

Vedlegg V0.09

MILJØTILTAK VED VRAKET AV U-864

Spesifisering av metyleringsforsøk

— DNV GL AS



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Miljøtiltak ved vraket av U-864
Spesifisering av metyleringsforsøk

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DNV GL AS
Project Management & Technical
Services Program
P.O.Box 300
1322 Høvik
Norway
Tel: +47 67 57 99 00

Utført av:

Jens Laugesen (DNV GL AS)
Morten Schaanning (NIVA)
Danny Reible (Texas Tech University)

Revidert av:

Carl Erik Høy-Petersen (DNV GL AS)

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Gjengivelse av deler av dette vedleggsdokument som kan føre til mistolkning er ikke tillatt

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1 INNLEDNING

I forbindelse med utredningen av tiltak for den tyske ubåten U-864 har det også vært fokusert på om det kan skje en metylering av kvikksølvlasten ved en tildekking.

Metylering er prosessen hvor uorganisk (rent) kvikksølv omdannes til organisk kvikksølv. For at dette skal kunne skje må det blant annet finnes en karbonkilde til stede.

Det er igangsatt to tester for å vurdere metylering av kvikksølvet fra U-864.

- En test ved Norsk Institutt for Vannforskning (NIVA) med forskningsleder Morten Schaanning som ansvarlig.
- En test ved Texas Tech University med professor Danny Reible som ansvarlig.

I testene gjenskapes situasjonen og effektene knyttet til kvikksølv sedimentene ved Fedje så nøyaktig som mulig, blant annet ved å bruke sedimenter fra området, og sjøvann med karakteristikk i form av oksygeninnhold og saltinnhold som er nær den vi finner ved Fedje. Tilsvarende tester som tar hensyn til de faktiske forholdene på Fedje har ikke blitt gjennomført tidligere. Dette vil derfor gi bedre svar på effekten av å tildekke den forurensede havbunnen på Fedje.

I denne rapporten er de to testene beskrevet.

2 METYLERINGSFORSØK VED NIVA

NIVA skal gjennomføre et eksperiment for å vurdere risiko for dannelse av metylkvikksølv ved tildekking av sedimenter forurenset med metallisk kvikksølv fra U-864. Forsøket skal gjennomføres i mesokosmos-laboratoriet ved Marin Forskningsstasjon Solbergstrand og alle analyser vil bli utført på NIVAs kjemiske laboratorium i Oslo.

På grunn av gode oksygenforhold og lite tilgjengelig organisk karbon vurderes risiko knyttet til dannelse av metyl-kvikksølv (met-Hg) i sedimentene ved Fedje som liten. Likevel kan det ikke utelukkes at noe organisk karbon vil kunne fanges sammen med det forurensete sedimentet under et fremtidig tildekkingslag. I dette forsøket vil det bli simulert en slik situasjon for å teste ut i hvilken grad dannelsen av met-Hg begrenses av tilgangen på organisk karbon.

Et Hg-kontaminert sediment hentet fra Fedje vil tilsettes fire nivåer av organisk materiale i form av marine mikroalger. Dannelse av met-Hg måles deretter månedlig gjennom et halvt år ved prøvetaking av vannet over sedimentene og et begrenset antall snitt nedover i sedimentene. Vannprøvene analyseres med lavest mulige deteksjonsgrense (0,02 ng/L). Disse prøvene vil øke sjansene for å detektere aktive metyleringsprosesser i sedimentet. Målingene av met-Hg suppleres med målinger av vertikalprofiler av O₂ og H₂S ved bruk av mikroelektroder med måleintervall ≤0,25 mm. Både utlekking og profiler av O₂ og H₂S måles non-destruktivt.

Forsøket igangsettes rundt 1. mai 2014. Forsøksperioden er på 6 måneder, analyser av alle prøver og rapportering vil være ferdigstilt et år fra oppstart, dvs. 1. mai 2015.

Bakgrunn og mer detaljer av forsøksoppsettet er beskrevet i den engelske teksten under.

