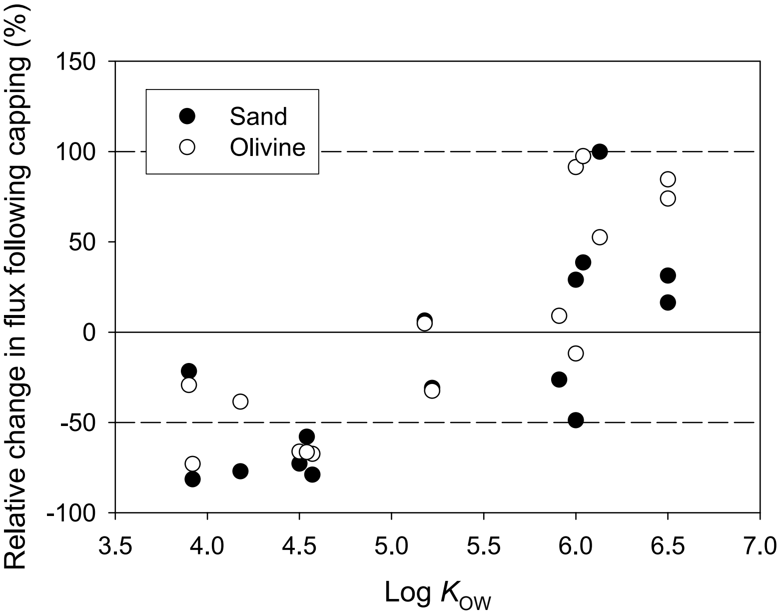


Figure 4. Percentage change in flux of PAHs following capping with sand or olivine. Dashed lines correspond to an increase/decrease in flux of a a factor or 2.

The significance of possible differences in the change in flux following capping with a relatively thin layer of sand or olivine was tested using the student's t-test on log-transformed flux values (at the 0.05 confidence level, n = 3). Differences appear mostly significant for the *increases* in post-capping fluxes observed for higher molecular-weight PAHs (4 benzene rings or more). Higher fluxes are measured with the olivine capping than with the sand caps.

Table 7. Differences and significance (95 % confidence) of fluxes observed following capping with sand and olivine

Analyte ID	$\Delta F_{OLIVINE}$-F_{SAND} (%)	Significance[a] [P value]
Acenaphthylene	-10.7	
Acenaphtene	31.5	Y [0,049]
Fluorene	62.8	Y [0,02]
Dibenzothiophene		
Phenanthrene	35.4	N [0,16]
Anthracene	-25.4	N [0,14]
Fluoranthene	-2.3	N [0,77]
Pyrene	-1.5	N [0,86]
Benzo[*a*]Anthracene	32.4	N [0,23]
Benzo[*k*]fluoranthene	41.9	Y [0,009]
Benzo[*e*]pyrene	32.6	Y[0,019]
Benzo[*a*]pyrene	29.8	Y[0,030]
Perylene	-31.1	N [0,55]
Indeno[*123 cd*]pyrene	33.1	Y [0,032]
Dibenzo[*a,h*]anthracene		
Benzo[*ghi*]perylene	28.9	Y [0,003]
Dibutyltin	67,3	[b]
Tributyltin	-337,2	N [0.07]
Triphenyltin	-80,0	[b]

[a]t-test on log-transformed values of fluxes for sand or olivine capped sediment ; [b]Insufficient number of value to run a t-test

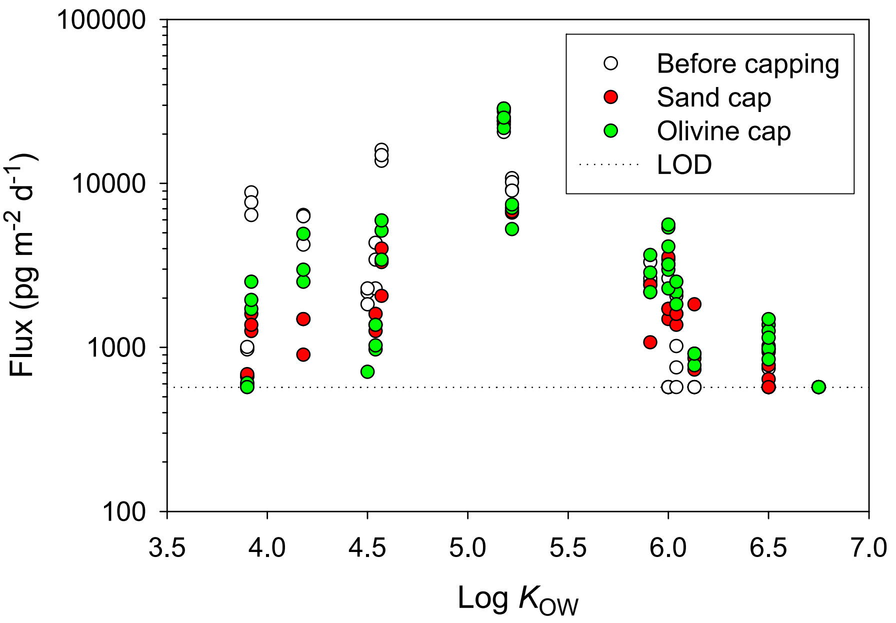


Figure 5. Comparison of PAH fluxes prior to and post capping with a 2-3 cm layer of sand and olivine

3.1.4 Modelling of contaminant fluxes observed prior to and post-capping

Modelling of PAH fluxes across active sediment layers (conceptual homogenous layer of sediment actually contributing to the flux of contaminant to the water phase) or across sediment-water interfaces using relatively simple or empirical models may help to understand and interpret results from experimental simulation.

In the present case, the temperature was significantly higher for the second SPMD exposure compared with the first one (by a factor of 2). Such a difference will have a direct impact on processes such as molecular diffusion in water that control the diffusive release of contaminants from sediments. In these experiments, contaminant diffusion in sediment pore water and across conceptual diffusive boundary layers present both at the surface of both the sediment and the SPMD are likely to have an impact on the overall mass transfer coefficient. Fluxes may be explained using empirical mass transfer approximation equations such as[7]:

$$F_{SPMD} = K_{OV}(C_{PW} - C_W) \qquad [2]$$

where C_{PW} and C_W are contaminant concentrations in pore and overlying water (ng L^{-1}), respectively, and K_{OV} the overall mass transfer coefficient across the both diffusive boundary layers when the flux is measured with an SPMD (F_{SPMD}). The driver for the flux C_W may be assumed to be negligible (very close to) the surface of the passive sampler, while C_{PW} may be estimated empirically using commonly used log K_{OC}-log K_{OW} relationships to estimating contaminant distribution coefficients, K_d, between sediments and pore water:

$$F_{SPMD} = K_{OV}\left(\frac{C_S}{K_d} - C_W\right) \qquad [3]$$

With:

$$K_d = \frac{C_S}{C_{PW}} = K_{OC} \times TOC \qquad [4]$$

With *TOC* the total organic carbon content of the sediment (approx. 4 % for this sediment) and the organic carbon content normalised partition coefficient K_{OC}, estimated through the following empirical relationship[8,9]:

$$\log K_{OC} = 0{,}989 \log K_{OW} - 0.346 \qquad [5]$$

---

[7] W Lick (2006) The sediment-water flux of HOCs due to "diffusion" or is there a well-mixed layer? If there is, does it matter? *Environmental Science and Technology.* Vol. 40 (18) pp. 5610-5617

[8] SW Karickhoff (1984) Organic pollutant sorption in aquatic systems. *J. Hydr. Eng.* Vol. 110 pp 707-735

[9] SW Karickhoff (1981) Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* Vol. 10 pp 833-846

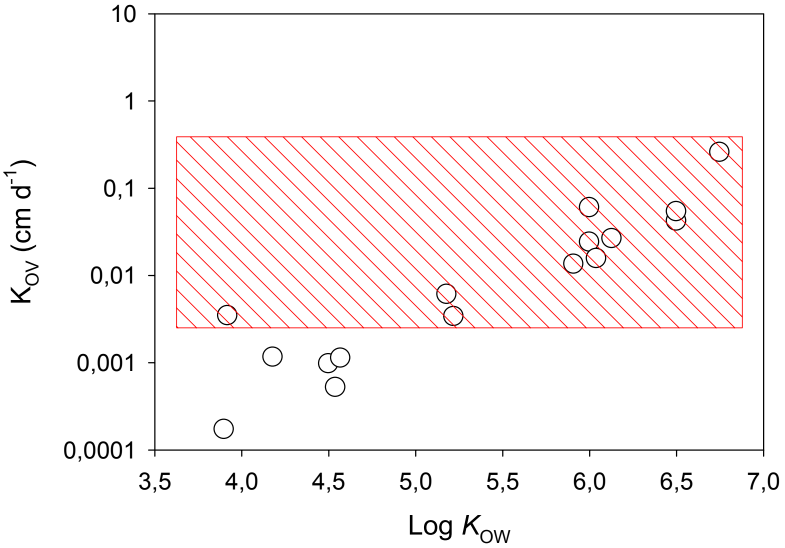


Figure 6. Overall mass transfer coefficient calculated for PAH diffusion out of the sediment prior to capping. The box represents a range of mass transfer coefficient generally observed for hydrophobic contaminant under biodiffusive transport in pore water or molecular diffusion of bioavailable compounds[10]

The mass transfer coefficient can also be formulated in terms of conceptual diffusive boundary layer thickness (δ_{DBL}) and contaminant diffusion coefficient in water and Equation [3] may be re-written:

$$F_{SPMD} = \frac{D_i}{\delta_{DBL}}(C_{PW} - C_W) \qquad [6]$$

with D_i influenced by temperature and C_{PW} is unknown. The thickness of the diffusive boundary layer (at the sediment and SPMD surfaces) is unlikely to have been affected by the capping layer.

