Contaminant Leaching from
Drill Cuttings Piles of the Northern
and Central North Sea: Field results
from the Beryl "A" cuttings pile

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Executive Summary

- This study was designed to establish the sedimentary distribution and mobility of metals (Ba, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, U, V, and Zn) in an offshore drill cuttings pile. Metal mobility ("leaching") was assessed through analysis of interstitial (pore) water.

- Unique results (the first in-situ measurements of reactants and products in cuttings piles) have been obtained using ROV technology, and micro electrodes capable of resolving rapid biogeochemical changes close to the sediment water - interface.

- Results and data interpretation of field (Beryl "A", block 9/13) investigations performed to study the following geochemical parameters within drill cuttings piles are presented:
  - a) the measurement of dissolved (<0.2 µm particle size diameter) and total (>0.2 µm particle size diameter) heavy metal (Cd, Co, Cr, Cu, Mo, Ni, Pb, U, V, Zn) concentrations within cuttings and seabed surrounding the Beryl "A" field, at 65, 165, 300 and 3500 m from the apex of the cuttings pile.
  - b) the simultaneous analysis of geochemical carrier substances (Mn and Fe oxyhydroxides), indicators of drill cuttings (Ba, hydrocarbons) and other biogeochemical parameters (e.g. dissolved oxygen and sulphide concentrations within the interstitial water of the sediment) were used to help describe the major processes controlling contaminant behaviour within the cuttings piles.
  - c) the analysis of the naturally - occurring radionuclide, $^{210}\text{Pb}$, to assess sediment mixing, by both organisms and physical processes of sediment disturbances.

- A rapid rate of organic matter decomposition (43.6 g C m$^{-2}$ y$^{-1}$) occurs within the cuttings pile. This is the first time such unequivocal information has been provided on the rate of organic matter decomposition and breakdown in cuttings piles and at the spatial resolution necessary to resolve the interfacial gradients.

- Precipitation of metal mono- and disulphides were directly observed within the pile.

- An increase in the specific activity of $^{210}\text{Pb}$ with distance from the platform, probably due to lower sediment accumulation rates, and less dilution of unsupported $^{210}\text{Pb}$, was observed.

- There is no sediment mixing at the station closest to the platform but mixing in the surface sediment increases with increasing distance from the platform.

- The most rapid biogeochemical reactions and fluxes take place at the 65 m site.

- The fluxes presented here suggest that low exchange rates of metals with overlying seawater are observed under the relatively protected quiescent conditions persisting in the cuttings pile when sampled.
1 INTRODUCTION AND OBJECTIVES

1.1 Objectives

This study was carried under support from both the NERC Thematic programme MIME (Managing Impacts on the Marine Environment) project and the Drill Cuttings Initiative sponsored by the UK Offshore Oil Association (UKOOA). The stated objectives were:

a) To obtain undisturbed sediment cores for metal, sulphide and hydrocarbon analysis.

b) To make in-situ oxygen, sulphide and pH measurements in and around the drill cuttings pile.

c) To collect bottom fish and crustaceans for liver and back muscle analysis of metals and hydrocarbons.

d) To suspend and collect semi-permeable membrane devices above the drill cuttings piles for later analysis of metals and hydrocarbons.

1.2 Introduction

There is a large reservoir of trace metals in the cuttings piles resulting from the drilling process during the exploration and production of hydrocarbons. Remobilization of these metals may be instrumental in determining porewater concentrations and fluxes out to the overlying water ("leaching"). The decomposition of organic matter, and/or the reductive dissolution of manganese and iron oxides may release metals into solution. Trace metals that are solubilised into the porewater will migrate either upward to the overlying water, possibly adsorbing onto Mn and Fe oxyhydroxides at the sediment water interface, or diffusing downward where they will become incorporated into pyrite, metastable Fe monosulphides and bisulphides like MnS. The exposure of these Fe sulphides to oxygen via bioturbation or sediment resuspension may lead to the release of the associated metals into the water column (Saulinier and Mucci, 2000; Huerta-Diaz et al., 1998). Dominating transport mechanisms contributing to the sediment - water exchange of dissolved metals are molecular diffusion, bioturbation and bioirrigation, turbulent process induced by the movement of the overlying water, and advective processes caused by bioroughness of the seabed. The relative importance of these processes depends on the sediment characteristics and the fauna composition, which in turn, are controlled by the hydrodynamical regime. Generally mass transport of solutes into the overlying water is controlled by the eddy diffusion, leading to a relative uniform distribution of dissolved material. Very close to the sediment surface, viscous forces and surface friction retard the turbulent water flow and the velocity of water approaches zero. In this region called the diffusive boundary layer, eddy diffusion becomes smaller than molecular diffusion and molecular forces dominate the transport of dissolved material. (Lohse et al., 1996). In areas of high organic matter decomposition steep depth associated concentration gradients develop where a maxima of dissolved metal concentrations will often result (Harper et al., 1998).

