



BARITE-BOUND MERCURY IN MARINE SEDIMENTS; POTENTIAL RELEASE AND BIOAVAILABILITY UNDER ARCTIC CONDITIONS

Literature review

Scientific Report from DCE – Danish Centre for Environment and Energy

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Abstract:	Comprehensive Arctic monitoring programmes have found that mercury is of high concern regarding bioaccumulation and biomagnification in Arctic food webs, and the health of marine mammals and humans in the Arctic. This review evaluates the potential rate of release and methylation of mercury entering the environment from oil exploration activities. Our review indicates that there is a lack of data on the rates of mercury methylation in Arctic sediments and we assess that the traditional methods for estimating solubility and partitioning coefficients, sediment porosity, diffusion coefficients and complex algorithms are insufficient and subject to uncertainty. Hence, realistic rates need to be established for the natural Arctic sediments considering their specific physical and chemical properties.
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1. Summary

The process of offshore oil well drilling produces as waste both drill cuttings and drilling mud that are added to optimise the drilling performance. The major component of drilling muds is the weight agent barite, which is used to control formation pressures to prevent blow-outs. If drilling mud is discharged to the sea, the sediments affected by these discharges, for instance in the North Sea, have frequently shown elevated concentrations of barium from barite and potentially toxic metals such as lead (Pb), mercury (Hg) and cadmium (Cd) from barite impurities. Adverse effects from this heavy metal load on benthic communities have frequently been documented for affected areas in the North Sea.

Comprehensive Arctic monitoring programmes have found that mercury, especially the methylated species, are substances of high concern regarding bioaccumulation and biomagnification in Arctic food webs, and the health of marine mammals and humans in the Arctic. Here, the concentrations and intake of mercury by humans are far beyond the limits for toxic effects. Some local food items, especially narwhal meat, have high mercury concentrations, implying that humans living in the Arctic have a mercury intake above the guideline levels. Monitoring within the framework of AMAP clearly indicates that methylated mercury (MeHg) is strongly bioaccumulated and biomagnified in Arctic food webs.

Mercury is, in general, a substance of worldwide concern regarding the health of the environment and of humans. This led to the implementation of the UN Minamata Convention in 2017, which includes regulations on the use and emission of mercury.

To evaluate the potential rate of release and methylation of mercury entering the environment from oil exploration activities, this literature review of the release and bioavailability of barite-bound mercury was performed.

The literature review shows that methylation of mercury does occur in natural sediments and also in the guts of benthos species and fish. One study shows that mercury from barite can be taken up by benthic fauna species. MeHg has a strong potential to be released from the sediment, to be taken up and bioaccumulated in organisms.

Our review of the literature indicates that there is a lack of data on the rates of mercury methylation in Arctic sediments. From our review, we assess that the traditional methods for evaluation and estimation of the release and bioavailability of mercury from barite and sediment are insufficient and subject to uncertainty. The traditional estimations are based on assumptions on solubility and partitioning coefficients, sediment porosity, diffusion coefficients and complex algorithms. However, as solubility and partitioning coefficients are determined under test conditions that do not mimic the variable physical and chemical conditions in natural sediments, the results of the calculations will be too uncertain to allow meaningful predictions of the release rates of inorganic mercury from barite, methylation rates of mercury in sediment and release of mercury from sediments to water under natural conditions.

The limited number of studies on mercury release rates from natural sediments indicate significantly higher release rates than the calculated estimates based on partitioning coefficients.

To estimate release and methylation rates of mercury in connection with barite-bound mercury contamination, realistic rates need to be established for the natural Arctic sediments considering their specific physical and chemical properties, including:

- Release rate of inorganic Hg from barite and following methylation
- Methylation rates of inorganic mercury from shallow and deep water Arctic natural sediments
- Flux measurements of MeHg from Arctic natural sediments cores.

On the background of the review conclusions, the following recommendations are put forward:

- It is recommended, due to the high concern of mercury in the Arctic environment and in particular the high mercury concentrations in marine mammals such as narwhals and seals, that mercury emissions from industry in the Arctic is minimized by strict regulation to protect the environment in accordance with the Minamata convention (2017)
- It is recommended, that barite is classified according to its concentration of mercury impurities. The background for this recommendation is that barite currently is listed by OSPAR as a PLONOR (Pose Little Or NO Risk to the environment) offshore chemical independently of mercury content.

2. Sammenfatning

Ved offshore olieboringer produceres affald fra selve boreprocessen i form af borespåner og boremudder. Sidstnævnte anvendes til at optimere boreprocessen. Den største bestanddel af boremudder er det tunge baryt (BaSO_4), som især anvendes til at modstå tryk i brønden og derved undgå udblæsning (blow-out). Hvis boremudder udledes til havet har man fx i Nordsøen observeret forhøjede værdier i miljøet af barium og tungmetaller, (fx kviksølv (Hg), bly (Pb), og cadmium (Cd)), der alle optræder som urenheder i baryt.

Der er tillige påvist effekter på bunddyr fra disse tungmetaller i områder påvirket af boremudder i Nordsøen.

Omfattende monitoringsprogrammer i Arktis under Arktisk Råd (Arctic Monitoring and Assessment Programme, AMAP), har vist at kviksølv, især de methylerede former, kan bioakkumulere og opkoncentreres i de arktiske fødekæder, i hvilke havpattedyr og mennesker indgår. Fx har især narhvalkød, som er en vigtig fødevarer i Arktis, et højt indhold af kviksølv. Mennesker indtager derfor i visse områder således kviksølv i mængder, der overskrider de anbefalede værdier og dermed grænsen for giftige effekter.

Der er på verdensplan en generel bekymring for forurening med kviksølv. Derfor implementerede man FNs Minamata Konvention i 2017, som indeholder regulering af brug og udledning af kviksølv.

Denne rapport om frigivelses og biotilgængelighed af barytbundet kviksølv er udført med henblik på, at kunne vurdere den mulige frigivelse og methyleringsrate af kviksølv, der udledes til miljøet i forbindelse med olieeftersøgningsaktiviteter.

Rapporten er baseret på en gennemgang af litteraturen og viser, at methylering af kviksølv kan ske i naturlige sedimentter og også i tarmene hos bunddyr og fisk. Idet uorganisk kviksølv er methyleret frigives det relativt let fra sedimentet, og optages og bioakkumuleres i organismer. Et studie viser endvidere at kviksølv frigivet fra baryt kan optages af bunddyr, og dermed kan medvirke til en methylering af den uorganiske kviksølv.

Vores gennemgang af litteraturen indikerer, at der er mangel på data om kviksølvmethylering i arktiske sedimentter. Vi vurderer at de metoder, der normalt bruges til evaluering og estimering af frigivelse og biotilgængelighed af kviksølv fra baryt og sedimentter, er utilstrækkelige og usikre. De sædvanlige beregninger bygger på antagelser om opløselighed og fordelingskoefficienter af kviksølvforbindelserne mellem sediment og vand, sedimentets porøsitet, diffusionskoefficienter og komplekse algoritmer. Da disse koefficienter fastlægges under eksperimentelle forhold, som ikke tager højde for de varierende fysiske og kemiske forhold i naturlige sedimentter, bliver resultaterne tilsvarende usikre. De bør derfor ikke anvendes til at sige noget mere konkret om frigivelsesrater af uorganisk kviksølv fra baryt, methyleringsrater af kviksølv i sedimentet og frigivelse af kviksølv til vandet fra sedimentet under naturlige forhold.