Background

Mercury-contaminated sediments from the site where the wrecks of the U-864 submarine are situated were collected in January this year. These sediments are known to be heavily contaminated with Hg from previous measurements. Capping the Hg-contaminated site around the U-864 wrecks with clean sediments has been proposed as a mitigation measure. The aim of this project is therefore to carry out microcosm lab experiments to study the effect of capping on mercury speciation in these Hg-contaminated sediments. There is special interest related to investigating how/if the presence of organic matter (in addition to other biogeochemical factors such as dissolved oxygen and other electron acceptors) affects Hg methylation with time. It is hypothesized that capping and the presence of organic matter in the sediments will alter the methylation-demethylation balance leading to an increase of in situ MeHg concentrations relative to uncapped controls. That is capping will encourage the activity of anaerobic bacterial populations, including sulfate reducing bacteria (and other bacteria that aid Hg methylation) at shallow depths beneath a capped Hg-contaminated sediment compared to the uncapped controls.

Microcosm experiments and location

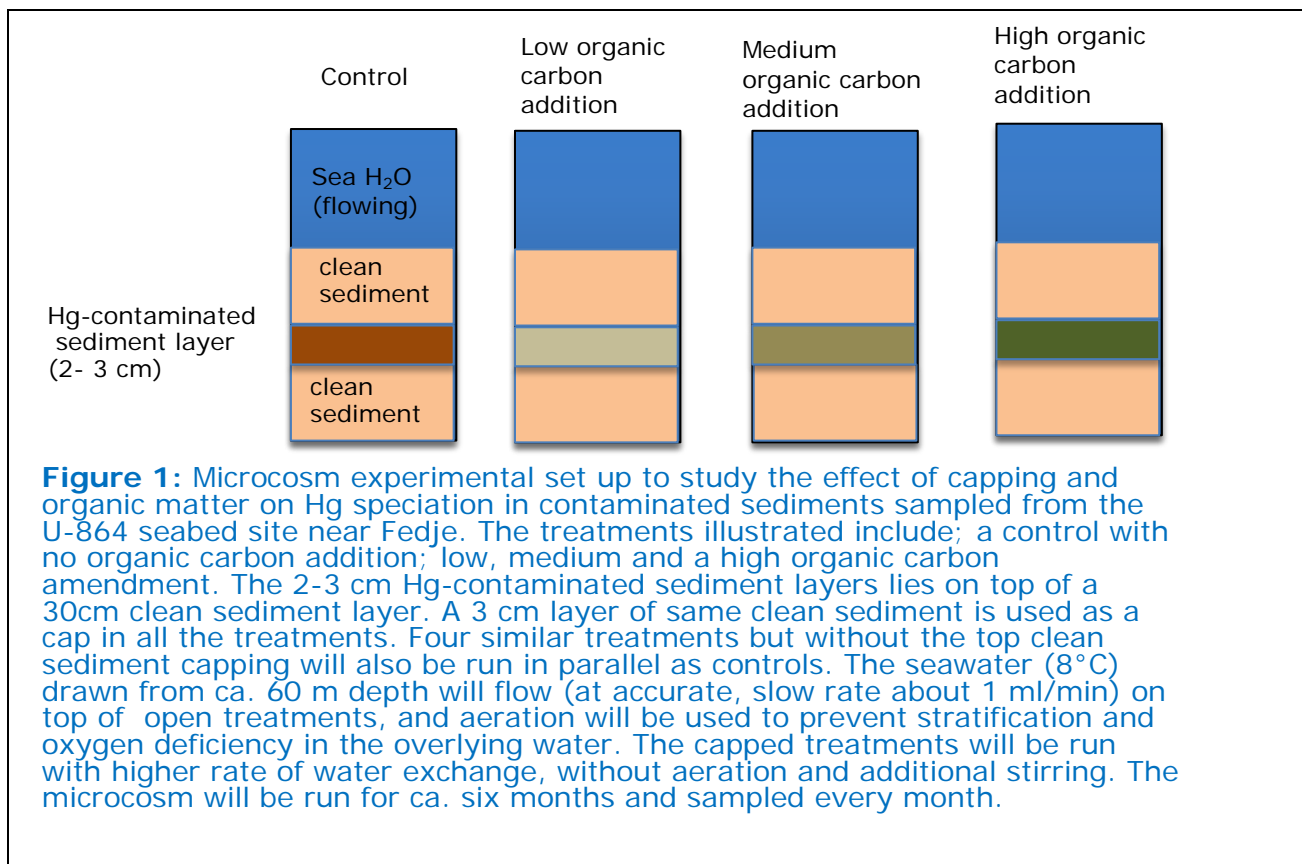
To test this hypothesis, eight microcosm experimental units (four capped and four uncapped) are set up with the following sediment treatments (see Figure 1 below);

