Marine Pollution Bulletin 204 (2024) 116518

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Mercury fingerprint: A comparative evaluation of lability in North Sea drill cuttings

Christoph Gade [a,b,*], Rebecca von Hellfeld [a,b], Lenka Mbadugha [b], Graeme Paton [b]

[a] National Decommissioning Centre, University of Aberdeen, Aberdeen, Scotland, UK
[b] School of Biological Sciences, University of Aberdeen, Cruickshank Building, St. Machar Drive, Aberdeen AB24 3UU, Scotland, UK

ARTICLE INFO

Keywords:
Thermofractionation
Diffusive gradient in thin-films
Offshore
Decommissioning
Legacy contamination

ABSTRACT

Quantifying impacts on marine ecosystems remains pivotal in estimating risks associated with offshore industry practices. Cuttings piles, formed during drilling operations, are commonly abandoned in situ, and left to attenuate on the seabed. In the present work, the presence and lability of mercury in samples obtained from drill cuttings piles of two decommissioned North Sea oil platforms (bp Miller and bp North West Hutton) and the surrounding sediment were investigated. Maximum concentrations of total mercury were measured at 0.23 and 0.37 µg/g dry weight (dw) for bp Miller and bp North West Hutton, respectively. Background concentrations of 3.6 and 8.3 ng/g dw were measured at reference sites at 3200 metre distance. Thermofractionation and DGT-analysis of the samples to assess the effective environmental impact of the measured mercury suggests that although total mercury concentrations are increased in the proximity of the cuttings pile, the effective environmental impact may be limited.

1. Introduction

More than two thousand North Sea oil wells are projected to be decommissioned within the next decade, necessitating environmental impact assessments for offshore assets (OEUK, 2022). Regulation 98/3 of the Convention for the Protection of the Marine Environment of the North-East Atlantic (also known as the Oslo Paris Convention, OSPAR) states that 'the dumping, and the leaving wholly or partly in place, of disused offshore installations within the maritime area is prohibited', which entails a full removal of topside structures and partial removal of submerged structures (OSPAR, 1998). Exempt from this legislation is the handling of drill cuttings piles that form during the initial well drilling, which are a mixture of rock, drilling fluids, and diverse reagents such as biocides and lubricants. These cuttings piles contain substantial quantities of barium sulphate (barite) and hydrocarbons, due to the additional use of drilling fluids (also termed 'drilling mud') used as a lubricant to protect drilling equipment and move crushed bedrock. Drilling muds either use heavy oils (oil based mud, OBM), synthetic hydrocarbon mixtures (synthetic based mud, SBM), or salt brine as lubricants (water based mud, WBM), depending on the geological parameters of the reservoir (e.g., depth). Although the potential risk associated with drill cuttings piles underneath offshore platforms in the North Sea has been assessed (Breuer et al., 2004; Candler et al., 1992; Grant and Briggs, 2002; Henry et al., 2017), the scientific understanding of the exact footprint and post depositional reactivity of cuttings piles is still fragmentary.

The bp Miller (BPM) and bp North West Hutton (NWH) oilfields were originally discovered in the 1970s in the UK sector of the North Sea, with drilling operations discharging OBM, SBM, and WBM cuttings in the 1980s and 90s (BP, 2005; BP Exploration, 2011). During the drilling operations of bp North West Hutton, approximately 52,000 t of drill cuttings were discharged to the environment including over 51,000 m^3 of drilling mud (Marsh, 2003).

Barite ore deposits are frequently contaminated with mercury sulphide inclusions, the concentration of which is dependent on regional and geological parameters (Candler et al., 1992; Neff, 2008). Consequently, drill cuttings piles can contain elevated concentrations of mercury, which poses a potential environmental hazard (Mikos-Szymańska et al., 2018). Sediment sequestered and insoluble mercury compounds are available for benthic microorganisms, some of which metabolise mercury by methylation under anoxic conditions (Zhang et al., 2014). The resultant methylmercury bioaccumulates and biomagnifies through the food web, leading to elevated concentrations in top marine predators and, ultimately, humans (Kimáková et al., 2018).

---

* Corresponding author at: School of Biological Sciences, University of Aberdeen, Cruickshank Building, St. Machar Drive, Aberdeen AB24 3UU, Scotland, UK.
E-mail address: c.gade.20@abdn.ac.uk (C. Gade).

https://doi.org/10.1016/j.marpolbul.2024.116518
Received 8 May 2024; Received in revised form 21 May 2024; Accepted 21 May 2024
Available online 23 May 2024
0025-326X/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

Mercury analysis remains challenging due to the difficulties arising from the combination of complex matrices and low natural concentrations (Hong et al., 2011). Bespoke mercury analysers, originally devised by Wittmann (1981), operate on the principle of thermal decomposition amalgamation atomic absorption spectrophotometry (TDA-AAS), which enables a sensitive and matrix independent mercury analysis. TDA-AAS is regarded as a 'green chemistry' method, as it does not require reagent consuming sample preparation and works with a small mass of sample material. A recent development for TDA-AAS systems is thermofractionation, allowing for a qualitative mercury fraction analysis in environmental samples (Bełdowska et al., 2018; Jędruch et al., 2018; Korejwo et al., 2020; Reis et al., 2012; Saniewska and Bełdowska, 2017). The identification of fractions with similar physicochemical properties, such as e.g. halides and chalcogenides, enables a qualitative assessment of a sample's environmental reactivity. Despite the limited number of studies conducted on this approach and the absence of a unanimous agreement on its protocol, it possesses the potential to emerge as an innovative tool for assessing the risk of environmental mercury (Reis et al., 2015).

Current environmental monitoring approaches increasingly consider the use of passive samplers to not only assess total concentrations but also their lability and potential bioavailability. For aquatic systems, diffuse gradient in thin films (DGTs) devices are popular due to their facile deployment and high versatility (Davison and Zhang, 2012, 1994). The steady accumulation of labile analytes enables a calculation of environmental concentrations and fluxes (Bretier et al., 2020). Sediment disturbance is recognised as a risk factor with the potential to mobilise cuttings pile-associated pollutants into the water column (OSPAR, 2019), affirming the use of DGTs in offshore industrial monitoring (DNV, 2013).

The study aims to comparatively examine the extent of anthropogenic mercury contamination of the seabed near these decommissioned offshore installations. Sediment core samples were collected around two offshore cuttings piles near the BPM and NWH platforms during an offshore expedition in October 2022, and their total mercury concentration was measured. Additionally, the environmental fate of the pile-associated mercury was evaluated using DGT passive samplers and a novel five-step thermofractionation method (Jędruch et al., 2018).

2. Materials and methods

2.1. Sampling

Sediment core samples (diameter: 10 cm; length: >15 cm) were collected during an offshore survey onboard the MRV Scotia (operated by the Scottish Marine Directorate) using a multicorer (Ocean Scientific International Ltd., UK). At BPM, two physical replicates were sampled in both north and south transects at distances of 50, 100, 200, 400, 800, and 1600 metres (m) from the cuttings pile with a single reference site at 3200 m distance to the north. At NWH the sampling strategy had to be adapted due to weather constraints. Samples were taken at 170, 230, 320, 500, 900, and 1700 m distance in the northern transect with a reference site at 3200 m. The southern transect was angled at −120° with fewer sampling points (100, 300, 700, 1500 m). Platform locations and sampling transects are presented in Fig. 1.