Selvom der kun er et begrænset antal studier af rater af kviksølvfrigivelse fra naturligt sediment, indikerer de en signifikant højere frigivelsesrate end dem, man har beregnet baseret på fordelingskoefficienter.

For at estimere frigivelses- og methyleringsrater af kviksølv fra baryt, bør realistiske rater for naturlige sedimenter i Arktis fastlægges. Ved fastlæggelsen af sådanne rater bør sedimenternes specifikke fysiske og kemiske forhold tages i betragtning, herunder:

- Frigivelsesrate af uorganiske kviksølv fra baryt og efterfølgende methylering
- Methyleringsrater af uorganisk kviksølv i arktiske sedimenter fra lavt og dybt vand
- Flux-målinger af MeHg i kerner af naturligt arktisk sediment.

På baggrund af litteraturgennemgangen har vi følgende anbefalinger:

- På grund af bekymringen for kviksølv i det arktiske miljø, og især de høje koncentrationer i havpattedyr såsom narhvaler og sæler, anbefales det, at industriel udledning af kviksølv minimeres ved tæt regulering for således at beskytte det arktiske miljø i overensstemmelse med Minamata Konventionen (2017)
- Det anbefales, at baryt, som står på listen over PLONOR (Pose Little Or NO Risk to the environment) kemikalier, udarbejdet af OSPAR (Oslo-Paris Convention for the Protection of the Marine Environment of the North-East Atlantic), omfattes af begrænsninger i forhold til indholdet af kviksølv. Dette vil også være i overensstemmelse OSPARs egne anbefalinger om BAT (Best Available Technique) og BEP (Best Environmental Practice).

3. Eqikkaaneq

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Kviksølvimik mingutsitsineq nunarsuarmi tamarmi aarleqqutigineqarpoq. Taamaammat Naalagaaffiit Peqatigiit Minamatami Angerfigeqatigiissutaat 2017-imi atulersinneqarpoq, taannalu kviksølvip atorneqarnera aniatinneqarneralu pillugit malittarisassanik imaqarpoq.

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lunilu nalinginnaasumik periaaserineqartartut amigarput nalorninaateqarlutillu. Naatsorsuinerit nalinnginnaasut kviksølvip arroqqajaassusianik ilisimagisanik aammalu marraap erngullu akornanni kviksølvip agguataarsimaneranik, marraap imermik tigusisinnaassusianik, marrarmi siamarsinnaassusianik ilisimagisanik kisitsinernillu pisariusunik tunngaveqarput. Annertussutsit tamakku misileraanikkut aalajangerneqartarmata, taak-kunanilu marraap pinngortitamiittup qanoq issusiisa qanorlu akoqartigine-risa allanngorarneri ilanngullugit isiginiarneqarneq ajormata, taava misileraalluni uuttortaanernit paasisat aamma taama nalorninarqartarput. Taamaammat barytimiit kviksølvip anianeranut, marrarmi pinngortitamiit-tumi kviksølvip uumassusilinnut akuliussinnaanngorluni allanngoriartor-neranut aammalu marrarmiit aniasarnerata annertussusianut naliliinermut naliliinerit taakku atorineqartariaqanngillat.

Marrarmit pinngortitamiittumiit kviksølvip aniasarneranik misissuinerit amerlagisassaannikkaluartut taamaattoq misissuineritigut malunnarpoq erngup marraallu agguataarnerat tunngavigalugu naatsorsukkaniit annertu-nerujussuarmik sukkassuseqarluni kviksølv aniasartuq.

Kviksølvip barytimeersup aniatinneqarnerata uumassusilinnullu akuleruti-asunngorluni allanngoriartarnerata sukkassusia missingersinnaajumal-lugit Issittumi marrarmi aniasarisa allanngoriartarnerisalu sukkassusii piviusorsortut paasilluarneqartariaqarput. Sukkassutsit tamakku paasinia-neranni marraat pissusii akuilu isiginiarneqartariaqarput, tamatumunnga ilanngullugu makku paasineqartariaqarput:

- Kviksølvip barytimit aniasarnerata sukkassusia kingornalu timimut aku-leruteqqajaasunngorluni allanngoriartarnerata sukkassusia.
- Kviksølvip issittup marraani ikkattumi itisuumilu timimut akuleru-teqqajaasunngorluni allanngoriartarnerata sukkassusia.
- Issittup marraani MeHg-ip allanngorarnerinik uuttuinerit

Allaaserisanik misissuineq tunngavigalugu makku kaammattuutigaavut:

- Issittumi avatangiisini kviksølvip aarleqqutigineqarnera pissutigalugu, pingaartumik miluumasuni imarmiuni soorlu qilalukkani qernertani aam-malu puisini kviksølvip annertunerujussua eqqarsaatigalugu sukumiisu-mik malittarisassaqaqtitsinikkut suliffissuarniit kviksølvip aniatinneqar-nera minnerpaatinneqassasut kaammattuutigineqarpoq, tamatumuunak-kut Minamatami angerfigeqatigiissut (2017) naapertorlugu issittumi ava-tangiisit illersorneqarsinnaassapput.
- Kaammattuutigineqarpoq baryt, avatangiisinut ulorianaateqanngingajat-tutut ulorianaateqanngitsutulluunniit nalunaarsugaasoq (Atlanikup avan-namut kangiani imaani avatangiisinik illersuineq pillugu Oslo-Parisimi angerfigeqatigiissutikkut OSPAR-imik taagukkakkut), kviksølv eqqassutsi naapertorlugit killilersugaassasoq. Tamannana OSPAR-ip nammineerluni atortorissaarutit periaatsillu pitsaanerpaat atorineqarmissaannik kaammatt-uuatut aamma naapertuutissaaq.

4. Introduction

Mercury occurs naturally in the environment but is also released into the environment through various anthropogenic activities including oil exploration (e.g. Neff 2008, Norwegian Research Council 2012).

The present review aims to compile and improve our knowledge and understanding of the release and bioavailability of mercury in drilling mud barite and contaminated sediment based on available literature on mercury in barite and the potential release and bioavailability of mercury in sediments. Furthermore, mercury release rates and bioavailability depending on different physical and chemical conditions in the sediment are evaluated.

AMAP (Arctic Monitoring and Assessment Programme), a working group within the Arctic Council, performed a comprehensive assessment of mercury in the Arctic environment; sources and contribution, fate, influence of climate change, levels in biota, toxicological effects and projection of mercury to the Arctic (AMAP 2011). The general information from this assessment serves as background information on mercury in the Arctic environment, while knowledge of mercury in barite, including release rates and potential bioavailability, mainly relies on primary sources.