Pore water concentrations at the surface of the sediment/cap layer prior to and post capping may be corrected to account for the differences in molecular diffusion coefficients in water under variable temperature conditions. The ratio of SPMD-measured fluxes may be expressed as:

$$\frac{F_{NC}}{F_C} = \frac{\frac{D_{NC}}{\delta_{NC}}(C_{PW,NC} - C_{W,NC})}{\frac{D_C}{\delta_C}(C_{PW,C} - C_{W,C})} \qquad [7]$$

where subscripts *C* and *NC* correspond to capped and non capped conditions, respectively. Assuming $C_{W,NC} \sim C_{W,C} \sim 0$ and $\delta_{NC} \sim \delta_C$, Equation [7] may be simplified to:

$$\frac{F_{NC}}{F_C} = \frac{D_{NC} \times C_{PW,NC}}{D_C \times C_{PW,C}} \qquad [8]$$

The ratio of molecular diffusion coefficients in water is directly related to the ratio of temperature (K) and viscosity of water (Pa s). For temperatures of 10 and 20 °C (283.15 and 293.15 K), the viscosity of water can be estimated to be 1.308E-3 and 1.003E-3 Pa s, respectively. This results in a D_{NC}/D_C ratio value of approximately 0.74. The effect of capping, corrected for possible differences in PAH

---

[10] L Thibodeaux & D Mackay (July-Aug 2007 issue) The importance of chemical mass-transport coefficients in environmental and geochemical models. SETAC Globe pp 29-31

diffusion coefficients in water at different temperature, may be observed on the diagram below. A factor of 1.2 to >7 in decrease in calculated pore water concentration is observed for PAH with log $K_{OW} < 6$ following cap with sand or olivine. No significant decreases in pore water concentration for a few larger PAHs are observed.

While values for diffusivities are assumed to be based on molecular diffusion only, one must bear in mind that the presence of ragworm in the sediment and the increase in ragworm activity over time, in combination with increase in temperature over time, is likely to play a significant role in these fluxes. While this is not accounted for in the present modelling, the effect of an increase in temperature on ragworm activity and resulting diffusive fluxes of contaminants is difficult to model.

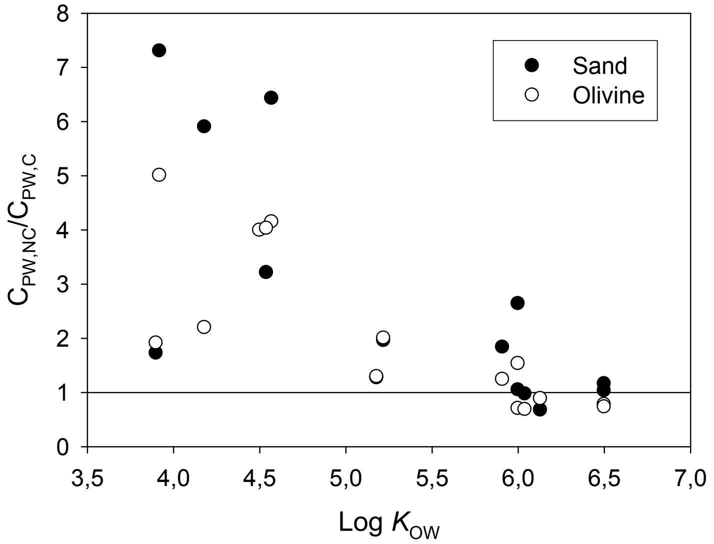


Figure 7. Ratio of calculated PAH concentrations in pore water prior to and post capping corrected for differences in molecular diffusion coefficients in water

3.1.5 Conclusions related to PAH/TBT fluxes

The following conclusions can be made related to PAH flux, pre- versus post-capping with relatively thin (several cm-thick) layers of olivine or sand:

- The placement of relatively thin capping layers of either fine-grained olivine or coarser-grained sand above contaminated sediments resulted in a decrease in sediment-water flux values for many PAHs (25-75 %), particularly those with log K_{OW} values of < 6. This was further confirmed by correcting fluxes for differences in contaminant diffusivities at different temperatures.

- No clear differences in the decrease in PAH fluxes following capping with olivine or sand can be observed

- Bioturbation by the ragworm, *Nereis virens* is likely to have significantly influenced overall fluxes of PAHs to SPMDs under both pre- and post-capping conditions. Increases in pore water advection for example, or transport of contaminated sediment particles through capping layers may have contributed to the observed fluxes. Despite this, fluxes appear generally low compared with other studies involving sediments with similar levels of contamination and investigating diffusional transport processes only.

- The increase in temperature and possible greater ragworm activity at higher temperature may contribute significantly to fluxes out of the sediment (experimental artefacts as we have not been able to run the experiment with temperature control). As well as weakening the integrity of the cap, ragworm movement was seen to bring contaminated sediments to the surface of the cap. The higher temperature during measurements following capping may also affect contaminant sorption and rates of desorption from contaminated sediments as well as promote biodegradation[11,12] of low molecular weight PAHs

- Since a reduction in flux of many PAH compounds was observed following capping with a relatively thin layer of material, the use of a relatively thicker capping layer when bioturbators are present is likely to improve the efficiency of capping with these materials.

- While capping did not appear to directly reduce sediment-water fluxes of tin species (DBT/TBT), lower fluxes from olivine capped sediments than sand capped sediment could be observed. These differences were close to being significant for TBT.

3.2 Effect of capping on fluxes of hexachlorobenzene, octachlorostyrene and polychlorinated biphenyls

Using a different sediment (from Gunnekleiv fjord), a similar experimental procedure, as described above, was conducted to evaluate pre- and post-cap, sediment-water fluxes of hexachlorobenzene (HCB), octachlorostyrene (OCS) and polychlorinated biphenyls (PCBs). The Gunnelkleiv fjord sediment is heavily contaminated with these constituents, including the PCB congener CB209. As shown by the contaminant masses accumulated in SPMDs during flux measurements, pentachlorobenzene (QCB) is also present in the sediment at a concentration sufficiently high to observe a significant flux out of the sediment.

3.2.1 Contaminant fluxes following capping with a relatively thin layer of olivine or sand

Results from the first (pre-capping) series of SPMD exposures are summarised below in Tables 8 and 9. Table 8 presents masses of HCB, OCS, PCBs and QCB accumulated in SPMDs over time (35 days) while Table 9 presents corresponding calculated sediment-water flux values. In general, SPMD masses and corresponding fluxes for these particular contaminants
As shown by the masses accumulated in SPMDs during flux measurements, pentachlorobenzene is also present in the sediment at a concentration sufficiently high to observe a significant diffusive flux out of the sediment. Masses accumulated and resulting fluxes presented in the tables below are of a similar order of magnitude as those masses and fluxes observed for the large molecular-weight PAHs in the other sediment.

As shown in Table 8, standard deviations (% RSD values) related to mass accumulation in SPMDs appear variable, but remain in a very acceptable range of 8-61 %. As shown in Table 9, calculated sediment-water fluxes of many PCBs remain below respective LOD values. HCB and QCB concentrations in sediment are in the range 6-20 mg kg^{-1} dry weight.

---

[11] BP Hedlund, AD Geiselbrecht, TJ Bair, & JT Staley (1999) Polycyclic aromatic hydrocarbon degradation by a new marine Bacterium, Neptunomonas naphthovorans gen. nov., sp. nov. Applied and Environmental Microbiology. Vol. 65 (1) pp. 251-259

[12] WK Chung and GM King (2001) Isolation, Characterization, and Polyaromatic Hydrocarbon Degradation Potential of Aerobic Bacteria from Marine Macrofaunal Burrow Sediments and Description of *Lutibacterium anuloederans* gen. nov., sp. nov., and *Cycloclasticus spirillensus* sp. nov. Applied and Environmental Microbiology. Vol. 67 (12) pp. 5585-5592

Table 8. Masses of PCBs, HCB, OCS and QCB accumulated in SPMDs exposed in Boxes 8, 9, 11 and 12 for 35 days prior to capping.

Analyte ID	Mass accumulated in SPMDs (ng) Mean[a]	Standard Deviation[a]	% RSD
CB28	<1		
CB52	<1		
CB101	<1		
CB118	<1		
CB105	<1		
CB153	1,50	0,91	61
CB138	<1		
CB156	<1		
CB180	<1		
CB209	5,23	2,63	50
Pentachlorobenzene (QCB)	5,03	0,74	15
HCB	5,35	0,45	8
OCS	6,78	2,29	34

[a]n=4

Table 9. Calculated sediment-water fluxes of PCBs, HCB, OCS and QCB (pg m^{-2} d^{-1}) measured with SPMD prior to capping.

Analyte ID	Sediment-water flux (pg m^{-2} day^{-1}) Mean[a]	Standard Deviation[a]	% RSD
CB28	<114		
CB52	<114		
CB101	<114		
CB118	<114		
CB105	<114		
CB153	171	104	61
CB138	<114		
CB156	<114		
CB180	<114		
CB209	597	301	50
Pentachlorobenzene (QCB)	574	84	15
HCB	611	52	9
OCS	774	262	34

[a]n=4

Results from the second (post-capping) series of SPMD exposures are summarised below in Tables 10 to 12.

Post-capping SPMD exposures resulted in the detection of CB52 and CB101, however values are generally close to respective LOD values (Table 10), and also close to analyte concentrations detected in the first series of pre-capping measurements. Standard deviations for triplicate measurements of post-capping fluxes are in an adequate range.

Calculated flux values following capping with either olivine or sand are generally similar to those values calculated prior to capping.

Nevertheless, for most contaminants, clear – and, in some cases, significant - differences were observed as a function of cap material type. In all cases, sediment-water fluxes for olivine-capped sediments were lower than fluxes for sand-capped sediments. At a 95 % confidence level (student's t-test), this difference was significant for CB101, CB209 and HCB (Table 12). Relative differences in contaminant fluxes between olivine- versus sand-capped sediment range from - 27.5 to - 82.5 %.