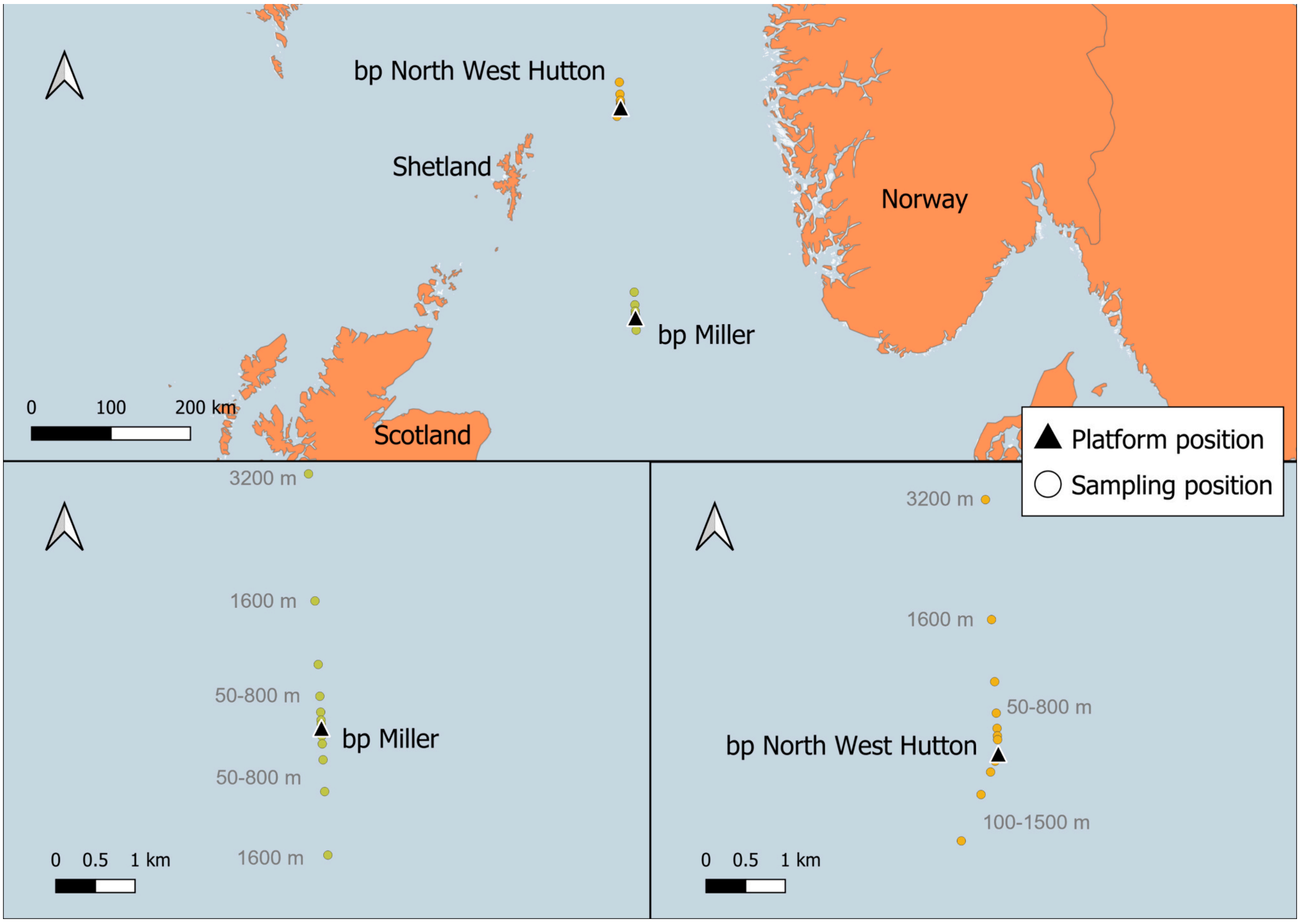

Fig. 1. Location of (top) and spatial distribution of the sampling points at the respective sites (bottom). Samples were taken at 50–1600 m distance with a single reference site 3200 m north from the former location of BPM. At NWH samples were taken at 170–1700 m distance in the northern transect with a reference site at 3200 m. The southern transect was angled at −120° with fewer sampling points at 100–1500 m distance. Coordinates of the platforms are Longitude (long) 1.307467 Latitude (lat) 61.10605 for NWH and long 1.400083295 lat 58.72173338 for BPM. Coordinates were cross referenced with Martins (2023).

Further operator-provided information on the cuttings piles can be found in Table 1. Cores of the top 15 cm of sediment/cuttings were subsampled every 5 cm and stored in separate polyethylene bags and 100 ml aluminium screw top jars at −20 °C until further processing. Once on shore, the samples were slowly thawed at 4 °C for 24 hours (h) and homogenised prior to analysis. This procedure was considered not to negatively impact subsequent analysis (Boer and Smedes, 1997). To convert wet-weight-concentrations into dry-weight-concentrations, ~1 g subsamples were dried in ceramic crucibles at 100 °C for 24 h.

2.2. *Total mercury analysis*

Approximately 250 ± 20 mg of wet sample material were weighed into nickel sample boats and measured directly for total mercury using a DMA-80*evo* direct mercury analyser (Milestone, Italy), herein referred to as DMA. The DMA operates on the principle of thermal decomposition gold amalgamation atomic absorption spectrophotometry (TDA-AAS) with a limit of detection of 0.001 ng. All analyses were conducted on this instrument. A certified reference material (estuarine sediment, ERM-CC580) was run every 12 samples to assess overall recovery and performance over time. Average sample mass was 1.3 mg, blank value was 0.03 ng, recovery was 93.32 ± 10.86 %, and relative standard deviation (RSD) was 8.82 %.

2.3. *DGT analysis*

Piston type DGT samplers were obtained from DGT Research Ltd. (Lancaster, UK). Probes consist of a polyethersulphone filter membrane, 0.8 mm agarose diffusive gel, and a 3-mercaptopropyl functionalised silica gel binding layer with an exposure window of 3.14 cm^2. To measure labile mercury in undisturbed porewater at the sediment-water interface, DGTs probes were inserted into the topmost core subsample (0–5 cm depth) and incubated in a cold room for one week. The temperature during exposure was 5.3 ± 0.18 °C, monitored hourly using a TinyTag Plus data logger (Gemini data loggers Ltd., UK). On removal, deionised water was used to rinse off any sediment traces that remained on the DGT surface. After opening the DGTs, the resin binding phase was extracted and transferred into a nickel sample boat and directly analysed for total mercury. DGT blanks and CRMs were analysed every 10 samples.