4.1 Mercury is of concern in the Arctic

The AMAP (2011) assessment led to the following concerns and conclusions:

- Mercury transfers into food chains where, as a result of biomagnification, it can reach levels of concern, particularly in the animals at the top of the Arctic's aquatic food webs.
- A high concentration of mercury is a serious problem for the indigenous peoples in the Arctic, who rely on hunting and fishing for their nutritional, social and cultural well-being.
- Methylmercury (MeHg) is of particular concern because high doses may cause neurological disorders and possibly myocardial infarction in humans.

The Minamata Convention entered into force in August 2017 and addresses the problems caused by mercury (<http://www.mercuryconvention.org/>). The aim of the convention is “to sustain an overall reduction in mercury levels in the environment over time thus protecting human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds”. Major highlights of the Minamata Convention include a ban on new mercury mines, the phase-out of existing ones, reduction of mercury use in a number of products and processes, as well as control measures on emissions to air and on releases to land and water (<http://www.mercuryconvention.org/Convention/tabid/3426/language/en-US/Default.aspx>).

4.2 Mercury forms

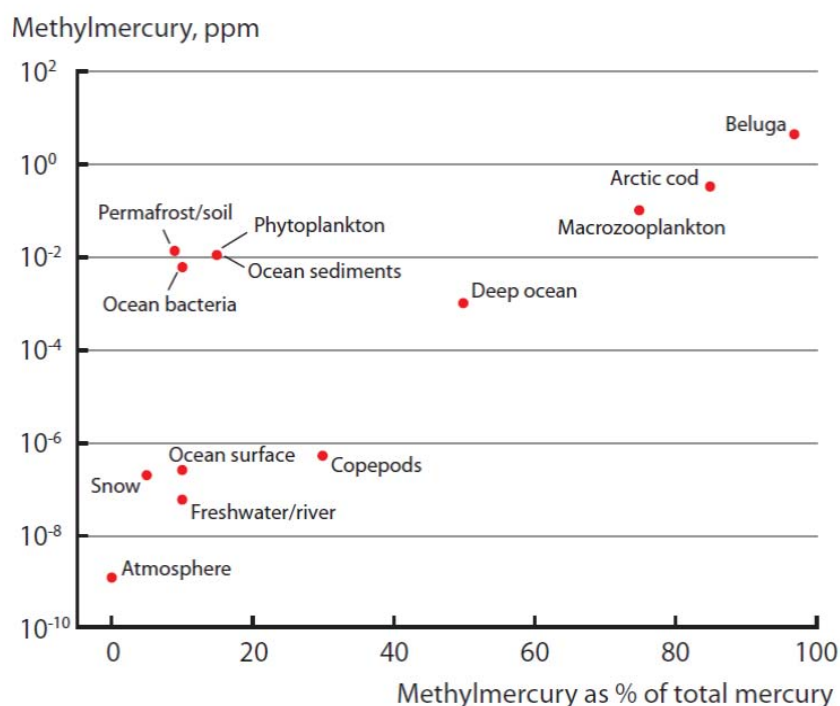
Elemental Hg₀ is the most abundant mercury form (98%) and it can be transported over long distances as it is highly volatile. From the state of elemental Hg₀, it can be oxidised to inorganic Hg (Hg²⁺ or Hg⁺ state), which is deposited on land or in water (AMAP 2011). Hg²⁺ is the prevalent inorganic Hg form in the environment. Via a process, catalysed under anoxic conditions by

primarily sulfate-reducing bacteria in water and sediments, inorganic Hg may be transformed to the organic form of Hg, methyl Hg (MeHg) (Chan 2003 and references herein). The transformation rate from inorganic to MeHg depends on environmental and physiological factors such as the chemical form and biochemical reactivity of Hg (Hg^+ or Hg^{2+}), the activity of microbial communities, redox conditions and the balance between dissolved versus particulate forms of Hg.

4.3 Bioavailability, bioaccumulation and biomagnification of mercury

According to Dutton (1998), and references herein), it is generally acknowledged that MeHg is significantly more bioavailable than inorganic Hg^{2+} and that it is highly absorbable from the diet (95 to 100%) compared with inorganic Hg (5 to 10%). MeHg strongly bioaccumulates and biomagnifies within marine food webs, because it is efficiently assimilated (bioavailable) in and only slowly sequestered from the body (AMAP 2011, Chan 2003, and references herein) (Figure 4.1). Therefore, high levels of mercury have been measured in Arctic indigenous peoples who among other items rely on marine mammals for food (AMAP 2011).

Figure 4.1. Biomagnification of MeHg and MeHg as an increasing proportion of total Hg from inorganic media (atmosphere, water bodies and soil) from the lowest trophic levels (bacteria and phytoplankton) to marine top predators such as toothed whale (beluga). From AMAP (2011).



As shown, both inorganic Hg and MeHg species may be bioavailable at the lowest levels of the food chain (bacteria, archaea, phytoplankton and other algae). However, as stated by AMAP (2011), only MeHg is bioaccumulated and biomagnified within food chains (see below) and thus poses the highest risk to the higher trophic levels and humans in the Arctic. AMAP (2011) states further: “Therefore, a critical question with respect to the bio-uptake of Hg into Arctic food webs concerns the mechanisms and locations where inorganic Hg^{2+} in the abiotic environment is predominantly transformed into MeHg and then assimilated into the lower levels of Arctic food webs”.

4.4 Mercury from oil exploration activities

The process of offshore oil exploration well drillings produces significant quantities of waste. This waste is a mixture of crushed bore hole minerals (cuttings) and drilling muds added to optimise the drilling performance. The major component of drilling muds is the weight agent barite (BaSO_4), suspended in a fluid phase, which is used to control formation pressures to prevent blow-outs. In cases where drilling mud has been discharged to the sea, the affected sediments, for instance in the North Sea, have frequently shown elevated concentrations of barium from barite and potentially toxic metals such as lead (Pb), mercury (Hg) and cadmium (Cd) from barite impurities. Adverse effects of this heavy metal load on benthic communities have frequently been documented for affected areas in the North Sea (e.g. Olsgard & Gray 1995, Grant & Briggs 2002).

It has been stated that mercury bound to barite is not expected to be released and methylate readily (Neff 2008, Trefry et al. 2008). The solubility of BaSO_4 in water is considered to be low, and because of the high concentrations of SO_4 in marine environments, the concentrations of dissolved barium ions also is expected to be low.

However, the study by Trefry et al. (2008) showed higher values of MeHg in sediments close to oil-producing activities (near-field sediments) where conditions might have favoured methylation (higher concentration of organic matter in anoxic and moderately reducing sediments). Furthermore, studies in Norway have indicated that some degree of bioavailability of barite-bound mercury cannot be ruled out (Norwegian Research Council 2012) (see Chapter 6 and 8).