Table 10. Masses of PCBs, HCB, OCS and QCB accumulated in SPMDs exposed for 35 days in boxes following capping with olivine or sand.

Analyte ID	Mass accumulated in SPMDs (ng)					
	Sand Mean[a]	Standard Deviation[a]	% RSD	Olivine Mean[a]	Standard Deviation[a]	% RSD
CB28	<1			<1		
CB52	1.53	0.12	8	1.20	0.28	23
CB101	1.47	0.06	4	1.15	0.07	6
CB118	<1			<1		
CB105	<1			<1		
CB153	1.37	0.38	-	<1		
CB138	<1			<1		
CB156	<1			<1		
CB180	<1			<1		
CB209	5.60	1.10	20	3.07	0.4	13
Pentachlorobenzene (QCB)	8.10	1.90	23	6.00	0.70	12
HCB	10.70	1.47	14	6.87	0.81	12
OCS	7.37	1.65	4.5	4.50	0.89	20

[a]n=4

Table 11. Calculated sediment-water fluxes of PCBs, HCB, OCS and QCB (pg m^{-2} d^{-1}) measured with SPMD following capping with olivine or sand.

Analyte ID	Sediment-water flux (pg m^{-2} day^{-1})			
	Sand Mean[a]	Standard Deviation[a]	Olivine Mean[a]	Standard Deviation[a]
CB28	<114		<114	
CB52	175	13	137	32
CB101	168	6,6	131	8,1
CB118	<114		<114	
CB105	<114		<114	
CB153	156	43	<114	
CB138	<114		<114	
CB156	<114		<114	
CB180	<114		<114	
CB209	640	126	351	46
Pentachlorobenzene (QCB)	926	217	686	80
HCB	1223	168	785	93
OCS	842	189	514	102

[a]n=3

Table 12. Differences and significance of contaminant fluxes observed following capping with olivine or sand.

Analyte ID	$\Delta(F_{OLIVINE}\text{-}F_{SAND})$ (%)	Significance [P value]
CB28		
CB52	-27,8	N [0,148]
CB101	-27,5	Y [0,011]
CB118		
CB105		
CB153		
CB138		
CB156		
CB180		
CB209	-82,6	Y [0,020]
Pentachlorobenzene (QCB)	-35,0	N [0,15]
HCB	-55,8	Y [0,017]
OCS	-63,7	N [0,057]

3.2.2 Conclusions related to HCB, OCS, PCB and QCB fluxes

The following conclusions relating to effect of capping with a relatively thin layer of olivine or sand on fluxes of HCB, OCS, PCBs and QCB out of contaminated sediments are:

- Pre- and post capping contaminant fluxes out of the sediment are generally similar irrespective of the capping material. A cap thickness such as that tested in the present experiment does not appear to reduce fluxes of these contaminants to the overlying water

- Nevertheless, contaminant fluxes from olivine-capped sediment are consistently lower than those measured in sand-capped sediment, with statistically significant differences observed for PCB congeners CB101 and CB209, and for HCB. Although not statistically significant, a difference in fluxes post capping may be observed for PCB congener CB153

- Lower fluxes of these organic contaminants through thin layers of fine-grained olivine may be the result, at least in part, to a presumed higher sorption capacity of fine-grained olivine for these hydrophobic contaminants (Table 1), when compared to that sorption capacity of natural sand

- Similarly to previous results observed for PAHs, it is likely that an increase in temperatures during the post-capping time period influenced (perhaps increased) total contaminant fluxes observed. Such potential flux increases could have been due to: increased ragworm activity; increased molecular diffusion (as a result of increased contaminant desorption and partitioning to pore-water phases); or both factors. The relative influence of these temperature-related factors as a function of cap type is unknown.

3.3 Measurement of Hg depth-concentration profiles in contaminated sediment following capping

3.3.1 Initial and post-capping Hg depth-concentration profiles

Core collection, incremental slicing and chemical analysis for total and dissolved (pore-water) mercury content was undertaken to establish depth-concentration profiles following application (4 weeks) of relatively thin layers of olivine or sand. One core (5-6 cm diameter) was collected from each box. Incremental slicing was undertaken with a 3 mm resolution for the top 5 cm of the core (thus encompassing the cap/sediment interface), then with a 1 cm resolution to the bottom of the core (15 cm; however analysis was only conducted for slices to a depth of 10 cm).

To provide adequate sample quantities for processing and analysis, depth-discrete slices from cores collected from replicate boxes capped with olivine or sand were physically pooled to provide a single, depth-discrete sample for each cap type. While it was difficult to undertake this work under oxygen-free conditions, the centrifuge was used on-site and sediment core slice samples were centrifuge shortly after sectioning to minimise possible changes in Hg speciation.
Analysis of sediment samples for the determination of total Hg concentrations was conducted in triplicate, per depth interval. Owing to smaller pore-water sample sizes, single analyses of total Hg concentrations in pore water were undertaken. To collect pore-water samples, centrifugation was undertaken for most samples, except for a few sand-cap samples, for which filtration (0.45 µm) was more suitable than centrifugation.

Table 13. Total and dissolved (pore-water) Hg concentration (ng g^{-1} dry weight and ng L^{-1}, respectively) depth profiles in sand-capped sediments.

Depth (mm)	Total Hg concentration in sediment (ng g^{-1} dw)			Total dissolved Hg concentration in sediment pore water (ng L^{-1})
	Mean	SD	% RSD	
0-3	220	64	*29*	134
3-6	123	16	*13*	179
6-9	121	62	*51*	112
9-12	275	91	*33*	261
12-15	1297	136	*10*	383
15-18[b]	6447	575	*9*	945
18-21[b]	9840	975	*10*	318
21-24	12000	755	*6*	606
24-27	10833	306	*3*	750
27-30	12200	624	*5*	587
30-33	11800	721	*6*	539
33-36	12153	2679	*22*	864
36-39	10850	1639	*15*	378
40-45	13367	643	*5*	398
45-50	18800[a]	1670	*9*	676
50-60	15080[a]	7779	*52*	278
60-70	19000[a]	6755	*36*	134
70-80	16400[a]	7255	*44*	179
80-90	20057[a]	16726	*83*	112
90-100	12897[a]	7666	*59*	

[a] Mean values from non-pooled samples from the three different cores showing the relative differences between Hg concentrations in the 3 boxes; [b] Cap material-contaminated sediment transition zone

Total Hg concentrations with depth clearly show a decrease towards the surface, across the sediment/cap interface (see Tables 13 and 14). The transition between the sand/olivine-cap materials and underlying contaminated sediment, as visually identified, was also confirmed by the clear increase in total Hg concentration with increased depth observed 15-21 and 9-15 mm below the cap surface (see Table 13) for sand and olivine capped sediments, respectively. Depth-discrete total Hg concentrations appear relatively variable (as illustrated by SD values), which demonstrates the inherent difficulty in achieving adequate homogeneity for sediments containing contaminants displaying very strong partitioning to sediment particles. This challenge becomes more apparent for measurements of total dissolved Hg in pore waters. Concentrations, however, are significantly lower for the cap layer. The recovered thickness of the olivine capping layers appears somewhat lower than recovered thicknesses of the sand capping layers. It may be that the method for olivine cap placement resulted in a wider mixed cap/sediment layer.

Concentrations in the sand cap appear 1-2 orders of magnitude lower than for the underlying contaminated sediment. Total Hg concentration in the cap is in the range 220-1297 ng g^{-1} while it reaches a maximum of > 20,000 ng g^{-1} deeper in the sediment. Pore water concentrations of Hg also tend to be lower in the sand cap (112-383 ng L^{-1}) than in the sediment below (112-945 ng L^{-1}). However, concentrations generally appear quite variable and differences, although apparent, are not very pronounced.

Total concentrations in the olivine cap material were in the range 96-577 ng g^{-1} while these values increased to a maximum of 5640 ng g^{-1} deeper in the contaminated sediment. Pore water concentrations are in a similar range to those obtained with the sand cap (62-260 ng L^{-1}), however pore water concentrations in deeper contaminated sediment appear to reflect the lower contamination of the sediment. The top layer of the cap for both sand and olivine present higher concentrations. These are likely to be the result of contaminated material brought to the surface by ragworm bioturbation and movement in and out of the sediment. Profiles were measured a few weeks following cap application and a significant level of bioturbation and reworking of the sediment and cap had obviously occurred. Mixing of sediment and cap most likely occurred through the burrowing activity of *Nereis virens* and ragworm hole filling with the very fine olivine particle. It is possible that overall lower sediment concentrations are observed as a result of mixing of burrow filling olivine material. This would be consistent with the slightly lower recovered thickness of the olivine cap.

Table 14. Total and dissolved (pore-water) Hg concentration (ng g^{-1} dry weight and ng L^{-1}, respectively) depth profiles in olivine-capped sediments.

Depth (mm)	Total Hg concentration in sediment (ng g^{-1} dw)			Total dissolved Hg concentration in sediment pore water (ng L^{-1})
	Mean	SD	% RSD	
0-3	315	15	*5*	142
3-6	96	5	*5*	62
6-9[b]	99	6	*6*	113
9-12[b]	577	104	*18*	260
12-15[b]	1033	40	*4*	217
15-18	1777	61	*3*	188
18-21	4633	605	*13*	297
21-24	4620	130	*3*	296
24-27	4530	128	*3*	570
27-30	2357	45	*2*	878
30-33	5640	53	*1*	467
33-36	3740[a]	2241	*60*	388
36-46	2287[a]	1934	*85*	220
46-56	2457[a]	1749	*71*	413
56-66	4527[a]	4359	*96*	171
66-76	3255[a]	1846	*57*	250
76-86	4620[a]	2560	*55*	142

[a] Mean values from non-pooled samples from the three different cores showing the relative differences between Hg concentrations in the 3 boxes; [b] Cap material-contaminated sediment transition zone.

