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Characterisation of the cuttings piles at the Beryl A and Ekofisk 2/4 A platform - UKOOA Phase II, task 1

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Scope:

The cuttings piles at Beryl A and Ekofisk 2/4 A have been characterised according to the recommendations in the OLF Guidelines. The characterisation parameters selected from these Guidelines were the most feasible ones based on RF's experience from sampling and characterisation of other cuttings piles in the North Sea. Analysis parameters not within the OLF guidelines have also been included.

PART 1: Contour mapping from recent surveys was used to plan the sampling program during the fieldwork. The selected physical parameters included: cone penetration, shear strength, grain size distribution and density. The selected chemical parameters were the organic contaminants: THC, PAH, NPDs, Decalines, and the metals: Al, V, Mn, Fe, Ba, Cr, Co, Ni, Cu, Zn, As, Sr, Cd, Pb and Hg as well as the chemical components: TOC, TON, pH, Redox potential (eH) and sulphide. These parameters were analysed on samples/cores taken at both cuttings piles. Other parameters not included within the OLF guidelines were; PCB ("Dutch 7"), mineralogy, radioactivity (NORM, carried out by TNO/D&M as part of task 2c) and screening of hormonal effects (endocrine disruption). Further work on metals speciation using a sequential extraction procedure to access the availability of metals has also been carried out. At the Ekofisk 2/4A, cuttings pile contaminants data were available from a previous investigation in 1998. These data were also assessed in the characterisation work. Sampling for benthos was also performed, and specimen taxa and diversity indexes calculated. The experience obtained from fieldwork on appropriate cuttings pile sampling methods have been included in the report and assessed.

In addition to collecting samples for the characterisation purpose, bulk material to be used in a series of other experiments within the UKOOA phase II were collected.

PART 2: Bioavailability of metals was investigated by sequential extraction and subsequent analyses.

PART 3: The potential for drill cuttings to cause endocrine effects was investigated together with potential impacts of PCBs.

Key words: Drill cuttings pile characterisation, sampling methods, physical characterisation, chemical characterisation, organic characterisation, THC, PAH, PCB, metals, benthos, hormonal effects

Stavanger, 20.12.01

Grethe Kjeilen, project manager

Part 1:

Characterisation of the cuttings piles at the Beryl A and Ekofisk 2/4 A platforms

Part 2:

Availability of trace metals in cuttings deposits - studied by sequential extraction

Part 3:

Endocrine Disruption from drill cuttings material

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Executive summary

The objective of the UKOOA phase II - task 1 project was to conduct a chemical, physical and biological characterisation of a water-based (WBM) and an oil-based (OBM) cuttings piles, based on the OLF Guidelines for characterisation of cutting piles (OLF, 2000). The characterisation task is part of the phase II initiative of UKOOA, that aim to identify and elaborate on relevant issues of drill cuttings as a part of field decommissioning. Apart from the cuttings pile characterisation itself, within the UKOOA phase II programme the characterisation task gives important input to short-term and long-term modelling of cuttings piles, as well as to other tasks focused at cuttings pile changes and impacts with time.

The two piles selected were both mapped (physical extent) from before, and they were classified as being ‘fairly large’. The two piles investigated were the cuttings piles at Beryl A (OBM) and Ekofisk 2/4 A. The Ekofisk pile was intentionally chosen to represent a water based pile (WBM). However in the later period of drilling activity at Ekofisk, also synthetic drilling fluids containing esters and poly-alfa-olefines (PBMs) were used at the 2/4 A platform. Although the main discharges (about 90%) have been purely WBM discharges, the characteristics of the pile is clearly different from that expected with a purely WBM pile.

The current report contains three parts, the main part (PART 1) dealing both with planning of survey and sampling locations, offshore sample collection, and analysis and interpretation of data. The offshore survey also included collection of samples (bulk material) for several other tasks within the UKOOA phase II program. The offshore survey took place late September 2000.

Contour mapping from recent surveys was used to plan the sampling program during the fieldwork. The selected parameters investigated included:

- The physical parameters: cone penetration, shear strength, grain size distribution and density,
- Mineralogy and main constituents,
- Organic contaminants: THC, PAH, NPD:s, Decalines, PCB (Dutch 7),
- Metals: Al, V, Mn, Fe, Ba, Cr, Co, Ni, Cu, Zn, As, Sr, Cd, Pb and Hg,
- Other chemical characteristics: TOC, TON, pH, Redox potential (eH) and sulphide.
- Biological: benthos
- In addition, NORM (radioactive scale) and alcylated nonylphenolethoxilates (endocrine disrupters) have been analysed by TNO as part of UKOOA task 2c. These results are also partly reported.

The listed parameters were analysed on core samples from both cuttings piles. At the Ekofisk 2/4A, cuttings pile contaminants data were available also from a previous investigation in 1998. These data were also assessed in the characterisation work. The experience obtained from fieldwork on appropriate cuttings pile sampling methods have been assessed.

The second part (PART 2) focuses particularly on metals speciation and the (bio)availability of trace metals of the cuttings material. In cases when elevated concentrations of metals are identified in cuttings material, a major concern is at what state the metals are present and particularly how bioavailable they are for the biota. This is investigated by using a sequential extraction approach followed by subsequent ICP-MS analyses.

The third part (PART 3) examines endocrine disturbances caused by components of cuttings material and effects related to the presence of polychlorinated biphenyls (PCB). Such issues are very complex and have not been related to drill cuttings piles previously. The objectives of the Part 3 are to provide pilot screening data on the occurrence of endocrine disruptive chemicals (EDCs) in drill cuttings from the North Sea, and to put this into context to EDCs in general. Further potential impacts of PCBs known to be present in the piles investigated are examined, also by a screening approach, and likewise put into context to PCBs in general, and particularly their relation to endocrine disruptive (ED) effects.

The main conclusions and observations made are summarised as listed below, each Part being presented separately.

Major findings and conclusions PART 1:

- The nature of the cuttings piles made traditional coring work difficult. The experience at both the cuttings piles sampled was that the coring equipment must be carefully selected to be able to retrieve samples and to reduce the number of failed attempts.
- The material found in the cuttings pile is extremely soft with very little bearing. The CPT measurements (in the field) could not distinguish between the material in the Beryl A and Ekofisk 2/4 A cuttings piles. Shear strength measurements on the material from the cores gave only small differences.
- The mineralogy results showed that Ba is one of the dominating main constituents and pyrite one of the crystalline phases found.
- Sulphide measurements directly on the cores sampled suggested presence of anoxic processes within both cuttings piles. The oxic/anoxic conditions in the piles seemed to vary. There was no apparent difference between the two piles.
- Both cutting piles contain significant amounts of hydrocarbons (THC). Clear differences could be seen between the two piles.
- The total load of THC in the Beryl pile is considerable higher than the Ekofisk pile. In Beryl, THC levels are high throughout the pile, and tend to increase vertically

into the pile (concentrations measured varied between 0.2 and 20%). At Beryl A, the hydrocarbon source is mainly mineral type oils.

- At Ekofisk, the main portion of the hydrocarbons was found in the surface layer (about 20cm), where concentrations up to 8% were measured. The THC in the Ekofisk surface layer is dominated by esters. Further down into the pile, THC levels decreased considerably, reflecting the use of water based muds (WBM) in earlier drilling activity.
- The PAH concentration was high at Beryl. The concentration of the carcinogenic PAH component B(a)P was not dramatically high, and was rather low compared to the sum PAH measured. It can clearly be seen by looking at the historical layers through the pile, that lower toxicity base oils with lower aromatic content has been used in the latest drilling periods.
- At Ekofisk 2/4 A, the concentration of the sum of PAH components was moderate and B(a)P was low. This reflects the different origin of the THC in this pile.
- No PCB was detected in the Beryl pile.
- In the Ekofisk pile, high concentrations of PCB were found in some layers (up to 1500 µg/kg sediment in a thin layer). The PCB contaminated layer was found in the oldest part of the cutting pile and is at present covered with cuttings layers where no PCB was detected.
- Both cuttings piles show very similar contamination patterns for metals. The highest contamination is found of Pb. Both piles also contain concentrations of Cu, Zn, Cd and Hg indicating a moderate contaminated marine environment.
- A hard crust layer was found on the surface of the Ekofisk pile. No such observations were made on the Beryl pile. After identification of crystalline phases and microscopic studies of the crust it was found that it was generated from discharged concrete.
- Both cuttings piles showed a rather similar pattern of the benthic fauna. The number of taxa found was in line with what could be expected in this area (i.e. when comparing with seabed survey in relevant areas). The dominating species in both cuttings was *Capitella Capitata*, which is usually found at contaminated sites.
- Analyses of alkylphenols (nonylphenol, 4-tert.octylphenol and alkylphenol etoxylates) were carried out by TNO. At the start of their experiment, no levels above detection limit (20, 20 and 200µg/kg respectively) was measured at Beryl or a North Sea reference sediment. No analysis was carried out on Ekofisk cuttings. This analysis was conducted on samples from the surface layer (0-40 cm) only.
- The NORM analysis (also by TNO) showed elevated concentrations of all isotopes measured for both Ekofisk and Beryl when compared to a North Sea reference station. However, the levels measured were not significantly higher than reported background levels for the North Sea as such. This analysis was conducted on samples from the surface layer (0-40 cm) only. Only for Ra-226 was there a clear

difference between Beryl and Ekofisk, Beryl having twice the concentration measured at Ekofisk.

- The major difference between the piles is seen in the organic contamination, which is mainly due to the nature of the drilling fluids used at the two sites, and in the crust layer which was only seen at Ekofisk.

Major findings and conclusions PART 2:

- When investigating the mobility of the metals in the cuttings material it is shown that metals of high environmental concern (Hg, Pb and Cd) are to a considerable extent bound in fractions of high mobility in regard to geochemical processes. However, at the higher metal contamination levels, the fraction (%) of the total pool of these metals in the most bioavailable fractions are reduced. Potential impacts to the environment thus do not increase linearly with the total concentration of these metals.
- The attempt to apply multivariate analysis (Principal Component Analysis - PCA) to relate the different metals to particular fractions did not enable a generalisation of the results, neither with respect to metals bound to specific fractions, location of the cuttings sample in the specific piles, or between the different piles.
- Data from other studies related to this indicate that Cd in the cuttings potentially will be bioavailable for biota.
- All metals generally associated with uptake by different biota, e.i. Zn, Cu, Cd, Hg, can be found in the more bioavailable fractions.

Major findings and conclusions PART 3:

- Signs of estrogenic, anti-estrogenic, androgenic and anti-androgenic activities were detected in drill cuttings pile samples from various oilfields in the North Sea (including Ekofisk 2/4A and Beryl A). Generally however, the effects found were weak and variable, and as such the conclusions that can be drawn from the results are limited. The study is therefore not conclusive with regard to the environmental risks linked to the eventual occurrence of endocrine acting substances in the cuttings piles material.
- The present investigation form a first step into the very complex issue of evaluating endocrine disruption (ED) activities of chemicals occurring in the numerous drill cuttings piles in the North Sea. This task is a challenge due to the fact that the piles typically vary a lot in composition and texture. This variation is seen not only between piles but also within piles. Identification of chemicals present in the cuttings piles being evaluated is important as a basis for selection of ED related test parameters and for interpretation of results. However, due to the chemical complexity and heterogeneous nature of the piles, this task could not be fully accomplished in the present study.
- Integrative cell-culture tests each indicating estrogenic, androgenic and dioxin related effects of the cuttings piles extracts were used. The study demonstrate that the occurrence of dioxin type toxicity in cuttings can be related to high levels of

PCBs. Additionally, a partly correlation of high BaP levels and anti-estrogenic effects was also indicated.

- The outcome of these pilot measurements was hampered by the presence of cytotoxic components in many of the cuttings samples, the results may though still be considered as valuable since signs of ED effects of various cuttings samples were recorded.
- Further studies are recommended to establish clear evidence with regard to the environmentally significance of the eventual presence of endocrine active compounds in drill cuttings. Such studies must put considerable emphasise in designing the test scheme in order to minimise the influence of cytotoxicity. This involves both selecting appropriate test organisms and using exposure doses in the sublethal dose range. More long-term studies addressing low-dose and chronic effects of EDs are suggested.

Acronyms

OBM	Oil based mud
WBM	Water based mud
PBM	Pseudo oil based mud (Esters, Olefines etc.)
UKOOA	United Kingdom Offshore Operators Association
OLF	Oljeindustriens Landsforening
SFT	Statens Forurensingstilsyn (Norwegian Pollution Control Authorities)
GC-FID	Gas Chromatography with flame ionisation detector
ICP-MS	Inductively coupled plasma mass spectrometry
LOI	Loss on Ignition
TON	Total organic nitrogen
THC	Total hydrocarbons
PAH	Poly-aromatic hydrocarbons
EPA 16 PAH	16 selected poly-aromatic hydrocarbons commonly used for monitoring purposes
NPD	Napthenes, Phenantrenes and Dibenzothiofenes
Decalines	A group of non-aromatic organic ring compounds
PCB	Polychlorinated biphenyls (all 209 congeners)
Dutch 7 PCB:s	The PCB congeners 28, 52, 101, 118, 153, 180, commonly used for monitoring purposes
NORM	Radioactivity of natural origin (Naturally Occurring radioactive material)
CPT	Cone penetration test for obtaining geo-physical data in a sediment
HI-PEP	Transponder on the gear sending signal to the ships dynamic positioning system, allowing positioning of the gear.
ROV	Remote operated vehicle
GPS	Global Positioning System
DGPS	Global Positioning System with a reference station to achieve higher accuracy in the positioning
DP2	Vessel classification category
SW	South West
NE	North East
XRF	X-ray fluorescence analysis
XRD	X-ray diffraction analysis
PCA	Principal Component Analysis

1 Introduction

The main objective of the UKOOA phase II - task 1 project was to do a chemical, physical and biological characterisation of two cuttings piles. The characterisation should be based on the OLF-Guidelines for characterisation of cutting piles (OLF, 2001), and the two piles were selected based on the criteria that:

- The piles should be mapped (physical extent) from before
- The piles should be fairly large
- One of the piles should contain discharged oil based cuttings
- One of the piles should contain primarily discharged water based cuttings

Based on these criteria, and ease of accessing possible piles, the Beryl A platform was selected as a representative for an oil based cuttings pile (OBM pile), while the Ekofisk 2/4 A platform was selected as a representative water based pile (WBM). The Ekofisk pile is not representing a purely water based pile as also synthetic drilling fluids containing esters and poly-alfa-olefines ('pseudo' oils, PBM) have been used during the drilling operations at the 2/4 A platform. The main discharge (about 90%) has, however, been purely WBM discharges.

Within the task 1, both planning of survey and sampling locations, offshore sample collection, and analysis and interpretation of data is included. The offshore survey also included collection of samples (bulk material) for several other tasks within the UKOOA phase II program.

The Beryl A platform is a concrete platform standing in 117 meters water depth. The structure has 19 hollow cylinders at the sea bottom, of which 3 are extended upwards to form legs (also used for drilling and utilities), while the remaining cylinders are used for oil storage. The platform is in the British sector of the North Sea, and the Beryl field is operated by Exxon-Mobil UK. In addition to the main platform, a satellite steel platform and a flare tower are connected, serviced by walkways. A total of 73 wells (or drilling incidents) have been drilled. The cuttings discharges have occurred from the south side of the platform. The mapped cuttings pile is situated below the tank base to the south, forming a rather steep pile, sheltered from the main currents and waves. Drilling activities took place from 1976-1997. The pile is mapped (SubSea 1996) to have a volume of 24 600 m^3 (Appendix 9). The pile has the highest point close to the discharge point at the concrete structure.

The Ekofisk 2/4 A platform is an eight-leg steel structure standing in 72 meters water depth in the Ekofisk field. The structure is located about 2 km from the main Ekofisk complex. The platform is in the Norwegian sector of the North Sea. The Ekofisk field is operated by Phillips Petroleum Norway (PPCoN). The cuttings pile is mainly situated underneath the jacket between the legs of the riser section. Drilling has taken place in the period 1973-94, and a total of 37 wells have been completed. The pile has been mapped (Cripps *et al.*, 1999) to have a volume of 5 300 m^3, and a peak height of 6 about meter (underneath the structure) (Appendix 8).

2 Mapping and surveys

2.1 Mapping

The Beryl A was mapped by SubSea (Document No: AB-R-RP-00132) in 1996. The full report can be found in appendix 9. The mapping was conducted by a sonargraphic technique with a sonar buoy positioned at a fixed point at the edge of the cuttings pile. The report contains contour maps of the cuttings pile from which the volume calculations was made. No new physical mapping data was produced during the survey. Details on the slope of the cuttings pile can be found in the report (Document No: AB-R-RP-00132). Based on the experience from this characterisation survey, the mapping performed in 1996 seems to be accurate. It can however not be ruled out that some changes of the pile, e.g. erosion, have occurred since the previous mapping was done. The Beryl pile was in 1996 mapped to have a volume of 24 600 m^3, a maximum height of 20 m, and an extension of about 70 m (see appendix 9) however the pile height drops quickly from the discharge point close to the structure.

The Ekofisk 2/4 A was mapped in 1998. The mapping were obtained landing the ROV on a station grid on and around the pile obtaining accurate depth from the ROV pressure sensor. The ROV operations were made by SubSea, and the mapping data were processed by Rogaland Research (Cripps et al., 1999). The Ekofisk 2/4A pile was measured to have a maximum height of 6.5m, a volume of about 5 300 m^3, covering an area of about 2 700 m^2 (see appendix 8). Rough estimations of erosion rates presented by Cripps et al. (1999) indicate that possibly 6% of the cuttings pile at Ekofisk might have become eroded from the time of mapping to the sampling occurred for this project. With the sample approach taken, it has not been possible to confirm this estimation.