The processes responsible for the removal of dissolved metals to the solid phase are adsorption, absorption, and surface precipitation. However, if porewater
concentrations are lower, and oxygen is introduced, then remobilization can occur. The toxicity of trace metals as well biogeochemical behaviour can be controlled by complexation with organic ligands (Wen et al. 1999).

2 SURVEY DESIGN AND SAMPLING

The sampling strategy was designed to optimise distance-related changes in chemical properties in order to assess the direction and magnitude of contaminant concentrations with respect to the Beryl field drill cuttings pile. The sampling was carried out to provide one distance related transect away from the pile in the direction of residual current. The station positions occupied during the cruise are shown in Figure 1. Temperature and salinity profiles are shown in Figures 2 and 3. The collection of mega-core samples and the deployment of the benthic landers was performed at four stations. Lander deployment was performed using ROV technology, the first time this has been carried out in the North Sea to our knowledge. Coral specimens were videoed, photographed and collected from several locations on the structures. Longline deployment was done at 500m off the Southwest of the platform. A summary of the cruise may be found in appendix 1. Precise station positions were determined using DGPS at the time of sampling. All stations are in UTM co-ordinates.

3 SAMPLING PROTOCOLS

3.1 Sediment geochemistry

Undisturbed sediment cores were taken from 4 stations using the mega-corer which preserves the sediment-water interface intact. Once collected, cores for dissolved and solid phase metal were sectioned at 0.5 cm intervals to 10 cm then 1 cm intervals to 15 cm when possible. This was performed under anaerobic conditions using trace-metal clean teflon and butyrate slicing rings, plates and spatulas. Samples for hydrocarbon analysis were obtained by sub-coring the collected cores at 0-2 cm, 2-5 cm, 5-10 cm using clean metal slicing materials.

3.2 In-situ sampling

3.2.1 Benthic Landers

The benthic landers were used in non-autonomous mode, without buoyancy and ballast, and were deployed and recovered using a Pioneer 11 work-class ROV and ship’s crane.

3.2.1a. "Profilur"

System developed at Dunstaffnage Marine Laboratory using designs from KC Denmark for measuring oxygen, sulphide and pH concentrations in the sediment at very fine resolution (50 - 250 µm) using microelectrodes.
Figure 1. Beryl "A" station positions.
Figure 2. Temperature profile for the water column at the Beryl "A" production platform measured using sensors onboard the ROV.
Figure 3. Salinity profile for the water column at the Beryl "A" production platform measured using sensors onboard the ROV.
3.2.1b. Oxygen

"Unisense" micro-electrodes with a sensing tip diameter of < 10 µm and 90% response time of 1s were mounted on the Profilur for in-situ measuring. Stabilisation of the lander on the seafloor for 1 hour was allowed to take place prior to commencement of measuring. An automatic titration system using the micro-winkler technique was used to obtain oxygen concentration values for the oxygen microelectrode calibrations. The oxygen microelectrodes were also calibrated against bottom water obtained from the water-sampling device attached to the lander.

3.2.1c Sulphide

The sulphide electrodes are only known to be linear up to sulphide concentrations of 1mM, and their behaviour in sulphide concentrations higher than this are not well known. The sulphide electrodes were calibrated in solutions of up to 4 mM sulphide because of the high expected sulphide concentrations within the cuttings piles.

4 Methods

4.1 Sediments

Sample collection of pore water was achieved using a modified Watson - Barnett SMBA multi-corer, the mega - corer (to retain intact the sediment-water interface), sample slicing and centrifugation under an N₂-atmosphere (to prevent oxidation and precipitation of dissolved metals), and analysis by inductively - coupled plasma mass spectrometry (ICP-MS; VG PQ3).

4.2 Microwave Digestion Method

The total dissolution of sediments for multi-element analysis was accomplished by microwave high pressure closed digestion with Aqua Regia (HNO₃ + HCl), perchloric acid and hydrofluoric acid (HF) in a microwave accelerated reaction system (MARS 5, CEM Corp.). An aliquot of dried sediment was transferred to special high pressure Teflon vessels. After the addition of acid the vessel was closed with a Teflon cap. Up to 12 vessels were placed on a rotating turntable in the microwave oven at maximum power (1200 W). Process blank (acid with no sediment) and reference materials were randomly included to verify no crossover contamination and satisfactory digestion.

4.3 Methodology for Heavy Metal Analysis by Inductively Coupled Plasma Spectrometry (ICP-MS)

The following description details the method of analysis of marine sediments by ICP-MS. This method uses a quadropole mass spectrometer to measure each element by its isotopic mass number and allows the determination of isotopic ratios if required. The instrument used for this analysis is a VG Elemental PlasmaQuad PQ3 and the standard instrument conditions are as follows:
Table 1. ICP-MS instrument conditions.