While analysis with the Lumex atomic absorption spectrophotometer does not allow us to distinguish various Hg species (i.e. inorganic Hg, methyl mercury, etc.), clear differences in peak shape may reflect differences in Hg speciation in the sediment and pore water samples (See Figure 10). Despite the qualitative nature of the information, peak shapes in most cases here were clearly different for samples from the cap material compared with those from further below the cap. This could be the result of different Hg species migrating through the cap, and/or the presence of differing redox or oxic/anoxic conditions in and below the cap that affect Hg speciation.

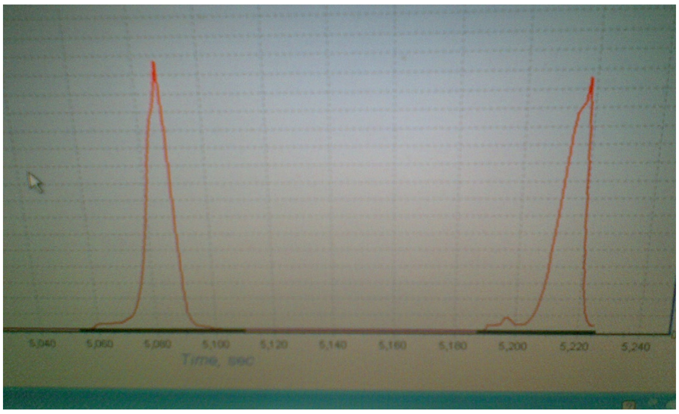


Figure 8. Two dissimilar Hg peaks on the Lumex analyser.

3.3.2 Subsequent and post-capping Hg depth-concentration profiles (3 months later)

Post-capping, Hg depth-concentration profiles were measured in a total of two of the boxes (one olivine and one sand) to determine total Hg as well as dissolved (pore-water) Hg concentrations three months after initial, post-capping Hg testing (Section 3.4.1)

Since only one core per box was collected during this phase of the work, thicker depth-discrete slices of material were needed in order to obtain sufficient amounts of pore water for Hg analysis. Slicing was undertaken with a 5 mm resolution along both the olivine- and sand-cap cores. Only the top (55 mm-thick) sections were analysed, rather than the entire recovered core lengths (approx. 15 cm).

Table 15. Total and dissolved (pore-water) Hg concentration (ng g^{-1} dry weight and ng L^{-1}, respectively) depth profiles 3 months after olivine or sand capping.

Depth (mm)	Total Hg concentration in sediment (ng g^{-1} dw)		Total dissolved Hg concentration in sediment pore water (ng L^{-1})
	Mean	SD	
Sand			
0-5	572	110	410
5-10	521	67	98
10-15[a]	1475	332	320
15-20[a]	4250	141	410
20-25	6545	49	850
25-35	10120	255	1180
35-45	10900	0	830
45-55	15150	636	640
Olivine			
0-5	595	30	35
5-10	510	13	131
10-15[a]	1255	49	122
15-20[a]	1715	64	94
20-25	3135	21	370
25-35	6520	410	260
35-45	6100	240	745
45-55	7165	474	220

[a] Cap-sediment intrface

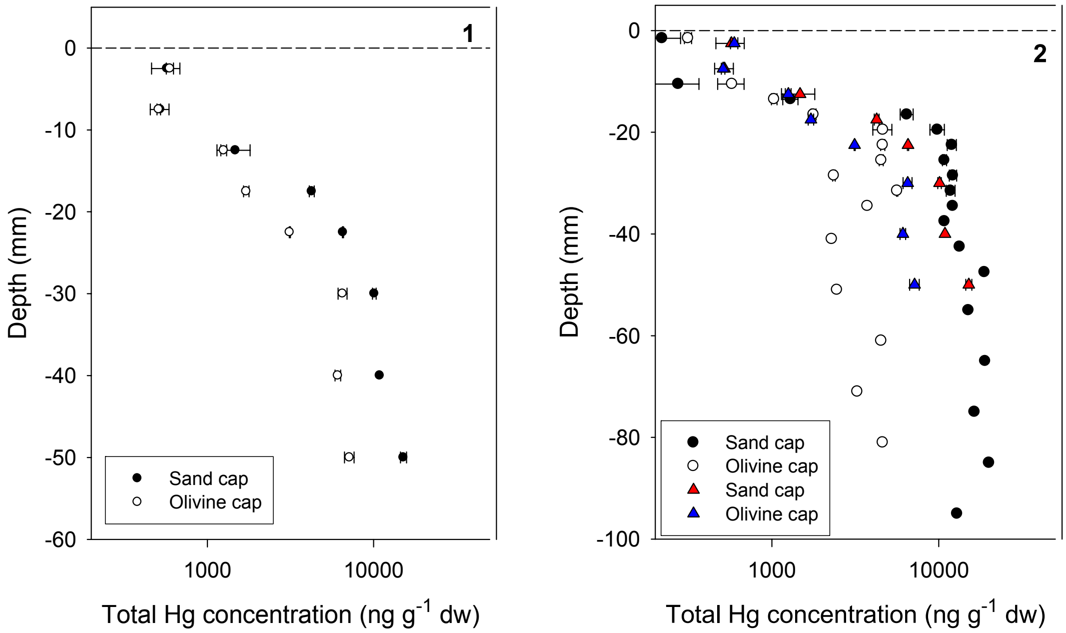


Figure 9. Depth profiles of total Hg concentration. Initial profiles (1, black and white) and subsequent profiles (2, colour code) are shown. The dashed line represents the cap-water interface

As shown in Figure 9, total Hg concentrations in both capped-sediment systems at three months were generally higher than those measured 1 month after cap placement. With high sediment-water distribution coefficients generally observed for Hg, it is unlikely that such an increase in concentration over such a short period of time is only the result of diffusion in pore water. Other processes, including bioturbation-related mixing of contaminated sediments with clean cap material as a result of ragworm activity, are likely to be much more significant.

Since data related to both total Hg concentrations and dissolved Hg concentrations in pore water are available for each section/ depth interval, it is possible to derive a rough estimate of *in situ* distribution coefficients (K_d values)[13] for Hg in depth-discrete portions of the sediment and in the cap material:

$$K_d = \frac{C_S}{C_{PW}} \qquad [9]$$

Depth profiles of estimated sediment- or cap-pore water distribution coefficients (log K_d values) developed using initial and three-month data sets are presented in Figure 12. Initially after capping, estimated log K_d values for the contaminated sediment vary between values of 4.0 and 4.5, whereas lower log K_d values, in the range of <3 to 4, were observed for both cap materials. Higher log K_d values may typically be expected for more organic-rich material such as the sediment used in this study (TOC values on the order of several percent).

Three months after capping, estimated log Kd values for capping materials are closer to those values estimated for the contaminated sediment (which remained similar to initial values).

---

[13] http://www.epa.gov/radiation/docs/kdreport/vol1/402-r-99-004a_ch3.pdf

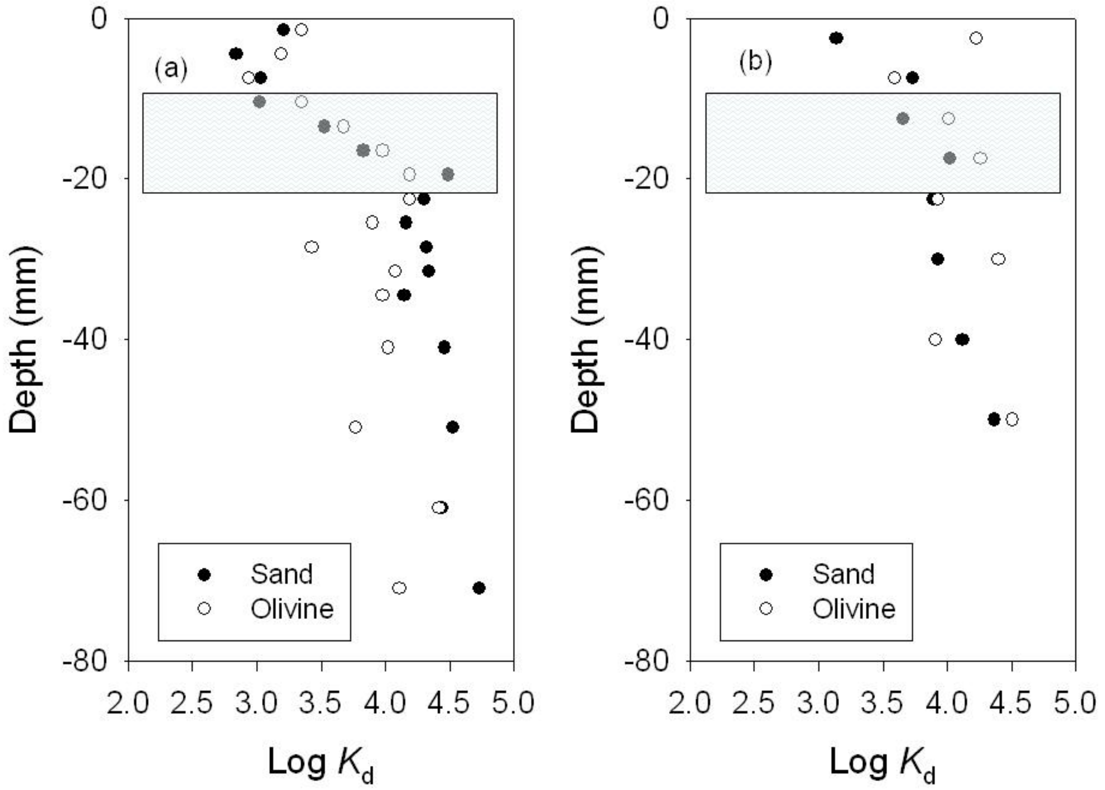


Figure 10. Depth profiles of sediment- and cap-water distribution coefficients for Hg 1 (a) and 3 (b) months following placement of relatively thin layers of olivine or sand. Shaded areas represent the cap-sediment interface

Mean values of distribution coefficients for the sediment, olivine and sand were calculated for both series of measurements. Mean values for the sediment were in the range 3.98 to 4.34 while mean values for sand and olivine increased slightly from 3.13 and 3.21 to 3.51 to 3.94, respectively. Although not significant, slightly higher K_d values were observed for the olivine material. These log K_d values are in agreement with operationally defined K_d values found in the literature under estuarine conditions or for wetlands for example[14,15].