With the height and shape of these two cuttings piles, we estimate that more than 90% of the pile cuttings material is within the mapped area, having a layer thickness >10cm.

2.2 Previous surveys

At Beryl, there are no data available from previous investigations of chemical or physical properties of the actual cuttings pile. There have however been investigations in the periphery of the cuttings pile with Benthic landers obtaining pore water profiles as well as measurements in the sediment (Shimmield et al., 2000).

At the Ekofisk 2/4 A, vibro-core samples of the cuttings pile were taken during the 1998 mapping survey (Cripps et al., 1999). These core samples were primarily used to match the cuttings layer thickness against the total pile map. The core samples were also analysed for most of the organic and inorganic compounds analysed during this

UKOOA task 1 work. The results from the current characterisation work will be compared to the 1998 survey results.

3 Sampling

The survey was conducted with the vessel Edda Freya chartered from DeepOcean subsea services. The vessel is classified as a “DP2 vessel”, which implies, amongst others, that the vessel was equipped with a dynamic positioning system achieving accurate positions from a differential GPS (DGPS) signal. All sampling operations took place close to the platform (within about 40 meters from the installation) and seabed pipelines being tied up to the platform.

In addition to the GPS signal, a moored transponder 300m from the platform and a laser beam reflected from a fixed point at the platform served as a back up system if the DGPS signal were weak or lost. To accurately position the sampling equipment at the sea bottom, all gear was supplied with HI-PEP transponders making it possible to achieve a position accuracy of at least 5 m when the equipment was used in the described manner. This positioning also made it possible to operate close to pipelines without simultaneous ROV surveillance. Despite the accurate positioning of the sampling equipment, some equipment (e.g. the coring device) proved difficult to position and operate on the cuttings surface (especially at Beryl).

3.1 Sampling equipment

Most analysis parameters (physical, chemical and biological) were measured on the collected samples, either directly on deck or later in the lab. In addition, physical parameters of the cuttings material was measured using a cone penetration system (CPT). To improve efficiency, a vibro-corer equipped with a CPT was used. The gear listed below was brought along either for main sampling or as backup. All equipment used during the field survey was included in the OLF Guidelines and suggested as proper tools for sampling in cuttings piles. The experience made and feasibility of using these gears are further discussed in the next section.

Gear	**Purpose**
• Vibro corer	Long sediment cores
• Gravity corer	Long sediment cores (Backup)
• Boxcorer. 0.25 m^2	Bulk material
• Boxcorer 0.1 m^2	Undisturbed sediment
• Smøgen grab (small Boxcorer) 0.1 m^2	Undisturbed sediment
• Multiple corer	Undisturbed short cores
• Van Ven Grab 0.1 m^2	Benthos

Pictures of most of the sampling equipment are presented in Appendix 11.

3.2 Experience

3.2.1 Boxcorer, multiple corer, Smøgen grab and Van Ven grab

The two boxcorers (both 0.1 and 0.25 m^2) both worked fine in both cuttings piles. Due to the different characteristics however, the boxcorer penetrated different in the two piles. It was therefore necessary to adjust the boxcorer to avoid too deep penetration that would destroy the top layer in the Ekofisk pile. At this pile it was possible to obtain 60 cm penetration.

At the Beryl A, the cuttings material was less penetrative. The deepest boxcorer penetration achieved in this pile was 40 cm, while the most common penetration depth was about 25 cm. The failure frequency of sampling with the boxcorers was low. This type of boxcorer has also been used when investigating cutting deposits at the Frigg area (Westerlund, 2000), with successful results.

The Smøgen grab was planned used to sample “undisturbed” samples of a predetermined size to be used in a separate phase II task. The Smøgen grab had been successfully used for this purpose in other environments. The Smøgen grab (“lightweight” boxcorer) was only tested at Beryl, but no successful sampling was made. Since they have the same size, the small boxcorer could replace the Smøgen grab when sampling. Due to the poor performance of the grab equipment at Beryl, it was not attempted used at Ekofisk. Based on this experience, we would not recommend the use of such Smøgen grab as the primary tool for sampling in cuttings piles.

The multiple corer was tested at both Beryl and Ekofisk. We did not manage to get any useful cores from the Beryl pile. We were slightly more successful in the Ekofisk pile, where, after a few attempts, sampling was successful. However not all the cores in the multiple corer were successfully sampled. It seems that the multiple corer is too sensitive, and whenever possible the boxcorer should be used. If, however, the feature of undisturbed cores with the overlaying water phase is needed for experiments or other reasons, the multiple corer still is a useful tool.

The van Veen grab worked satisfactory. The sampling of sediment for Benthos does not need very deep penetration of the tool to achieve good samples, and hence this grabs is quite suitable and easy to handle, with little failure when sampling. Consequently the van Veen grab is useful when only the top layer of the cuttings pile is needed.

3.2.2 Coring

The most difficult samples to retrieve from a cuttings pile is deep cores vertically into the pile. Fairly successful coring have been made with a vibro-corer in several of the cuttings piles at the Ekofisk area by Cripps et al. (1999). At this occasion, a medium weight vibro corer with a total weight of 1 ton (from Alluvial mining, UK) was used. There are several factors that could affect the vibro-core sampling, where the most important apparently is the elevation of the cuttings pile surface. The more horizontal the surface in the sampling area, the easier it is to carefully position the gear on the surface. A soft surface of the cuttings pile may also cause problems in positioning the equipment as it may sink into the cuttings material.

Within the current project, the main coring device used was a vibro-corer with built-in CPT (cone penetration torque). The corer is rather heavy (about 2 ton), but has the useful operational characteristic that it can be operated hanging from a crane (so-called dynamic load). If the sediment, or in this case, the cuttings pile surface is soft or have a high elevation, the gear could still be operated if the weather conditions allow it.

Deep cores were successfully obtained from both platform sites, but several unsuccessful attempts were made (especially where the slope of the cuttings pile was steep). The weather conditions during this survey, which most of the time was within the upper acceptable level in terms of wave and wind conditions, did not allow the feature releasing the vibro corer under dynamic load to be used. The lighter vibro-core used in fieldwork 1998 (Cripps et al., 1999) seemed to be more suitable for sampling in cutting piles, at least when the dynamic load release could not be used.

The use of the gravity-corer for sampling of these cutting piles was not very successful. Larger cores (e.g. 30-60 cm long) were more easily achieved by sub-sampling the box-corer samples. The Gravity corer seems to be less suitable for coring sampling of cuttings piles even if the cuttings layers are thin.

4 Field work

The field work took place from 18th to 30th September 2000, using the supply ship, Edda Freya, supplied with a large offshore crane. Geocore AS was responsible for most of the sampling equipment, while Danish Geotechnical Institute (DGI) operated the vibrocorer. The ship was equipped with a working class ROV, and this was used for some limited inspection of the cuttings piles as part of a test run of the newly installed ROV. (The ROV was not hired for use in this survey).

The equipment used, the type of samples retrieved and the type of analysis performed on them are summarised in Table 1 and Appendix 1.

Table 1: Summary of the status for different sampling equipment based on experiences from three different field surveys of cuttings piles

Device	**Purpose**	**Succesrate**	**Turnover time**	**Equipment status**
Cuttings sampling		%	Hours	
Vibrocorer	Long sediment cores 1- 5 m	20	1-2	Availble vibro cores not very efficient in cuttings piles
Large Boxcorer 0.25 m2	Bulk material, Cores<60 cm	95	0.25-1	
Large Boxcorer 0.1 m2	Bulk material, Cores<60 cm	95	0.25-0.75	Efficient tool, works well in virtually all kind of sediment
Van Ven Graab	Bulk material, Biota samples	95	0.25	Efficient tool, works well in virtually all kind of sediment
Multiple corer	Undisturbed cores<30 cm	50	0.75	Efficient tool, works well in virtually all kind of sediment
CPT-measurements	Geophysical profiling		1	The geophysical results obtained in cuttings not very useful to other purpose than defining the thickness of the cuttings layer

4.1 Coring

The proposed sampling plan scheduled 3 vibrocore samples to be taken at Beryl A. A map showing the sampling locations is plotted in Figure 2. The 3 sample locations for deep cores were selected based on the pile size, height and location relative to the platform. The maximum possible penetration depth of the vibrocorer used is 6 m, while the mapping of the pile showed that the pile thickness at the sampling point closest to the platform was about 12 m thick. The three sampling points were hence chosen so that from the two outermost sampling points, cores penetrating through the pile and into the underlying sediment could be retrieved. The core that was taken in the peripheral part penetrated through the entire cuttings layer. At this location successful CPT measurements were also carried out.

At Ekofisk 2/4A, one vibrocore sample was scheduled to be taken from the NE side of the platform. A map showing the sampling locations at Ekofisk can be seen in Figure 2: Sampling locations at the Beryl A platform in UTM coordinates grid 32. During the field survey, samples were collected for several projects within the UKOOA phase II programme. The label denotations reflects this: SINTEF – bulk material boxcore. The main part of the cuttings pile at Ekofisk 2/4 A is placed underneath the platform. Since it was not possible to sample with the vibrocorer underneath the structure, the cuttings thickness in the selected sampling area was well within the limits set by the equipment. One successful vibrocore sample was retrieved from the planned location, and CPT measurements were also made. In the investigation of cuttings piles at Ekofisk in 1998, a core sample was taken on the SW side of the platform. Data from this core are also used in the characterisation of the chemical components at the Ekofisk pile.

4.1.1 Pile coverage by the coring

The coring at Beryl was problematic and no penetration through the pile was achieved at the thicker part even though the whole pile was located in front of the platform. This will rise uncertainties if important pile characteristic exist in the relatively large cuttings deposits in the historical layers that we not succeeded to sample.

The coring at Ekofisk 2/4A will most likely to a large extent cover all different layers in the cuttings pile with cores penetrating all through the cuttings layer on both side of the platform. Additionally data from the surface layer at this location helps us also to evaluate the possibility to trace the historical layer in a relatively short core in the periphery.

4.2 Boxcorer

The boxcorer was primarily used to sample bulk material to be used in several of the other tasks within the UKOOA drill cuttings programme. The sampling progressed with no or minor problems and well within expected time limits (actually down to 15 minutes working time per boxcorer sample). The success in sampling with this equipment was much a result of proper planning and organisation of the sampling process onboard. To achieve this, rather extended adjustments were done on the ship deck during mobilisation. The system was set up so that the whole content of the boxcorer was dumped directly into a plastic box lined with polyethylene foil. The sampling locations are shown in figures 1 and 2.

4.3 Grab samples

Grab samples were taken for benthos analysis only (as part of the characterisation work). The benthos samples were collected at one location within each pile, and one reference station 1000 m downstream of each pile. Five (5) replicate grab samples were taken at each of these four locations.

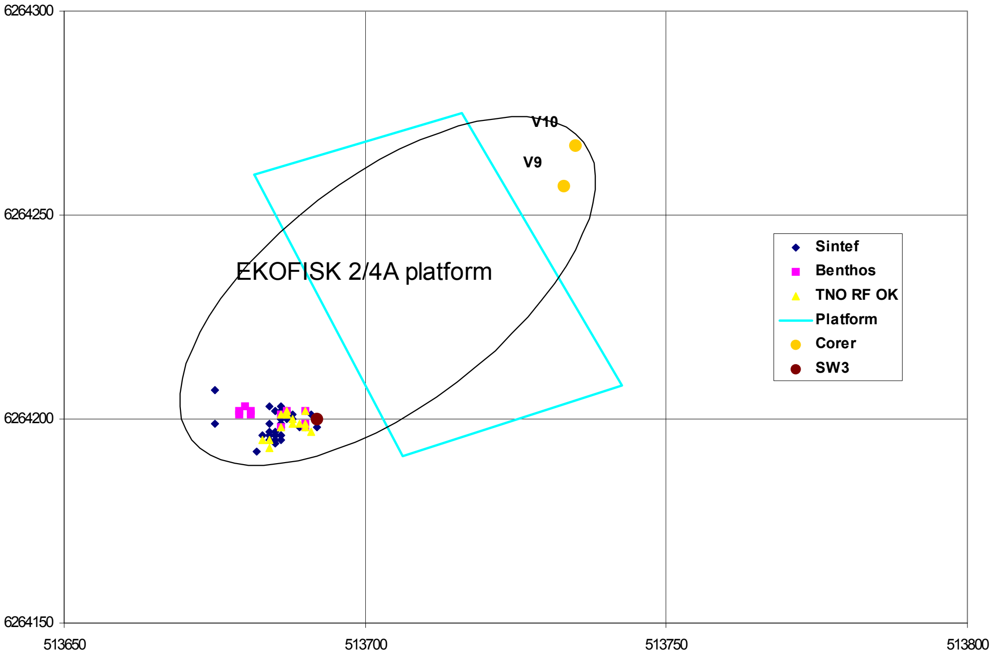


Figure 1: Sampling locations at the Ekofisk 2/4 A platform in UTM co-ordinates grid 32. During the field survey, samples were collected for several projects within the UKOOA phase II programme. The label denotations reflects this: SINTEF – bulk material boxcorer samples, part of task 3, TNO – bulk material samples, task 2c, RF CEFAS OK – bulk material samples for task 3 and 1 (RF), task 2c (CEFAS) and addition to task 3 (OK – University of Oklahoma), core samples – deep/vibrocore samples for task 1.

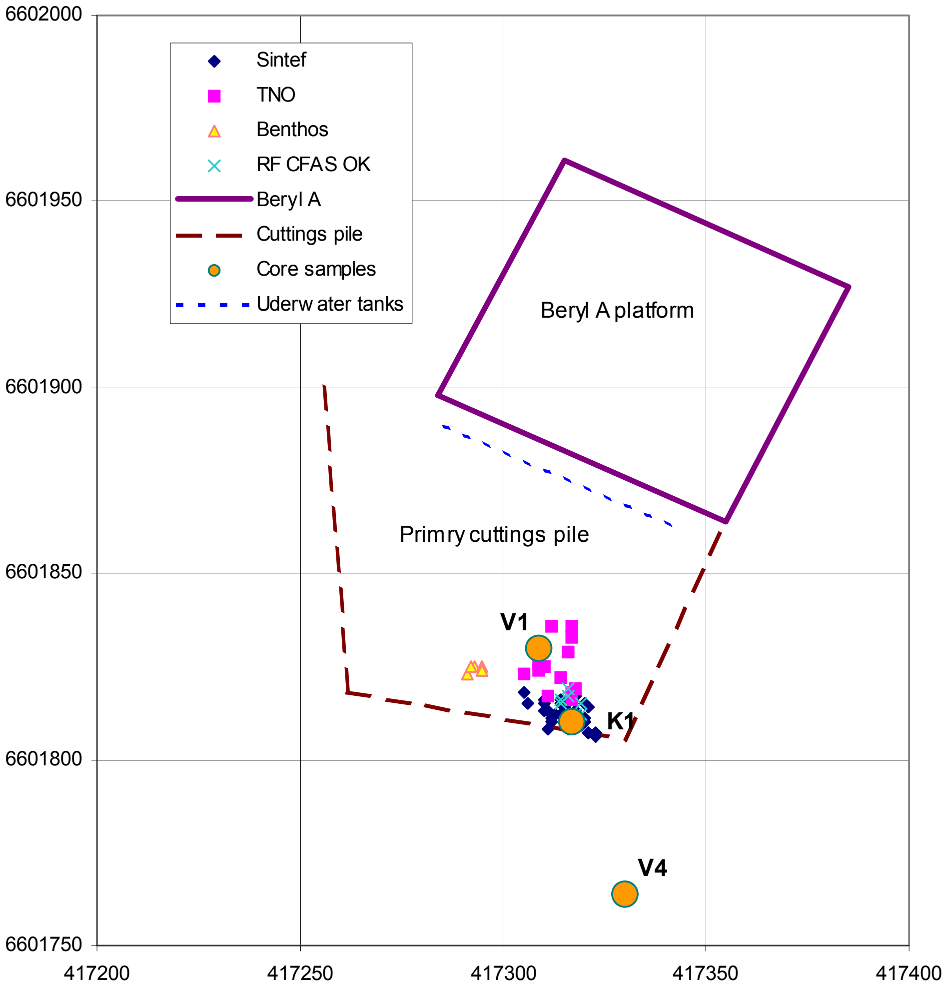


Figure 2: Sampling locations at the Beryl A platform in UTM coordinates grid 32. During the field survey, samples were collected for several projects within the UKOOA phase II programme. The label denotations reflects this: SINTEF – bulk material boxcorer samples, part of task 3, TNO – bulk material samples, task 2c, RF CEFAS OK – bulk material samples for task 3 and 1 (RF), task 2c (CEFAS) and addition to task 3 (OK – University of Oklahoma), core samples – deep/vibrocore samples for task 1.

5 Methods

The characterisation work basically follows the intention of the OLF guidelines for characterisation of cuttings piles (OLF, 2000). These guidelines are, at present, prepared as a list of relevant analysis parameters and sampling equipment that might be feasible for cuttings pile characterisation. The input data, e.g. previous experience, has not been sufficient to draw conclusions on what actually turns out to be feasible in different situations.

The selection of proper analysis parameters for the characterisation of the two piles included in this work was based partly on earlier experience from cutting piles investigations (Westerlund and Cripps, 1999, Westerlund and Olsen, 2000). A selection of the most relevant chemical and physical parameters described in the OLF guidelines has been analysed. In addition, some more parameters have also been included, i.e. mineralogy, trace metal bioavailability (Part 2) screening test for endocrine disrupting effects, PCB:s (both Part 3) and NORM (naturally occurring radioactive material).