- i) Control: i.e. no organic matter added
- ii) Low organic matter amendment (ca. 30 g-C/m² sediment surface area)
- iii) Medium organic matter amendment (ca. 90 g-C/ m² sediment surface area)
- iv) High organic matter amendment (ca. 270 g-C/ m² sediment surface area)

The capped treatments will be carried out in parallel with a similar set of four control treatments without a cap, i.e. a total of eight treatments.

Microcosm site

The microcosm experiment will be set up and run at NIVA's field marine station at Solbergstrand. The station has the necessary resources in terms of equipment (including access to piped fjord seawater from 60 m depth) and personnel and has successfully performed several similar experiments before. The microcosms will be set up in clean polycarbonate aquaria containers with a surface area of ca. 0.1 m². A three-centimeter layer of well homogenized Hg-contaminated sediment will be placed on top of a 30 cm clean layer of uncontaminated sediment in each container. The sediment in three of the treatments will be amended with organic matter (a commercially available mixture of four marine microalgae) at three levels while the fourth will not be amended and will act as a control. The capped treatments will be covered with a 3 cm layer of uncontaminated sediment. A similar set of four microcosms but without any cap will be run in parallel. Fjord seawater drawn from a depth of 60 m in the fjord (salinity of 34, temp 6-8°C) will flow over the sediments in all the microcosms. The microcosm layout is depicted in Figure 1 below. In the absence of bioturbation, this will be enough to prevent O₂ penetration to contaminated layer.



Sampling and Analysis

The microcosm experiments will be run for six months and sample both water, sediment and sediment pore water monthly for measurement of;

- i) MeHg and tot.-Hg concentration in both the inflowing and outflowing surface seawater to calculate the sediment-water fluxes of MeHg and tot.-Hg for the uncapped sediment treatments
- ii) MeHg and tot.-Hg (at least one time) concentration depth profile. For each of the monthly sampling, a small core through the Hg-contaminated sediment layer will be extracted using double polypropylene tubes. The outer core will be left in the sediment to prevent collapse and stratification disturbance after each sampling. The core collected in the inner tube will be sectioned into 1-3 cm slices and analysed for measurement of total MeHg. Vertical profiles of dissolved oxygen and hydrogen sulfide in pore water will be measured using a microelectrode array.

Mercury speciation analysis; NIVA lab

Water

The methods for determining total mercury (TotHg) and methylmercury (MeHg) in water is based on The United States Environmental Protection Agency (USEPA) Method 1631 (USEPA 2002) and USEPA Method 1630 (USEPA 1998) respectively. In short, MeHg is determined by distillation, aqueous ethylation, purge and trap, and cold vapor atomic fluorescence spectrometry (CVAFS) and TotHg by oxidation, purge and trap and CVAFS. The method detection limits (MDL) are 0.02 ng/L for MeHg and 0.1 ng/L for TotHg (3 standard deviations (STD) of blanks). Precision (as relative standard deviation (RSD) of parallel samples) is < 10 % for both methods.

Sediments

Determination of MeHg in sediments is done by organic phase extraction. Samples are first leached with acid and then extracted into dichloromethane (DCM) before back extraction into water. MeHg is then determined by aqueous ethylation, purge and trap, and CVAFS. An aliquot of 2.0 mL of sample is added to approximately 40 mL of DI water in amber glass vials and added acetate buffer solution (2M, 0.600 mL). The MDL is < 0.1 ng/g (3 STD of blanks for 0.1 g dried sample).

References

- USEPA. 1998. Method 1630 Methylmercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. ed. W. A. Telliard. US Environmental Protection Agency - Office of Water.
- USEPA. 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. ed. U. S. E. P. Agency.