<table>
<thead>
<tr>
<th>Lens Voltages</th>
<th>Volts</th>
<th>Gas Flows</th>
<th>L/min</th>
<th>Misc. settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lens 4</td>
<td>-90</td>
<td>Cool gas</td>
<td>12.5</td>
<td>Pole Bias</td>
</tr>
<tr>
<td>Lens 3</td>
<td>5.0</td>
<td>Aux gas</td>
<td>0.60</td>
<td>R.F. power</td>
</tr>
<tr>
<td>Lens 2</td>
<td>0.5</td>
<td>Neb gas</td>
<td>0.78</td>
<td>Peri speed</td>
</tr>
<tr>
<td>Lens 1</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collector</td>
<td>-4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extraction</td>
<td>-320</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The digested sediments were diluted to give a maximum solid concentration of 0.1 wt % and aspirated using a glass expansion nebuliser and a water-cooled spray chamber. A suite of elements were analysed using a set of standards, prepared from CLARITAS PPT certified reference solutions, to cover the expected range of concentrations. These standards were inserted every 5 samples within the analysis procedure. Any drift in the instrument performance was assessed using internal standards (indium and bismuth) in each sample and a low and a high certified reference solution every 10 samples. Any sample that was outwith the dynamic range of the calibration line was diluted further and reanalysed. Appropriate interference equations were applied to take account of any polyatomic interferences. The elements, V, Cr, Fe and Cu were analysed using matrix-modified standards to account for the affect of the sediment matrix. Instrument detection limits and the detection limits in the solid sediment for each sample are detailed in Table 2.

Table 2. Instrument and sample detection limits.

<table>
<thead>
<tr>
<th>Element</th>
<th>Instrument Detection Limit ppb (ng/g)</th>
<th>Sediment sample Detection Limit ppm (ug/g)</th>
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<tbody>
<tr>
<td>V</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe</td>
<td>2.69</td>
<td>2.69</td>
</tr>
<tr>
<td>Ni</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Zn</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>Cu</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Cd</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Ba</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Pb</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*The instrument detection limit was calculated as 3 times the standard deviation on the blank. Detection limits in the sediment were calculated using the instrument blank and the dilution factor that is required to achieve a solution containing 0.1 wt % solid content (1000x).*
4.4 Sediment radiochemistry - $^{210}$Pb

The down core distribution of the naturally-occurring radionuclide, $^{210}$Pb, was determined to assess the sediment mixing and sedimentation rate within the study area. The $^{210}$Pb was measured by alpha particle decay of its short-lived daughter, $^{210}$Po, assuming the daughter is in secular equilibrium. $^{210}$Po is plated onto silver discs with another isotope, $^{208}$Po, of known activity. $^{210}$Pb is the product of the following decay:

$$^{226}\text{Ra} \rightarrow ^{222}\text{Rn} \rightarrow ^{210}\text{Pb}$$

Half-life: $1600 \text{ y}$, $3.83 \text{ d}$, $22.3 \text{ y}$

by $\alpha$-particle emission for each decay. The radionuclide $^{226}$Ra commonly occurs in proportion to dissolved silicate and is relatively soluble in seawater, whereas $^{222}$Rn is the result of nuclear decay in continental rocks and is found as a gas in the atmosphere. The rate of nuclear production for both these reactions can be found and used to predict the rate of $^{210}$Pb supply to the sediment (Cochran et al., 1990). Once the downcore distribution of $^{210}$Pb is determined then the quantity of excess $^{210}$Pb (the level above $^{226}$Ra found within the sediment) can be determined using the asymptotic activity at the deepest sample depths. Sediment accumulation rates may then be estimated by appropriate curve fitting techniques.

5. Results and Discussion

5.1 Sediment description and observations

Preliminary inspection of vertical distributions within the cores collected in the area revealed generally two or three layers: a light, sandy coloured upper layer consisting of fine sand, a lower dark grey to black layer consisting of drill cuttings and then at the outer station (3500m), a sandy layer. With the exception of the most proximal station (65m) the sediment appeared to be very porous with a low water content, and was abrasive and non-cohesive. The 65m station contained mainly drill cuttings and had a high water content, high H$_2$S concentration and was very thixotropic in texture. Shell fragments were evident in all cores with a very high shell content in the core from the 300m station. The problem in achieving deep cores at the outer stations was due to the sandy, rocky terrain associated with pipeline laying and natural sediment, along with the inability to lower the megacorer at sufficient speed.