The analytical parameters selected include:

Physical properties
- Core description
- Cone penetration (CPT) Point resistance
- Shear strength
- Grain size distribution
- Density and water content

Mineralogy
- Major components
- Total of minor components
- Crystalline phases on whole rock and clay fraction

Chemical properties
- Organic contaminants
  - THC, PAH, NPD:s, Decalines, PCB (Dutch 7)
- Metals
  - Al, V, Mn, Fe, Ba, Cr, Co, Ni, Cu, Zn, As, Sr, Cd, Pb and Hg
- TOC, TON, Loss on ignition and density
- pH , Redox potential (eH) and sulphide
- NORM

Biology
- Benthos diversity index

Trace metal availability (bioavailability)
- Availability of trace metals in cuttings deposits-studied by sequential extraction.(Part 2)

Endocrine disruption
- Endocrine Disruption from drill cuttings material (Part 3)

Most chemical parameters were analysed on several layers of the core samples, both the vibrocore samples and sub-sampled cores from the boxcores (i.e. a total of about 70 samples from both piles were analysed for most of the organic parameters). Some of the physical parameters were analysed directly while sampled (i.a. on board), or when preparing the core samples for further analysis. Other physical parameters were analysed on the same fractionated material that was analysed for the selected chemical parameters.

6 Results

The result section is divided into four main sub-sections: preparation (e.g. sub-sampling of different layers) and visual observation of core samples, physical, chemical and biological properties.

No cores penetrating down to the underlying sand was obtained from the deeper parts of the Beryl A cuttings pile in the thicker part of the pile (e.g. the 5-15m thick layers). This can imply that unidentified levels of contaminants can be present in historical layers not sampled. However the obtained cores from the top sections of the thick sections of the pile together with the peripheral samples show correlation in contaminant type and concentration layer-wise, the thicker layer being represented in the central part of the pile. Based on this, the peripheral samples would most likely contain a thin layer of the most historic layer. If this thin layer would have a dramatic different contamination picture this would show on the contaminants data. Earlier experiences of cutting piles, (e.g. Ekofisk piles (Cripps et al., 1999) and others) indicate also that there is correlation between contaminant content and layer thickness based on pile thickness. However, neither in these cases has it been possible to compare with cores penetrating all the way to the underlying sediment in the clearly thickest parts of the pile. Even though we believe that the samples from Beryl A is representative for the cuttings pile the uncertainties with what might be buried in the most historic layer has to be kept in mind.

6.1 Preparation and slicing of cores

The sampled cores consist of a large number of layers with different colours and texture. The cores were sliced according to the visual layering structures. A schematic drawing of the layering structure in the different cores can be seen in Figure 3, and is also illustrated by the pictures in Figure 4 and 5. The characteristics of the different layers are summarised in Table 2 and 3 below. Photographs were taken of all cores during the slicing procedure, for documentation. Figures 4 and 5 show examples of the layering structures at Beryl and Ekofisk respectively.

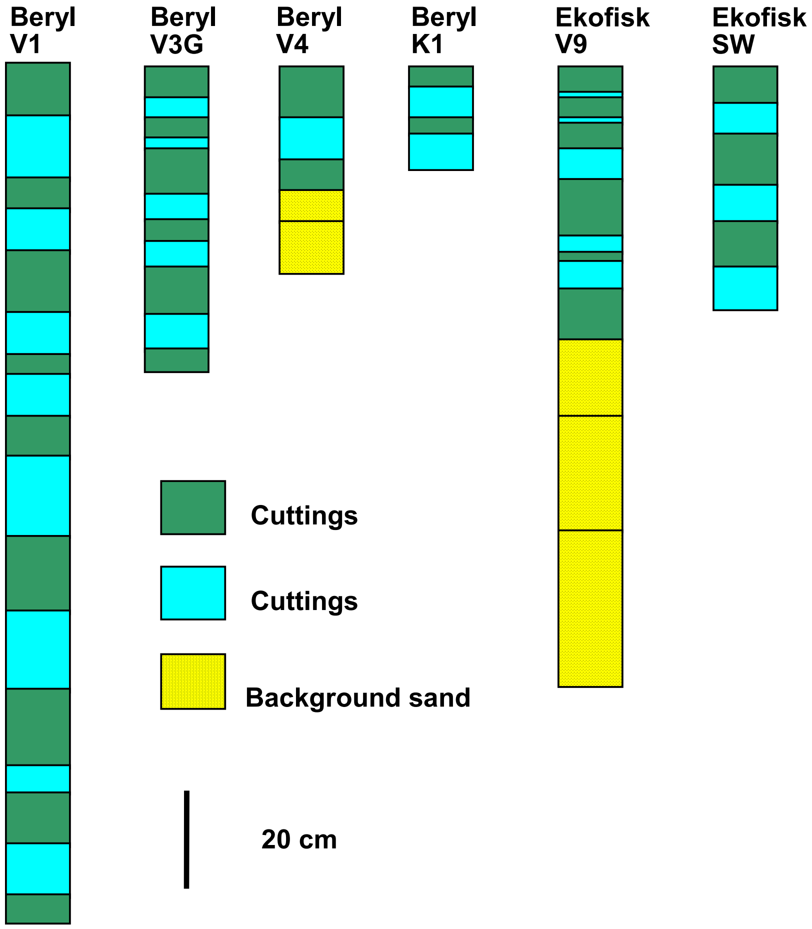


Figure 3: layering structure of the cores from Beryl A and Ekofisk 2/4A. The core numbering is the same as referred to in appendix. The two different shadings for the cuttings represent the successive layers (thickness) that the cores were divided into based on the visual observations of their layering structure. In the cases where the core penetrated through the cuttings layers and into the underlying sand this is shown by the different shading.

Table 2:Description of the cores from Beryl A. The core numbering is the same as referred to in appendix 1. Unless otherwise stated, the samples are drill cuttings. The reported smell of the samples is quite subjective, but gives an indication of what samples were most alike.

BERYL					
Core	**Slice (cm)**	**Colour**	**Smell**	**Texture**	**Comments**
V1	**0-10**	Black	Syntethic oil		Small clumps
V1	**10-22**	Brown	Syntethic oil		Small clumps
V1	**22-28**	Light brown	Syntethic oil		Small clumps
V1	**28-36**	Grey-black	Syntethic oil		Small clumps
V1	**36-40**	Grey-olive	Syntethic oil		Small clumps
V1	**40-48**	Light brown	Syntethic oil		Small clumps
V1	**48-56**	Grey-black	Oil		
V1	**56-60**	Light Grey-black	Oil		
V1	**60-68**	Grey-black	Oil	white dots	
V1	**68-76**	Brown-black	Oil		Dry
V1	**76-91**	Brown-black	Oil		Dry
V1	**91-106**	Brown-black	Oil	white dots	Dry
V1	**106-121**	Brown-black	Oil		Dry
V1	**121-136**	Brown-black	Oil		Dry
V1	**136-141**	Grey-black	Oil		Dry
V1	**141-151**	Grey-brown	Oil		Dry
V1	**151-161**	Grey-brown-green	Oil		Dry
V1	**161-166**	Grey-brown-green	Oil	coarser	Dry
V3G	**0-6**	Black	Oil		
V3G	**6-10**	Grey	Oil		
V3G	**10-14**	Grey-black	Oil		
V3G	**14-16**	Grey	Oil		
V3G	**16-25**	Black	Oil		
V3G	**25-30**	Black	Oil		
V3G	**30-34**	Black	Oil		
V3G	**34-39**	Black	Oil		Dry
V3G	**39-48**	Brown	Oil		
V3G	**48-56**	Grey-black	Oil		
V3G	**56-60**	Grey-brown	Oil		
V3G2	**0-6**	Grey-black			
V3G2	**6-13**	Black			
V3G2	**13-28**	Black-brown			Clumps
V3G2	**28-37**	Grey-brown			
V4	**0-10**	Black	Rotten		
V4	**10-18**	Light brown	Oil		
V4	**18-24**	Black	Oil		
V4	**24-30**	Olive green			Sand before cutting deposits
V4	**30-40**	Olive green			Sand before cutting deposits
K1	**0-4**	Black	Oil		
K1	**4-10**	Grey	Oil		Thin brown layer
K1	**10-13**	Grey-black	Oil		Weak smell
K1	**13-20**	Grey	Oil		Weak smell

Figure 4: Lower part of vibrocore1 (V1) from Beryl. The layering seen on the picture corresponds to the layers into which the cores were divided for further analysis.

Table 3:Description of the cores from Ekofisk 2/4 A. The core numbering is the same as referred to in appendix 1. Unless otherwise stated, the samples are drill cuttings. The reported smell of the samples is quite subjective, but gives an indication of what samples were most alike.

Core	Slice (cm)	Colour	Smell	Texture	Comments
EKOFISK					
V9	**0-5**	Black	Synthetic		Coarse
V9	**6-5**	Brown	Synthetic		
V9	**6-10**	Black	Synthetic		
V9	**10-11**	Grey	Synthetic		
V9	**11-15**	Black-brown	Synthetic		
V9	**15-22**	Grey	Synthetic		
V9	**22-33**	Grey-brown	Synthetic		
V9	**33-36**	Grey	Synthetic		
V9	**36-38**	Brown	Synthetic		
V9	**38-43**	Grey	Synthetic		Black parts
V9	**43-53**	Olive green			Sand before cutting deposits
V9	**53-68**	Olive green			Sand before cutting deposits
V9	**68-90**	Olive green			Sand before cutting deposits
V9	**90-120**	Olive green			Sand before cutting deposits
V10	**1-10**	Black	Oil		
V10	**10-13**	Olive green			Sand mixed cuttings
V10	**13-21**	Black			
V10	**21-28**	Olive green			Sand mixed cuttings
V10	**20-30**	Black			
V10	**30-35**	Olive green			Sand
SW3	**0-7**	Black	Synthetic		
SW3	**7-13**	Black-grey	Synthetic		
SW3	**13-15**	Black-brown-grey	Synthetic		
SW3	**15-23**	Black-brown-grey	Synthetic		Several layers
SW3	**23-30**	Black	Synthetic		Coarse layer
SW3	**30-39**	Grey	Oil		Fine grained layer
SW3	**39-47**	Light grey	Synthetic		

Figure 5: Sub-core (SW3) from a box corer taken at Ekofisk 2/4A. The layering seen on the picture corresponds to the layers into which the cores were divided for further analysis.

6.2 Physical properties

6.2.1 Cone penetration test

The CPT probe has three different sensors measuring:

- Local friction
- Pore water pressure
- Shear strength

When measuring a sample, the calculated values given take into account the difference from the readings obtained in both the water and the sediment. A raw data curve from the CPT measurements can be found in Appendix 7.

A summary of the results from both piles is presented in Table 4. The data referred to as sand is measured in the sand layer underneath the cuttings. The data given for glacial clay is from literature data, which have been included for comparison. The pore water pressure gave no relevant information with regard to physical properties of the cuttings pile. Sand has no shear strength if there is no confining stress. The corresponding parameter for sand is the Constrain modulus.

Table 4: CPT test results (both Ekofisk and Beryl are reported together). The data for glacial clay is added for comparison.

	Friction	**Shear strength**	**Constrain modulus**
	Deg.	**kPa**	**MPa/m^2**
Cuttings	0-25	0-2	
Sand	>45		30
Glacial clay*		>50-1000	

* Literature data

The CPT data had little significance in describing the piles. It was not possible to measure significant differences between the layers. Judging from these results, the information from this type of measurements in cutting piles is obviously very limited. The intention to record the layering structure of cuttings material by *in situ* measurements using this instrument was consequently not successful. The CPT tool was only useful to record the depth of the cuttings layer.

6.2.2 Shear strength measurements using a Wing Tool

To gather additional information about the physical properties of the cuttings material, the shear strength of the cores were also measured with a wing tool. The wing tool used makes it possible to measure lower shear strengths than what was the case with the CPT used offshore. Table 4 summarises the shear strength measurements from the two piles when using the wing tool.

Table 5: Shear strength from the wing tool measurements.

Beryl	**Sample**	**kPa**
V1	Core catcher	9,8
RF1	Bulk sample	7
		6
RF2	Bulk sample	5
Ekofisk		
RF6	Bulk sample	1,2
		4
RF7	Bulk sample	2
		4
SW1	Core Top	2,4
	Core Bottom	1,6
RF REF	Bulk sample	12
		14

The data show that the shear strength measurements vary slightly in the piles. The measured values are lower in the Ekofisk pile than in the Beryl pile. Shear strength measurements from other cutting piles (Bell et al., 1999) gave values in the same range (e.g. <2-40 kPa), and confirms that the cuttings material consists of soft material with low resistance.

6.2.3 Grain size distribution

A total of 29 samples were analysed for their grain size distribution, 18 from Beryl and 11 from Ekofisk. The samples were taken from different layers of the core samples, as specified in Appendix 1.

The grain size distribution was measured with two different techniques to cover a larger particle size interval. The same sample was analysed with both methods. For the large particles (e.g. >63 µm), sieving with a set of sieves of different mesh sizes were conducted. This sieving procedure also quantifies the total weight of the fine fraction which were further analysed by a coulter multisizer (the fine fraction was quantified down to 4 µm). Figures 6 to 9 show a selection of data representing typical grain size distribution of the cuttings material from the two sites. All data are available in Appendix 3.

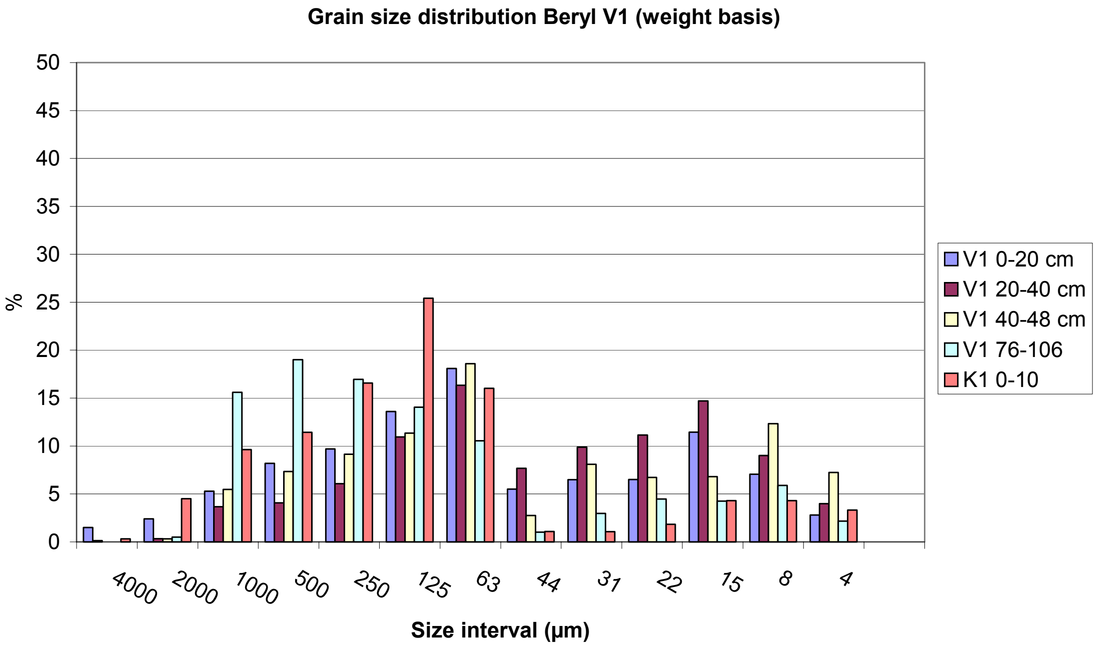


Figure 6: Example of grain size distribution at Beryl. Layers indicated are all cm thickness.

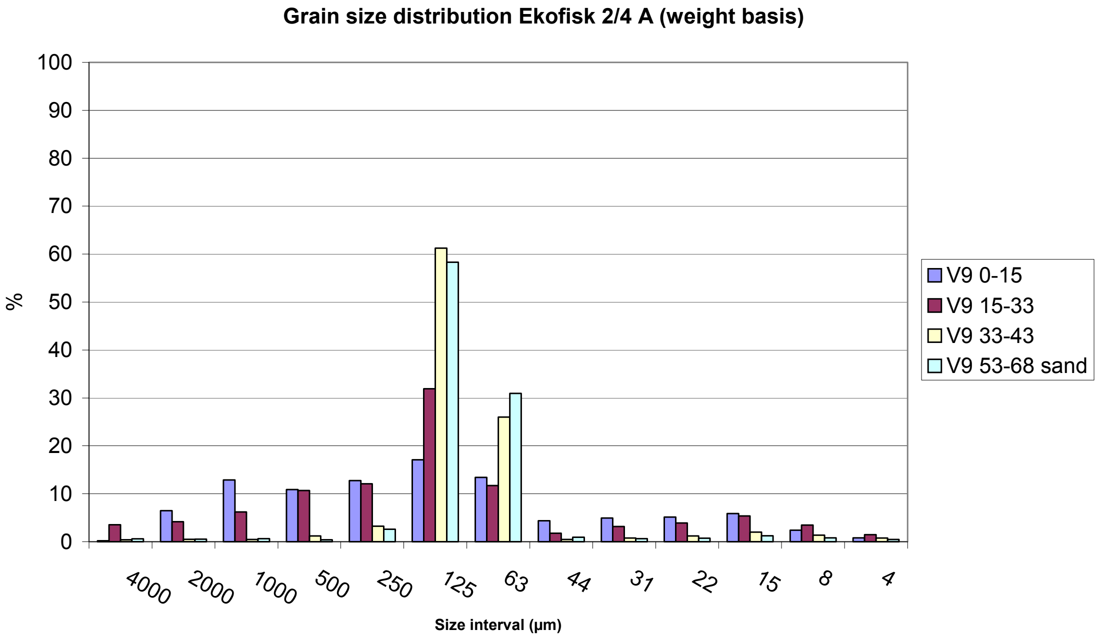


Figure 7: Example on grain size distribution at Ekofisk 2/4A. The V9 53-68 section is from the sand below the cuttings pile. Layers indicated are all cm thickness.