Table 16. Mean log K_d values determined for Hg in sediment sand and olivine

Mean log K_d	**1 month**			**3 months**		
	Sediment	**Sand**	**Olivine**	**Sediment**	**Sand**	**Olivine**
	4.34 ± 0.24[a]	**3.13 ± 0.26**	**3.21 ± 0.19**	**4.07 ± 0.19**	**3.51 ± 0.32**	**3.94 ± 0.33**
	3.98 ± 0.26			**4.20 ± 0.27**		

[a] 2 values are for olivine and sand capped sediments

---

[14] KA Merritt & A Amirbahman (2007) Mercury mobilization in estuarine sediment porewaters: A diffusive gel time-series study. *Environmental Science & Technology.* Vol. 41 (3) pp. 717-722

[15] http://www.epa.gov/radiation/docs/kdreport/vol1/402-r-99-004a_ch3.pdf

3.3.3 Conclusions related to Hg testing results

The following conclusions can be made regarding the measurement (1 and 3 months following capping, respectively) of total and dissolved Hg concentration-depth profiles following sediment capping with a relatively thin (1-2 cm as shown by Hg profiles) layer of sand or olivine:

- The placement of a thin layer of both capping materials could be clearly observed both through visual inspection and measurement of depth-concentration profiles for both total Hg sediment concentrations and total dissolved Hg concentrations in extracted pore water.

- Initially measured Hg concentrations in pore waters of both capping materials were generally lower than those observed in pore waters of the underlying contaminated.

- One month after capping, relatively high pore water concentrations of Hg were observed in pore waters of both cap types (though concentrations in caps were still lower than within respective underlying sediments). Although reasonably variable, pore-water Hg concentrations appeared slightly lower in the olivine cap than in the sand cap. Differences in Hg concentrations in underlying sediments as well as different material sorption capacities towards Hg (fine-grained olivine presumed to possess a higher sorption capacity than coarser-grained sand) may be responsible for this.

- Three months after capping, higher Hg concentrations (total and dissolved?) were observed in both cap types. Molecular diffusion of Hg resulting in such an increase in concentrations in caps over such a short period of time is improbable. Instead, more likely explanations for such increases include: (1) bioturbation-related mixing of cap and contaminated sediment material as a result of ragworm activity; and (2) consolidation-induced advection of Hg-contaminated pore waters up into capping layers. In view of the substantial ragworm activity observed within both cap types, together with the likelihood that the vertical extent of pore-water advection would probably be different for the different cap types, bioturbation-induced transport processes likely had the largest effect on the Hg depth trends observed.

- Estimates of in-situ solid-water Hg distribution coefficients (log K_d values) measured in both caps appeared lower than those measured in deeper layers of the relatively organic-enriched sediment. Although not significant, slightly higher log *K*d values were observed for layers of the fine-grained olivine cap compared with than for the coarser-grained sand. While this may imply a slightly more sorptive olivine towards Hg compared with sand, other factors may have contributed to these differences. Considering the approach used here to derive these in situ Kd values, solid-water distribution coefficients in cap layers may be influenced by (i) the intrinsic capacity of the capping materials to bind various species of Hg (ii) non-equilibrium conditions, (iii) mixing of cap material and underlying contaminated sediment particles or (iv) depth or time-dependent changes and variability in Hg speciation, including transformation to less strongly sorbing methyl mercury.

3.4 Changes at the sediment-water interface with time

A relatively thin layer (1-2 cm thick) of capping material was placed in all boxes (see Figure 4). The finer particles sizes allowed the olivine move along and fill ragworm burrows as shown by the holes that emerged at the surface of the olivine cap as early as 48 hrs after cap placement.

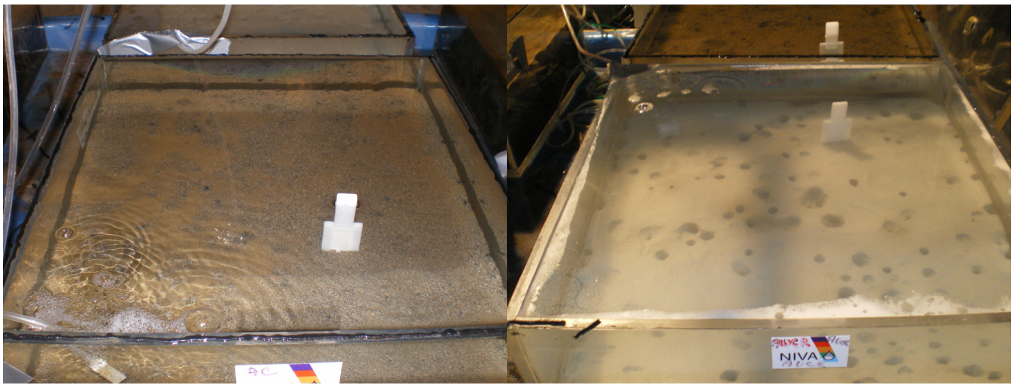


Figure 11. Sand (left) and olivine (right) caps 3 months after cap placement. Note: DGT probe measurement in progress.

Within a few months following cap placement, the surfaces of both cap types appeared to differ significantly from respective visual states observed following cap application. The effects of bioturbation by ragworms was clearly visible with the development over time of a thin and darker layer composed of detritus and contaminated sediments brought to the surface by worm movement through bioturbation. This may have further implications in the efficiency of a given capping layer. The numerous holes through the cap due to ragworm activity are also likely to affect contaminant fluxes.

Figure 12. Sand (left) and olivine (right) caps 3 months after cap placement. Note: sediment layer integrity is preserved with the use of a tube placed following coring (right)

4. Summary and conclusions

4.1 Assumptions

Mesocosm experiments were undertaken to assess and compare the capacity of a relatively thin layer (1-2 cms) of fine-grained olivine and coarser sand placed above contaminated marine sediments to reduce sediment-water fluxes of a range of hydrophobic organic contaminants, tributyltin and mercury.

The two distinct sediments used for this study were contaminated with polycyclic aromatic hydrocarbons (PAHs), tin species (TBT and TPhT), hexachlorobenzene (HCB), octachlorostyrene (OCS), polychlorinated biphenyls (PCBs) and mercury (Hg).

Semipermeable membrane devices (SPMDs) were used in these mesocosms as infinite sink device in order to accumulate contaminants (hydrophobic organics and organotins) released by the sediment into the water column. This provided a mean to quantify the release and resulting fluxes of these contaminants out of non-capped and olivine or sand-capped sediments. For Hg, the efficiency of both capping layers were assessed by measuring depth profiles of total and pore water Hg concentrations after two intervals following capping. A relatively natural density of benthic bioturbating organisms was added to the sediment as a mean to improve the representativeness of these mesocosm experiments and the habitat compatibility of both capping material on *Nereis virens*. Organisms were introduced into the mesocosms at the start of the experiment and prior to applying caps to the boxes.

4.2 Conclusions

To conclude:

- This work demonstrates some differences between contaminant fluxes observed following capping of contaminated sediments with finer-grained olivine versus capping with relatively coarser sand. However, in many cases, these differences are limited.
- Based on these results and for these particular experimental conditions, olivine’s efficiency appears similar to that of sand, material commonly used for isolation or thin layer capping purposes (where for example, decreases in pore water concentrations may be expected in surficial sediment layers). Alternative experimental designs may be implemented in order to corroborate these finding.
- It is likely that increasing the thickness of the cap will result in an increase in the efficiency of olivine to reduce sediment-water contaminant fluxes when it is used for isolation capping purposes.
- Based on these result limited efficiency of passive thin layer capping with olivine may be expected, however the combination of olivine with other types of materials such as activated carbon may improve remediation efficiency of both thin-layer and isolation capping.

4.3 Summary of conclusions related to specific contaminants

4.3.1 Fluxes of PAHs and TBT

- The placement of relatively thin capping layers of either fine-grained olivine or coarser-grained sand resulted in a decrease (25-75 %) in sediment-water flux values for PAHs with log K_{OW} values of < 6. For larger molecular weight PAHs, no obvious effects were observed and this may be the result of ragworm bioturbation and transport of contaminated sediments to the surface of the cap. It may be that factors (temperature) and processes controlling the release and movement of PAHs out of this contaminated sediment and into the SPMD devices differ as a function of the hydrophobicity, partitioning and availability of these compounds in the sediment.

- No clear differences in pre- versus post-capping flux decreases were observed as a function of capping material type. This, despite a presumed higher sorption capacity of fine-grained olivine for hydrophobic contaminants PAHs (Table 1), when compared to that sorption capacity of natural sand. Definitive sorption testing (including collection of comparative K_d data) of olivine versus sand towards PAH compounds is needed to confirm this.

- Bioturbation-related contaminant or contaminated particle transport related to obvious ragworm activity in both olivine- and sand-capped sediments likely increased total PAH fluxes to SPMDs to some unknown degree, over and above fluxes expected through molecular diffusion processes alone, though these fluxes remain significantly lower than those observed by other researcher using a similar sediment (with generally similar contaminant concentrations) and investigating molecular diffusion only.

- It is likely that an increase in system temperatures during the latter phase of the experiment influenced (perhaps increased) the total PAH fluxes observed. Such potential flux increases could have been due to: increased ragworm activity; increased molecular diffusion (as a result of increased contaminant desorption and partitioning to pore-water phases) or both factors. The relative influence of these temperature-related factors as a function of cap type is unknown.

- Slightly lower fluxes of TBT could be observed when capping with olivine compared with sand. However these measurement of TBT fluxes show high variability and differences were not significant.