To measure labile mercury in perturbed sediment, 50.00 g of wet sediment and 50.00 g artificial seawater, prepared according to Cold Spring Harbor Protocols (2012), were added into a 100 ml glass Erlenmeyer flask to produce a slurry. Artificial seawater was adjusted to pH 8.1 and left to cool to incubator temperatures for 24 h before use. The DGT probes were placed on top of the 250 ml Erlenmeyer flasks, effectively capping them. Then, the flasks capped with DGT probes were sealed with parafilm before being placed upside down in a 250 ml polypropylene beaker (Fig. 2). The flasks were incubated in a cooled shaking incubator and left to accumulate for 1 week at 5.3 ± 0.6 °C and 130 rpm before being retrieved. After removal of the DGTs, beakers were left for 1 h to let the slurry settle before sampling 1 ml of supernatant water into 2 ml microcentrifuge tubes. To reduce the impact of suspended solids on total mercury analysis, supernatant samples were centrifuged at 14.3 G for 60 s. DGT binding resins and supernatant were analysed for total mercury. Blank value was 0.08 ng, recovery was 100.56 ± 13.43 %, and relative standard deviation (RSD) was 10.12 %.

Table 1
General description of BPM and NWH cuttings piles.

Platform	BPM	NWH
Time of discharge	1989–1996	1982–1992
Pile area [m^2]	9488	23,750
Max pile height [m]	6	5.5
Density of pile [t/m^3]	1.839	1.67
Volume of pile [m^3]	9535	30,000
Pile water content [%]	38.6	45

Data taken from the decommissioning reports (BP, 2005; BP Exploration, 2011).

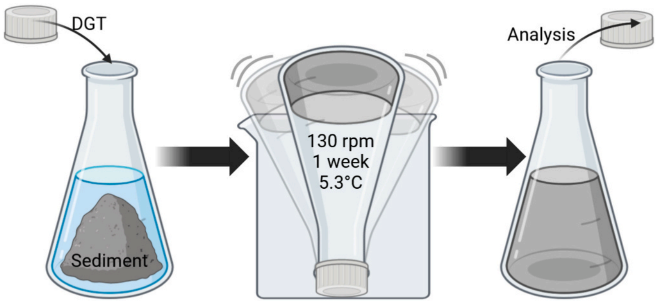

Fig. 2. Experimental setup to measure labile mercury in perturbed sediment using piston-type DGT probes.

2.4. *Benthic efflux assessments*

In the context of this manuscript the term 'efflux' refers to the flux of labile mercury from the pore water to the binding phase of the DGT device and serves as a proxy for bioavailability. To ascertain the possible matrix impact of the sediment slurry on mercury uptake in the sediment disturbance experiment, an additional uptake experiment in pure artificial seawater was conducted, allowing the comparison of the derived values. The diffusion coefficient was determined at 5.3 °C in duplicate to match the exposure conditions. Using the procedure described earlier, beakers containing 50 ml of artificial seawater with a concentration of 600 ng/l were capped with a DGT probe and placed in a refrigerated shaking incubator at a speed of 130 rpm. After 2, 4, and 6 h, the beakers were taken out and the binding resins were promptly analysed for total mercury. Two blanks deployed for 2 and 6 h were analysed concurrently. The resulting data were used to calculate the effective diffusion coefficient. Time averaged sediment mercury effluxes [ng cm^{-2} day^{-1}] were calculated through:

$$F = \mathrm{M}t{*}A \tag{1}$$

where A is the area of exposed gel [cm^2], M is the mass of mercury accumulated in the binding phase [ng], and t is the exposure time [day].

2.5. *Thermofractionation*

Mercury fractionation was performed by sequential thermodesorption on the DMA-80*evo*. The fractionation process followed a 5-step method, wherein each sample underwent heating at five distinct temperature ranges ranging from 150 °C to 750 °C. The first fraction (fraction 1), labelled "HgLAB 1a, " desorbs at 150 °C and comprises labile mercury halides. The second fraction (fraction 2), referred to as "HgLAB 1b, " desorbs at 230 °C and consists of strong mercury complexes with both organic and inorganic ligands, as well as methylmercury. The third fraction (fraction 3), labelled as "HgS," desorbs at 330 °C and primarily encompasses water-insoluble and highly stabilized mercury sulphide. The fourth fraction (fraction 4) denoted as "HgLAB 2," desorbs at 475 °C and includes additional mineral forms of mercury such as oxides, sulphates, and fluorides. Lastly, the fifth fraction (fraction 5), known as "HgRES," desorbs at 750 °C and comprises mineral inclusions. While the original fraction names given by the method developers (Jędruch et al., 2018) inform the mercury forms found within it, the fractions will be referred as fractions 1 to 5 within this manuscript. Thermofractionation is not speciation analysis but rather a more practical approach to evaluate environmental mercury fractions with distinct physicochemical properties. Furthermore, mercury compounds exhibit fraction overlapping effects due to the thermochemical formation of intermediary mercury compounds (Rumayor et al., 2013). This, along with matrix-caused thermodesorption artifacts (e.g. Reis et al., 2015) adds to the uncertainty associated with the thermofractionation technique. For a more comprehensive understanding of the method and the identified fractions, please refer to Jędruch et al. (2018). Blank value was 0.03 ng, recovery was 85.86 ± 8.97 %, and relative standard deviation (RSD) was 7.91 %.

2.6. Statistics and data visualisation

All data were processed using MS Excel® (Microsoft, USA) and visualised using SigmaPlot (v. 15.0, Systat Software Inc. USA). Maps were generated using QGIS (v. 3.3, Open Source Geospatial Foundation Project).

2.7. Assumptions and limitations

To place the findings of the work presented here in context, scientific publications are cited where possible. However, due to the nature of this research, commissioned reports and industry communications had to be included where no peer-reviewed scientific articles could be obtained. We acknowledge that data and claims derived from these sources do not conform to the standards of peer-reviewed scientific publishing but provides the context necessary for the present work. Their use in the context of this manuscript is chosen carefully and mainly serves the purpose of appraising the observations and empirically derived data in this study.

3. Results

3.1. Extent of cuttings piles

As drilling operations ceased at BPM in 1996, a new layer of sediment (2–5 cm) has settled on the dark hydrocarbons of the cuttings pile (Fig. 3). Overall sediment texture was sandy with increasingly gelatinous, visco-elastic texture and strong diesel odor with decreasing distance. Sediment cores collected at NWH were similar in appearance (images not available). The physical extent of the BPM and NWH piles was qualitatively confirmed from the sediment cores sampled at varying distances. Sediment drying revealed a change in the cumulative fraction of substances evaporating at 100 °C, with reference sites at 3200 m distance typically losing 22.8 ± 3.9 % and cuttings pile samples (50 m) losing up to 40 % weight (average 31.9 ± 3.8 %). However, it was not possible to ascertain whether observed weight losses were purely caused by water or the evaporation of light hydrocarbons.

3.2. Total mercury concentrations

Background concentrations of total mercury measured at the control sites average 3.3 ± 1.2 and 7.1 ± 2.0 ng/g for BPM and NWH. Significantly elevated mercury concentrations compared to the reference sites were measured as far as 200 and > 700 m away from BPM and NWH (Fig. 4). Maximum average concentrations of total mercury were 0.23 and 0.37 μg/g at 50 m distance for BPM and NWH respectively. In the case of BPM, average concentrations consistently decrease with depth and reduced by up to 45 % at 10–15 cm depth and 50 m distance. For NWH this trend is less pronounced, although total concentration is reduced by up to 90 % at 10–15 cm depth and 150 m distance. Data variability was highest at 50 m distance for both sites at maximum 32.9 and 14.1 % relative standard deviation for BPM and NWH respectively. Coefficients of variation increased with sediment core depth and distance to platform up to 200 m for both sites.