The grain size distribution at both sites shows a similar pattern. The size distribution is moraine-like with material in all size categories. The expected particle size distribution to be found in offshore marine sediments would be a normal distribution with the dominating fraction of material found in a much more limited part of the size distribution spectra.

In understanding the distribution of contaminants, the fine particle fraction is the most interesting. The fine particles have on weight basis the largest surface area. Contaminants is normally adsorbed or bonded to the surface of fine particles with more or less weak bindings. Figure 8-9 shows that the fraction of small particles in the cuttings is relatively large compared to the surrounding sediment. Consequently there is a potential to keep contaminants adsorbed in the pile.

The major source of the fine particles is barite used with the drilling mud. Although the remaining fine fraction in the piles is relatively large (in this case, for Beryl >40%, and for Ekofisk >30%), it is still small compared to the portions of mud used when drilling (e.g. a ratio of mud:cuttings of 4:1 could be expected, Kjeilen et al., 2001). This indicates that a significant portion of the fine particles are removed either during the settling of the discharged material into the pile, or later.

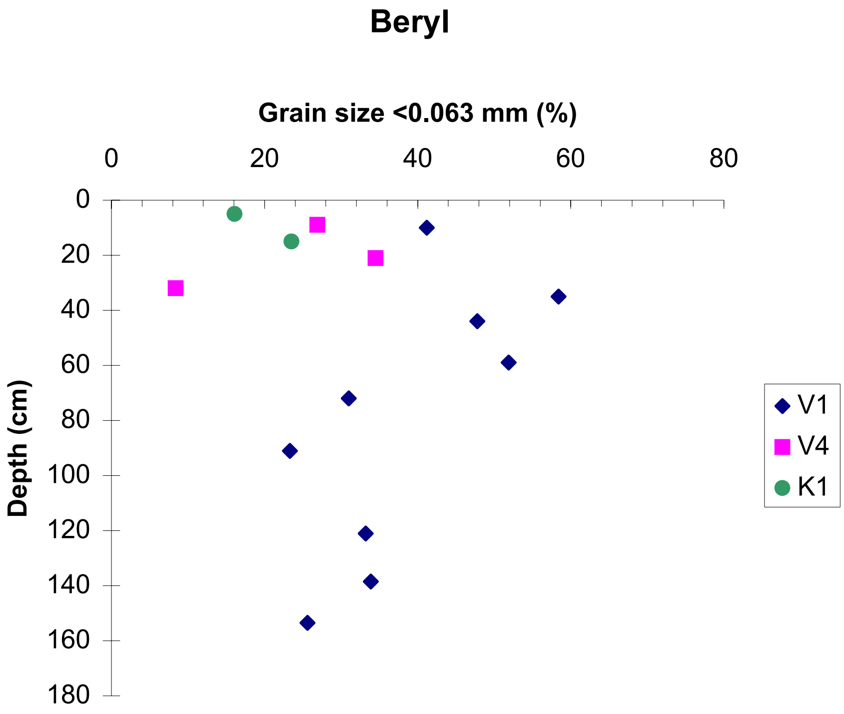


Figure 8: Fine fraction at Beryl

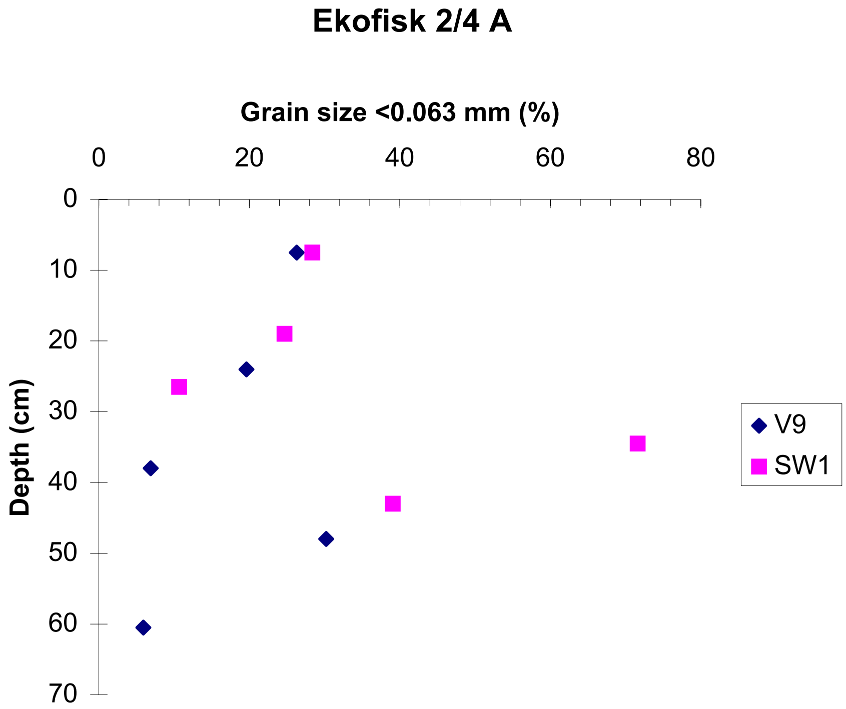


Figure 9: Fine fraction at Ekofisk 2/4A

6.2.4 Organic carbon

The organic matter is reported under this heading since the organic matter data also gives information of the physical characteristics of the material. The organic matter was quantified in two ways on a limited data set (Appendix 2):

- Measurements of total organic carbon (TOC) with elemental analyser (NIVA, Oslo)
- Loss on ignition (LOI) at 550^{o} C

LOI can be found for the whole dataset in appendix 3 where LOI is labelled glødetap. Additional LOI data can also be found in appendix 13 in the mineralogy data set.

The TOC measure only the organic carbon that can originate from the oil components or debris from biota accumulated in the cuttings. In the cuttings it is most likely that the TOC manly originates from oil and other drilling chemicals. The LOI measures all material that decomposes at 550 degrees. However there are several sources for error in the LOI measurements if the data should be used for interpretation of the content of organic material (Loss of crystalline bound water in the clay material, weight loss from oxides by loss of oxygen). The TOC data from Ekofisk 2/4 A shows a good fit with the THC in the top layer where the POB drilling fluid was found. Comparison between the TOC and measurements compared with the THC data from Beryl gives bad fit indicating that the TOC procedure might not be suitable for cuttings material. The LOI measurements can be seen plotted in the mineralogy section. The higher LOI compared to the North Sea background is a typical feature of a cuttings material and is one simple parameter that could be used to distinguish cuttings material from the substrate.

6.2.5 Density

The density of the cuttings material was measured on the same samples that were analysed for Grain size distribution. A summary of the data is presented in Table 6. The details are presented in Appendix 2.

Table 6: Summary of the density measurements at Beryl A and Ekofisk 2/4 A. In the third column the dry weight measurement is used to calculate the density of the dry material to be able to calculate the load of the different contaminants. The dry weight parameter is needed as all contaminants are quantified on dry weight basis.

Station	**Density**		
	Wet weight Range g/cm^3	**Average g/cm^3**	**Dry weight Average g/cm^3**
Beryl	1.75-2.6	1.97	1.58
Ekofisk 2/4A	1.68-2.04	1.80	1.36

The results obtained are in the same range as reported from other cuttings piles (Cordah and more). It could be noted that the cuttings deposits at Beryl A is slightly heavier than the cutting deposits found at Ekofisk 2/4 A.

6.3 Mineralogy

6.3.1 Methods

The samples to be analysed for mineralogy parameters were selected from the dried and homogenised samples previously prepared for the characterisation work (see below). The samples were stored in sealed plastic bags during the time from preparation to shipment for mineralogy analysis. X-ray Mineral SERVICES LTD UK performed the mineralogy analysis. The mineralogy work included:

– **Identifying major crystalline phases by:**

- Whole rock mineral X-Ray diffraction (XRD)
- Clay minerals (<2 µm) XRD

– **Determination of the total content of major and minor elements:**

- Major elements by X-Ray fluorescence (XRF) on a glass bead
- Minor elements by XRF on a powdered pellet

6.3.2 Sample preparation

Whole rock minerals:

To obtain a semi-quantitative measurement of the mineral components of a rock or soil sample, it is gently disaggregated using a pestle and mortar and then 'micronised' using a McCrone Micronising Mill to obtain an x-ray diffraction 'powder' with a mean particle diameter of between 5 - 10 microns. The slurry is then dried and packed into an aluminium cavity mount, producing a randomly orientated sample for presentation to the x-ray beam. Each sample is analysed between 5° to 60°2θ (theta), at a step size of 0.05°/sec using x-ray radiation from a copper anode at 40kV, 30mA.

Clay minerals:

Separating the <2 micron fraction is achieved by ultrasound, shaking and centrifugation. The total weight of clay extracted is obtained by removing 20ml of the clay suspension and evaporating to dryness. Size fractions other than <2 micron (e.g. 2-16 micron) are obtained by varying the centrifuge speed and time. The clay XRD mount is obtained by filtering the clay suspension through a Millipore filter and drying the filtrate on the filter paper. The samples are analysed as untreated clay, after 'glycolation 'overnight and following 'heating' at 380°C for 2 hours and 550°C for one hour. The initial scan for these four treatments is between 3° and 35° 2θ (theta) at a step size of 0.05°/sec using x-ray radiation from a copper anode at 40kV, 30mA. The untreated sample is also analysed between 24-27° 2θ (theta) at a step size of 0.02°/2 sec to further define kaolinite/chlorite peaks.

Major elements analysed for:

The major elements included in the XRF measurements were; SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, SO_3, Cl and BaO. In the later calculations it is assumed that the above compounds constitute 100% of the sample content.

Powdered samples were first weighed accurately (0.7000g), then mixed with a fixed weight of Lithium Metaborate of 2.3000g. This mixture was then fused at 1100°C for 20 minutes then cast into a 32mm diameter Glass "Bead". The detection limits for the elements were between 50-200 mg/kg depending on the compound.

Minor elements:

The minor elements included in the XRF measurements were; V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr,Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, I, Cs, La, Hf, Ta, W, Hg, Tl, Pb, Bi, Ce, Pr, Nd, Th, and U. The samples were crushed in Tungsten Carbide then milled. Approximately 10g of the powdered sample was mixed with Polyvinylalcohol binder (Movial) and pressed at 12 ton to produce a 32mm Pressed Powder Pellet. The detection limits for these elements were about 5 mg/kg for all elements. However, the high Ba content of the cuttings samples made the Cr results less reliable.

The samples were then analysed using a **Spectro X-Lab** Energy Dispersive Polarised X-ray Fluorescence (EDPXRF) analyser at following conditions:

ANODE :	Rhodium
DETECTOR :	Si(Li)
TARGETS :	Majors: Co, Al, HOPG Traces: Mo, Al_2O_3, B_4C, Co, HOPG.

The XRF was fully calibrated using International Rock, Soil, Ore, Sediment, Ash, Oil and Water standards to ensure repeatable and accurate analysis.

Loss of ignition

Loss of ignition (LOI) was in this set of samples determined as weight loss of a dried sample after ignition at 975 degrees. The LOI results in Appendix 2–3 are performed according to Norwegian standard 4764 with drying for 2 hours and then ignition at 550 degrees. The sample material for the mineralogy and grain size distribution was sliced differently.

6.3.3 Mineralogy results

The data from the mineralogy can be found in Appendix 13. The major elements are traditionally calculated as oxides in % of total. In addition to the elements measured by XRF, results from loss of ignition (LOI) are included in the matrix before it is added up to 100%. The determination of the minor elements showed that Sr could have been included in the major element matrix (considering the amount of Sr compared to total volume). A separate sheet with a less traditional mode of calculating the major elements can also be found in appendix, where Ba is calculated as Barite and remaining sulphur as S. It is most likely that the Ba in these samples is predominately barite ($BaSO_4$).

6.3.3.1 Minor components XRF

For the minor elements there are good agreement between the XRF results and the ICP-MS results (using the NS4770 digestion method for sample processing) for the elements Cu, Ni, Zn, Pb and Fe. A likely explanation for this is that large parts of these metals are bound as sulphides that will dissolve in the nitric acid, while mineral bound metals will only be partly dissolved in the acid. The V and Cr (in the samples below cuttings) show higher concentrations indicating strong mineral bound metals as expected for these elements.

In the data sets for Sr there are large differences between the two analysis methods. The XRF results show that the total Sr concentration is 10 times higher than the acid soluble Sr (ICP-MS). A reasonable explanation for this is that most of the Sr originates from the barite. The Sr is known to replace Ba in the barite crystals (Deer, et al. 1969) and this will explain the low recovery of Sr from acid extraction.

6.3.3.2 Beryl A

The measurements of the main components show that the dominating component of the cuttings is quarts (SiO_2) and Ba ($BaSO_4$). They are both found at similar concentrations in the Beryl cuttings. It could also be noted that there is an excess of sulphur, which is not bound as sulphate in the barite. In the substrate layer found below the layers of the Beryl core (core V4) containing cuttings material, quarts is the dominating component, as expected. An illustration of the main components is shown in Figure 10 below.

Figure 11 shows the crystalline phases found in the cuttings at Beryl A. Sediments in anoxic basins usually contain Pyrite (FeS_2) that is formed in the water column, and then settles on the sea bottom. The rather large fraction of pyrite found in the cuttings pile

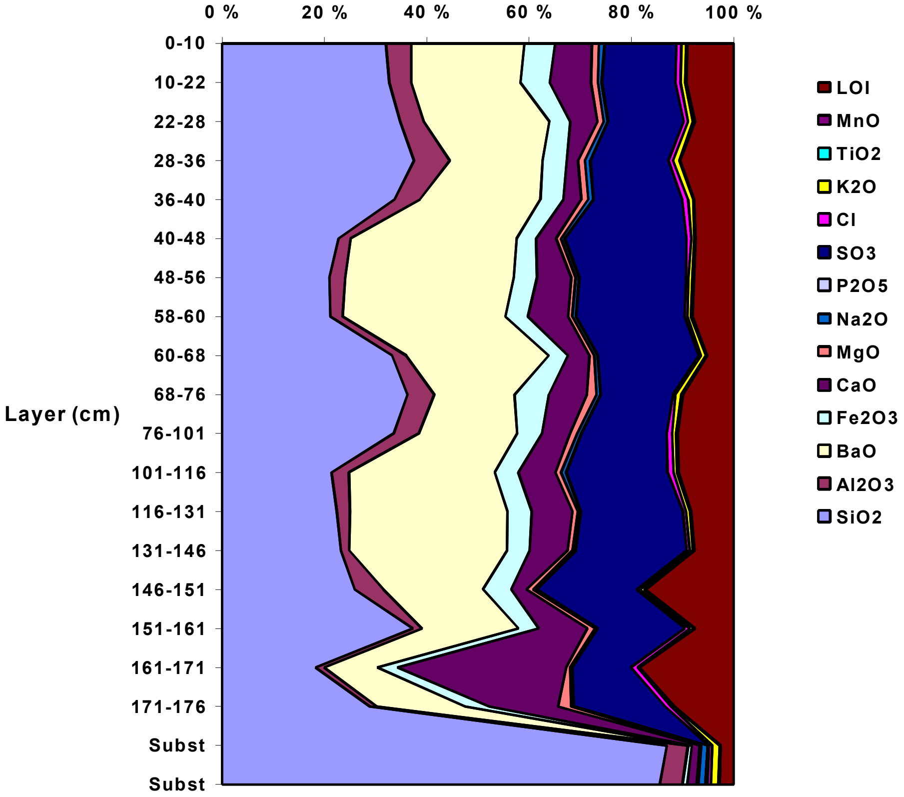


Figure 10 : Beryl A, core V1 main components calculated as oxide phase and organic matter (LOI). The substrate layer (bottom of figure) is the underlying sand layer from core V4.