3 METYLERINGSFORSØK VED TEXAS TECH UNIVERSITY

Formålet med de foreslåtte forsøkene er å foreta en vurdering av det mobile kvikksølvet (THg) og potensialet for metylering til metylkvikksølv (MeHg) under de anaerobe forhold som vil utvikle seg under tildekkingslaget. Kvikksølvforurensede sedimenter fra U-864 mottatt fra NIVA vil få lov til å utvikle anaerobe forhold. Redoksprofiler og endringer i Hg og MeHg vil bli målt som en funksjon av tiden. Det primære målet er en estimering av MeHg i porevann over lang tid, det vil si når sedimentene er fullt redusert. Det er dette MeHg som kan migrere inn i tildekkingen og potensielt redusere effekten av tildekkingslaget. To forskjellige oppsett vil bli brukt i forsøkene:

1. Ampuller inneholdende omtrent 20 ml sediment plasseres i et anaerobt kammer og hvor porevannet prøvetas og analyseres for Hg og MeHg hvoretter sedimentet fjernes og analyseres for Hg og MeHg i fast fase.
2. Det brukes mesokosmer inneholdende ca. 1 liter med sedimenter hvor naturlige redoksprofiler får lov til å utvikle seg. Overvåkingen av mesokosmene vil være fokusert på å vurdere gradientene i redoksforholdene og dynamikken av reduksjonen i sedimentene.

Resultatene fra forsøkene vil bli brukt i modellen CapSim for å forutsi migrasjonen (spredningen) av THg og MeHg gjennom tildekkingslaget. CapSim er et numerisk modelleringsverktøy for tildekkingslag utviklet i Texas Tech University's laboratorium (Reible og Lampert , 2014) . Disse numeriske simuleringene vil gi en oppdatering av tidligere simuleringer (DNV, 2008) for å forutsi hvordan tildekkingen vil oppføre seg.

Forsøkene forventes å gi et estimat på sannsynlige (mobile) porevannskonsentrasjoner av THg og MeHg i de tildekkede sedimentene og fordelingskoeffisienter av THg og MeHg i sedimentene. Fordelingskoeffisientene kan brukes til å estimere porevannskonsentrasjoner av THg og MeHg på andre steder med lignende sedimenter, men hvor det er forskjellige konsentrasjoner av kvikksølv i sedimentene. Konsentrasjonene av den mobile fasen kan brukes til å oppdatere estimater for THg og MeHg fluks gjennom tildekkingen.

Forsøket igangsettes rundt 1. mai 2014. Forsøksperioden er ca. 6 måneder, analyser av alle prøver og rapportering forventes å være ferdigstilt før utgangen av 2014.

En mer detaljert beskrivelse av forsøket er gitt i den engelske teksten under.

Methods

Sediments received from NIVA are expected to be homogenized and contain approximately 8.89 mg/kg THg and 0.59 µg/kg MeHg. The sediment will be subsampled and THg and MeHg in solids will be measured for confirmation. Porewater concentrations in the sediments as received will also be measured by the methods described below.

Weighed aliquots of sediments will be placed into two physical systems as outlined above, that is, vials containing approximately 20 mL of sediments and mesocosms containing approximately 1 L of sediments. 20 vials are expected to be used for the vial experiments and 1-2 mesocosms will be employed depending upon the availability of

sediments and the desire to reserve some sediments for potential future studies. The manner in which each of these experiments will be conducted is described below.

Vial Experiments

The vials will be filled and retained in an anaerobic chamber under a reducing atmosphere. The maintenance of the samples in an anaerobic environment will simulate the effect of thick cap layer in which oxygen and other easily reduced species will not be expected to penetrate to the underlying sediment. Five vials will be removed at 2 weeks, 1 month and 2 months after the initiation of the experiment and analysed. 5 vials will be reserved and maintained in the anaerobic chamber for possible later analysis if needed to achieve steady state conditions.

Diffusion gradient in thin films (DGT) will be employed for porewater analysis for THg and MeHg. Figure 1 depicts the vial with DGT inserted.