- Observed flux results may have also been affected by the occurrence some unknown degree of biodegradation of some PAH compounds, particularly lower-ring PAHs.

4.3.2 Fluxes of HCB, OCS, PCBs and QCB

- Sediment-water contaminant flux values following thin-layer capping with either olivine or sand are generally similar to measured pre-cap flux values.

- Contaminant fluxes from olivine-capped sediment are consistently lower than fluxes from sand-capped sediment, with statistically significant decreases (pre- versus post-capping) observed for PCB congeners CB101 and CB209, and for HCB.

- Lower fluxes of these organic contaminants through thin layers of fine-grained olivine are likely due, at least in part, to a presumed higher sorption capacity of fine-grained olivine for hydrophobic contaminants like PCBs (Table 1), when compared to that sorption capacity of natural sand, Definitive sorption testing (including collection of comparative K_d data) of olivine versus sand towards these specific contaminants is needed to confirm this.

- As for results of PAH flux testing, bioturbation by ragworms and the increase in temperature may have affected sediment-water fluxes for HCB, QCB, OCS and PCBs.

4.3.3 Hg testing

- The placement of thin capping layers of olivine or sand could be clearly observed, both visually and through measurement of depth-concentration profiles for both total Hg sediment concentrations and dissolved Hg concentrations in extracted pore water.

- Initially measured, total dissolved Hg concentrations in pore waters of both capping materials were generally lower than total dissolved concentrations observed in pore waters of the underlying contaminated sediment.

- One month after capping, relatively high concentrations of total dissolved Hg were observed in pore waters of both cap types (though concentrations in caps were still lower than within respective underlying sediments). Although reasonably variable, pore-water Hg concentrations appeared to be slightly lower in the olivine cap than in the sand cap. This difference could be due to initially different total Hg concentrations in underlying sediments as well as different material sorption capacities towards Hg.

- Three months after capping, higher total sediment and pore water concentrations of Hg were observed in both cap material. Molecular diffusion of Hg resulting in such an increase in Hg concentrations in caps over such a short period of time is unlikely. Instead, more likely explanations for such increases include: (1) bioturbation-related mixing of cap and contaminated sediment material as a result of ragworm activity; and (2) consolidation-related advection of Hg-contaminated pore waters up into capping layers. In view of the substantial ragworm activity observed within both cap types, together with the likelihood that the vertical extent of pore-water advection would probably be different for the different cap types (had no bioturbators been involved), bioturbation-related transport processes likely had the largest effect on the Hg depth trends observed.

- *In situ* partition coefficients could be calculated from measurements of total and pore water concentrations of Hg. As expected, estimated solid-water Hg distribution coefficients (log K_d values) for both capping material types appeared lower than log K_d values for relatively organic-enriched sediment. Nevertheless, and although not significant, slightly higher log K_d values were observed for the fine-grained olivine material than for the coarser-grained sand, implying that the olivine may be slightly more sorptive towards Hg than sand.

- Considering the approach used here to estimate *in situ* Hg-cap material distribution coefficients, a number of factors may have affected the K_d value estimates derived here. Such factors may include, but may not be limited to: (i) non-equilibrium conditions (ii) influence of pore-water advection resulting from cap loading, or (iii) variable Hg speciation with depth and over time owing to differences in factors such as pH or microbial transformation (that may lead to the production of less strongly sorbing methyl mercury).

4.4 Lessons learnt

From the start of the experiment as well as during the measurement of sediment-water fluxes of contaminants prior to capping, significant sediment reworking could be observed. Relatively thin layers (1-2 cms) of olivine and sand were added on top of the contaminated sediment beds in all mesocosm boxes using laboratory scale techniques. These techniques may differ from those used for larger-scale cap placement owing to evident differences in volumes of sediment deposited, water depth and tools used for the cap application including the ability to change the water level above the sediment bed. Techniques used for the application of both olivine and sand caps resulted in relatively little mixing of cap and sediment materials during placement of both caps, Visual inspection further confirmed relatively discrete cap/sediment interfaces. Some variability in the thickness of the caps following application could be observed. This is mainly the result of an uneven surface caused by ragworm activity and through minimising the mixing of contaminated sediment with cap material during cap. Following cap application and during the remaining phase of the experiment no significant changes in ragworm activity could be seen. From a habitat perspective, both capping materials appeared to be physically compatible with ragworm populations, as shown by the significant bioturbation and burrowing activity observed in both cap types over time. No significant differences in the activity (number of worm burrows at the surface or movement/activity during feeding) could be seen following capping with olivine or sand.

As summarised above for specific sediment contaminants, olivine material has the potential to be incorporated into different sediment capping strategies, i.e. thin-layer capping (enhanced natural recovery) as well as isolation capping. However, it must be clearly recognised that, by definition, the strategy of thin-layer sediment capping is not intended to completely isolate sediment contaminants from the overlying water column, and from bioturbating organisms. Rather, the placement of thin layers of capping material only reduces, rather than completely eliminates, contaminant fluxes and organism exposure. Relatively thin (2-4 cm thick) layers of capping material were applied in the present experiments to take into account the size of the boxes, surface of sediment, volume of water above the sediment and importantly the time-scale for conducting these experiments. The application of thin caps aimed at investigating the reduction in contaminant fluxes that could be obtained using different cap materials. It was expected that results from this smaller-scale experimental design could, in part, be applicable to more realistic conditions where thicker isolation caps are applied. However, since contaminant fluxes measured upon capping with olivine or sand are likely to be linked to contaminant pore water concentrations, lower fluxes observed for certain compounds may be linked to differences in pore water concentrations in the capping layer or the layer. These differences (and reduction) in pore water concentrations are an important component of enhanced natural recovery. The extent of contaminant flux reductions when undertaking thin layer capping can be considered more-or-less “proportional” to the thickness of material placed. Indeed, considering typical bioturbation depths of marine benthic organisms of up to 10 cm or more, in combination with the target thickness of capping material placed in this study, at least some degree of bioturbation-related mixing across the cap/sediment interface, as well as flux increases associated with such biological processes, should be expected. If complete isolation of sediment contaminants is desired through capping with olivine materials, the strategy of isolation capping – rather than thin-layer capping – should be followed, where the chemical isolation layer component of the cap remains, by design, unaffected by bioturbation in overlying capping layers.

Appendix A. PAH concentrations in sediment 1

ANALYSERAPPORT Interne saksbehandlere

Utskrift: 05.05.2008

OBS!! Klagefrist 4 uker f.o.m godkjenningsdato. Prøvene kastes 30 dager etter godkjenningsdato, hvis ikke annet er avtalt.

Rekvisisjonsnr : **2008-00622** Mottatt dato : **20080408** Godkjent av : **EHA** Godkjent dato: **20080505**
Prosjektnr : **O 28150**
Kunde/Stikkord : **OLICAP**
Kontaktp./Saksbeh. : **IAL**

Analysevariabel		TTS/%	NAP-Sm	ACNLE-Sm	ACNE-Sm	FLE-Sm	DBTHI-Sm	PA-Sm	ANT-Sm	FLU-Sm
Enhet ==>		%	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.
Metode ==>	TESTNO	B 3	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3
PrNr PrDato Merking Prøvetype										
1 ! 20080403 Pr 1 sedis	2008-00622	44	410	65	30	120	110	790	360	760

Analysevariabel	PYR-Sm	BAA-Sm	BKF-Sm	BEP-Sm	BAP-Sm	PER-Sm	ICDP-Sm	DBA3A-Sm	BGHIP-Sm	Sum PAH
Enhet ==>	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.
Metode ==>	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3	H 2-3	Beregnet*
PrNr PrDato Merking Prøvetype										
1 ! 20080403 Pr 1 sedis	950	250	83	170	120	45	66	19	67	5035

Analysevariabel	Sum PAH16	Sum KPAH	Sum NPD	MBT-Sm	DBT-Sm	TBT-Sm	MPhT-Sm	DPhT-Sm	TPhT-Sm	9BBJF-Sm
Enhet ==>	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg MBT/kg	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.	µg/kg t.v.
Metode ==>	Beregnet*	Beregnet*	Beregnet*	H 14-1*	H 14-1*	H 14-1*	H 14-1*	H 14-1*	H 14-1*	H 2-3
PrNr PrDato Merking Prøvetype										
1 ! 20080403 Pr 1 sedis	4710	778	1310	8.5	40	29	<1	1.8	2.7	240

Analysevariabel	9CHR-Sm
Enhet ==>	µg/kg t.v.
Metode ==>	H 2-3
PrNr PrDato Merking Prøvetype	
1 ! 20080403 Pr 1 sedis	380

* Analysemetoden er ikke akkreditert.

PrNr 1 PAH: Et sertifisert referansemateriale ble analysert parallelt med prøven. Resultatet for dibenz(ah+ac)perylen var lavere enn nedre aksjonsgrense. SnOrg: Et sertifisert referansemateriale ble analysert parallelt med prøven. Resultatet for monobutyltinn (MBT) var lavere enn nedre aksjonsgrense.

Informasjon om analyseusikkerhet finnes på K:\Kvalitet\Godkjente_dokumenter\Akkreditering\Diversedokumenter\Y3Usikker.doc, eller kan fås ved henvendels til laboratoriet.

Appendix B. Contaminant masses accumulated in SPMDs (prior to capping)

ANALYSERAPPORT Interne saksbehandlere

Utskrift: 24.06.2008

OBS!! Klagefrist 4 uker f.o.m godkjenningsdato. Prøvene kastes 30 dager etter godkjenningsdato, hvis ikke annet er avtalt.