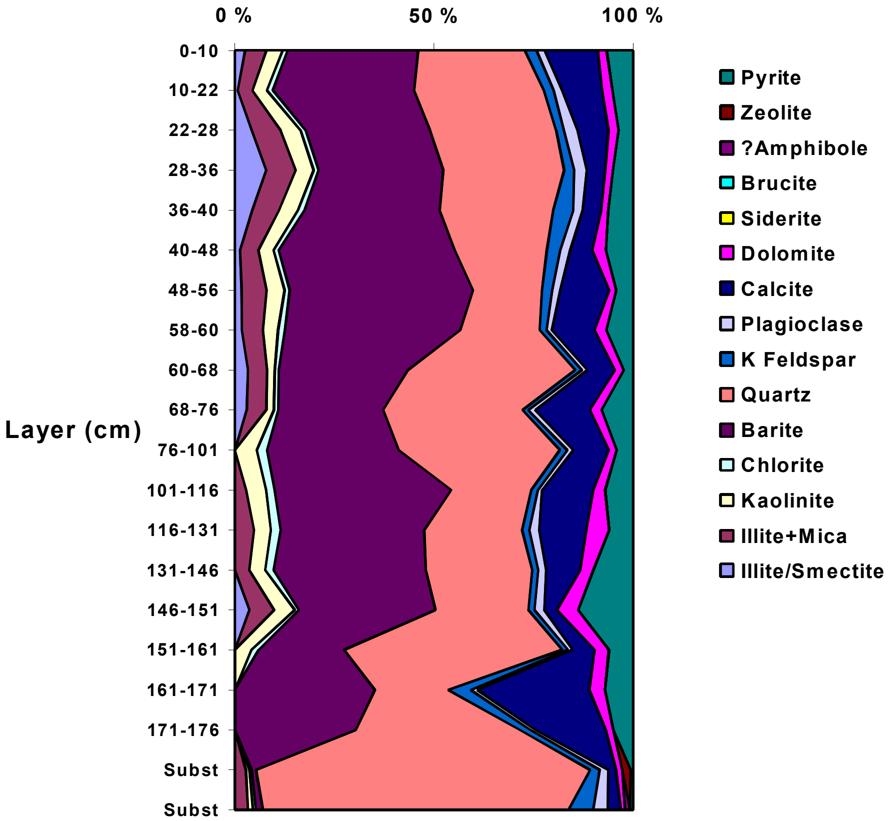


Figure 11: Beryl A, core V1. Semi-quantitative results for the crystalline phases. The substrate is the underlying sand layer from core V4.

was most likely formed either in the drilling process or during anoxic degradation processes within the cuttings pile. The latter is probably the most realistic explanation.

Table 7: *Modelling the Fe mineral composition from the major component data.*

	Beryl A				Ekofisk 2/4 A		
Core	**Slice (cm)**	**Fe/S mol ratio**	**Fe/S mol ratio**	**Core**	**Slice (cm)**	**Fe/S mol ratio**
		100% S in Fe	**50% S in Fe**			**100% S in Fe**
V1-1	0-10	1.05	2.11	V9	0-5	0.45
V1-1	10-22	0.80	1.59	V9	5-11	0.45
V1-1	22-28	0.86	1.72	V9	11-15	0.52
V1-1	28-36	0.39	0.78	V9	15-22	1.10
V1-1	36-40	0.41	0.81	V9	22-23	0.46
V1-1	40-48	0.26	0.52	V9	33-36	1.05
V1-1	48-56	0.54	1.08	V9	36-38	0.66
V1-1	58-60	0.42	0.85	V9	38-43	0.54
V1-1	60-68	0.33	0.66	SW3	0-7	0.74
V1-1	68-76	0.55	1.09	SW3	7-13	0.42
V1-2	76-101	0.35	0.71	SW3	13-15	0.64
V1-2	101-116	0.42	0.85	VC2-1	0-9	1.13
V1-2	116-131	0.54	1.08	VC2-1	9-12	0.94
V1-2	131-146	0.36	0.71	VC2-1	12-15	1.12
V1-2	146-151	0.28	0.56	VC2-1	15-30	0.49
V1-2	151-161	0.27	0.54	VC2-1	30-41	0.48
V1-2	161-171	0.32	0.63	VC2-1	44-50	1.10
V1-2	171-176	0.26	0.51	VC2-1	50-56	1.61
V4	0-10	0.35	0.70	VC2-1	58-68	0.44
V4	10-18	0.39	0.78	VC2-1	68-77	0.53
V4	18-24	0.43	0.86	VC2-1	77-89	2.05

Table 7 shows the modelling of the Fe from the main constituent's data when the remaining sulphur is used for Fe to form Fe-sulphides. With a molar ratio for Fe/S of 0.5, the Fe is bound as pyrite (FeS_2) while a ratio of 1 indicate that the Fe is found as FeS. A ratio less than 0.5 indicate that the remaining sulphur has to be bound to some other constituent or exist as elemental sulphur. A ratio above 1 suggests that there is not sufficient sulphur to bind all Fe as Fe-sulphides, and that the residual Fe then most likely is found as oxides. The data from Beryl A shows that it is likely that the Fe in most layers is bound in pyrite. However, in the deepest sampled part elemental sulphur might exist.

The results from the XRD measurements of the clay fraction of Beryl are shown in Figure 12. The results are shown as % of the clay fraction. Results with the % figures calculated on the total minerals can be found in appendix 13.

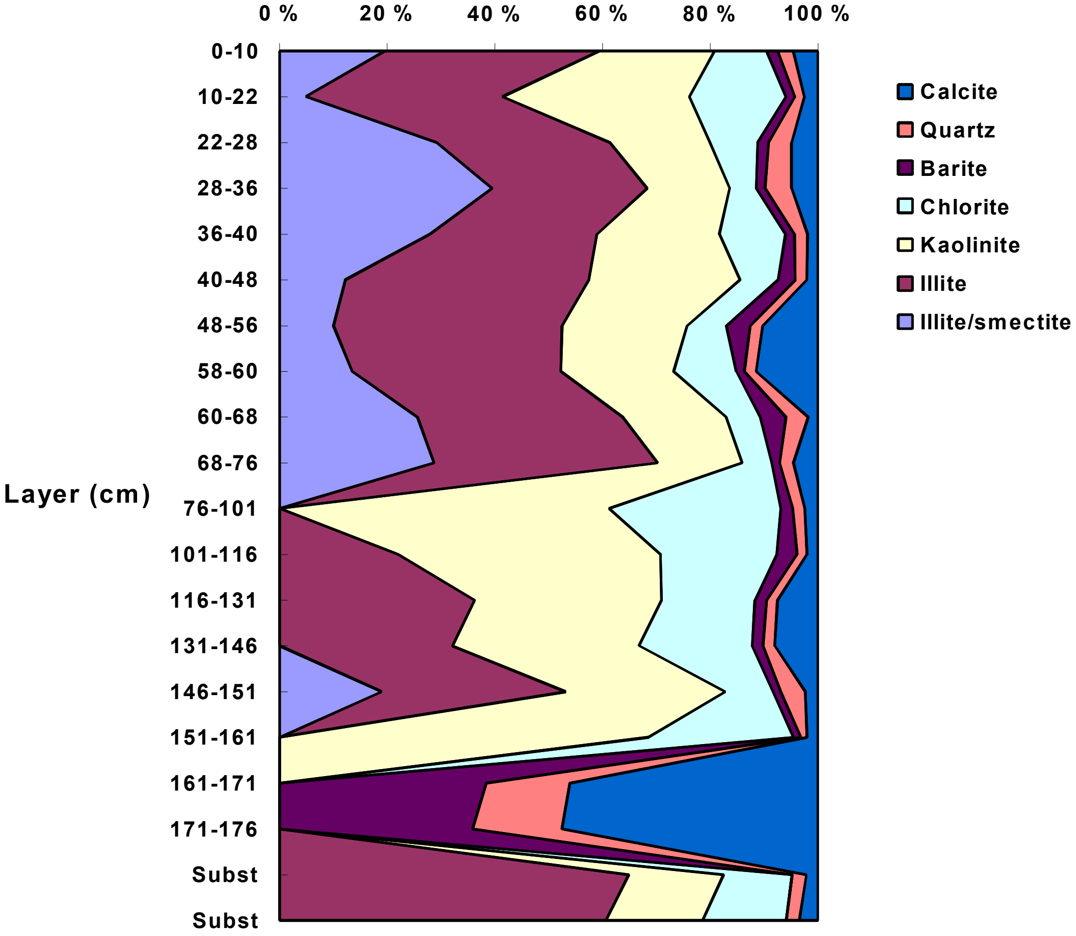


Figure 12: Beryl A core V1. Clay fraction (<2µm) results for crystalline phases. The subst is the underlying sand layer from core V4. The results is shown as % of the clay fraction.

6.3.3.3 Ekofisk 2/4 A

The mineralogy of the Ekofisk 2/4 A cores is presented in Figure 13-15 below. There is much similarity in the major components between the two piles, with the dominating components being barite and quarts. However, the deeper part of the Ekofisk 2/4 A cuttings pile contains less Ba. This can be seen from the cores at both sides of the cutting pile.

For the crystalline phases there is one layer of the core at the south west side that deviates largely from the general pattern seen, with a high content of brucite. This layer consisted of courser material than what was normally observed. The brucite may originate from concrete and is probably remainings from discharged concrete. The crust found on this part of the cuttings pile was found to consist of concrete (see crust section,6.4.12).

It could be noted that all samples from the Ekofisk 2/4 A also contained pyrite. The fit with Fe at this pile shows that most Fe is likely bound to sulphur.

The results from the XRD measurements of the clay fraction of Ekofisk A are shown in Figure 14-15. The results are shown as % of the clay fraction. Results with the % figures calculated on the total minerals can be found in appendix 13.

More comments can be found in the Beryl A section above.

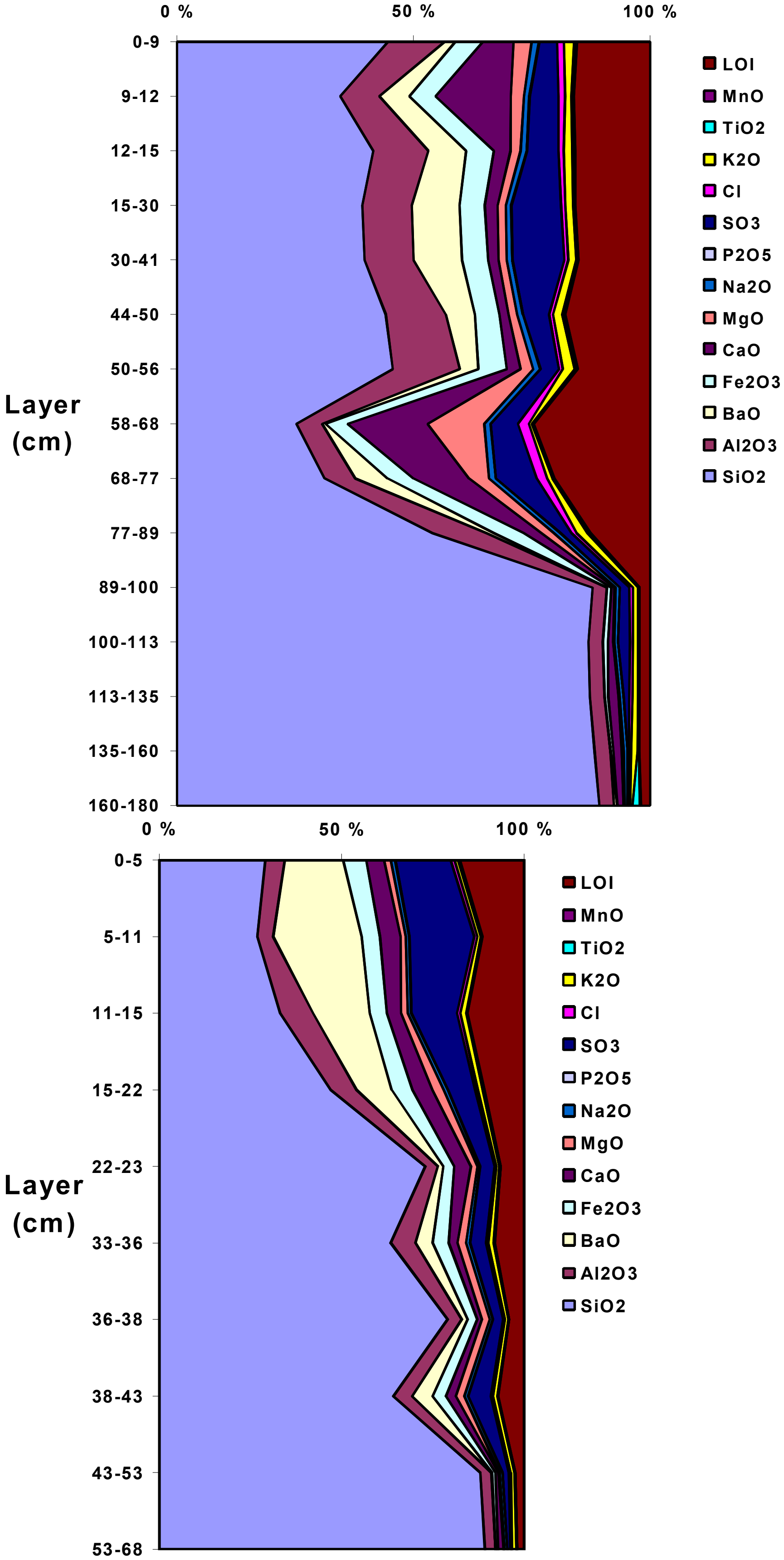
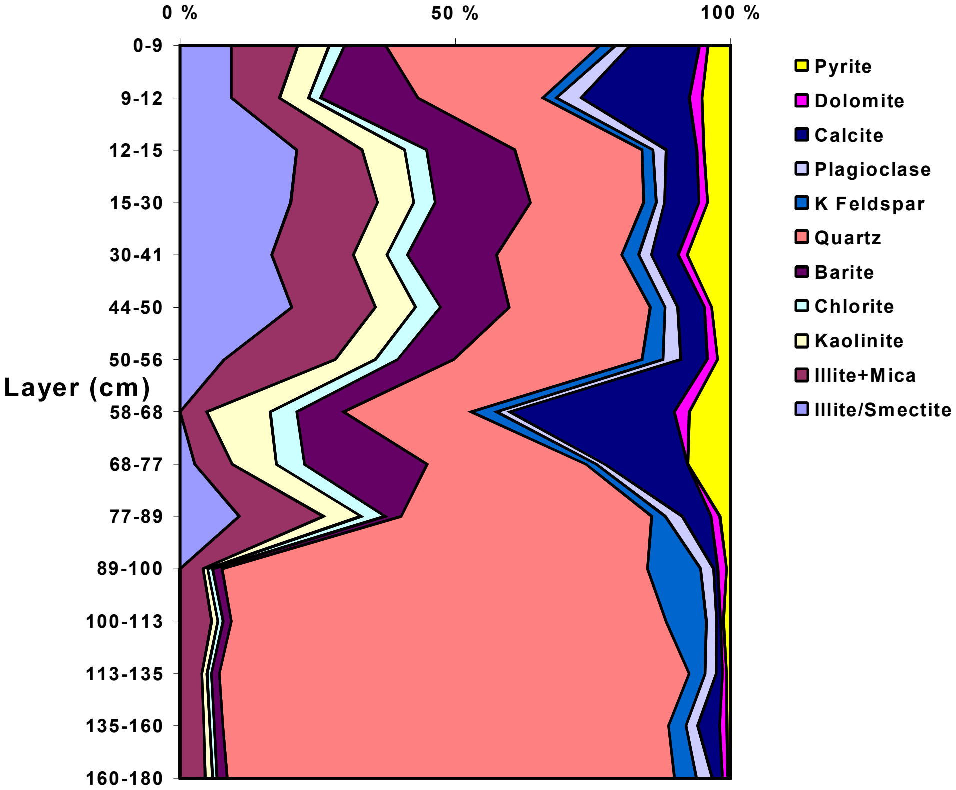


Figure 13: Main components in the Ekofisk 2/4 A cutting pile. Upper figure show VC2 core from the south-west side of the structure. Lower figure is core V9 from the north east side the structure.



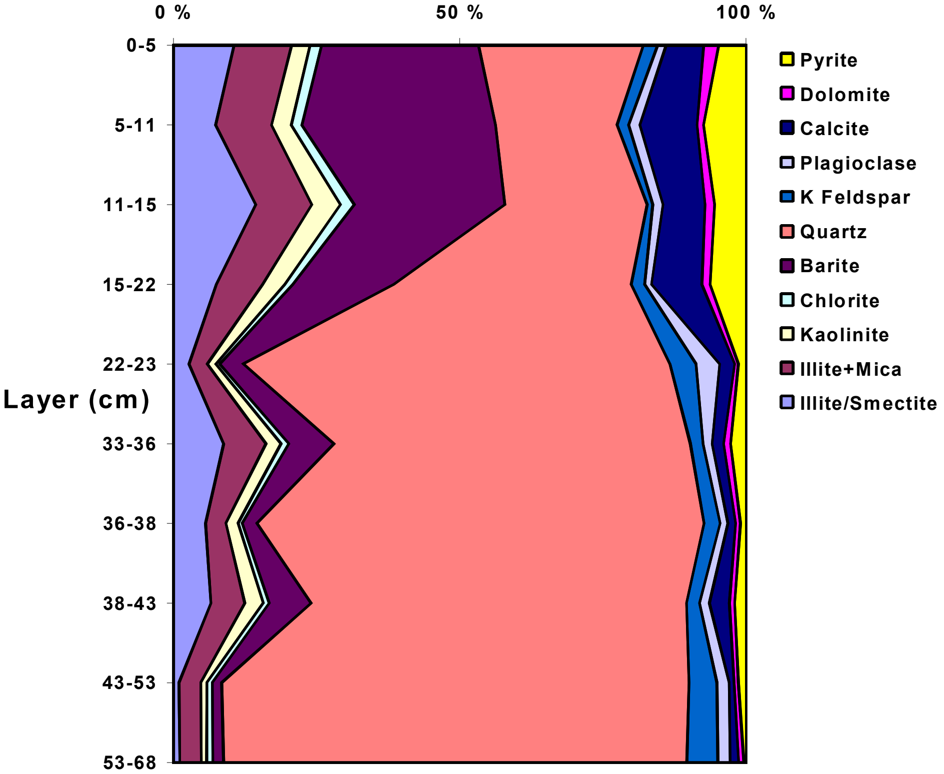


Figure 14: Semi-quantitative results for crystalline phases at Ekofisk 2/4 A cuttings pile. Upper figure show VC2 core from the south-west side of the structure. Lower figure is core V9 from the north east side the structure.