5.2 The biogeochemistry of microbially-mediated biogeochemical reactions in the cuttings pile.

It has long been recognised that microbially-mediated diagenetic reactions taking place in organic-rich sediments follow a predictable sequence that may be modelled on the energy yield per mole of organic matter being mineralised by the microbial reactions. This diagenetic sequence has been verified in many environments from the deep ocean to shallow continental shelf sediments. The typical diagenetic sequence is as follows:
Table 3. Theoretical diagenetic sequence within marine sediments

**Aerobic Respiration**

\[ 138O_2 + (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O \]

**Denitification**

\[ 94.4 \text{ HNO}_3 + (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 236^+N_2 + 106CO_2 + 16 \text{ NH}_3 + H_3PO_4 + 366H_2O \]

**Manganese Reduction**

\[ 236\text{MnO}_2 + (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 472H^+ \rightarrow 106CO_2 + 55.2\text{Mn}^{2+} + H_3PO_4 + 177.2H_2O \]

**Iron Reduction**

\[ 212\text{Fe}_2O_3 + (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 848H^+ \rightarrow 424\text{Fe}^{2+} + 106CO_2 + 16\text{NH}_3 + H_3PO_4 + 530H_2O \]

**Sulphate Reduction**

\[ 53\text{SO}_4^{2-} + (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 106CO_2 + 16\text{NH}_3 + 53S^{2-} + H_3PO_4 + 106H_2O \]

**Disproportionation**

\[ (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 53\text{CH}_4 + 16\text{NH}_3 + H_3PO_4 \]

In this sequence, the utilisation of oxygen as an electron acceptor in the reaction sequence provides the greatest free energy yield for the microbial reaction. It is this process that leads to the development of anoxia within the sediment pile; all the available oxygen from the overlying seawater having been consumed in the diagenetic reaction. Examining the theoretical diagenetic sequence would predict the subsequent sequence of denitrification, the dissolution of iron and manganese oxides, the liberation of dissolved iron and manganese into the pore water and the consumption of seawater sulphate producing higher concentrations of dissolved sulphide.

In addition to predicting the distribution of dissolved solutes in the pore water, it is also possible to measure the down core distribution of the concentration of the constituents in order to estimate the diffusion gradient into or out of sediments. The typical interpretation of pore water profiles is provided in Figure 4.

This theory indicates the significant importance of solid and pore water phase analysis within sedimentary sequences suffering significant diagenesis. The ability to provide mass balance estimates of metal transport into and out of the overlying seawater (the flux of leachate from the cuttings piles) and the depth zonation of the key biogeochemical reactions is crucial for understanding the environmental impact of extant cuttings or during subsequent disturbance.
It is also predicted that cuttings piles contain high levels of labile organic matter which will be subject to severe diagenetic reaction within millimetres to centimetres of the sediment - water interface. The challenge, therefore, is to conduct suitable measurement and sampling techniques that allow both in-situ solid and aqueous phase analysis of key constituents at sufficient resolution to observe the biogeochemical cycle operating within the cuttings pile.

An important process operating near the sediment water interface of all marine deposits is the process of benthic mixing. Benthic mixing may occur by either the infaunal and epifaunal biota, or as a consequence of physical disturbance by bottom currents or human (industrial or fishing) activity. Within the marine geochemical literature it has been well established that the use of naturally-occurring radioisotopes (especially $^{210}$Pb, half life 22.3 years, $^{234}$Th, half life 24 days) are excellent tracers for examining and modelling the act of benthic mixing within the near subsurface sedimentary regime. We have employed the technique of alpha spectroscopy to measure the activity of naturally occurring $^{210}$Pb and to interpret the resulting profiles in terms of mixing and sediment accumulation rate. This provides an excellent insight into the dynamics operating in the cuttings pile down to the natural sediment interface and allows interpretation of the biogeochemical signals to be conducted.

5.3 Oxygen and sulphide distribution.

5.3 Oxygen and sulphide distribution.

Figure 5 presents the down sediment profiles of dissolved oxygen measured in the interstitial water from 3 sites at 65, 165 and 300 metres distance from the apex of the cuttings pile at the Beryl platform. These profiles have been obtained using the Dunstaffnage Marine
Laboratory Profilur System attached to ROV deployment instrumentation. The use of *in-situ* $O_2$ and sulphide microelectrodes within the piles has allowed us to measure the distribution of these constituents at a very high spatial and temporal resolution (Gundersen and Jorgensen, 1990) which would not have been possible otherwise. By inserting them into the cuttings with sub-millimetre resolution, the concentration gradients can be identified without significant disturbance of the sediment structure.

Figure 5a, 5b, 5c provides evidence for the heterogeneity in the dissolved oxygen profile in that 2-3 electrodes mounted on the same electrode holder have been inserted into sediment simultaneously. This provides qualitative information on the heterogeneity of oxygen consumption by microbial activity over about 30 cm$^2$ of the surface of the sediment.