As the concentration of mercury impurities in barite varies with geographical origin, discharge of mercury to the environment can be minimised by using barite with low concentration of mercury. Barite from suppliers in Vietnam and Norway has very low mercury concentration levels, 0.05 ppm, (TTM VIET NAM (https://www.alibaba.com/product-detail/High-quality-Barite-Powder-4-2_50031453561.html?spm=a2700.7724857.normal-List.33.65a07765NX880s), Neff 2008). Also, the mercury level in barite from China and India is relatively low, while those in barite from Scotland and Spain reach 7.18 and 3.37 ppm, respectively (Holmes et al. 2008).

4.5 Regulation of mercury concentrations in barite for use as weighing agent in drilling mud

In OSPAR (Oslo-Paris convention on reducing pollution in the North Atlantic Sea), barite is considered as 'Posing Little Or NO Risk to the environment (PLONOR)' according to OSPAR's HOCNF (Harmonized offshore Chemical Notification Format) categorisation. HOCNF is an international system for phasing out critical chemicals regarding toxicity, biodegradation and bioaccumulation used in the oil industry. There are four colour categories: green (PLONOR), yellow, red and black. Discharge of drilling mud additives, categorised as green, is allowed. In barite (BaSO_4), barium is a biologically inactive heavy metal and, therefore, considered PLONOR. However, the concentration of the mercury impurity in barite is not directly regulated through OSPAR. However, OSPAR recommends that Best Available Technology (BAT) is used and has set a Background Assessment Criterion (BAC) for mercury in sediments at 0.050 ppm. This limit corresponds to the natural level of mercury in sea floor sediments set by AMAP (2011).

In Norway, there are no limits set regarding the concentration of mercury impurities in barite used as weighing agent in drilling mud (Klima- og Forurensningsdirektoratet, now Norwegian Environmental Agency, pers. contact), but the concentration must be as low as possible to comply with § 66 of the Norwegian regulation for oil drilling activities (http://www.ptil.no/aktivitetsforskriften/category379.html#_Toc470090965). This legislation states that the operator shall use the drilling mud chemicals that pose the lowest possible risk to the environment, including heavy metals in drilling mud weighing agents.

In Greenland, the concentration of mercury impurities in the barite used in oil exploration drilling activities was < 1ppm (< 1mg Hg/kg dry weight of sediment) (Wegeberg et al. 2013). This limit was based on the corresponding US limit set by US EPA (2004) and used in US EPA Permit No. AKG-31-5000 from the Mexican Gulf. The natural level of mercury in the sediments of the Gulf of Mexico reaches 0.06 ppm (Trefry et al. 2008), the same level as that measured in samples from surface sea floor sediments in Greenland (Asmund & Nielsen 2000).

As mercury is of high concern for the environment and human populations in Arctic areas, as mentioned above, and for the future regulation of oil exploration activities, it is important to understand and minimise the potential transfer of mercury from drilling mud to the environment and the food web.

To evaluate the potential rate of release and methylation of mercury discharged to the environment from oil exploration, we performed a literature review on the release and bioavailability of barite-bound mercury.

5. Overview of the selected literature

For the literature review, a bibliographic search was performed, including:

- 1) Search using Google Scholar including relevant English words and their combinations as well as their translation to Norwegian: e.g., mercury, methylmercury, barite, ilmenite, toxicity, bioavailability, bioaccumulation, release, partitioning, k-value, flux.
- 2) Search in reference lists of relevant articles/reports (snow balling).

The resulting references were screened for relevance and all scientific articles, reports and memos considered relevant were included in the review (Table 5.1).

Furthermore, a search in the literature was conducted for:

- Release rates of Hg from barite
- Methylation rates in the environment
- Bioavailability of Hg from barite in biota
- Sediment profiles of MeHg and total Hg
- Concentration of mercury (Hg and MeHg) in sediments
- Concentration of mercury (Hg and MeHg) in pore water
- Concentration of mercury (Hg and MeHg) in benthic biota.

Table 5.1. Selected scientific articles and reports obtained from the literature search and their topic and main content.

Reference	Content / conclusions
AMAP 2011. AMAP Assessment 2011: Mercury in the Arctic. Arctic Monitoring and Assessment programme (AMAP), Oslo, Norway. xvi + 193 pp.	A comprehensive assessment of mercury in the Arctic environment; sources and contribution, fate, influence of climate change, levels in biota, toxicological effects and projection of mercury.
Breedveld G, Ruus A. 2015. Risikovurdering av forurenset sediment. Veileder. [Guidelines for risk assessment of contaminated sediments]. Miljødirektoratet M409. 106 pp.	Norwegian guidelines for assessment of the risk of release of hazardous compounds from contaminated sediments, the impact on human health and on the ecosystem.
Covelli S, Faganeli J, De Vittor C, Predonzani S. 2008. Benthic fluxes of mercury species in a lagoon environment. <i>Applied Geochemistry</i> 23: 529-546	The calculated flux of mercury as diffusive flux from pore water to seawater based on K_d values and the flux measured in situ in benthic chambers were found to vary with several orders of magnitude.
Dutton MD. 1998. Methyl mercury bioaccumulation, a study of factors influencing uptake and elimination in fish.	The results showed that MeHg was significantly more bioavailable than the inorganic Hg^{2+} and highly absorbable from the diet (95-100%) compared with inorganic Hg (5-10%).
Grant A, Briggs AD. 2002. Toxicity of sediments from around a North Sea oil platform: are metals or hydrocarbons responsible for ecological impacts? <i>Marine Environmental Research</i> 53: 95-113.	Mercury was not included in the chemical analyses and hence not ecotoxicologically tested.
Heyes A, Mason RP, Kim E-H, Sunderland E. 2006. Mercury methylation in estuaries: Insights from using measuring rates using stable mercury isotopes. <i>Marine Chemistry</i> 102: 134-147.	The rates of Hg methylation and MeHg demethylation in sediment of the Hudson River, Chesapeake Bay and Bay of Fundy were measured by using stable isotopes of Hg and MeHg. Methylation was more important than demethylation in controlling the differences in MeHg concentrations among ecosystems. The in situ MeHg concentration is a good indicator of methylation activity in sediment across ecosystems in sampled and spiked cores.
Li Q, Lingyan J, Dingyong W, Xu L. 2015. Sediment profile and fluxes of mercury and methyl mercury in Weihe Watershed in Henan, China. <i>Bulletin of Environmental Contamination and Toxicology</i> 95: 51-55.	The conclusion was drawn that in situ benthic flux chambers provided the most environmentally realistic measurement of the exchange of mercury types at the sediment/water interface.
Mason RP, Kim, E-H, Cornwell J, Heyes D. 2006. An examination of the factors influencing the flux of mercury, methylmercury and other constituents from estuarine sediment. <i>Marine Chemistry</i> 102: 96-110.	The flux of Hg and MeHg was measured from sediments collected in Baltimore Harbor, USA. For Hg and MeHg, there appeared to be little relationship between their flux and that of major metals, or sulfide, or DOC. For MeHg, it was suggested that processes occurring at the sediment/water interface, including methylation, may play a major role in determining the extent of the MeHg flux to the water column.
Muresan B, Cossaa D, Jézéquelb D, Prévotb F, Kerbellica S. 2007. The biogeochemistry of mercury at the sediment water interface in the Thau lagoon. 1. Partition and speciation. <i>Estuarine, Coastal and Shelf Science</i> 72: 472-484.	Diffusive fluxes of total Hg and MeHg from the sediment to the water column in the warm period were estimated in a Mediterranean lagoon in France by Fick's first law for calculation of release rates.
Ndungu K, Schaanning M, Braaten HFV, 2016. Effects of organic matter addition on methylmercury formation in capped and uncapped marine sediments. <i>Water Research</i> , 103, 401-407.	An investigation of whether the addition of organic carbon (OC) to Hg-contaminated marine sediments beneath an in situ cap would initiate and/or enhance MeHg formation of the inorganic Hg present. The results showed that MeHg production was limited by the available amount of organic carbon.
Neff JM. 2008. Estimation of bioavailability of metals from drilling mud barite. <i>Integrated Environmental Assessment and Management</i> 4: 184-193.	The conclusion was made that mercury in metal sulfide inclusions in barite from deposited drilling muds and cuttings is highly stable and insoluble in sediments near offshore platforms.