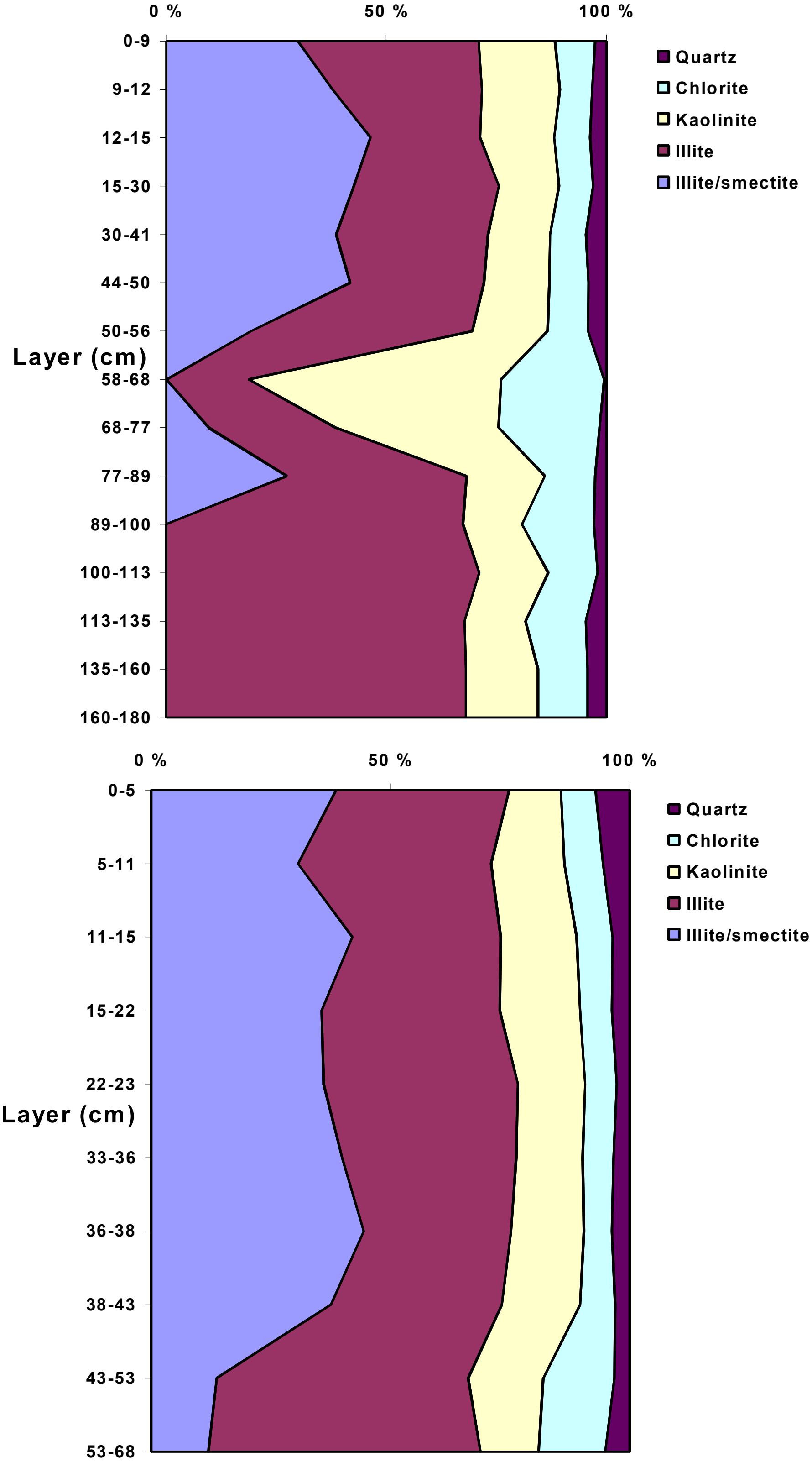


Figure 15: Clay fraction (<2µm) results for crystalline phases at Ekofisk 2/4 A cuttings pile. Upper figure show VC2 core from the south-west side of the structure. Lower figure is core V9 from the north east side the structure.

From the mineralogy results it seems evident that microbial diagenetic processes mobilises significant amounts of sulphur from the barite. There is evidently no other sulphate sources available that are large enough to provide the sulphur that seems to be present in the cuttings pile. This support the findings by Shimmield *et al*, (2000) who found a diffusive flux of Ba from the Beryl cuttings pile. From what we see here, the flux of Ba from the cuttings pile must be considerably larger. This issue might however be more complex than assumed, as though it is likely that transport of Ba from the deeper part of the pile is a slow process. It could for instance be that mobilisation of sulphur is a rapid process occurring at a short time-scale at the time of cuttings discharge. Such a theory is supported by the observation that no strong anoxic environment was found in any of the samples analysed from the two cutting piles. Redox and sulphide measurements indicate an oxic environment at Beryl A at the position for core V1 while sulphide was detectable at the position for V4 (see 6.4.1). Shimmield *et al*. (2000) measured sulphide at the location close to V4 with an in-situ profiler and found 300µM sulphide on 15 mm depth. These observations then don't support the suggested theory.

6.4 Chemical properties

The main chemical parameters analysed for were the organic components of oil or related compounds, and metals. Samples analysed for the organic parameters were processed together, while processing for the metal analysis were carried out separately. A total of about 70 samples from various core samples have been analysed, and when appropriate, references to the previous characterisation (Cripps *et al.*, 1999) work at Ekofisk has been included. Redox conditions, pH and sulfide have also been measured.

In discussing the importance of the levels of the different contaminants analysed for, references have been made to the SFT classification of marine sediments, as presented in section.

6.4.1 Redox, pH and sulphide

To establish the sediment condition in the cuttings layers, electrode measurements were performed on the exposed surfaces of the cores after they had been cut to proper lengths to be transported ashore.

The pH electrode was calibrated with NBS buffers prior to the measurements. The redox electrode was calibrated towards a redox-buffer to be able to correct the measurements to the absolute redox scale. The sulphide electrode was used directly without any calibration, however, a test was made to check that the mV readings fell within the working range for the electrode. The sulphide measurements only show if there was sulphide present or not. A summary of the obtained results is presented in Table 8.

Table 7: Summary of the measurements of pH and redox potential indicating the sediment conditions in the cuttings piles at Beryl A and Ekofisk 2/4A.

		pH	eH vs SHE mV	Sulphide
Beryl	V1-0	10.1	91	
Beryl	V1-80	9.7	110	
Beryl	V1-160	9.1	242	
Beryl	V4-0	8.6	-21	Sulphide present
Beryl	V3-0	9.4	-71	Sulphide present
Ekofisk	SW1-0	8.4	-72	Sulphide present
Ekofisk	SW1-0	8.5	-63	Sulphide present
Ekofisk	SW1-60	8.8	-64	Sulphide present

6.4.2 Analytical methods

6.4.2.1 Trace metals

The sediments were digested according to Norwegian Standard NS 4770. This digestion procedure, together with the pre-treatment method described below, is recommended by SFT (The Norwegian Environmental Pollution Control Authority). This is the protocol being used when monitoring possible contaminants from oil installations arising from offshore operations, on the Norwegian Shelf.

The sediment samples were, after arrival at the laboratory, dried at 50°C to a weight that remained constant. After drying, the samples were crushed and homogenised in an agate mill.

For digestion of the sediment, approximately 1 g of sediment was placed in a vessel, and 10 ml 7 M HNO_3 was added. The vessel was sealed and placed in an autoclave. Temperature in the autoclave was maintained at 120°C, for 30 min. The autoclave was then allowed to cool and the samples were diluted with water to 50 ml. Reference material, MESS-1 and BEST-1, were similarly digested, for quality control of the analytical procedure. The results are presented in Appendix 5, together with all raw data. This method based on digestion with nitric acid is not strong enough to dissolve the refractory part of elements like Al, Cr or Ba. However the SFT Guidelines used to assess the results from the metal analysis is at a large extent based on baseline data from nitric acid digestion. The element Ba and Sr will be difficult to compare directly to data produced with other digestion methods due to the low solubility of $BaSO_4$. The results from the determination of the major components (see mineralogy) showed clearly that most of the Ba was indissoluble of this digestion procedure.

Analyses. Analyses of all metals were performed by inductively coupled plasma mass spectrometry (ICP-MS), using a VG-PQ2+ system with standard mienard nebulizer and Ni sampling and Skimmer cones. In addition to the usual standard curves, Indium was used as an internal standard. The Hg analysis was performed by cold vapour atomic absorption spectroscopy (CV-AAS) in an automated flow injection system (FIMS) from Perkin-Elmer.

Precision. The response from the reference materials was according to what is normally achieved with this type of digestion procedure. The precision based on replicate digestion of the reference material was between 5 - 10 %, while the precision based on replicate digestion of samples from the experimental site was slightly higher, due to in-homogeneity in this coarser sediment.

Precision in the cuttings samples. To achieve a better idea on the precession on these specific samples a number of replicate analyses were performed The data can be found in the data report in appendix 5. Most replicates are within 10%, however considerably larger differences can be seen on some samples, particularly for elements where a higher contamination in the cuttings is found. The data set from the sequential extraction procedure can also be used for evaluation of the accuracy of the data.

6.4.2.2 Organic analysis

The hydrocarbons were extracted from the wet sediment in four steps:

1. Saponification with KOH.
2. Extraction with dichloromethane.
3. Purification of the extract on a silica column.
4. Evaporation of the excess solvent.

The THC and drilling fluids were determined with GC-FID (Gas Chromatography with flame ionisation detector). The PCB, PAH, NPD and decalines were determined by GC/MS/SIM (Gas Chromatography, Mass spectrometry, Simultaneous Ion Monitoring). The values were corrected to dry weight basis after the analysis.

The olefine-based drilling fluid was quantified from the GC-FID chromatograms. The identification if ester-based drilling fluid was present was made from the retention time in the chromatograms. No attempt to derivatisation of the extract for increased recovery of non-volatile compounds was made.

The precision obtained was 15 % RSD. Values less than 10 times the detection limit (such as those from the underlying sand) can, in the worst case, have an uncertainty of up to 50 %. The procedure and analytical data are presented in appendix 4.

The alkylphenols: nonlyphenol, 4-tert.octylphenol and alkylphenol ethoxylates were analysed on a mixed sample from several mesocosm units from the upper 20-40 cm of the Ekofisk, Beryl and North Sea reference station respectively. These analyses were carried out by TNO (TNO project 31644).

6.4.2.3 Total organic nitrogen (TON)

Total nitrogen was measured in the same set of sediment samples as the organic and metals fraction. The samples were treated with sulphuric acid, hydrogenperoxide and salicylic acid in the presence of a catalysator. The sample is further made alkaline by sodium hydroxide, and titrated with hydrochloric acid after removing ammoniac with steam distillation. The precision obtained was 10 % RSD. The procedure and analytical data are presented in appendix 4.

6.4.2.4 NORM

NORM, as Bq/kg DW, was measured on a mixed sample from several mesocosm units from the upper 0-40 cm of the Ekofisk, Beryl and North Sea reference station respectively. The Isotopes analysed for included: Uranium 238, Radium 226 and 228, Lead 210 and Thorium 228. These analyses were carried out by TNO (TNO project 31644).

6.4.3 SFT classification

As a reference, the metals and organic contaminant parameters are compared to the SFT classification system for marine sediments. The SFT marine sediment classification system (Molvær *et al.*, 1997) consists of 5 classes. The classification was designed for use in fjords and coastal environments mainly for clay type sediment. The relevance of this classification to offshore environments is debatable; however to our knowledge it is the only classification system presently available.

The five classes are:

Class 1 - minor or uncontaminated coastal environments;
Class 2 - moderately polluted;
Class 3 - markedly polluted;
Class 4 - strongly polluted;
Class 5 - very strongly polluted environments.

Again, it should be noted that this system has been designed for use in fjords and coastal waters in Norway. It does nevertheless give a general indication of the severity of any contamination, and is the only such system available. The classification should therefore not be used as an absolute measure, but rather as a general indicator.

The benefit of comparing the cuttings pile contaminant levels to this SFT classification system is to identify what components are of most concern to the environment. It is however still a task for the authorities to decide what are acceptable contaminants levels in the relevant environment, and no such judgements have been made in this report. Also within the SFT classification system, there are no specific action initiatives attached to the contaminant levels/classes per se.

Figure 16 shows how the respective SFT classes are presented in the figures of the chemical components found in the cuttings piles. The SFT classes have been indicated on relevant figures in Section 6.4. The analysed elements that are also included in the SFT classification system is presented in appendix 12.

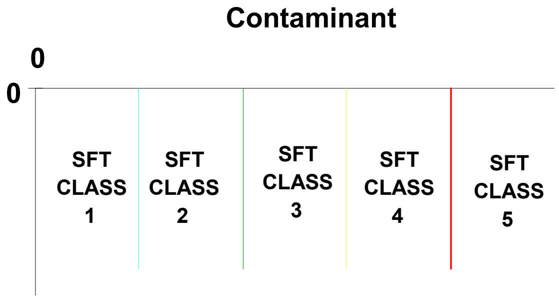


Figure 16: Colour coding as it is presented in the figures of contaminants. The coloured lines represent the upper limit for each class.

6.4.4 Main results

A summary of the results from the analysis of metals and organic contaminants can be found in the Table 9 below. More details are presented in the following sections and in the Appendixes.

The results in Table 9 contain all samples identified as cuttings in the description of the cores during the slicing process (see Table 1 and 2 and Appendix 1). The samples not used in the calculations are only those identified as sand originating from the substrate under the cuttings pile. For the calculations for Ekofisk 2/4 A only data from the 2000 sampling is used, however the concentrations for most contaminants measured at Ekofisk in the samples from 1998 (Cripps *et al.*, 1999) and in this investigation are similar and will not affect the values to any larger extent. (see data can be found in appendix 5).

Table 8: Chemical data from the cuttings deposits at Beryl A and Ekofisk 2/4 A. All results are on dry weight basis.

Contaminant	Beryl A						Ekofisk 2/4 A					
	Average	Median	Min	Max	S.D.	S.D.%	Average	Median	Min	Max	S.D.	S.D.%
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%
Lithium	17	17	2	35	8	45	11.5	9.0	1.9	26.7	7.7	66.3
Aluminium	12401	12225	2729	23186	4808	39	6844	7008	1956	9966	1947	28.4
Vanadium	37	36	5	72	13	36	19.2	17.9	6.4	37.4	7.4	38.7
Manganese	616	559	124	1378	273	44	857	719	101	1812	492	57.5
Iron	26422	26148	8472	44895	7241	27	21410	19601	5870	53145	8915	41.6
Barium	468	300	65	1696	435	93	476	267	114	1452	400	83.9
Chromium	51	46	15	215	30	59	32.1	28.2	8.4	85.6	18.3	57.0
Cobalt	14	13	4	25	5	34	14.9	13.3	3.9	43.5	7.5	50.1
Nickel	32	29	10	73	13	41	34.7	33.1	6.7	83.0	16.6	47.7
Copper	67	54	20	188	40	60	72	48	5	678	121	168
Zinc	316	264	59	987	209	66	377	346	55	1204	256	68
Arsenic	17	13	3	61	13	73	10.5	9.5	2.8	25.6	5.4	51.4
Strontium	347	304	78	765	197	57	230	243	65	411	108	47.0
Cadmium	0.74	0.46	0.05	5.60	1.01	137	0.85	0.59	< 0.00	3.53	0.85	99.3
Lead	291	215	12	1136	260	89	195	149	29	600	150	76.6
Hg	0.56	0.46	0.05	1.36	0.40	72	0.24	0.19	0.03	0.73	0.17	70.1
THC (mg/kg TS)	57294	47000	670	200000	52877	92	23673	1700	16	79000	30116	127
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	%	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	%
SUM PAH	12609	5589.5	0	57983	14988	119	1035	1095	16	3189	814	79
SUM PAH- naftalen	9117	6337	195.1	42983	9676	106	927	869	14	3089	769	83
Sum Dekalines	757669	626000	13400	2730000	660310	87	19793	18600	0	63000	16269	82
SUM NPD	233460	85300	2803	1563600	355733	152	13451	14879	24	38550	10039	75
Sum 3-rings	7048	3405	0	38200	8561	121	644	653	5	1557	520	81
Sum 4-rings	1106	717	0	5891	1246	113	206	124	7	1760	373	181
Sum 5-rings	141	72	0	683	164	117	53	30	2	467	99	185
Sum 6-rings	64	22	0	290	87	137	25	21	5	108	21	84
Naftalen	4639	1900	26	21000	5937	128	108	105	2	310	85	79
Asenaftylen	897	520	10	4700	1037	115	104	21	1	390	125	120
Asenaften	853	720	16	3300	826	97	166	35	2	780	249	150
Fluoren	1621	930	25	8800	1969	121	89	100	6	280	65	73
Fenantren	3709	1700	0.8	23000	4962	134	267	260	3	940	238	89
Antrasen	496	170	6.2	4900	898	181	34	19	0	200	44	130
Fluoranten	275	160	0.2	1200	292	106	69	39	2	660	141	205
Pyren	642	340	0.4	5120	910	142	68	44	3	560	119	174
Benzo(a)antrasen	73	49	2.5	340	78	106	24	10	0	300	65	271
Krysen/trifenylen	191	120	7.6	960	200	105	45	28	1	240	52	117
Benzo(b+j+k)fluoranten	103	66	0.7	410	107	104	36	20	2	310	66	182
Benzo(a)pyren	48	40	1.1	180	48	100	14	7	1	150	32	224
Indeno(1,2,3-c,d)pyren	39	34.5	1.9	120	37	94	9	6	2	54	13	143
Benzo(g,h,i)perylen	59	45	4.6	210	61	104	18	16	3	54	11	62
Dibenzo(a,h)antrasen	32	27	1	93	33	102	4	3	1	7	2	55
PCB (Dutch 7)							239	5	0.5	1427	475	198
Total Nitrogen mg/kg	460	385	300	1000	177	39	813	750	430	1800	344	42
Dry weight %	77	77.95	66.5	84.1	5	6	74	74	60	85	7	10

6.4.5 Organic contaminants: Beryl A

The results of the organic parameters analysed in the Beryl A cuttings piles represent sets of sediment profiles from two locations in the pile; one core taken as close as possible to the platform (VC 1), and one core taken in the periphery of the pile (VC4). The core from the periphery penetrated down to the underlying sand. Based on the knowledge of pile structure found in other cuttings piles (Westerlund and Olsen, 2000), the core in the periphery should pick up a thin layer of the older cuttings. If there are any dramatically different contamination profiles in the more historic layers, which would be below maximum core depth of the central sample from inside the pile there would be a good probability that this could be seen in even though the layer is thin. A complete set of data from all samples analysed, and also a wider spectra of organic components, can be found in Appendix 4.