The information from the three sites has been averaged to produce a composite plot in Figure 5d that illustrates clearly the differences in oxygen consumption (Biological Oxygen Demand) at the three sites. Figure 5d dissolved oxygen concentrations are presented as µmole l$^{-1}$ for flux determinations later in this section. The down sediment consumption of oxygen may be interpreted as a) rapid microbially-mediated diagenesis of labile organic matter decreasing in microbial activity with greater distance from the apex of the cuttings pile, and b) higher compaction and less oxygen diffusion close to the apex of the cuttings pile with increased irrigation and oxygen diffusion to depth in the sediment moving with distance from the apex (after 300 metres).

Using the stoichiometry of the reaction sequence identified in Table 3 it is possible to estimate the total amount of organic matter required to produce the observed decrease in dissolved oxygen. We have made an assumption about the average composition of organic matter (the so-called Redfield composition of average marine plankton detritus). Figure 6 reproduces the *in-situ* oxygen profile taken from the 65 m site. Both visual evidence from the ROV and sediment cores, along with geochemical data, verifies this location to be part of the drill cuttings pile. From this profile we can clearly see that the steepest declination of the oxygen concentration gradient occurs between 0 and 1 mm below the sediment surface. This gradient of 234.4 mol/m$^3$ is shown in Figure 6. By using Fick’s First Law in one dimension:

$$J = \mathcal{D} \times D_s \times (\partial C/\partial z)_{x,y}$$

with the oxygen coefficient, $D_{sO2} = 8.5 \times 10^{-10}$ and a porosity ($\mathcal{D}$) of 0.75 the resulting annual flux of oxygen is 4.73 mol m$^{-2}$ y$^{-1}$. To determine carbon oxidation we assume that the oxygen reacts in the sediment only with organic carbon in the ratio of 106/138 (Froleich et al., 1979). This yields the following rates of organic matter degradation for the cuttings pile: $R_{ox,Corg} = 43.6 gC m^{-2} y^{-1}$. This estimate takes in the assumption that all the oxygen is utilised in the oxidation of organic C and that the ratio of 106/138 holds true for the cuttings pile.

Notwithstanding the limitations in this assumption, it is clear that a rapid rate of organic matter decomposition occurs within the cuttings pile. This is the first time such unequivocal information has been provided on the rate of organic matter decomposition and breakdown in cuttings piles and at the spatial resolution necessary to resolve the interfacial gradients.
Examination of Table 3 also predicts the appearance of dissolved sulphide in the pore water on the consumption of seawater sulphate. This is shown in Figure 7a, 7b and 7c. Again, there is a consistent interpretation based on the most rapid diagenetic reactions occurring closest to the apex of the pile, yielding very rapid reduction of dissolved sulphate in the pore water. Such high levels of dissolved sulphide allow the potential stabilisation of heavy metals as sulphide minerals within cuttings. Organic - rich drill cuttings piles provide an ideal substrate for sulphate reduction and organic matter remineralisation in keeping with observations from organic rich marine sediments (Canfield et al., 1993). The cycling of sulphide is a key component in biogeochemical processes in the aquatic environment. It plays a major role in reactions at oxic-anoxic interfaces, as in the formation of metal precipitates and oxidation by phytotrophic or chemolithotrophic bacteria, respectively (Jeroschewski et al., 1996). The variation of porewater concentration of sulphide with depth in the sediment is also one of the major controls of the dissolved concentration and toxicity of trace metals (Teasdale et al., 1999). The presence of filamentous, colourless sulphur bacteria *Beggiatoa* spp. on the Beryl "A" pile is indicative of a sulphide - rich area. *Beggiatoa* mat formation occurs where diffusing sulphide from below and oxygen from above meet. The filaments oxidise sulphide, with oxygen competing efficiently with the spontaneous chemical oxidation, thereby establishing steep, opposed gradients of oxygen and sulphide.

*The likely outcome of this process is the precipitation of metal mono- and disulphides within the pile, which may have different degrees of stability with respect to reoxygenation. This latter point is important when considering the potential of the pile to oxygenation on disturbance, perhaps associated with the decommissioning process.*

Figure 7 presents the first measured *in-situ* dissolved sulphide concentrations from the northern North Sea and clearly indicates the validation of the typical diagenetic sequence in Table 1. The vertical dislocation in the depth at which dissolved oxygen reaches zero and dissolved sulphide starts to make an appearance in the pore water, is probably controlled by the level of nitrate reduction and dissolution of higher manganese oxyhydroxides.