Table 5.1, continued

Olsen M, Schaanning MT, Braaten HFV, Eek E, Moy FE, Lydersen E. 2017 The influence of permanently submerged macrophytes on sediment mercury distribution, mobility and methylation potential in a brackish Norwegian fjord. <i>Science of the Total Environment</i> . STOTEN-D-17-02562R2.	An investigation of how a meadow with permanent colonies of submerged macrophytes in a contaminated brackish fjord in southern Norway influenced the conditions for sulfate-reducing microbial activity, methyl-Hg (MeHg) production and availability of MeHg. Enhanced availability of MeHg within the meadow was demonstrated.
Olsgard F, Gray JS. 1995. A comprehensive analysis of the effects of offshore oil and gas exploration and production on the benthic communities of the Norwegian continental shelf. <i>Mar Ecol Progress Series</i> 122: 277-306.	Mercury was included in the chemical analyses, whereas the ecotoxicological effects of metals were not studied. Focus was on the diversity and distribution of benthos with respect to sedimentation (Ba).
Research Council of Norway. 2012. Long-term effects of discharges to sea from petroleum-related activities The results of ten years' research. Report. 45 pp.	A summary of the long-term effects of discharges of drilling cuttings and mud. Regarding Hg, studies conducted in Norway indicated that some degree of bioavailability of barite-bound mercury cannot be ruled out.
Rudd JWM, Furutania A, Turner MA 1980. Mercury methylation by fish intestinal contents. <i>Applied and Environmental Microbiology</i> 40: 777-782.	The studies showed that the intestinal content of fish (six freshwater species) can convert Hg ²⁺ to MeHg.
Saloranta TM, Ruus A, Borgå K. 2011. Identification of the most influential factors in the Norwegian guidelines for risk assessment of dispersion of contaminants from sediments. <i>Integrated Environmental Assessment and Management</i> 7: 657-667.	Identification of the most influential factors and parameters on the flux and transport of mercury from sediment: flux of organic carbon to the sediment, bioturbation activity diffusion factor, sediment-water partitioning coefficient, benthic biota-water bioconcentration factor, mass of resuspension of fine material.
Schaanning M, Ruus A, Bakke T, Hylland K, Olsgard F. 2002. Bioavailability of metals in weight materials for drilling mud. Report from Norwegian Institute for Water Research. 35 pp.	Evidence was found of bioaccumulation of mercury in a polychaete and a gastropod species exposed to barite with a mercury concentration of 0.37 ppm (Barite Zelmou/Safi).
Schaanning MT, Trannum HC, Pinturier L, Rye H. 2011. Metal partitioning in ilmenite- and barite-based drill cuttings on seabed sections in a mesocosm laboratory. <i>SPE Drilling & Completion</i> June 2011: 268-277.	A positive correlation between metal concentrations in drill cuttings or weight material (barite, ilmenite) and the interstitial water concentration was confirmed, including mercury. Flux measurements supported the relatively high mobility of mercury.
STF 2007. Revidering av klassifisering av metaller og organiske miljøgifter i vann og sedimenter. TA-2229/2007.	State classification regarding level of pollution, including concentration of mercury in water (µg Hg L ⁻¹) (Table 7).
Tong Y, Zhang W, Chen C, Chen L, Wang W, Hud X, Wang H, Hu D, Ou L, Wang X, Wang Q. 2014. Fate modeling of mercury species and fluxes estimation in an urban River. <i>Environmental Pollution</i> 184: 54-61.	QWASI (Quantitative Water–Air–Sediment Interaction) model was selected to estimate the levels of total mercury and three mercury species in water and sediment and used to quantify the fluxes of mercury at water/air and sediment/water interfaces of an urban river.
Trefry JH, Trocine RP, McElvaine ML, Rember RD, Hawkins LT. 2008. Total mercury and methylmercury in sediments near offshore drilling sites in the Gulf of Mexico. <i>Environmental Geology</i> 53: 375-385	The conclusion was reached that even under oxidising conditions, mercuric sulfide is extremely stable and does not dissolve rapidly, particularly if the concentration of sulfate is high, as is the case in marine sediments. Also elevated concentrations of MeHg were found where optimal conditions for methylation occur. Profiles of MeHg and total Hg are shown, but fluxes are not included, and the diffusion from sediment to seawater is thus not quantified.

Table 5.1, continued

<p>Wegeberg S, Asmund G, Fritt-Rasmussen J, Lassen P, Mosbech A. 2013. Post drill monitoring evaluation, environmental assessment and recommendation of Cairn's drilling campaign 2011. DCE-Danish Centre for Environment and Energy. Memo dated 7th February 2013. 29 pp.</p>	<p>The post drill monitoring results on mercury were evaluated and concerns were raised about the elevated concentration levels in sediments.</p>
<p>Weltens R, Goossens R, Puymbroeck S van. 2000. Ecotoxicity of contaminated suspended filter feeders (<i>Daphnia magna</i>). Archives of Environmental Contamination and Toxicology 39: 315-323.</p>	<p>The study did not include mercury but showed a significantly increased toxicity of cadmium to filter feeders when it is attached to particles .</p>
<p>Westerlund, S., Eriksen, V., Beyer, J., & Keilen, G. 2001. Characterisation of the cuttings piles at the Beryl A and Ekofisk 2/4 A platform - UKOOA Phase II, task 1. Rogaland Research Report No. RF 2001/092, 162 pp.</p>	<p>Leaching studies of metals from historic cuttings material found mercury (and other metals) in fractions loosely bound to particles, indicating that these elements have a potential to accumulate in biota.</p>
<p>Westerlund S, Bechmann RK. 2006. Metals in tissues of mussels, scallops and cod exposed to suspended particles of water based drilling mud. In: Bechmann RK, Westerlund S, Baussant T, Taban IC, Pampanin DM, Smith M, Lowe D. 2006. Impacts of drilling mud discharges on water column organisms and filter feeding bivalves. Report IRIS – 2006/0388: 21-38.</p>	<p>The study did not include mercury but concluded that, even though the metals may not be leached from particles, they may be taken up from particles in contact with tissue. It was found that metal concentrations increased more in filter feeders than in fish, but predators on filter feeders may take up metals from their prey due to low pH in the digestive system.</p>

6. Review and discussion

6.1 Effects of barite

There are two main concerns about the impact on marine organisms by discharged barite: 1) the physical impact from particle smothering, which may bury and/or inhibit filtration of benthic organisms, and 2) potentially toxic effects from heavy metal impurities in the barite.