3.2.1. DGT efflux assessment

The empirically derived diffusion coefficient was determined to be 4.21 ± 0.38 10^{-8} cm^2s^{-1} in artificial seawater at 5.3 °C. Analysing the sediment slurry supernatant concentration produced a matrix matched diffusion coefficient of 4.89 10^{-8} cm^2s^{-1} at 5.4 °C. At both sites, the background benthic efflux was similar at ~0.03 and 0.045 ng cm^{-2} day^{-1} for BPM and NWH, respectively. Overall, DGT-derived benthic effluxes decreased significantly at 800 m and for both sites (Fig. 5). This trend was observed in both static and slurry exposure, although efflux rates were notably increased in the slurry, indicating a higher resupply flux. Benthic efflux rates at 50 m distance were 0.004 and 0.003 ng cm^{-2} day^{-1} for BPM and NWH, respectively. Maximum efflux rates (0.03 and 0.08 ng cm^{-2} day^{-1}) were observed at 1600 and 400 m distance for BPM and NWH, respectively.

3.3. Mercury thermofractionation

Background fractionation was congruent at both reference sites and changes dramatically with proximity to the platform (Fig. 6). While Fraction 1, 2, and 4 decrease significantly, Fraction 5 increases up to almost sevenfold. The change in fractionation is very local and is ameliorated after about 800 m for both platforms. The thermofractionation profiles derived from lower depth samples (5–10 cm and 10–15 cm) mirror the profiles of the top sediment core samples (data not shown).

Fig. 3. Sediment core samples from BPM taken at 3200 m (left), 400 m (middle), and 100 m (right). A distinct layer of emerging black hydrocarbon contamination as well as newly deposited sediment can be seen in cores taken at proximity (400 m and 100 m).

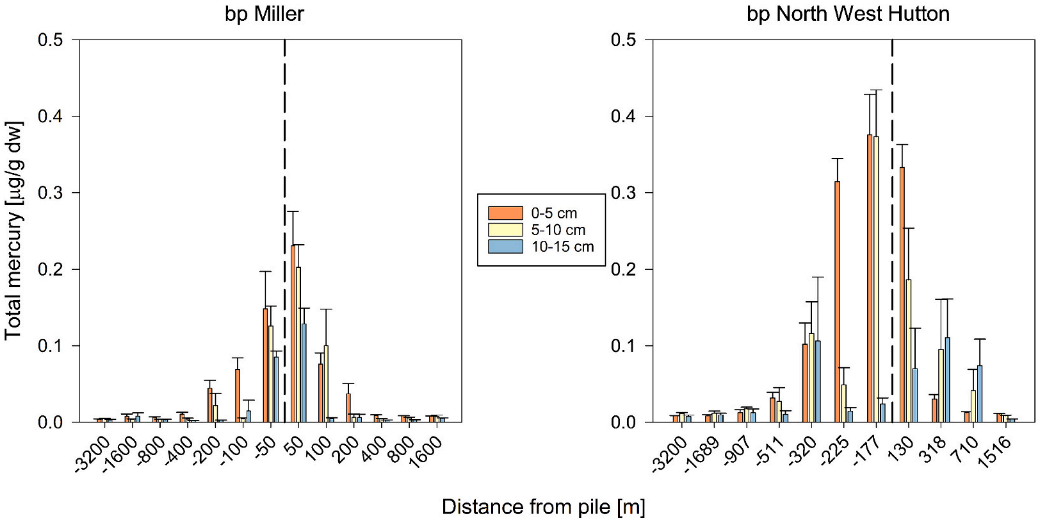

Fig. 4. Total mercury concentration [µg/g, dw] of sediments around the BPM and NWH cuttings piles. Core samples were taken in a north-south transect (left to right) and were sliced in 5 cm increments from the top. Bars show the mean of triplicates, whiskers denote the standard deviation. The location of the former platforms is indicated by the vertical dashed black line.

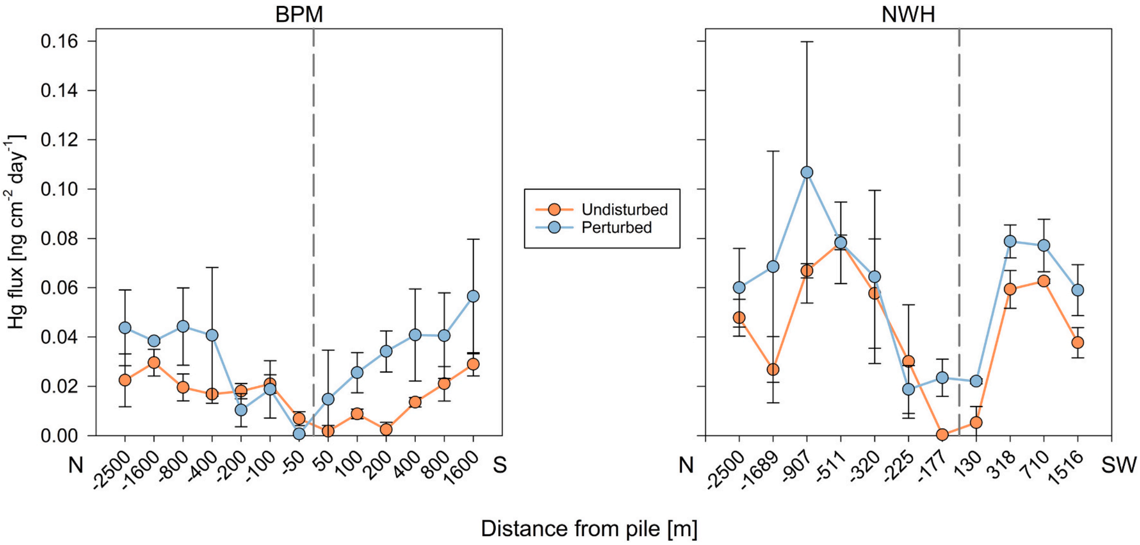

Fig. 5. Benthic efflux rates [ng mercury cm^{-2} day^{-1}] from undisturbed and perturbed sediment around offshore platforms BPM and NWH measured by DGTs at the sediment/water interface. Core samples were taken in a north-south transect (left to right). Bars show the mean of duplicates, whiskers denote the standard deviation. The location of the former platforms is indicated by the vertical dashed grey line.

4. Discussion

4.1. Mercury concentrations and lability

The impact of offshore oil and gas assets on the surrounding seabed has long been studied, with elevated mercury concentrations (up to 0.42 µg/g) being reported near assets all over the world (Henry et al., 2017; Sompongchaiyakul et al., 2018; Trefry et al., 2003). The maximum average concentrations measured here (0.23 and 0.37 µg/g; BPM and NWH) in the respective piles are consistent with previously reported values for other North Sea cuttings piles and surpass the Estimated Acceptable Concentrations (EAC) set by OSPAR (Table 2). However, in the case of NWH, the extent of mercury contamination far exceeds the previously reported radius of 200 m from the pile (OSPAR, 2019). Since mercury is only a trace contaminant in the overall high pile-associated metal burden, other elements including chromium, copper, and cadmium may also contaminate a wider area than previously assumed. Still, in comparison with other North Sea drill cuttings piles (see Table 2), the sites studied here show a lower mercury contamination (Sheahan et al., 2001). The gravimetrically determined average water content in sediments sampled within a 50 m radius from the pile (~27–40 %) is slightly below the values stated in the decommissioning reports (38–45 %), which may be due to a difference in methodology (BP, 2005; BP Exploration, 2011). Although the background concentrations measured in this study are lower than the previously reported values for the North Sea (see Table 2), it is important to note that sediment heavy metal concentrations in the North Sea exhibit spatiotemporal variability (Larsen and Hjermann, 2023).