*In summary, this unique data set obtained using in situ microelectrode techniques yields incontrovertible evidence for high rates of biogeochemical diagenetic reaction close to the apex of the cuttings pile, decreasing rapidly with radial distance, and the sharp interfacial gradients in oxidant and reactants within the pore water of the cuttings pile. The production of dissolved sulphide leads to the potential mechanism of heavy metal stabilisation associated with the process of redox diagenesis. This is examined further below.*
Figure 5. Interstitial dissolved oxygen concentrations for Beryl "A". The dashed line at 0 mm depth marks the position of the sediment - water interface.
Figure 6. Dissolved oxygen gradient within the interstitial water of the Beryl "A" cuttings pile, 65 m from the apex.
Figure 7. Interstitial dissolved constituents for Beryl "A" at 65 m from the pile apex.
5.4 The diagenesis of redox-sensitive metals (Mn, Fe and Mo).

As indicated above, the distribution of redox-sensitive metals to be controlled by microbially mediated reactions requiring the usage of free dissolved oxygen and sulphate as energy sources, is well known in the marine environment.

In Figure 8 we present the distribution of solid phase (µg g\(^{-1}\)) and dissolved phase (ng g\(^{-1}\)) of manganese, iron and molybdenum with depth and radial distance from the apex of the cuttings pile. Typically, manganese and iron show similar behaviour in that the dissolution of solid phase manganese and iron oxyhydroxides found under oxic environmental conditions, yields higher concentrations of dissolved iron and manganese in the pore waters. The depth at which the redox reaction Mn\(^{4+}\) to Mn\(^{2+}\) and Fe\(^{3+}\) to Fe\(^{2+}\) (identified within the diagenetic scheme in Table 3), predicts that the iron redoxcline is found at deeper depth within the sediment than the manganese redoxcline. The control on manganese and iron solubility in the pore water is exercised by concentration of dissolved sulphide. At higher levels of dissolved sulphide the potential for precipitation of manganese and iron sulphides, as solid phase minerals, controls the concentration of the dissolved phase.

The generation of iron sulphide may play a significant role in trace metal distribution in sediments. The diagenetic products of iron sulphide proceeds via two pathways in conjunction with bacterially-generated sulphide (Shimmield and Pedersen 1990):

1) \(\text{Fe}^{2+} + \text{HS}^- = \text{FeS} + \text{H}^+ \Rightarrow \text{FeS} + S^0 = \text{FeS}_2\)
2) \(\text{Fe}^{2+} + Sx^{2-} + \text{HS}^- = \text{FeS}_2 + S_{x-1}^{2-} + \text{H}^+\)

Examining Figure 8, it is clearly possible to discern the rapid dissolution of manganese oxyhydroxide close to the sediment water interface at the 65-metre site and the rapid increase in dissolved Mn\(^{2+}\) in the pore water. With depth down the core the dissolved manganese falls as a consequence of manganese precipitation in sulphide minerals. This is clearly most marked at the 65-metre site as sulphide tension is the highest.

It is worth noting that the near surface sediment at the 300-metre site is dominated by shelly material, likely to cause dilution of the solid phase signal. It is also to be noted that the highest dissolved manganese concentration is found at the 65-metre site.

In all cases, the subsurface concentration in the pore water metal is higher than the immediately overlying concentration in the water column. This would therefore predict a diffusion gradient, such that the metal will tend to flux out of the cuttings pile into the overlying water, or downwards into the sediment where it may be fixed as a sulphide mineral. This qualitative interpretation provides the basis for estimating fluxes in the discussion below.

The distribution of molybdenum is controlled by the redox chemistry of the element and the passive uptake onto oxyhydroxides or incorporation into sulphide phases. Again the distribution of the solid and dissolved phase is consistent with established biogeochemical theory and identifies the most rapid reaction and fluxes that take place at the 65-metre site.
Figure 8. The distribution of solid and dissolved manganese, iron and molybdenum
5.5 Natural radionuclide $^{210}\text{Pb}$ activities.

The total $^{210}\text{Pb}$ activity profiles versus depth (cm) for the four stations are shown in Figure 9. $^{210}\text{Pb}$ activities within sediment can be used to determine sediment accumulation rates and provide a qualitative indication of the extent of mixing within the sediment core. The length of the profiles shown reflect the depth of the core retrieved. In the case of station the 3500 m site, the maximum depth of the core is 3 cm. This station was mainly sand and the shortness of this core reflects the difficulty in obtaining cores from this type of sediment. The surface $^{210}\text{Pb}$ concentrations vary from 110 to 180 Bq kg$^{-1}$, with the station furthest from the platform having the highest surface activity of $^{210}\text{Pb}$. The general trend in activity is a decrease with sediment depth, however the profile nearest to the platform at station B1, 65m, has an erratic profile which does not reflect the classic trend of deposition and decay of $^{210}\text{Pb}$ as is shown in the profile from station B2, 165m. The profile from B1 may reflect the increased and variable deposition of material on the seabed at this site. The profile does begin to show some structure nearer to the surface, which may reflect a decline in discharge over recent years. It is important to note that there is no indication of mixing in this core at the surface.