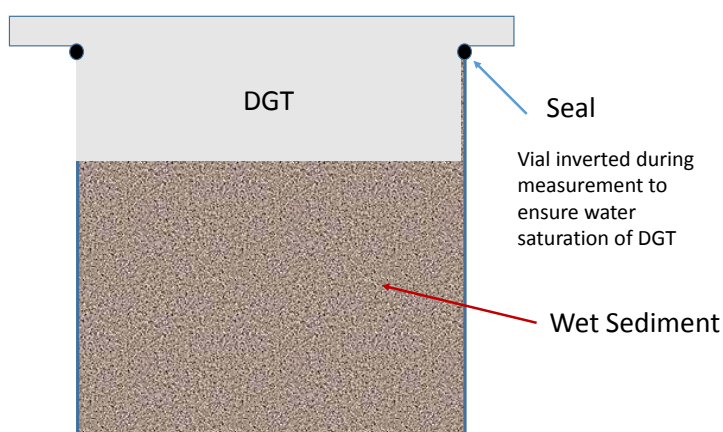


Figure 1: Vial with DGT inserted for THg and MeHg in porewater analysis. Approximately 20 mL of wet sediment fills the vial.

Analysis of each vial will include:

1. DGT analysis for porewater THg and MeHg. The vials used for these studies are especially designed to allow a DGT sampler to be inserted and sealed at the mouth of the vial and maintain contact with the wet sediment. The vials will be inverted to insure water saturation of the sampler. The exposure to the DGTs will be conducted prior to removal from the anaerobic environment since several days of exposure to the sediment are required to measure porewater concentrations of THg and MeHg. The DGT method is described in more detail below.

2. Voltammetric measurements of specific redox couples within the vials. These will be conducted outside of the anaerobic chamber and focused on a location at the sediment mid-depth away from any rapid redox changes that may occur at the sediment surface due to exposure to air. Oxygen (if any), reduced manganese, reduced iron or reduced sulphur (sulphides) are measured by the technique, based upon that developed by Brendel and Luthy, 1996. The measurement approach is described in more detail below.

3. Removal of the sediment from the vials and analysis for solid phase THg and MeHg. THg follows EPA Method 7471 with hot acid digestion while MeHg analysis follows EPA Method 1630.

Mesocosm Experiment

The experimental mesocosm to be used in these studies are shown in Figure 2

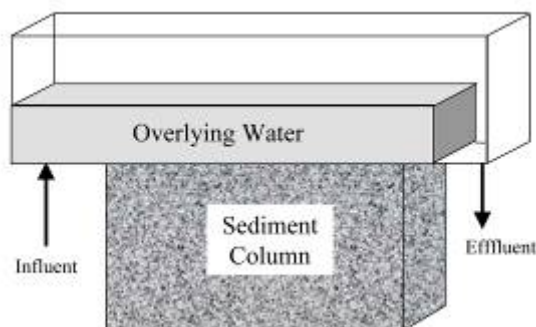


Figure 2: Schematic of experimental mesocosms. Approximately 20 cm x 10cm x 5 cm (LxHxW) sediment layer with 3 cm overlying water

The primary purpose of these mesocosms is to allow development of natural redox conditions with depth over time. Although the sediments are expected to be capped, effectively driving the entire sediment layer anaerobic, the rate at which this occurs will be studied through voltammetry in this system. Voltammetric measurements will be conducted every 2 weeks while water essentially saturated with air will be passed over the surface. The upper layers will remain oxygenated and aerobic while the bottom will eventually become anaerobic. This is expected to require 3-6 months due to the low labile organic matter expected in the sediments. In addition the fully developed redox environment could be available if later studies of particular cap material may be deemed useful. At the end of the stabilization period, DGT profilers can be used to measure vertical profiles of THg and MeHg if desired. Due to the time potentially required for stabilization, these measurements may not be part of the initial reporting.