The decrease of total metal concentrations opposing increasing porewater sulphide concentration with depth is congruent with findings by bp (BP Exploration, 2011), and has previously been reported for cuttings piles by Breuer et al. (2008). They attributed this decrease to a redox process at the oxic-suboxic interface. In this cycle, the depletion of O_2 within the first few millimeters of pile depth results in the reductive

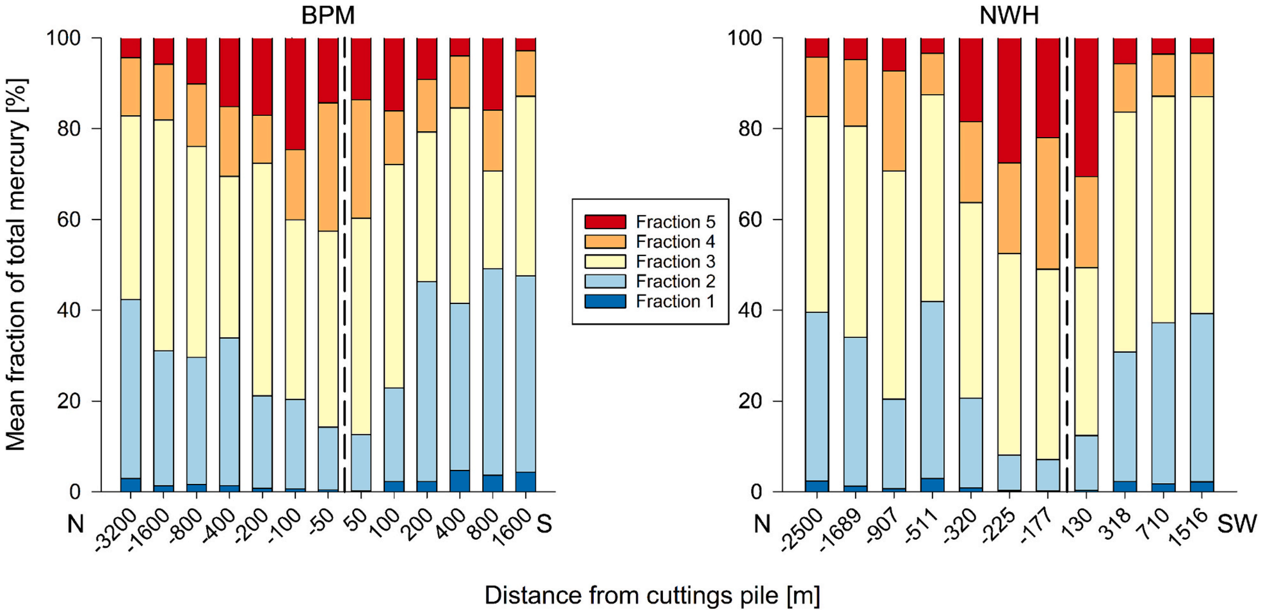

Fig. 6. Mercury thermofractionation profile from the BPM and NWH cuttings piles top sediment layer (0–5 cm). The location of the former platforms is indicated by the vertical black line. Core samples were taken in a north-south transect (left to right). The fractions and their desorption temperatures are as follows: Fraction 1 up to 150 °C, Fraction 2 up to 230 °C, Fraction 3 up to 330 °C, Fraction 4 up to 475 °C, Fraction 5 up to 750 °C.

dissolution of the highly abundant ferric and manganese (oxyhydroxides) (Kujawska and Cel, 2017; Peiffer and Wan, 2016; Versteegh et al., 2021). As a result, other minerals, including barite, may be mobilised into the porewater, leading to a diffusive flux of metals towards the oxic/suboxic front above where they precipitate (Breuer et al., 2008; Versteegh et al., 2021; Zan et al., 2020). The steady removal of solute metals results in a slow enrichment in this top most layer, which could explain the decrease of total mercury concentrations with depth observed in this study and others (XodusGroup, 2019). The long-term effects of this redox-driven mineral weathering remain to be fully understood, yet they have the potential to transform the spatial and chemical composition of cuttings piles.

The use of DGTs to evaluate pile associated metal lability and bioavailability remains to be established, although their deployment is already recommended to monitor environmental impacts during drilling operations (DNV, 2013). Hartley and Watson (1993) and Breuer et al. (2002) conducted comparative studies on the NWH cuttings pile using sequential extraction and in situ DGT deployment to ascertain metal bioavailability. The extraction data mentioned in the Hartley and Watson study could not be found and may never have been published. Similarly, the in situ DGT deployment presented by Breuer et al. failed, thus not producing any data. Here DGT-derived efflux data suggests that, although total concentrations are increased in the direct vicinity of assets, their lability is low.

The diffusion coefficient obtained through empirical means exhibits a significant disparity in magnitude when compared to the diffusion coefficient derived from calculations using the Stokes-Einstein equation as suggested by Zhang and Davison (1995). The main reason for this discrepancy may be that the experiments were conducted in artificial seawater and at low temperature to emulate environmental conditions. The diffusion coefficients of mercury are directly affected by temperature and ionic strength (Gade et al., 2024). Nevertheless, the close agreement between the diffusion coefficients derived from pure water and matrix matched samples (difference of ~11.8 %) confirms the reliability of the benthic efflux data obtained in this study under environmental conditions. Background efflux rates of ~0.05 ng cm^{-2} d^{-1} are in good agreement with previously reported values for comparable marine environments (Bełdowski et al., 2009; Koron and Faganeli, 2012).

The thermofractionation data mirrors the DGT assessment. The dominant fractions in the reference sites are fraction 2 and 3, accounting for 70–80 % of total mercury. This indicates that most of the naturally occurring mercury in marine sediments is either organically sequestered or in mineral form with only negligible amounts of labile or unsequestered species. Close to the cuttings pile, fraction 5 shows a distinct peak most likely related to barite embedded mercury species (Jędruch et al., 2018; Parker and Smith, 2004). At the same time, fraction 3 does not distinctly change, but fractions 1, 2, and 4 decrease significantly. This suggests a decrease in overall mercury lability in the proximity of the cuttings pile. The change in fractionation close to the cuttings pile (increase of fraction 5) is congruent with the assumption that the source of mercury in cuttings pile is mainly the therein contained barite (Denney, 2003).