![Figure 9. Downcore distribution of $^{210}\text{Pb}$ (Bq kg$^{-1}$) measured by alpha spectrometry.](image-url)

The profile for the 165 m site, indicates that there is mixing (either physical, biological or both) within the top 1 to 1.5 cm of this core and thereafter there is a decrease in activity to a minimum of 22 Bq kg$^{-1}$ at 6 cm depth. This profile maybe used to determine a sediment accumulation rate for this area, which is shown in Figure 10. In Figure 10 the vertical depth scale has been converted to cumulative density - corrected scale, using sediment dry bulk densities measured from the sedimentary water content for each sample. This corrects for compaction effects that
would otherwise render the simple length scale unreliable in this rapidly - compacting cuttings pile sediment. The $^{210}$Pb profile indicates that a sediment accumulation rate of 28 mg cm$^{-2}$ y$^{-1}$ is occurring at this site. This would indicate that the sediment from the surface to 1.5 cm depth (0.85 g cm$^{-2}$) is mixed giving a time interval of 30 years, i.e. the last 30 years of sediment is within the mixed layer zone.

The $^{210}$Pb activity versus depth profile for the core at the 300 m site is unusual in that the activity of $^{210}$Pb within the first cm is considerably lower than at depth. The sediment from 0-1 cm contained a large amount of shells, which has resulted in a dilution affect by calcium carbonate. This affect is also evident in other analyte profiles for this station. The $^{210}$Pb concentration below the shell band is approximately 200 Bq kg$^{-1}$ and then decreases with depth. The spike at a depth of around 5 cm may be due to bio-irrigation, i.e. material from the 1 cm layer maybe being deposited at the 5 cm horizon as a consequence of an infaunal organism feeding and egestion.

![Figure 10](image)

**Figure 10.** Estimate of sediment accumulation rate at the site 165 m from the apex of the Beryl “A” cuttings pile using $^{210}$ Pb

The overall conclusions from the $^{210}$Pb profiles are;

- With increased distance from the platform the specific activity of $^{210}$Pb increases. This is probably due to a dilution affect of the cuttings discharge.
There is no mixing at the station closest to the platform, but mixing in the surface sediments increases with increasing distance from the platform.

The sedimentation rate in the area 165m from the platform is 28mg cm\(^{-2}\) y\(^{-1}\).

There are only 3 samples from station B4, 3500m. The \(^{210}\)Pb surface concentration is 180 Bq kg\(^{-1}\) and decreases slightly with depth. It is difficult to draw any conclusions from so few points, however the lack of any major decrease in activity over 3 cm would suggest there is a higher degree of mixing at this site.

5.6 Heavy metals

Having set the biogeochemical scene of the principal oxidants and reactants involved in the biogeochemical reactions, it is appropriate to consider the down core distribution of dissolved and particulate heavy metals.

Figure 11 displays the particulate and dissolved concentrations of barium, nickel and uranium at the three sites along the transect from the apex of the cuttings pile. In all cases the highest concentration of particulate metals in the cuttings pile occurs closest to the platform jacket (65 metres from the apex). Barium is the principal elemental constituent of the cuttings pile and occurs as the mineral barite (BaSO\(_4\)), an agent used in drilling mud. Up to 20 weight percent of barium is found in the sediment. This concentration is higher than reported in most reviews probably because we are sampling very close to the centre of the pile and also because the analysis is performed by a total sediment dissolution, in the presence of hydrofluoric and perchloric acids, using microwave digestion techniques.

The general increase in dissolved barium with depth is considered to be due to the process of barite dissolution in the presence of sulphate reduction biogeochemical processes. The sulphate reduction enhances the solubility of the barite mineral releasing more dissolved Ba to the pore waters, which then fluxes out to the overlying water. Other heavy metals are probably liberated to the pore water on dissolution of the barite lattice, and in some cases, the high sulphide activity will help to reduce the concentration in the pore water and susceptibility to leaching. This is the case for nickel, and the redox sensitive element, uranium. In nearly all cases the presence of sulphide in the pore waters below about 4-5 cm depth, reduces the solubility of the heavy metal phases.

Figures 12 and 13 report the dissolved and particulate concentrations of other heavy metals analysed (vanadium, chromium, copper, cobalt and cadmium). In particular, Cr and Cd display strong control by sulphide precipitation leading to low concentrations in the porewater.

5.7 Biogeochemistry discussion

The results obtained from the transect study at Beryl "A" show clearly that significant biogeochemical reactions and diagenesis are taking place in the cuttings pile fuelled by the organic matter of the hydrocarbon-rich substrate.