However, Schaanning et al. (2002) summarizes the environmental effects of barite as such, and conclude that the effects on benthic communities by metals present in drilling muds are often difficult to distinguish from the effects of other factors related to mud composition (e.g. organic fluids), high sedimentation rates (smothering) and altered substrate properties (particle size and shape). Adverse effects from metals associated with drill cuttings are rarely described in the scientific literature.

6.2 Bioavailability of mercury from barite

Based on values on the solubility of barite in water and sediments, Neff (2008) stated that most of the heavy metal impurities in barite (besides mercury also lead and cadmium) are relatively immobile and non-bioavailable to benthos. He refers to the circumstances 1) that the solubility of barite in marine sediments and drill cuttings piles is controlled by the sulfate concentration in sediment pore water; 2) that sulfate-reducing bacteria use sulfate as an alternate electron source in oxygen-depleted sediments and generate sulfide that combines with and precipitates sediment metals; and 3) that, even under oxidising conditions, mercuric sulfide is extremely stable and does not dissolve rapidly, particularly if the concentration of sulfate is high as is the case in marine sediments. Thus, Neff (2008) concludes that mercury in metal sulfide inclusions in barite from deposited drilling muds and cuttings is highly stable and insoluble in sediments near offshore platforms.

The estimates of bioavailability of barium, cadmium, copper, lead and mercury presented by Neff (2008) are, firstly, based on the assumption that the bioavailable fraction is metals soluble in seawater or pore water. Secondly, the estimates by Neff (2008) are based on partition coefficients (K_d) of the metal between water and solid/sediment and these are obtained from the literature. The concentration of the metal in the pore water is subsequently calculated by simple multiplication of the K_d and the concentration of the metal in drill mud/sediment ($C_{\text{porewater}} = C_{\text{sediment}} \times K_d$). Thirdly, the release of dissolved metals from solid barite presumably depends on the solubility products of the metal sulfides.

However, K_d values obtained from literature are extremely variable due to heterogeneity in and between sediment types and the redox potential. The variation may span several orders of magnitude (Schaanning et al. 2011). Furthermore, based on experimental evidence, Schaanning et al. (2011) recommended using a $\text{Log}K_d$ value of 3.3, whereas Neff (2008) recommended using a $\text{Log}K_d$ value of 6.6, which results in a considerably lower solubility/mobility/flux of mercury from the sediment.

It has been shown that the calculated flux of mercury as diffusive flux from pore water to seawater based on K_d values is several orders of magnitude lower than the release/flux measured in situ in benthic chambers (Covelli et al. 2008, Schaanning et al. 2011).

Hence, the estimates by Neff (2008) are doubtful as they are based on K_d values obtained from the literature and thus do not mimic realistic environmental conditions. Furthermore, Neff (2008) assesses the bioavailability of mercury in barite from estimates of solubility. Hence, he does not include the formation of methylmercury or mercury-organic complexes in the sediments in contrast to Ndungu et al. (2016) who showed that MeHg production was correlated with the available amount of organic carbon. Nor does Neff (2008) include uptake of particle-bound mercury in organisms.

6.3 Bioaccumulation of mercury from barite

Schaanning et al. (2002) performed controlled experiments investigating the bioaccumulation of metals in benthic organisms exposed to various drilling mud weighing agents. The aim of the experiments was to compare bioaccumulation of metals from sediments spiked with barite from different ores (Barite Zelmou, Barite Safi and Barite Zelmou/Safi) with two alternative weight materials for drilling muds, Ilmenite (an oxide of iron and titanium) and Hematite (an oxide of iron). Bioaccumulation of metals was determined after 28 days in polychaetes (*Nereis diversicolor*) and gastropods (*Nassarius reticulatus*). The results indicated significantly higher concentrations of barium, titanium, lead, mercury and copper in organisms exposed to various test substances than in organisms exposed to non-spiked control sediments. Schaanning et al. (2002) showed, by Al and Li analyses, that the concentrations of heavy metal in the animals originated from uptake of the metals and that the elevated mercury concentrations were not caused by barite particles in the animals in solid form. The results hence indicated bioaccumulation of mercury in benthic organisms exposed to barite with a mercury concentration of 0.37 ppm (Barite Zelmou/Safi).

6.4 Fluxes of Hg and MeHg across the sediment/water interface

Measurements of mercury in sediment profiles can help us to determine accumulation and fluxes of mercury. However, because of the rapid formation, degradation and movement of MeHg in sediments, it is difficult to study mercury dynamics using sediment profiles alone. Additional data on MeHg and THg (total mercury) fluxes between sediment and water are needed to determine the transport and fate of MeHg.

Li et al. (2015) tested and discussed the multiple approaches applied to examine the fluxes of Hg and MeHg across the sediment/water interface.

For this purpose, they conducted a study of the mobility of THg and MeHg across the sediment/water interface of river sediments. Flux estimates were based on THg and MeHg concentration profiles in the sediments as well as in situ measurements of sediment fluxes using benthic chambers. Use of benthic chambers, designed as boxes, bell jars and cylindrical micro-/mesocosms, is a generally accepted approach for in situ measurements of fluxes of elements/substances across the water sediment interface in natural sediments. The measurements will include release of MeHg from the natural sediment.

The authors found that higher summer temperatures may have enhanced the bacterial methylation process of inorganic Hg in the sediments and thereby increased the ratio of MeHg in the sediments from the range of 0.39-0.77% in winter to 0.48-1.12% in summer. They also found an increasing concentration of MeHg with depth, which suggests that the most recent sediment (0-10 cm) could be a source of MeHg for the water column. Furthermore, their in situ investigations showed that both total Hg and MeHg flux patterns differed greatly depending on the redox conditions in the sediment; MeHg concentrations were lower when the redox was low and higher under aerobic conditions. In addition, Li et al. (2015) found that the measured fluxes of MeHg in in situ chambers were 5 to 8 times larger than the flux estimates based on the MeHg profile in the sediment. This illustrates the limitation of interpretation of MeHg profiles. Also Muresan et al. (2007), studying MeHg profiles and fluxes in the sediments of a Mediterranean lagoon in France, found that the calculated diffusive fluxes were low compared with those obtained using benthic chambers and that their magnitude strongly depended on the evolution of the redox state of the sediment-water interface.

In a mesocosm experiment with boxcore samples of fjord sediments, Shaanning et al. (2011) investigated fluxes of metals across the water-sediment interface. They found a positive correlation between the metal concentration in drill cuttings or weight material (barite, ilmenite) and the interstitial water concentration of metals. Flux measurements indicated a relatively high mobility of mercury in the sediment.