4.2. State of literature on cuttings pile-associated mercury

Mercury is classified as hazardous to the environment with long-lasting effects, due to its potential to become methylated under environmental conditions. The organic moiety results in a higher bioavailability and toxicity and is considered to be a major factor in environmental risk assessment due to its bioaccumulation potential (von Hellfeld et al., 2023). Apart from accumulating dissolved mercury in porewater, methylating bacteria are known to absorb and methylate particulate mercury species, thus mobilising sequestered fractions and serving as a springboard to enter a wider food web (Zhang et al., 2012). Historically, North Sea assets have been drilled using barite with above average mercury contents (8.1 mg/kg; Hartley et al., 2003). Similar to other OBM cuttings piles, total mercury concentrations in the here studied piles by far exceeded OSPAR EAC levels, thus being technically classified as toxic. Yet, the impact of cuttings pile associated mercury is disputed as mercury impurities in barite exhibit low water and porewater solubility ($LogK_D = 5.3–5.5$; Neff, 2008), thus amounting to a negligible environmental significance (Parker and Smith, 2004). This is further supported by leaching studies, showing that <1 % of total mercury may enter the water column under environmental conditions (Candler et al., 1992; Crecelius et al., 2007). However, Wegeberg and Gustavson (2019) state that, in the case of barite-sourced mercury, $LogK_D$ partitioning coefficients alone were a poor predictor of potential

Table 2
Published total mercury concentrations in North Sea cuttings piles and adjacent sediments. Background and OSPAR benchmark concentrations are highlighted in grey. All concentrations are given on a dry weight basis (dw).

Location/asset	Type	Mercury [µg/g]	Reference
Murchison	Drill Cuttings Pile Core 1	1.73	(BMT Cordah, 2013)
	Drill Cuttings Pile Core 2	3.89	
	Drill Cuttings Pile Core 3	2.86	
	St.4–250 m SE Murchison	2.33	
	Sediments (0–500 m)	0.35 ± 0.01	
	Sediments (750–2000 m)	0.28 ± 0.25	
	Sediments (5000-10,000 m)	0.22 ± 0.21	
Dunlin Alpha	Cuttings Surface	0.08–1.28	(Xodus Group, 2019)
	Cuttings Cores	0.002–1.44	
North Cormorant	Cuttings Pile	0.61–1.57	(OSPAR, 2019)
Heather “A”		1.24	(Environment and Resource Technology Ltd., 1994)
Miller		0.03–2.25	(Genesis, 2016)
Ekoflak 2/4A		0.16	
North West Hutton		0.45	(AURIS, 1993)
Beryl A		0.56	(Hartley et al., 2003)
Maureen A		2.44	
Ekofisk 2/4A		0.24	
Frigg		0.03	
Auk		0.005–0.456	(Repsol Sinopec Resources UK Ltd., 2021)
Fulmar		0.004–0.619	
Eider		0.45–0.89	(TAQA Bratani Ltd., 2023)
Ninian Northern		1.86	(CNR International, 2017)
	Northern and central North Sea	<0.02–0.45	(Breuer et al., 1999)
Benchmark values	Background Concentration	0.05	(OSPAR, 2019)
	Background Assessment Concentration (BAC)	0.07	
	Estimated Acceptable Concentration (EAC)	0.22	
	Effect Range Low[a]	0.15	

[a] The ERL indicates the concentration below which toxic effects are scarcely observed or predicted.

environmental release as microbial methylation may have a significant impact on mobilisation. A similar view is endorsed by the UKOOA Drill cuttings initiative report that advocated caution when linking chemical extractability to bioavailability (UKOOA, 2002).

Bioaccumulation studies on barite sourced mercury continue to be underrepresented in comparison to other cuttings pile associated heavy metals (e.g., cadmium, chromium, copper, lead, zinc) as noted by the EPA (1984). To date only two studies with contradicting results on the bioaccumulation of barite sourced mercury exist. Schaanning et al. (2002) measured a significant uptake by polychaetes while Denney (2003) could not establish a relevant direct tissue uptake by macrofauna despite barite particle ingestion. Sheahan et al. (2001) reported an increased bioavailability of total mercury in North Sea cuttings piles in the direct vicinity of piles (0–500 m; 40 %) in comparison with reference sites (>5000 m; 25 %). Similarly, Henry et al. (2017) reported a profound impact of mercury on the benthos at a distance of 895 m. Contrastingly, Crecelius et al. (2007) measured a dose-dependent increase in methylmercury concentrations in barite spiked sediments (~60 %), however the authors state that barite sourced mercury was not available for methylation. Similar conclusion were drawn by Trefry et al. (2003), who measured total mercury and porewater methylmercury concentrations near assets in the Gulf of Mexico. Although elevated methylmercury porewater concentrations were measured, no sediment to seawater diffusion was quantified. Methylmercury levels are determined by a balance between the benthic efflux and the redox dependent formation thus demanding a flux assessments (Tang et al., 2020).

In their comparative assessment on the systemic impacts of cuttings piles on the marine environment, Hartley et al. (2003) concluded that ‘on the basis of existing data there is no evidence that cuttings piles have significant effects on the wider food chain or present a risk to human health’. In contrast, Wegeberg and Gustavson (2019) recommend the reclassification of barite ‘according to its concentration of mercury impurities’, thus challenging its status as an offshore chemical which poses little or no risk (PLONOR) (OSPAR, 2021).

5. Conclusion

With the increasing decommissioning activities in the North Sea, environmental risk assessments may benefit from updating as current practices of determining total, rather than available, concentrations during required benthic surveys are called into question. The use of passive samplers, like DGTs, may aid in more accurately determining environmentally relevant benthic effluxes, as is already practice for hydrocarbons. The here reported concentrations attest a local anthropogenic enrichment of mercury in cuttings piles however, data derived from passive samplers and a novel thermofractionation analysis suggest a low environmental lability. Although the presented results highlight the high degree of sequestration of pile associated mercury, the risk of potentially increased environmental contamination due to mineral weathering should not be underestimated and remains to be fully addressed. The main ecological impacts of cuttings piles is thought to be the hydrocarbon contamination, which accounts for the majority of adverse effects observed in the underlying and surrounding benthos. However, currently published research is contradictory in its evaluation of the release and subsequent bioaccumulation of legacy contaminants from barite, including mercury. Future risk assessment would benefit from improved approaches to evaluate the environmental fate of all drill cuttings constituents.

Funding

CG is funded by Chevron through its Anchor Partnership with the UK National Decommissioning Centre. We also acknowledge funding and in-kind support from the Net Zero Technology Centre and the University of Aberdeen through their partnership with the UK National Decommissioning Centre.

CRediT authorship contribution statement

Christoph Gade: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Rebecca von Hellfeld:** Writing – review & editing, Investigation. **Lenka Mbadugha:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition. **Graeme Paton:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

Data availability

Data will be made available on request.

Acknowledgements

We would like to thank the Scottish Marine Directorate and Daniel Stewart for the opportunity to join cruise 1422S. Sampling and general support was provided by chief scientist Robert Watret, and scientists Danny Copland, Paul Stainer, and Jack Lucas, as well as the captain and the entire crew of the MRV Scotia.

References

AURIS, 1993. Environmental Survey of the Beatrice Field Block 11/ 30.

Bełdowska, M., Saniewska, D., Gębka, K., Kwasigroch, U., Korejwo, E., Kobos, J., 2018. Simple screening technique for determination of adsorbed and absorbed mercury in particulate matter in atmospheric and aquatic environment. Talanta 182, 340–347. https://doi.org/10.1016/j.talanta.2018.01.082.