The analytical methodology employed allows the calculation of fluxes into and out of the cuttings pile using the shape of the pore water profile near the sediment water
interface. Assuming that the leaching process may be modelled using Fick’s First Law it is possible to calculate the leaching rate or uptake rate for heavy metals. This data reveals the flux of barium to the overlying water, and also the uptake of heavy metals into the cuttings pile where they are stabilised with the sulphide minerals. This process is similar to that documented in mine tailings, an analogue to drill cuttings found in the fjordic settings of British Columbia (Pedersen et al., 1993; Pedersen and Losher, 1988; Pedersen, 1984, 1985). Table 4 presents the results using this approach.

Table 4. The vertical diffusional flux, J, for dissolved metals from Beryl "A" at the 65 m and 165 m sites. (Minus (-) indicates a flux out of the sediment.

<table>
<thead>
<tr>
<th>Site</th>
<th>Ba ug/cm²/yr</th>
<th>Cu ug/cm²/yr</th>
<th>Ni ug/cm²/yr</th>
<th>Cr ug/cm²/yr</th>
<th>Mn ug/cm²/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>65 m</td>
<td>-22.089</td>
<td>-0.109</td>
<td>-7.120</td>
<td>-0.328</td>
<td>2.614</td>
</tr>
<tr>
<td>165 m</td>
<td>-3.403</td>
<td>-0.288</td>
<td>0.202</td>
<td>-0.225</td>
<td>-1.124</td>
</tr>
</tbody>
</table>

Note: The vertical diffusional flux, J, was calculated from the dissolved porewater gradient \( \frac{\partial C}{\partial z} \) \( x, y \) and Fick’s first law in one dimension: \( J = \mathcal{O} \times D_s \times \left( \frac{\partial C}{\partial z} \right) \) \( x, y \) where \( \mathcal{O} \) is the porosity and \( D_s \) is the diffusion coefficient in porewater. \( J \) was calculated using the following assumptions:
1) negligible viscosity and ionic charge effects
2) no solid phase incorporation of dissolved species near the sediment water interface.

Dissolved concentration gradients are linear \( \left( \frac{\partial C}{\partial z} \right) \) \( x, y \) = \( \Delta \)

Other unpublished studies that we have carried out indicate that the decrease in diagenetic reaction rate away from the apex of the cuttings pile is consistent at all the sites we have surveyed. Furthermore, the process of barite dissolution is now well documented from three other sites, as is the control on metal solubility by sulphate reduction and sulphide formation in the pore waters. Subsequent unpublished studies (carried out as part of the NERC MIME programme) of the cuttings in controlled laboratory experimental conditions reveal that this heavy metal fixation as sulphide is indeed metastable and on resuspension in oxygenated seawater, substantial metal release can occur to the dissolved phase.

*The fluxes presented here suggest that low concentrations of exchange of metals with overlying seawater is observed under the relatively protected quiescent conditions persisting in the cuttings pile when sampled.*

6 Additional Comments

6.1 Liver and back muscle analysis of bottom fish and crustaceans for metals and hydrocarbons

No fish or crustaceans were caught on this short field trip.

6.2 Semi-permeable membrane devices above the drill cuttings piles for later analysis of metals and hydrocarbons.

The short time frame for the cruise made the suspension of semi permeable membrane devices above the pile unfeasible.

6.3 pH

No successful pH measurements were ever obtained.
Figure 11. The distribution of solid and dissolved barium, nickel and uranium.
Figure 12. The distribution of solid and dissolved vanadium, chromium and copper
Figure 13. The distribution of solid and dissolved cobalt and cadmium
7 Conclusions

- A rapid rate of organic matter decomposition (43.6 g C m\(^{-2}\) y\(^{-1}\)) occurs within the Beryl "A" cuttings pile. This is the first time such unequivocal information has been provided on the rate of organic matter decomposition and breakdown in cuttings piles and at the spatial resolution necessary to resolve the interfacial gradients.

- Precipitation of metal mono- and disulphides were directly observed within the pile controlling the solubility of Mn, Fe, Mo, Ni, U, Cr and Cd in particular.

- An increase in the specific activity of \(^{210}\)Pb with distance from the platform, probably due to lower sediment accumulation rates, and less dilution of unsupported \(^{210}\)Pb, was observed.

- There is no sediment mixing at the station closest to the platform but mixing in the surface sediment increases with increasing distance from the platform.

- The most rapid biogeochemical reactions and fluxes take place at the 65 m site.

- The fluxes presented here suggest that low exchange rates of metals with overlying seawater are observed under the relatively protected quiescent conditions persisting in the cuttings pile when sampled.

- There is a potential for increased metal fluxes and metal release to occur on oxidation of metal mono- and disulphides should the cuttings pile be substantially disturbed.

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8. REFERENCES