In a study performed by Westerlund et al. (2001), sequential extraction of metals from cuttings material and drilling mud was used to obtain information on the potential mobility of metals during various geochemical processes and, hence, release to the sea water. For the metals of high environmental concern (Hg, Pb and Cd), the largest fraction was bound in a state suggesting high geochemical mobility, pointing to possibly high release and bioavailability.

Total concentrations of mercury and methylmercury in near-field and far-field sediments to offshore drilling sites in the Gulf of Mexico were published by Trefry et al. (2008). Total Hg levels at the near-field sites were in general high, within the range 25-558 ppb, whereas total Hg levels at the far-field sites were distinctly lower, ranging between 11 and 92 ppb. Furthermore, a strong correlation between barium and total mercury concentrations in the sediments was demonstrated, which confirmed that barite from drilling mud most probable was the main source of the mercury contamination in near-field sediments. Regarding methylmercury, the concentrations ranged from 0.11-1.05 ppb in the far-field sediments and <0.03-2.7 ppb in all the near-field sediments. Accordingly, in contrast to the results for total Hg, the concentrations of MeHg in surficial (0-2 cm) sediments did not vary significantly between the near- and far-field stations. From these findings, Trefry et al. (2008) concluded that 1) contaminated total Hg in the sediments at the drilling sites studied was associated with barite and 2) that Hg introduced with barite during offshore drilling could not be directly linked to the raised levels of MeHg in the near-field sediments. However, considerable variability was observed in the MeHg concentrations in the upper 2 cm of the sediment, and interpretation of sediment data may be difficult and complex. MeHg concentrations are a balance between the net formation of methylmercury in the sediment, which is strongly regulated by the sediment redox, and the flux out of the sediment. The latter depends on the porosity of the sediments, sorption con-

ditions and bioturbation. Correspondingly, the interpretation of vertical sediment profiles is complicated and cannot stand alone as a proxy for the flux out of the sediment.

6.5 Methylation of Hg in the environment

Bioavailability of mercury is controlled by many environmental and physiological factors, including the chemical form and biochemical reactivity of Hg, the activity of microbial communities, redox conditions and the balance between dissolved and particulate forms of Hg.

The change in speciation of mercury from inorganic to methylated forms is the first step in the aquatic bioaccumulation process. MeHg bioaccumulates strongly in organisms because it is highly absorbable from the diet (95 to 100%) compared with inorganic Hg (5 to 10%) and efficiently assimilated into tissues and successively only slowly degraded or eliminated from the body (AMAP 2011, and references herein, Chan 2003).

Mason et al. (2006), studying the potential importance of the diffusive sediment flux of Hg and MeHg, found that the redox status of the sediment surface may be the most important factor in determining to which extent any Hg is methylated within the sediment and the extent of the MeHg release to the water column. This is in continuation with Gill et al. (1999), who showed that MeHg fluxes from sediments were related to the overall water column oxygen concentration and that the fluxes increased as water column oxygen decreased.

The proposed factors controlling Hg methylation can be grouped into those affecting the bioavailability of Hg for methylation and those affecting the activity of the methylating bacteria (Heyes et al. 2006). The factors controlling the bioavailability of Hg depend on the dissolved and solid phase speciation of Hg. Sulfate-reducing bacteria (SRB) have been identified as the most important group of Hg-methylating bacteria in saline waters, implying that factors affecting the activity of SRB will also effect Hg methylation (Heyes et al. 2006). Hence, microbial activity and the formation of sulfide appear to be at least as important as the Hg concentration in controlling the MeHg concentration in estuarine sediment.

In sediments from a Mediterranean lagoon in France, Muresan et al. (2007) found that the distribution of MeHg in sediment profiles was characterised by a main peak in the superficial sediments and another peak deeper in the core within the sulfide-accumulating zone. In addition, high dissolved MeHg concentrations and methylated percentages were found in the epibenthic water. Furthermore, the study of Muresan et al. (2007) indicated that Fe- and Mn-oxides played a major role in controlling total and methylmercury mobility throughout the sediment-water interface.

The concentration of MeHg may also be a result of methylation and, for instance, bacterial demethylation as found by Heyes et al. (2006). They measured methylation and demethylation in sediment from the Hudson River, Chesapeake Bay and Bay of Fundy using stable isotopes of Hg and MeHg. They reached the conclusion that methylation was more important than demethylation in controlling the differences in MeHg concentrations among ecosystems.

AMAP (2011) synthesises studies that confirm methylation of Hg in oxic environments in Arctic oceans – methylation of Hg²⁺ occurs as part of the biodegradation of detritus, and increased levels of MeHg are thus associated with oceanic nutrient maxima. This MeHg, which is produced from the abiotic Hg²⁺ reservoir in the ocean rather than the particulate Hg carried by detritus, may enter food webs by upwelling of nutrient-rich bottom water or through vertical migration of zooplankton.

According to AMAP's (2011) synthesis on the methylation of Hg²⁺ in the Arctic, sulfate reductive microorganisms in anoxic environments can also methylate Hg²⁺. However, sediments favorable to sulfate reducers and exhibiting a declining oxygen profile may accommodate methylation to a greater extent than anoxic environments. Such conditions, with a gradient in redox conditions, are found widely in the Arctic oceans.

Two pathways for inorganic Hg uptake by microorganisms that can lead to Hg methylation are considered: 1) passive diffusion of dissolved uncharged Hg species (Hg associated with sulfide (S)) through the bacterial membranes; or 2) active transport of Hg species (e.g., by the amino acid transport system). Hence, transport from microorganisms to other unicellular organisms (microalgae, protozoans) is considered as an entrance of MeHg into the aquatic food webs, either through consumption by heterotrophs of the MeHg-containing microbial populations or the release of dissolved MeHg into water followed by its assimilation by phytoplankton (AMAP 2011, and references herein). Specific information regarding bacterial Hg uptake and methylation rates in the Arctic seas is, however, sparse.

6.6 Modelling of and estimation methods for release of mercury from contaminated sediments

Different methods have been used for estimation of released mercury from contaminated sediment. Methods for estimation release/fluxes of Hg and MeHg from contaminated sediments include for instance:

- 1) Simplified methods where estimation is based on solubility and partitioning coefficients of the elements in the sediment (e.g. Neff 2008).
- 2) Complex methods where estimation is based on interpretation of concentration profiles of the elements in sediment and pore water combined with a model for diffusive release using Fick's first law (e.g. Muresan et al. 2007).
- 3) Complex multi-media models such as the generic QWASI (Quantitative Water Air Sediment Interaction) model, where the distribution and fluxes of mercury species in a lake or river are estimated (e.g. Tong et al. 2014).
- 4) Estimation based on direct measurement of the release of Hg and MeHg from natural sediment to water in benthic flux chambers (e.g. Covelli et al. 2008, Mason et al. 2006, Schaanning et al. 2011, Ndungu et al. 2016, Olsen et al. 2017).