Rekvisisjonsnr : **2008-00929** Mottatt dato : **20080513** Godkjent av : **EHA** Godkjent dato: **20080624**
Prosjektnr : **O 28150**
Kunde/Stikkord : **OLICAP**
Kontaktp./Saksbeh. : **IAL**

Analysevariabel					CB28-SPMD	CB52-SPMD	CB101-SPMD	CB118-SPMD	CB105-SPMD	CB153-SPMD	CB138-SPMD	CB156-SPMD	CB180-SPMD
Enhet ==>					ng/SPMD	ng/SPMB	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				TESTNO	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*
PrNr	PrDato	Merking	Prøvetype										
1	20080513	Box 8	SPMD	2008-00929	<1	1.4	1.7	<1	<1	2.7	2.0	<1	1.1
2	20080513	Box 9	SPMD	2008-00929	<1	<1	<1	<1	<1	1.3	<1	<1	<1
3	20080513	Box 11	SPMD	2008-00929	<1	<1	1.1	<1	<1	<1	<1	<1	<1
4	20080513	Box 12	SPMD	2008-00929	<1	<1	<1	<1	<1	1.5	<1	<1	<1
5	20080513	Blank 2	SPMD	2008-00929	<1	<1	<1	<1	<1	<1	<1	<1	<1

Analysevariabel				CB209-SPMD	QCB-SPMD	HCHA-SPMD	HCB-SPMD	HCHG-SPMD	OCS-SPMD	DDEPP-SPMD	TDEPP-SPMD
Enhet ==>				ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*
PrNr	PrDato	Merking	Prøvetype								
1	20080513	Box 8	SPMD	8.7	5.9	<1	5.7	1.3	9.7	<1	<2
2	20080513	Box 9	SPMD	2.9	5.0	<1	5.4	1.4	5.1	<1	<2
3	20080513	Box 11	SPMD	3.5	5.1	<1	5.6	1.5	4.8	<1	15
4	20080513	Box 12	SPMD	5.8	4.1	<1	4.7	1.5	7.5	<1	10
5	20080513	Blank 2	SPMD	<1	<0.5	4.6	<0.5	2.4	<1	<1	<2

* Analysemetoden er ikke akkreditert.

Informasjon om analyseusikkerhet finnes på K:\Kvalitet\Godkjente_dokumenter\Akkreditering\Diversedokumenter\Y3Usikker.doc, eller kan fås ved henvendels til laboratoriet.

Appendix C. Contaminant masses accumulated in SPMD (prior to capping)

ANALYSERAPPORT Interne saksbehandlere Utskrift: 03.09.2008

OBS!! Klagefrist 4 uker f.o.m godkjenningsdato. Prøvene kastes 30 dager etter godkjenningsdato, hvis ikke annet er avtalt.

Rekvisisjonsnr : **2008-00930** Mottatt dato : **20080513** Godkjent av : **BEL** Godkjent dato: **20080903**
Prosjektnr : **O 28150**
Kunde/Stikkord : **OLICAP**
Kontaktp./Saksbeh. : **IAL**

Analysevariabel					NAP-SPMD	ACNLE-SPMD	ACNE-SPMD	FLE-SPMD	DBTHI-SPMD	PA-SPMD	ANT-SPMD	FLU-SPMD	PYR-SPMD
Enhet ==>					ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				TESTNO	H 2-2*	H 2-2*	H 2-2*	H 2-2	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*
PrNr	PrDato	Merking	Prøvetype										
1 !	20080513	Box 2	annet	2008-00930	24	8.5	77	56	19	120	30	80	200
2	20080513	Box 3	annet	2008-00930	<9	5.2	67	55	16	140	20	94	240
3	20080513	Box 4	annet	2008-00930	9.8	8.8	56	37	20	130	38	89	220
4 !	20080513	Box 5	annet	2008-00930	m	m	m	m	m	m	m	79	180
5	20080513	Blank 1	annet	2008-00930	100	<5	<5	<5	<5	12	<5	<5	<5

Analysevariabel				BAA-SPMD	BKF-SPMD	BEP-SPMD	BAP-SPMD	PER-SPMD	ICDP-SPMD	DBA3A-SPMD	BGHIP-SPMD	Sum PAH	Sum PAH16
Enhet ==>				ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	Beregnet	Beregnet
PrNr	PrDato	Merking	Prøvetype										
1 !	20080513	Box 2	annet	22	<5	<5	18	<5	<5	<5	<5	<717.5	<688.5
2	20080513	Box 3	annet	29	<5	19	8.9	<5	<5	<5	<5	<772.1	<732.1
3	20080513	Box 4	annet	23	<5	14	6.6	<5	<5	<5	<5	<713.2	<674.2
4 !	20080513	Box 5	annet	19	28	23	<5	<5	<5	<5	6.5	m<389.5	m<361.5
5	20080513	Blank 1	annet	<5	<5	<5	<5	<5	<5	<5	<5	<198	<183

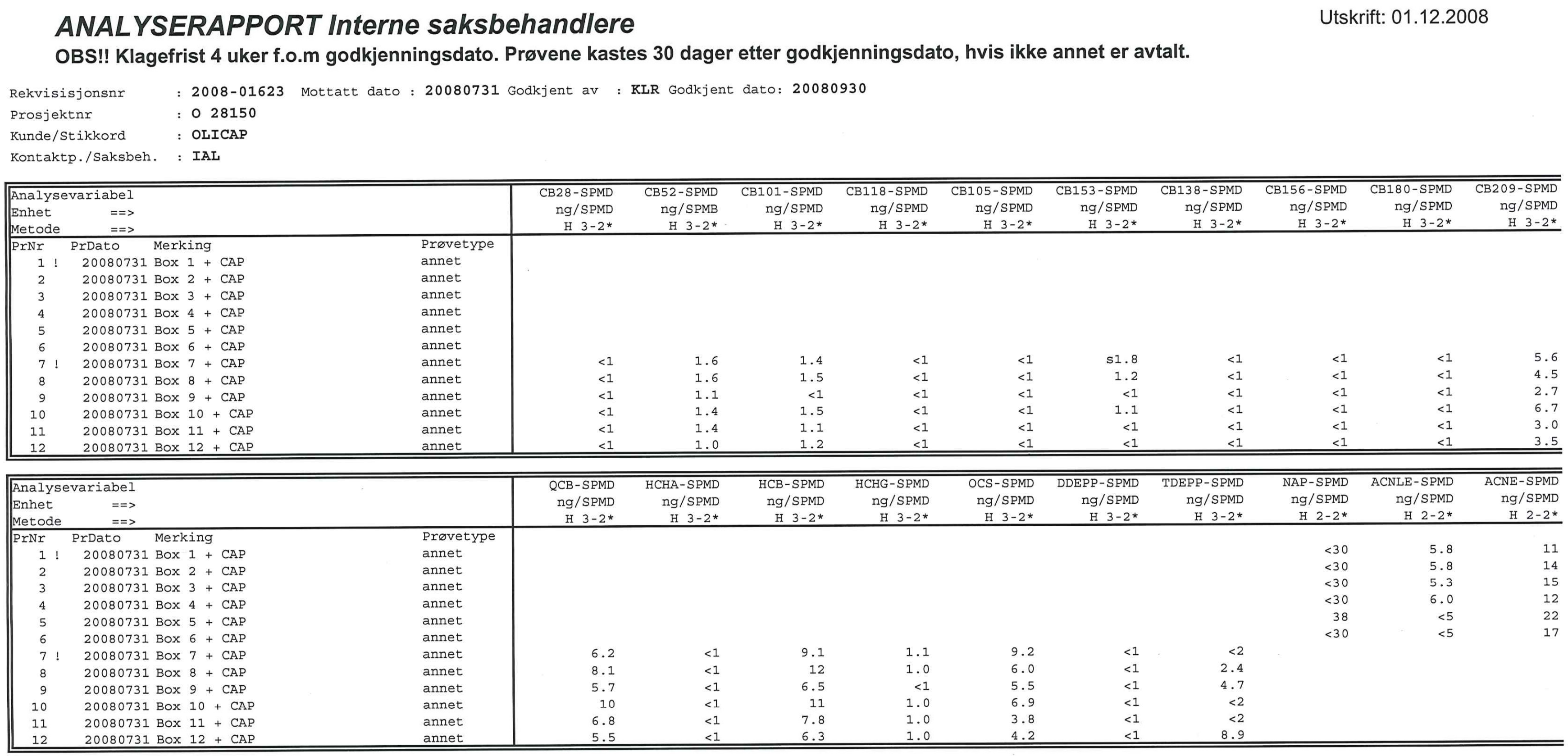
Analysevariabel				Sum KPAH	DBT-SPMD	TBT-SPMD	TPhT-SPMD	9ACNED10	9BBJF-SPMD	9CHRD12	9CHR-SPMD	9FLED10	9PAD10
Enhet ==>				ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				Beregnet	Intern*	Intern*	Intern*	H-2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*
PrNr	PrDato	Merking	Prøvetype										
1 !	20080513	Box 2	annet	<72	2.5	2.4	<1	550	17	1600	16	690	1800
2	20080513	Box 3	annet	<75.9	<2	<2	<1	280	23	1600	21	360	1100
3	20080513	Box 4	annet	<62.6	<2	2.7	<1	520	18	1600	18	680	1800
4 !	20080513	Box 5	annet	<74	<2	2.4	<1	m	12	1600	22	m	m
5	20080513	Blank 1	annet	<31	<2	<2	<1	2600	<6	1600	<5	2400	2900

* Analysemetoden er ikke akkreditert.
m Analyseresultatet mangler. Se kommentar nedenfor.

PrNr 1 PAH prøve 4 (se kommentar på prøven): Ved et uhell har prøven tørket og det ble derfor ikke mulig å kvantifisere de 10 flyktigste forbindelsene.
PrNr 4 PAH: Ved et uhell har prøven tørket og det ble derfor ikke mulig å kvantifisere de flyktigste forbindelsene. Dette gjelder ACNED10, FLED10, PAD10, NAP, ACNLE, ACNE, FLE, DBTHI, PA og ANT.

Informasjon om analyseusikkerhet finnes på K:\Kvalitet\Godkjente_dokumenter\Akkreditering\Diversedokumenter\Y3Usikker.doc, eller kan fås ved henvendels til laboratoriet.