6.4.5.1 THC

THC levels in the Beryl pile are high and variable (from 0.17 – 20%). When evaluating the chromatograms from the GC-FID analysis of the samples it could be concluded that the THC found in the cuttings pile at Beryl mainly originate from mineral oil(s). No evidence could be seen from the data sets that pseudo oils (esters, olefines etc.) which could have been used as additives to the drilling mud, are present, at least the concentrations are low. This also corresponds with the reported discharge data. There is large spread in the THC concentration found in the Beryl A cuttings pile.

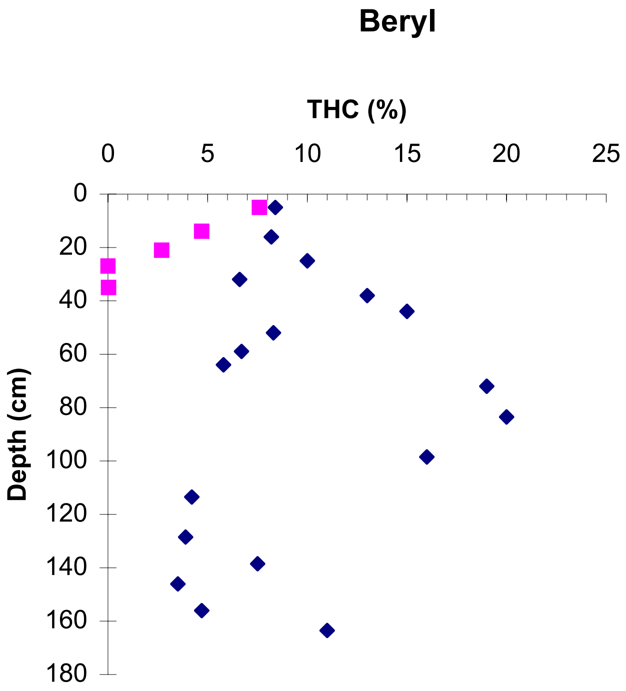


Figure 17: Total hydrocarbons in Beryl A cuttings pile. ◆ Vibrocore 1 Close to discharge ■ Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.

6.4.5.2 PAH

The PAH components represents the potentially more harmful part of the hydrocarbon components. At the Beryl A, both THC (Figure 17) and PAH:s (Figure 18) are high, which is expected in a cuttings pile where oil based muds have been discharged.

While PAH:s in general represents the most toxic part of the hydrocarbons, the B(a)P consentration normally is chosen to represent the carcinogenic potential of the PAH mixture. Figure 19, presenting B(a)P levels, show that the Sum PAH reach a higher risk class as defined by SFT than the concentration of B(a)P alone.

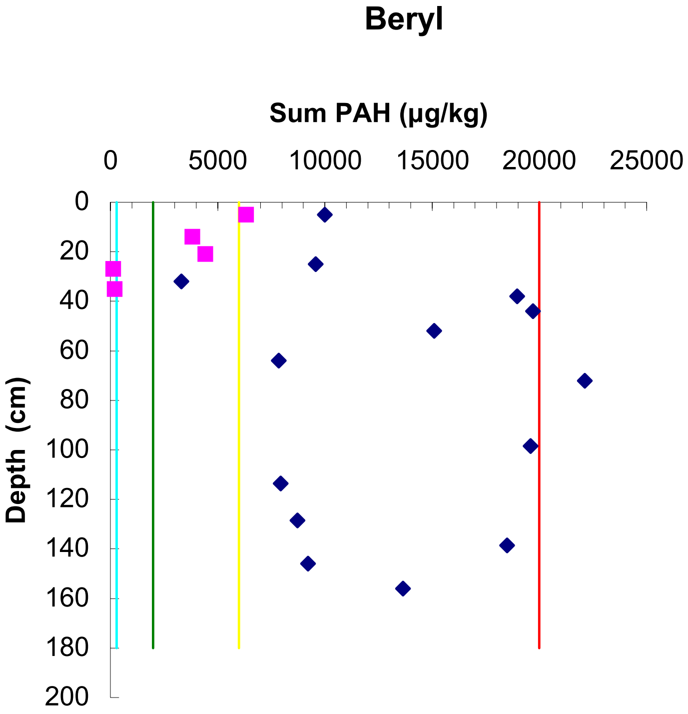


Figure 18: Total PAH:s with Naphthalene subtracted in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ■ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

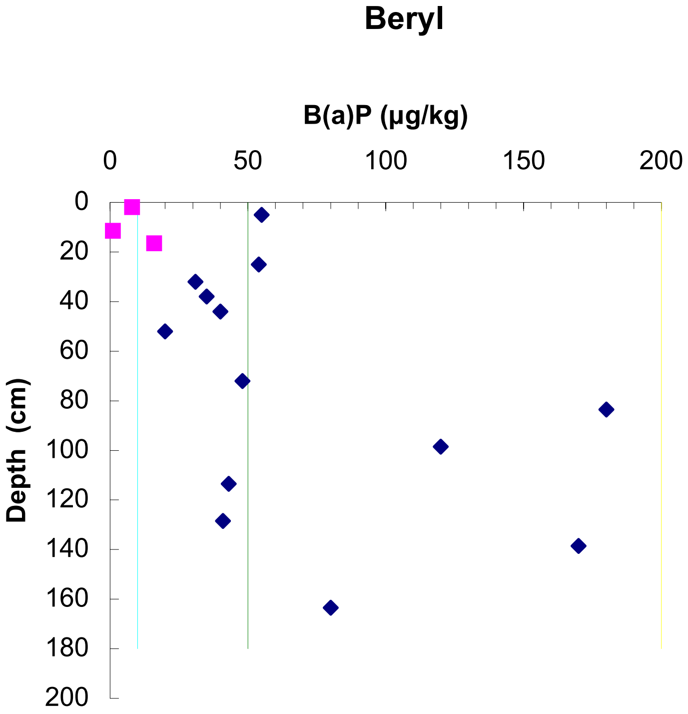


Figure 19: Total B(a)P in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ■ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand*

6.4.5.3 PCB

No detectable PCB was found in any of the Beryl samples.

6.4.5.4 TON

Of the 41 total nitrogen analysis carried out, 17 were below the detection limit of 300 mg/kg TS, while the rest varied between 300 and 1000 mg/kg, with an average concentration of 460 mg/kg. Details are presented in Appendix 4.

6.4.6 Metals: Beryl A

The result from the measurements of metals in the cuttings from the Beryl A is shown in a set of plots (Figure 20-33). All data are also presented in Appendix 5. The selected metals include a number of metals (e.g. Fe, Mn, Co, V, Ba, Sr) that has no major concern in sense of pollution. However, these metals are of value to understand processes and the origin of components found in the cuttings.

For the elements where environmental classification is available (SFT code), this is illustrated by colour coded lines in the respective graphs (see section 6.3.2 and Figure 16).

The metals found in the cuttings pile may have different origins. The most important likely metals sources are listed below, indicating which metals may originate from the different sources:

- The rock milled during the drilling process (Fe, Li)
- Drilling mud (Ba)
- Contaminants in the drilling mud (Pb, and possibly others; Hg, Zn, As)
- Produced water (Hg, Zn, As)
- Other unspecified sources not directly attributable to the oil production activities can also be envisioned

The material found in the cuttings pile has a composition that largely differs from the sandy sediments normally found on the North Sea continental shelf. Sandy sediment has a high content of quarts in contrast to clay sediment, which results in the sandy sediment having a lower concentration of most metals. As indicated below, the sediment type found in the cuttings pile is comparable with clay sediment. Presuming that the cuttings material is more comparable with clay than sediment, it is expected that the concentrations of all metals are higher than in the surrounding sand and in the sand found underneath the cuttings pile (see Figure 20-32).

6.4.6.1 Individual metals

Judging from the **Fe**-content (Figure 20), The sediment type found in the cuttings pile is more comparable with a clay sediment, however, there are fairly large variations within the cuttings pile.

Cu and **Zn** show one common feature. For both, the concentrations found in the samples from Vibrocore 4 in the assumed most historic layer are higher than within the rest of the core. However, based on only these data and the few outlying high data points from Vibrocore 1, it is difficult to conclude that the most historic layers in the whole pile will have these high concentrations found in the oldest layers in the peripheral part.

The general pattern within the cuttings pile is that the highest lead (**Pb**) concentration is found deep down in the pile. This supports the well-established fact that the barite used in earlier days could contain high concentrations of Pb. When this was established, barite was generally replaced by barite from other sources having lower concentrations of lead was

For most of the metals, the data as presented shows surprisingly few outliers deviating from the general pattern in the cores. However, there are a few extreme values measured for **Cd**. There is no reason to believe that this represents any general pattern of metals in the pile. The source of these outliers is more likely to be a dropped item like a rechargeable battery or other item from the platform or support vessels.

In contrast to most of the other metals analysed for, the highest concentrations of **Hg** in the Beryl A cuttings pile was found in the top layer closest to the discharge point. The levels of Hg are significantly higher than background levels. Little is known about the possible sources for the Hg:

- presence/concentrations of Hg in barite is normally not reported,
- presence of Hg in other drilling chemicals is suggestive
- the reservoir rock as a source of Hg is a possibility (e.g. Hg is found in produced water at concentrations higher than injected sea water, Trefry et al. (1995), Jacobs et al. (1992)), and hence both cuttings and produced water might be a possible source for a Hg accumulation within the cuttings pile.

The **As** distribution is fairly similar to the Pb distribution with higher concentration in the older layers that most likely are originating from a period in which a barite with high lead concentrations were used. It is possible that this same barite also contains elevated levels of As. The same pattern has been observed also in cuttings piles at Ekofisk (RF report). The concentration of As is still moderate (SFT classification).

As mentioned in previously section, the barium levels measured are not absolute values, as the method used does not allow complete extraction of the compound. However, the method used does give relative concentrations, and can also be used to distinguish cuttings samples from underlying sand (see method section).

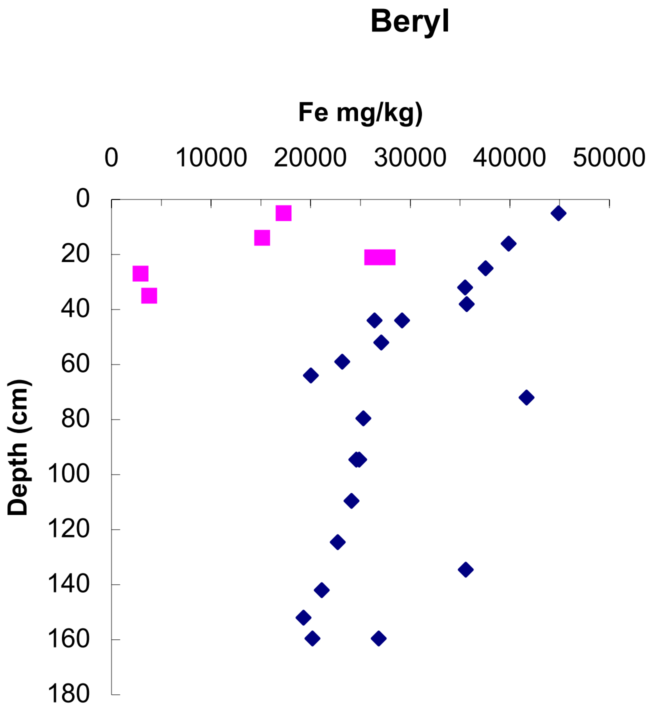


Figure 20: Fe in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ▰ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand*

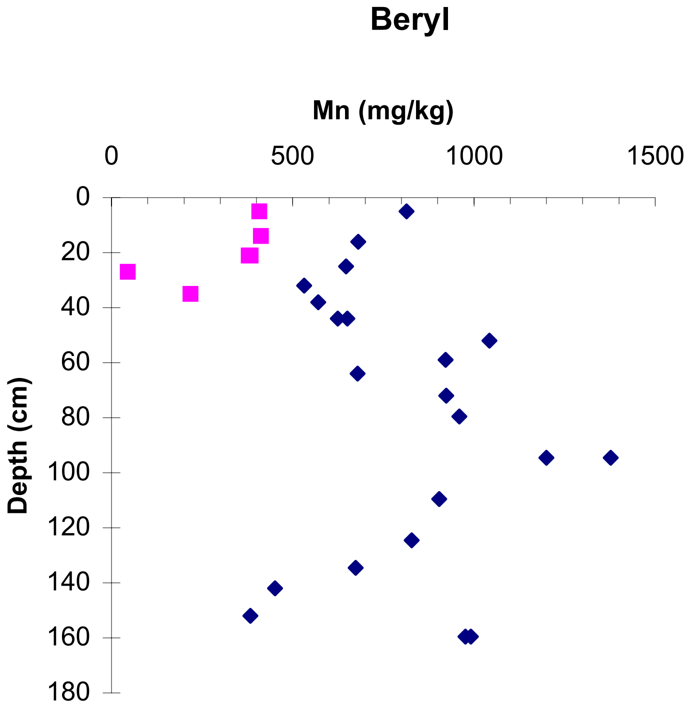


Figure 21:Mn in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ▰ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

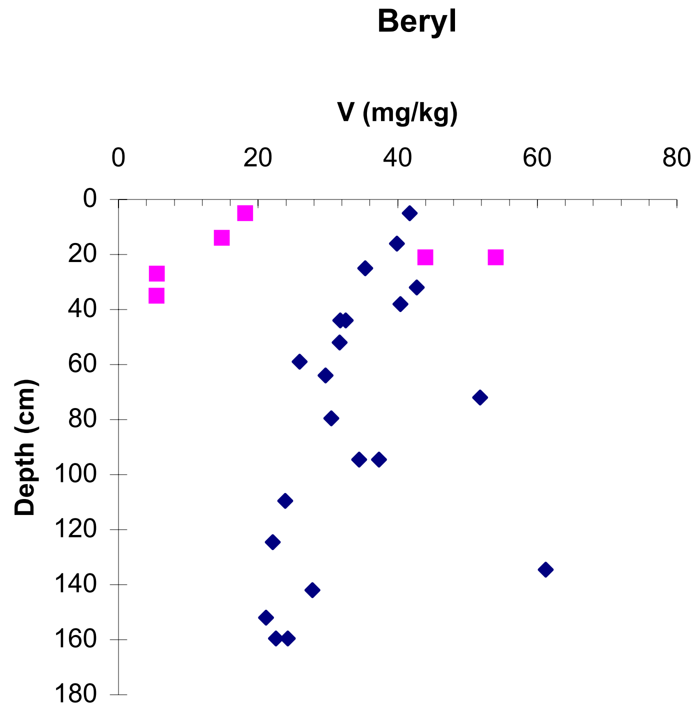


Figure 22: V in the Beryl A cuttings pile. ◆ Vibrocore 1 Close to discharge ▰ Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.

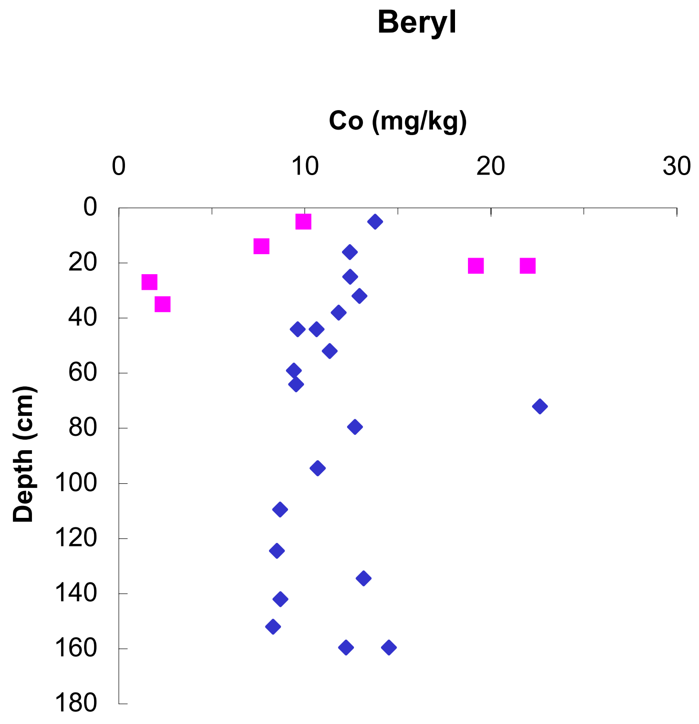


Figure 23: Co in the Beryl A cuttings pile. ◆ Vibrocore 1 Close to discharge ▰ Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.