Bełdowski, J., Miotk, M., Pempkowiak, J., 2009. Mercury fluxes through the sediment water interface and bioavailability of mercury in southern Baltic Sea sediments. Oceanologia 51, 263–285. https://doi.org/10.5697/oc.51-2.263.

Boer, J. De, Smedes, F., 1997. Effects of storage conditions of biological materials on the contents of organochlorine compounds and mercury. Mar. Pollut. Bull. 35, 93–108. https://doi.org/10.1016/S0025-326X(97)00198-7.

BP, 2005. North West Hutton Decommissioning Programme.

BP Exploration, 2011. Miller Decommissioning Programme MLR-A-D0-PM-PRO-00217.

Bretier, M., Dabrin, A., Billon, G., Mathon, B., Miège, C., Coquery, M., 2020. To what extent can the biogeochemical cycling of mercury modulate the measurement of dissolved mercury in surface freshwaters by passive sampling? Chemosphere 248, 126006. https://doi.org/10.1016/j.chemosphere.2020.126006.

Breuer, E., Howe, J.A., Shimmield, G.B., Cummings, D., Carroll, J., 1999. Contaminant Leaching from Drill Cuttings Piles of the Northern and Central North Sea: A Review.

Breuer, E., Peppe, O.C., Shimmield, G.B., 2002. A Novel Approach for the Study of North Sea Drill Cuttings Accumulations: The Combined Use of an ROV and Benthic Lander for <I>In situ</I> Measurements. Underw. Technol. 25, 77–82. doi:https://doi.org/10.3723/175605402783219190.

Breuer, E., Stevenson, A.G., Howe, J.A., Carroll, J., Shimmield, G.B., 2004. Drill cutting accumulations in the Northern and Central North Sea: a review of environmental interactions and chemical fate. Mar. Pollut. Bull. 48, 12–25. https://doi.org/10.1016/j.marpolbul.2003.08.009.

Breuer, E., Shimmield, G., Peppe, O., 2008. Assessment of metal concentrations found within a North Sea drill cuttings pile. Mar. Pollut. Bull. 56, 1310–1322. https://doi.org/10.1016/j.marpolbul.2008.04.010.

Candler, J.E., Leuterman, A.J.J., Wong, S.-Y.L., Stephens, M.P., 1992. Sources of mercury and cadmium in offshore drilling discharges. SPE Drill. Eng. 7, 279–283. https://doi.org/10.2118/20462-PA.

CNR International, 2017. Ninian Northern Platform Late Life & Decommissioning Project.

Cold Spring Harbor Protocols, 2012. Artificial Seawater. Cold Spring Harb Protoc 2012, pdb.rec068270. doi:https://doi.org/10.1101/pdb.rec068270.

Cordah, B.M.T., 2013. Environmental Assessment of Options for the Management of the Murchison Drill Cuttings Pile.

Crecelius, E., Trefry, J., Mckinley, J., 2007. Study of Barite Solubility and the Release of Trace Components to the Marine Environment Study of Barite Solubility and the Release of Trace Components to the Marine Environment.

Davison, W., Zhang, H., 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. Nature 367, 546–548. https://doi.org/10.1038/367546a0.

Davison, W., Zhang, H., 2012. Progress in understanding the use of diffusive gradients in thin films (DGT) – back to basics. Environ. Chem. 9, 1. https://doi.org/10.1071/EN11084.

Denney, D., 2003. Fate of mercury in drilling-fluid barite in the marine environment. J. Petrol. Tech. 55, 66–67. https://doi.org/10.2118/0703-0066-JPT.

DNV, 2013. Guideline: Monitoring of Drilling Activities in Areas With Presence of Cold Water Corals. Norwegian Oil and Gas Association (27 pp.).

Environment & Resource Technology Ltd, 1994. Predication of the Profile and Long Term Fate of the Cuttings Pile at Heather “A”. Environmental Report.

EPA, 1984. Regulating Cadmium and Mercury in Drilling Fluid Discharges.

Gade, C., Mbadugha, L., Paton, G., 2024. Use of diffusive gradient in thin-films (DGTs) to advance environmental mercury research: development, growth, and tomorrow. Trends in Environmental Analytical Chemistry e00230. doi:https://doi.org/10.1016/j.teac.2024.e00230.

Genesis, 2016. OSPAR OIC Characterisation of cutting piles (Report J73971A-Y-TN-24000).

Grant, A., Briggs, A.D., 2002. Toxicity of sediments from around a North Sea oil platform: are metals or hydrocarbons responsible for ecological impacts? Mar. Environ. Res. 53, 95–116. https://doi.org/10.1016/S0141-1136(01)00114-3.

Hartley, J., Trueman, R., Anderson, S., Neff, J., Fucik, K., Dando, P., 2003. Drill cuttings initiative: Food chain effects literature review. https://doi.org/10.13140/RG.2.1.2450.7766.

Hartley, J.P., Watson, T.N., 1993. Investigation of a North Sea Oil Platform Drill Cuttings Pile. All Days. OTC, in, pp. 749–752. https://doi.org/10.4043/7341-MS.

Henry, L., Harries, D., Kingston, P., Roberts, J.M., 2017. Historic scale and persistence of drill cuttings impacts on North Sea benthos. Mar. Environ. Res. 129, 219–228. https://doi.org/10.1016/j.marenvres.2017.05.008.

Hong, Y.S., Rifkin, E., Bouwer, E.J., 2011. Combination of diffusive gradient in a thin film probe and IC-ICP-MS for the simultaneous determination of CH 3 hg + and hg 2 + in Oxic water. Environ. Sci. Technol. 45, 6429–6436. https://doi.org/10.1021/es200398d.

Jędruch, A., Bełdowska, M., Kwasigroch, U., Normant-Saremba, M., Saniewska, D., 2018. Mercury fractionation in marine macrofauna using thermodesorption technique: method and its application. Talanta 189, 534–542. https://doi.org/10.1016/j.talanta.2018.07.047.

Kimáková, T., Kuzmová, L., Nevolná, Z., Bencko, V., 2018. Fish and fish products as risk factors of mercury exposure. Ann. Agric. Environ. Med. 25, 488–493. https://doi.org/10.26444/aaem/84934.

Korejwo, E., Saniewska, D., Bełdowska, M., 2020. Fractionation of mercury in aerosols of the southern Baltic coastal zone. Atmos. Environ. 235, 117623 https://doi.org/10.1016/j.atmosenv.2020.117623.

Koron, N., Faganeli, J., 2012. Benthic fluxes of mercury during redox changes in pristine coastal marine sediments from the Gulf of Trieste (northern Adriatic Sea). J. Soil. Sediment. 12, 1604–1614. https://doi.org/10.1007/s11368-012-0602-1.

Kujawska, J., Cel, W., 2017. Mobility of metals from Drill cuttings. Int J Waste Resour 07. https://doi.org/10.4172/2252-5211.1000285.

Larsen, M., Hjermann, D., 2023. Status and Trend for Heavy Metals (Mercury, Cadmium and Lead) in Fish (Shellfish and Sediment).