Appendix D. Contaminant masses accumulated in SPMD (post-capping)



Utskrift: 01.12.2008

ANALYSERAPPORT Interne saksbehandlere

OBS!! Klagefrist 4 uker f.o.m godkjenningsdato. Prøvene kastes 30 dager etter godkjenningsdato, hvis ikke annet er avtalt.

Rekvisisjonsnr : **2008-01623** Mottatt dato : **20080731** Godkjent av : **KLR** Godkjent dato: **20080930**
Prosjektnr : **O 28150**
Kunde/Stikkord : **OLICAP**
Kontaktp./Saksbeh. : **IAL**

Analysevariabel				CB28-SPMD	CB52-SPMD	CB101-SPMD	CB118-SPMD	CB105-SPMD	CB153-SPMD	CB138-SPMD	CB156-SPMD	CB180-SPMD	CB209-SPMD
Enhet ==>				ng/SPMD	ng/SPMB	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*
PrNr	PrDato	Merking	Prøvetype										
1 !	20080731	Box 1 + CAP	annet										
2	20080731	Box 2 + CAP	annet										
3	20080731	Box 3 + CAP	annet										
4	20080731	Box 4 + CAP	annet										
5	20080731	Box 5 + CAP	annet										
6	20080731	Box 6 + CAP	annet										
7 !	20080731	Box 7 + CAP	annet	<1	1.6	1.4	<1	<1	s1.8	<1	<1	<1	5.6
8	20080731	Box 8 + CAP	annet	<1	1.6	1.5	<1	<1	1.2	<1	<1	<1	4.5
9	20080731	Box 9 + CAP	annet	<1	1.1	<1	<1	<1	<1	<1	<1	<1	2.7
10	20080731	Box 10 + CAP	annet	<1	1.4	1.5	<1	<1	1.1	<1	<1	<1	6.7
11	20080731	Box 11 + CAP	annet	<1	1.4	1.1	<1	<1	<1	<1	<1	<1	3.0
12	20080731	Box 12 + CAP	annet	<1	1.0	1.2	<1	<1	<1	<1	<1	<1	3.5

Analysevariabel				QCB-SPMD	HCHA-SPMD	HCB-SPMD	HCHG-SPMD	OCS-SPMD	DDEPP-SPMD	TDEPP-SPMD	NAP-SPMD	ACNLE-SPMD	ACNE-SPMD
Enhet ==>				ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 3-2*	H 2-2*	H 2-2*	H 2-2*
PrNr	PrDato	Merking	Prøvetype										
1 !	20080731	Box 1 + CAP	annet								<30	5.8	11
2	20080731	Box 2 + CAP	annet								<30	5.8	14
3	20080731	Box 3 + CAP	annet								<30	5.3	15
4	20080731	Box 4 + CAP	annet								<30	6.0	12
5	20080731	Box 5 + CAP	annet								38	<5	22
6	20080731	Box 6 + CAP	annet								<30	<5	17
7 !	20080731	Box 7 + CAP	annet	6.2	<1	9.1	1.1	9.2	<1	<2			
8	20080731	Box 8 + CAP	annet	8.1	<1	12	1.0	6.0	<1	2.4			
9	20080731	Box 9 + CAP	annet	5.7	<1	6.5	<1	5.5	<1	4.7			
10	20080731	Box 10 + CAP	annet	10	<1	11	1.0	6.9	<1	<2			
11	20080731	Box 11 + CAP	annet	6.8	<1	7.8	1.0	3.8	<1	<2			
12	20080731	Box 12 + CAP	annet	5.5	<1	6.3	1.0	4.2	<1	8.9			

ANALYSERAPPORT Interne saksbehandlere

Utskrift: 01.12.2008

OBS!! Klagefrist 4 uker f.o.m godkjenningsdato. Prøvene kastes 30 dager etter godkjenningsdato, hvis ikke annet er avtalt.

Rekvisisjonsnr : **2008-01623** Mottatt dato : **20080731** Godkjent av : **KLR** Godkjent dato: **20080930**
Prosjektnr : **O 28150**
Kunde/Stikkord : **OLICAP**
Kontaktp./Saksbeh. : **IAL**

Analysevariabel				FLE-SPMD	DBTHI-SPMD	PA-SPMD	ANT-SPMD	FLU-SPMD	PYR-SPMD	BAA-SPMD	CHRD12	CHR-SPMD	BBJF-SPMD
Enhet ==>				ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				H 2-2	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*
PrNr	PrDato	Merking	Prøvetype										
1 !	20080731	Box 1 + CAP	annet	7.9	<5	18	11	58	210	9.4	1700	31	32
2	20080731	Box 2 + CAP	annet	13	<5	29	14	60	210	21	1700	32	33
3	20080731	Box 3 + CAP	annet	22	<5	30	8.5	62	250	25	1600	50	52
4	20080731	Box 4 + CAP	annet	13	<5	35	12	59	250	21	1700	28	41
5	20080731	Box 5 + CAP	annet	43	<5	45	9.0	46	190	19	1600	41	41
6	20080731	Box 6 + CAP	annet	26	6.2	52	12	65	220	32	1600	63	54
7 !	20080731	Box 7 + CAP	annet										
8	20080731	Box 8 + CAP	annet										
9	20080731	Box 9 + CAP	annet										
10	20080731	Box 10 + CAP	annet										
11	20080731	Box 11 + CAP	annet										
12	20080731	Box 12 + CAP	annet										

Analysevariabel				BKF-SPMD	BEP-SPMD	BAP-SPMD	PER-SPMD	ICDP-SPMD	DBA3A-SPMD	BGHIP-SPMD	Sum PAH	Sum PAH16	Sum KPAH
Enhet ==>				ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	H 2-2*	Beregnet	Beregnet	Beregnet
PrNr	PrDato	Merking	Prøvetype										
1 !	20080731	Box 1 + CAP	annet	13	28	12	16	5.6	<5	8.2	<516.9	<467.9	<138
2	20080731	Box 2 + CAP	annet	15	30	14	7.5	6.8	<5	8.9	<554	<511.5	<156.8
3	20080731	Box 3 + CAP	annet	26	47	19	6.8	8.6	<5	12	<679.2	<620.4	<215.6
4	20080731	Box 4 + CAP	annet	15	31	14	6.4	5.0	<5	8.5	<596.9	<554.5	<159
5	20080731	Box 5 + CAP	annet	20	36	16	8.0	7.4	<5	11	<607.4	<558.4	<187.4
6	20080731	Box 6 + CAP	annet	28	49	22	8.0	10	<5	13	<717.2	<654	<244
7 !	20080731	Box 7 + CAP	annet										
8	20080731	Box 8 + CAP	annet										
9	20080731	Box 9 + CAP	annet										
10	20080731	Box 10 + CAP	annet										
11	20080731	Box 11 + CAP	annet										
12	20080731	Box 12 + CAP	annet										

ANALYSERAPPORT Interne saksbehandlere

Utskrift: 01.12.2008

OBS!! Klagefrist 4 uker f.o.m godkjenningsdato. Prøvene kastes 30 dager etter godkjenningsdato, hvis ikke annet er avtalt.

Rekvisisjonsnr : 2008-01623 Mottatt dato : 20080731 Godkjent av : **KLR** Godkjent dato: 20080930
Prosjektnr : O 28150
Kunde/Stikkord : **OLICAP**
Kontaktp./Saksbeh. : **IAL**

Analysevariabel				MBT-SPMD	DBT-SPMD	TBT-SPMD	MPhT-SPMD	DPhT-SPMD	TPhT-SPMD	9ACNED10	9FLED10	9PAD10
Enhet ==>				ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD	ng/SPMD
Metode ==>				Intern*	Intern*	Intern*	Intern*	Intern*	Intern*	H-2-2*	H 2-2*	H 2-2*
PrNr	PrDato	Merking	Prøvetype									
1 !	20080731	Box 1 + CAP	annet	<6	3.8	57	<1	<1	3.1	110	160	670
2	20080731	Box 2 + CAP	annet	<1	3.6	26	<1	<1	1.2	170	230	860
3	20080731	Box 3 + CAP	annet	<7	1.9	1.9	<1	<1	<1	120	150	620
4	20080731	Box 4 + CAP	annet	<7	<1	18	<1	<1	1.1	88	130	660
5	20080731	Box 5 + CAP	annet	<7	10	2.0	<1	<1	<1	110	140	540
6	20080731	Box 6 + CAP	annet	<6	22	2.1	<1	<1	<1	190	250	910
7 !	20080731	Box 7 + CAP	annet									
8	20080731	Box 8 + CAP	annet									
9	20080731	Box 9 + CAP	annet									
10	20080731	Box 10 + CAP	annet									
11	20080731	Box 11 + CAP	annet									
12	20080731	Box 12 + CAP	annet									

* Analysemetoden er ikke akkreditert.
s Det er knyttet større usikkerhet enn normalt til kvantifiseringen.

PrNr 1 SPMD= EU 150.107 E
PrNr 7 s= Forbindelsen er delvis dekket av en interferens i kromatogrammet av prøven. Det er derfor knyttet noe større usikkerhet til kvantifiseringen.

Informasjon om analyseusikkerhet finnes på K:\Kvalitet\Godkjente_dokumenter\Akkreditering\Diversedokumenter\Y3Usikker.doc, eller kan fås ved henvendels til laboratoriet.

NIVA: Norway's leading centre of competence in aquatic environments

NIVA provides government, business and the public with a basis for preferred water management through its contracted research, reports and development work. A characteristic of NIVA is its broad scope of professional disciplines and extensive contact network in Norway and abroad. Our solid professionalism, interdisciplinary working methods and holistic approach are key elements that make us an excellent advisor for government and society.

NIVA
Norwegian Institute for Water Research

Gaustadalléen 21 • NO-0349 Oslo, Norway
Telephone: +47 22 18 51 00 • Fax: 22 18 52 00
www.niva.no • post@niva.no