Although the QWASI (Quantitative Water Air Sediment Interaction) model used by Tong et al. (2014) in a study of the fate and transfer of mercury in an urban river gave predicted estimations of mercury levels in water and sediments close to the measured values, this model was based on several assumptions. First, this calculation assumes steady-state conditions, which means that the mercury concentrations in the water and sediment remain stable during the study period. In addition, the QWASI model did not take into account the rates of methylation of mercury in the water and sediment.

The available methods for evaluation and estimation of the release and bioavailability of mercury from barite and sediment are thus assessed as insufficient and subject to uncertainty.

Mechanisms behind the release of Hg and MeHg from sediments to the water column are not well resolved and the literature indicates that the release depends on numerous factors such as redox conditions and bioturbation.

Often the estimations are based on assumptions on solubility and partitioning coefficients, sediment porosity, diffusion coefficients and complex algorithms. However, as solubility and partitioning coefficients are determined under test conditions that do not mimic the variable physical and chemical conditions in natural sediments, the results will be too uncertain to allow reliable predictions of the release of mercury. Furthermore, a number of studies on mercury release rates from natural sediments have measured a significantly higher release than the calculated estimates based on partitioning coefficients.

Modelling results, irrespective of the method used, may thus be extremely uncertain when evaluating a specific case of contamination. However, for risk assessments of specific activities, calculations/estimations may be performed for, for example, development of regulations. In such cases, it is often necessary for decision makers to work on the basis of uncertainties. The estimates should hence be conservative according to the precaution principle and all uncertainties and assumptions must be clarified and presented.

The Norwegian Environment Agency's guideline for environmental risk assessment of contaminated sediments (Miljødirektoratet 2016) focus on the risk of release of hazardous compounds from contaminated sediments and on the impact on human health and on the ecosystem (Breedveld & Ruus 2015). The assessment is based on a three-level tiered approach (Tier 1, Tier 2 and Tier 3), with increased complexity and demand for local data. The scope of this guideline is to identify marine sediment areas for possible implementation of measures to reduce load and exposure of the environment to mercury. Tier 1 is an evaluation based on the short-term toxicity of hazardous substances in sediments. Since the main concerns about mercury relate to the long-term effect of bioaccumulation and biomagnification, the Tier 1 assessment is not relevant in this case. Tier 2 involves calculations of the flux from the sediment to other parts of the ecosystem. The relatively simple calculations are based on default values on solubility and partitioning coefficients, sediment porosity, diffusion coefficients etc. However, as solubility and partitioning coefficients are mostly determined under test conditions that do not mimic the variable physical and chemical conditions in natural sediments, the results of these calculations will be too uncertain. With respect to methylmercury contamination of the sediment, the guideline recommends a Tier 3 assessment based on measurements such as, for instance, of redox conditions in the sediment and of flux in benthic flux chambers.

7. Knowledge gaps

Our review indicates that the existing rates regarding Hg release from barite and methylation of mercury in sediments are not sufficient to allow reliable estimations of the release of mercury from barite and sediment mercury contamination. Release and methylation depend strongly on the specific physical and chemical properties of the sediments, resulting in pronounced variations due to differences in grain size, organic content, light etc. To estimate the specific release and methylation rates of mercury, an experimental environment must be established to validate calculations of:

- Release rates of inorganic Hg from barite
- Methylation rates of inorganic mercury from shallow and deep water Arctic natural sediments
- Flux measurements of MeHg from Arctic natural sediment cores.

8. Conclusions and recommendations

Comprehensive Arctic monitoring programmes show that bioaccumulation and biomagnification of mercury, especially methylated species, affect the health of marine mammals and humans in the Arctic, which is of great concern. Observations of concentrations and intake of mercury by Arctic marine mammals far beyond the limits for toxic effects have been made.

World-wide, mercury is a substance of concern due to its adverse effects on the health of the environment and humans. Therefore, the UN Minamata convention came into force in 2017 and it contains regulation on the use and emission of mercury.

Information obtained from the conducted literature review shows that methylation of mercury occurs in natural sediments but also in the guts of benthic fauna and fish. One of the studies included demonstrates that mercury from barite can be bioaccumulated in some species of benthic fauna.

MeHg has a strong potential to be released from the sediment and to be taken up and bioaccumulated in organisms.

The AMAP monitoring clearly indicates pronounced bioaccumulation and biomagnification of MeHg in Arctic food webs.

Our literature review revealed large variations with regard to Hg partitioning in sediments, and so far mercury release and methylation rates have not been properly investigated in Arctic sediments.

The traditional methods for evaluation and estimation of the release and bioavailability of mercury from barite and sediment are subject to uncertainty and considered insufficient for assessing specific contamination cases. The estimations are often based on assumptions regarding solubility and partitioning coefficients, sediment porosity, diffusion coefficients and complex algorithms. However, as solubility and partitioning coefficients are determined under test conditions that do not mimic the variable physical and chemical conditions in natural sediments, the results of the calculations involve high uncertainty with respect to release and methylation rates under natural conditions. The limited number of studies available on mercury release rates from natural sediments indicate significantly higher release rates than the calculated estimates based on partitioning coefficients. Release rates of total Hg can be calculated based on sediment concentrations and literature data on partitioning. However, to calculate realistic release rates of inorganic mercury from, for instance, contaminated sediments, local partitioning coefficients need to be established for the natural sediments.

In addition, rather than total mercury, methylmercury is the primary toxic Hg species, and the methylation process, rates of formation and bioaccumulation at low trophic levels are generally not well known, and particularly data from Arctic environments are scarce.

Therefore, based on the review conclusions, the following recommendations are made:

- Due to the high concern regarding mercury in the Arctic environment, in particular the high mercury concentrations in marine mammals such as narwhals and seals, mercury emissions from industry in the Arctic should be minimised by strict regulation in order to protect the environment in accordance with the Minamata convention (2017).
- Barite, figuring on the list of offshore chemicals assessed as PLONOR (Pose Little Or NO Risk to the environment) by OSPAR (Oslo-Paris Convention for the Protection of the Marine Environment of the North-East Atlantic), should be amended with restrictions on the content of mercury impurities. This will be in accordance with OSPAR's recommendations regarding BAT (Best Available Technique) and BEP (Best Environmental Practice).

9. References

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BARITE-BOUND MERCURY IN MARINE SEDIMENTS; POTENTIAL RELEASE AND BIOAVAILABILITY UNDER ARCTIC CONDITIONS

Literature review

Comprehensive Arctic monitoring programmes have found that mercury is of high concern regarding bioaccumulation and biomagnification in Arctic food webs, and the health of marine mammals and humans in the Arctic. This review evaluates the potential rate of release and methylation of mercury entering the environment from oil exploration activities. Our review indicates that there is a lack of data on the rates of mercury methylation in Arctic sediments and we assess that the traditional methods for estimating solubility and partitioning coefficients, sediment porosity, diffusion coefficients and complex algorithms are insufficient and subject to uncertainty. Hence, realistic rates need to be established for the natural Arctic sediments considering their specific physical and chemical properties.

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