Marsh, R., 2003. A database of archived drilling records of the drill cuttings piles at the north west Hutton oil platform. Mar. Pollut. Bull. 46, 587–593. https://doi.org/10.1016/S0025-326X(03)00041-9.

Martins, M.C.I., 2023. Offshore energy structures in the North Sea: past, present and future-march 2023 (dataset). Doi:10.17630/338d5ba4-5e09-443f-9c08-013d24050c81.

Mikos-Szymańska, M., Rusek, P., Borowik, K., Rolewicz, M., Bogusz, P., Gluzińska, J., 2018. Characterization of drilling waste from shale gas exploration in central and eastern Poland. Environ. Sci. Pollut. Res. 25, 35990–36001. https://doi.org/10.1007/s11356-018-2365-8.

Neff, J.M., 2008. Estimation of bioavailability of metals from drilling mud barite. Integr. Environ. Assess. Manag. 4, 184–193. https://doi.org/10.1897/IEAM_2007-037.1.

OEUK, 2022. Decommissioning Insight (Aberdeen).

OSPAR, 1998. Ministerial Meeting of the OSPAR Commission. Sintra, Portugal.

OSPAR, 2019. Assessment of the Disturbance of Drill Cuttings during Decommissioning (London).

OSPAR, 2021. OSPAR Agreement 2013–06: List of Substances Used and Discharged Offshore which Are Considered to Pose Little or no Risk to the Environment (PLONOR) (Gothenburg).

Parker, M.E., Smith, J.P., 2004. Environmental significance of mercury in drilling discharges, in: proceedings of SPE international conference on health, safety, and environment in oil and gas Exploration and production. Society of Petroleum Engineers. https://doi.org/10.2523/86697-MS.

Peiffer, S., Wan, M., 2016. Reductive Dissolution and Reactivity of Ferric (Hydr)Oxides: New Insights and Implications for Environmental Redox Processes. Iron Oxides. Wiley, in, pp. 31–52. https://doi.org/10.1002/9783527691395.ch3.

Reis, A.T., Coelho, J.P., Rodrigues, S.M., Rocha, R., Davidson, C.M., Duarte, A.C., Pereira, E., 2012. Development and validation of a simple thermo-desorption technique for mercury speciation in soils and sediments. Talanta 99, 363–368. https://doi.org/10.1016/j.talanta.2012.05.065.

Reis, A.T., Coelho, J.P., Rucandio, I., Davidson, C.M., Duarte, A.C., Pereira, E., 2015. Thermo-desorption: a valid tool for mercury speciation in soils and sediments? Geoderma 237–238, 98–104. https://doi.org/10.1016/j.geoderma.2014.08.019.

Repsol Sinopec Resources UK Ltd, 2021. Auk. Fulmar & Auk North Area Decommissioning Environmental Appraisal Report, Aberdeen.

Rumayor, M., Diaz-Somoano, M., Lopez-Anton, M.A., Martinez-Tarazona, M.R., 2013. Mercury compounds characterization by thermal desorption. Talanta 114, 318–322. https://doi.org/10.1016/j.talanta.2013.05.059.

Saniewska, D., Bełdowska, M., 2017. Mercury fractionation in soil and sediment samples using thermo-desorption method. Talanta 168, 152–161. https://doi.org/10.1016/j.talanta.2017.03.026.

Schaanning, M., Ruus, A., Bakke, T., Hylland, K., Olsgard, F., 2002. Bioavailability of Metals in Weight Materials for Drilling Muds.

Sheahan, D., Rycroft, R., Allen, Y., Kenny, A., Irish, R., 2001. Contaminant Status of the North Sea.

Sompongchaiyakul, P., Bureekul, S., Sombatjinda, S., 2018. Impact of Natural Gas Exploration and Production on Mercury Concentrations in Surface Sediment of the Gulf of Thailand, in: Day 1 Mon, November 12, 2018. SPE.. https://doi.org/10.2118/192739-MS.

Tang, W.-L., Liu, Y.-R., Guan, W.-Y., Zhong, H., Qu, X.-M., Zhang, T., 2020. Understanding mercury methylation in the changing environment: recent advances in assessing microbial methylators and mercury bioavailability. Sci. Total Environ. 714, 136827 https://doi.org/10.1016/j.scitotenv.2020.136827.

TAQA Bratani Ltd, 2023. Eider Alpha Topside Decommissioning Environmental Appraisal 91.

Trefry, J.H., Trocine, R.P., McElvaine, M.L., Rember, R.D., 2003. Concentrations of total mercury and methylmercury in sediment adjacent to offshore drilling sites. Society of Petroleum Engineers - SPE/EPA/DOE Exploration and Production Environmental Conference 2003, EPEC 2003. doi:https://doi.org/10.2523/80569-ms.

UKOOA, 2002. Drill Cuttings Initiative: Final Report.

Versteegh, G.J.M., Koschinsky, A., Kuhn, T., Preuss, I., Kasten, S., 2021. Geochemical consequences of oxygen diffusion from the oceanic crust into overlying sediments and its significance for biogeochemical cycles based on sediments of the northeast Pacific. Biogeosciences 18, 4965–4984. https://doi.org/10.5194/bg-18-4965-2021.

von Hellfeld, R., Gade, C., Koppel, D.J., Walters, W.J., Kho, F., Hastings, A., 2023. An approach to assess potential environmental mercury release, food web bioaccumulation, and human dietary methylmercury uptake from decommissioning offshore oil and gas infrastructure. J. Hazard. Mater. 452, 131298 https://doi.org/10.1016/j.jhazmat.2023.131298.

Wegeberg, S., Gustavson, K., 2019. Barite-Bound Mercury in Marine Sediments; Potential Release and Bioavailability under Arctic Conditions.

Wittmann, Z., 1981. Determination of mercury by atomic-absorption spectrophotometry. Talanta 28, 271–273. https://doi.org/10.1016/0039-9140(81)80056-2.

Xodus Group, 2019. Dunlin Alpha Drill Cuttings Technical Report.

Zan, B., Yan, J., Liu, S., Mou, C., Ran, B., 2020. Llandovery (lower Silurian) nodular barite from the northern margin of Yangtze Block, South China, and its paleoceanographic implications. Palaeogeogr. Palaeoclimatol. Palaeoecol. 537, 109415 https://doi.org/10.1016/j.palaeo.2019.109415.

Zhang, Hao, Davison, William, 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. Anal. Chem. 67, 3391–3400. https://doi.org/10.1021/ac00115a005.

Zhang, T., Kim, B., Levard, C., Reinsch, B.C., Lowry, G.V., Deshusses, M.A., Hsu-Kim, H., 2012. Methylation of mercury by Bacteria exposed to dissolved, Nanoparticulate, and microparticulate mercuric sulfides. Environ. Sci. Technol. 46, 6950–6958. https://doi.org/10.1021/es203181m.

Zhang, T., Kucharzyk, K.H., Kim, B., Deshusses, M.A., Hsu-Kim, H., 2014. Net methylation of mercury in estuarine sediment microcosms amended with dissolved, Nanoparticulate, and microparticulate mercuric sulfides. Environ. Sci. Technol. 48, 9133–9141. https://doi.org/10.1021/es500336j.