Analytical methods

Porewater concentrations will be measured by diffusion gradient in thin film devices (DGTs) that we have used in multiple studies of mercury contaminated sediments. DGT approach originally developed of the analysis of metals in aqueous systems by Bill Davison and Hao Zhang of Lancaster University in England (Davidson et al., 1994), to the practical measurement of mercury and methyl mercury in porewater of sediments. Diffusion gradient in thin films (DGT) is a well-developed technique for sampling heavy metals in bulk water and has also been used in sediments. DGT measures the labile portion of heavy metals in typical time frames of 12-48 hours. The technique is quite powerful as it can be used to evaluate major metal pools (organic, inorganic, colloidal bound) as well as to some extent the kinetics of metal supply from the sorbed state to the interstitial. Its use in sediments is not as well developed and the more dense suspension of colloidal and other complexation media typically found in interstitial water may complicate the dynamic response of the DGT sampler.

A schematic of a typical DGT device is shown in Figure 3 below. The shown device is a two dimensional profiler and a smaller piston style sampler is expected to be used in the

vial studies. The layered construction is the same but the exposed surface is simply a 2 cm² circular disk. Dissolved contaminants of interest will diffuse across the membrane filter and diffusive gel layer and become sorbed in the underlying resin layer. The DGT device can be implanted into the system of interest (here the sediments) for a short period of time (typically 24-48 hours) and the amount of the contaminant of interest sorbed into the gel over that time is directly related to the concentration in the adjacent porewaters. Specificity can be achieved through proper choice of the diffusion gel layer and the sorbent layer. An agarose diffusive gel and a 3-mercaptopropyl functionalized silica gel resin, which is specific for mercury ions, will be employed for the measurement of mercury as demonstrated by Docekalova and Divis (2005). Divis et al. (2005) and Clarisse and Hintelmann (2006).

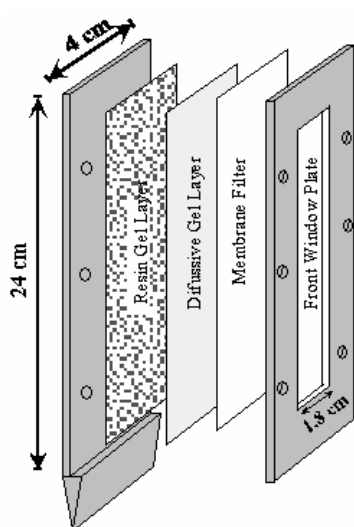


Figure 3: DGT profiler. These will be employed in the mesocosms but a smaller cylindrical piston shape will be used in the vials

The resin layer will be analyzed via digestion in HCl and EPA Method 1631 for THg and via EPA Method 1630 for MeHg. Bulk solid analysis in the vials will be conducted via THg follows EPA Method 7471 with hot acid digestion while MeHg analysis follows EPA Method 1630. Instrumentation that will be used is a Brooks Rand MERX 1400 for automated THg analysis and a Brooks Rand MERX 4400 for automated methyl mercury analysis.

Voltammetry

Over a period of several weeks to months, the development of quasi-steady redox conditions in the mesocosms will be monitored via voltammetry (Brendel and Luther 1995, Himmelheber et al. 2008, Johnson et al. 2009). Profiles of dissolved geochemical species in sediment porewater will be obtained at a vertical resolution of <3mm using a single axis automated micromanipulator (Analytical Instrument Systems, Flemington, NJ). Analytes include O₂, Mn²⁺, Fe²⁺, and dissolved sulfide (DS). The voltammetric electrodes respond to all reduced forms of dissolved sulfide (H₂S and HS⁻) and measurements do not need to be adjusted for pH. Microelectrodes will be prepared in the laboratory using the method of Brendel and Luther (Brendel and Luther 1995). At the beginning of each profiling event, electrodes will be calibrated for oxygen using a 2-point

calibration, and the method of standard additions will be used for iron, manganese, and sulfide in synthetic seawater with 2mM acetate or HEPES buffers. Scan parameters and detection limits will be the same as those reported in Brendel and Luther (Brendel and Luther 1995). Calibration checks will be performed on electrodes after each profile. Triplicate scans will be made at each depth and duplicate or triplicate electrodes will be spaced 2-3 cm apart.

Voltammetry will also be employed to evaluate redox conditions at the mid-depth in the vials before removal of sediments for solids analysis.

References

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