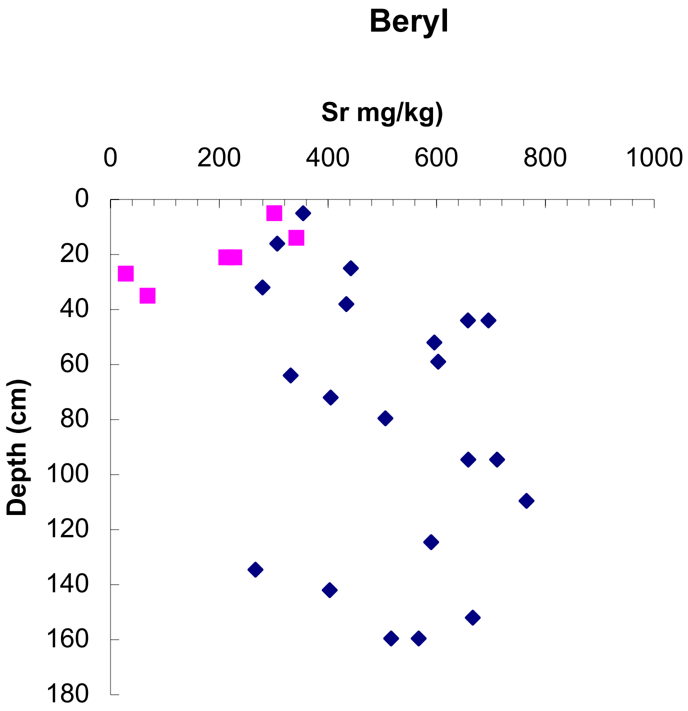


Figure 24: Sr in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge*
▰ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

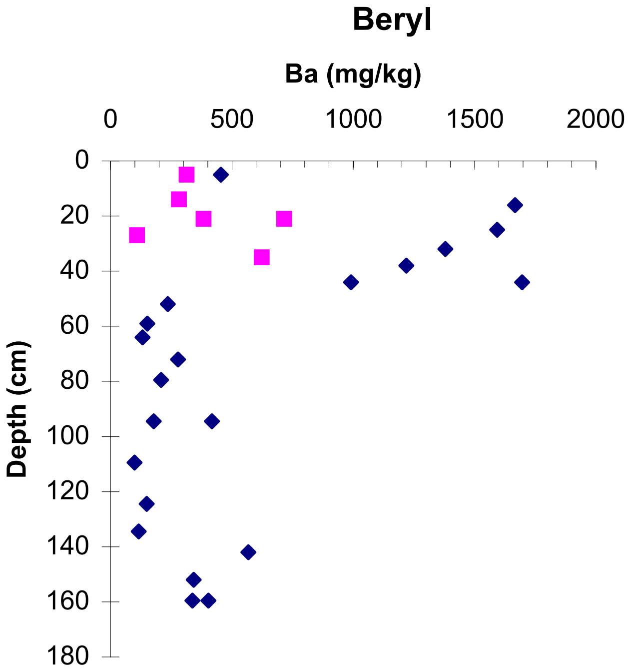


Figure 25: Ba in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge*
▰ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

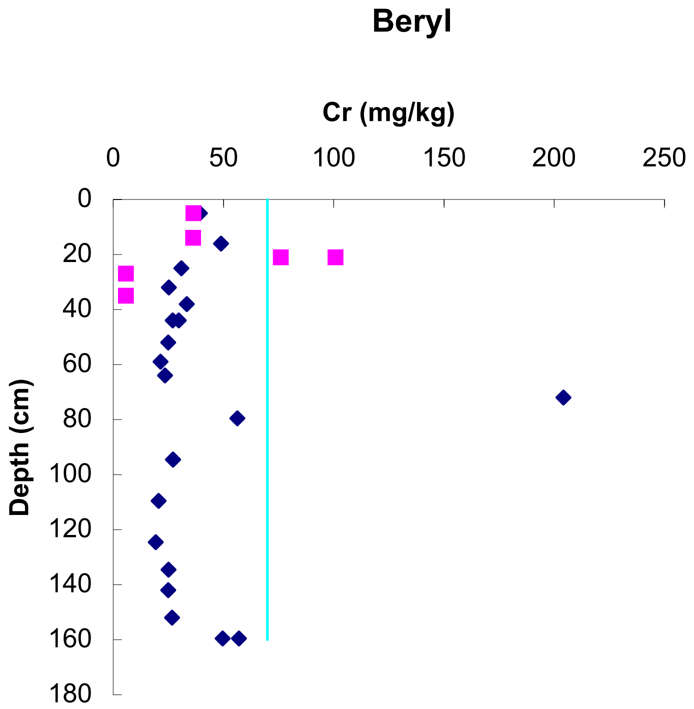


Figure 26: Cr in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ■ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

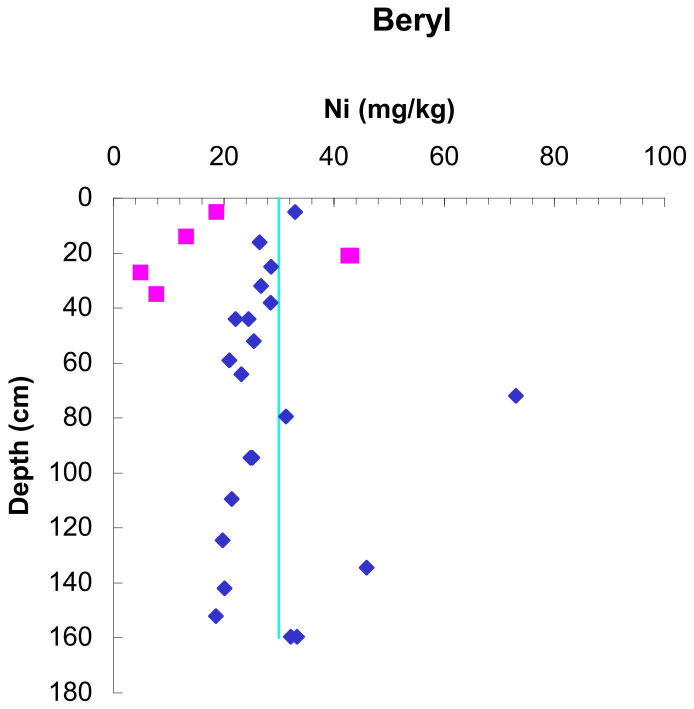


Figure 27: Ni in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ■ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

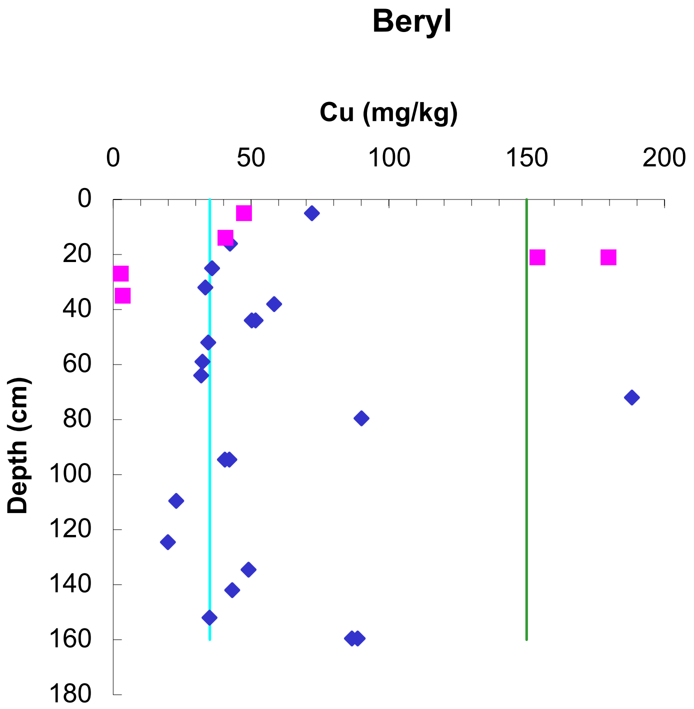


Figure 28: Cu in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ■ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

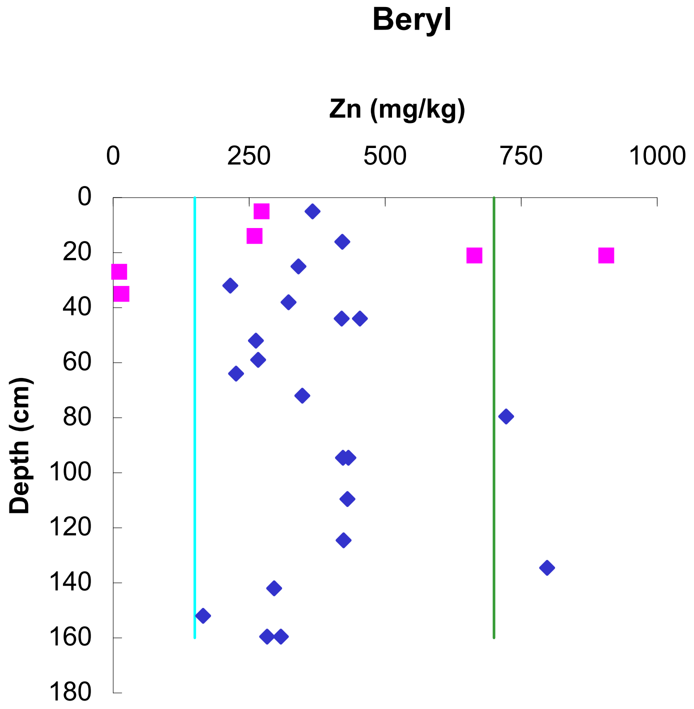


Figure 29: Zn in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ■ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

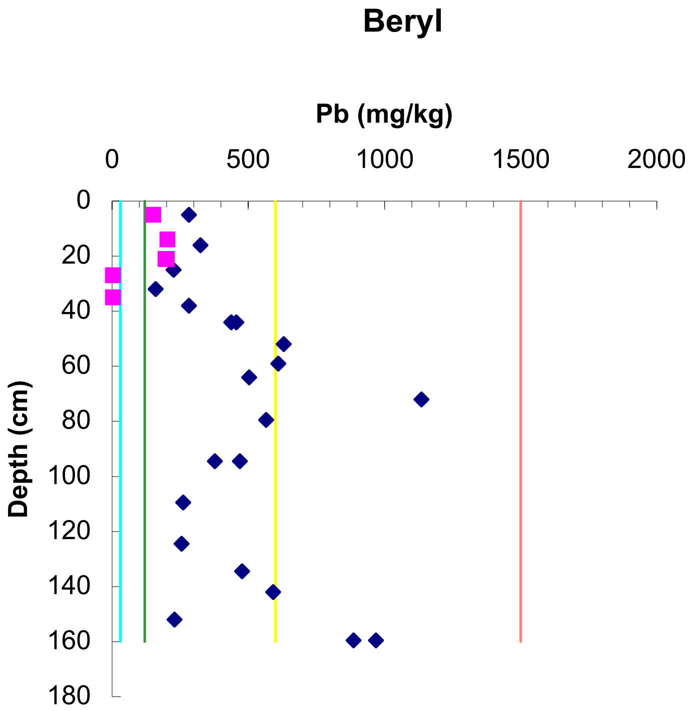


Figure 30: Pb in the Beryl A cuttings pile. ◆ Vibrocore 1 Close to discharge ■ Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.

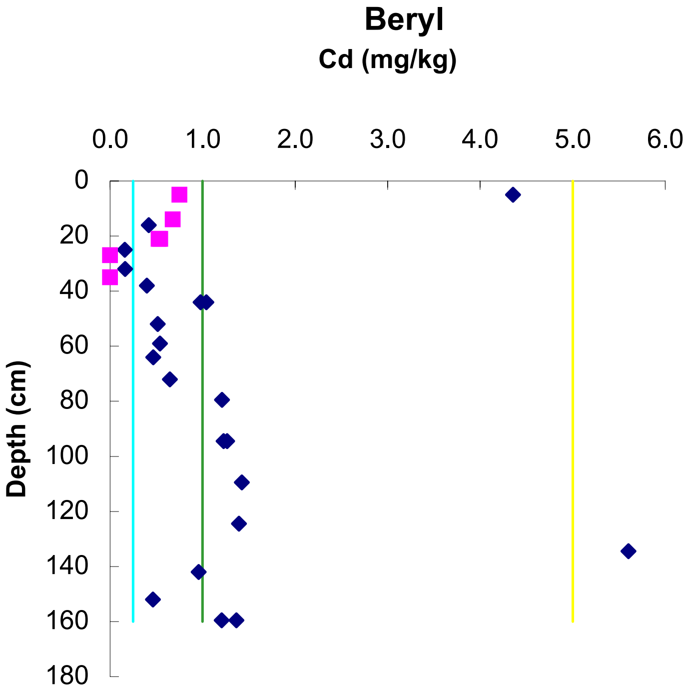


Figure 31: Cd in the Beryl A cuttings pile. ◆ Vibrocore 1 Close to discharge ■ Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.

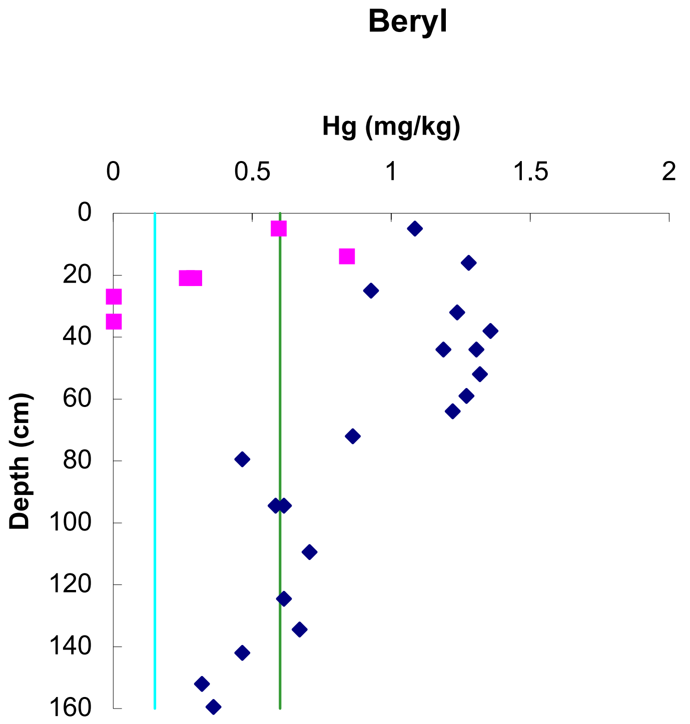


Figure 32: Hg in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ▰ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

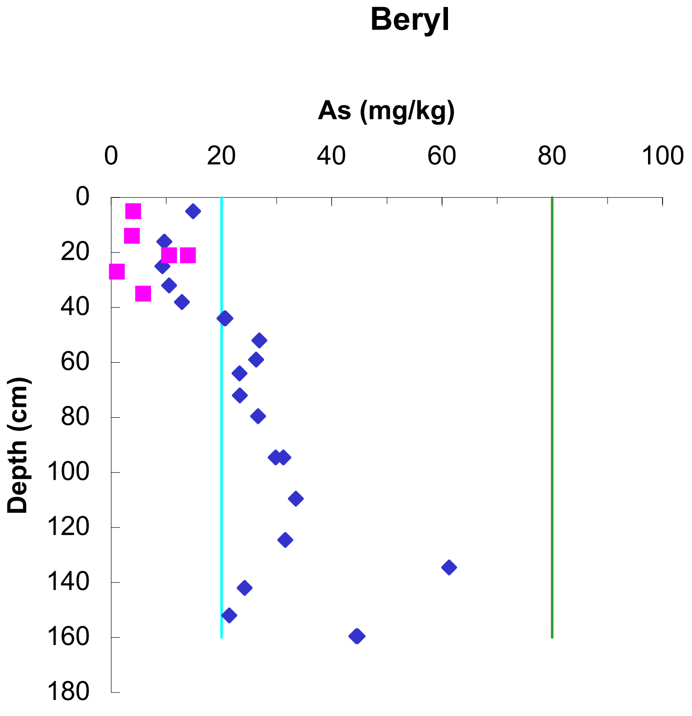


Figure 33: As in the Beryl A cuttings pile. ◆ *Vibrocore 1 Close to discharge* ▰ *Vibrocore 4 Peripheral part of the pile. Core 4 penetrated down to underlying sand.*

6.4.6.2 Metals Beryl A: summary

The most striking feature of the metal distribution found in the Beryl A could be summarised in the points below.

- The sediment type, based on the content of Fe, is to be characterised as a clay sediment, which consequently implies higher “natural” background concentrations than the surrounding sand.
- The highest Pb concentrations could be found deep down in the pile. The same pattern is observed also for As, however the degree of contamination is much less.
- The highest Hg concentrations are found in the top layer closest to the platform.
- The only elements that are considerable higher in the assumed most historic layers are Cu and Zn.
- Most metals of environmental concern are found at elevated concentrations compared to background levels. Most metal concentrations do however fall into SFT class I or II (minor to moderately contaminated), except for Pb that has concentrations corresponding to SFT class III (markedly polluted).

6.4.7 Organic contaminants : Ekofisk 2/4A

The main data presented on organic contaminants from the Ekofisk pile are the analysed core samples from the NE side of the platform, and data from the 1998 survey, when a core was taken on the SW side of the platform. The analytical program for the 1998 samples was not identical to the current, so consequently some components are missing.

6.4.7.1 THC

The hydrocarbon (THC) content of the Ekofisk 2/4A cuttings pile (Figure 34) is high in the top layer. The hydrocarbons found in this layer (representing 45% of the THC found) of the cuttings pile consists mainly of esters, as verified by the GC-FID chromatograms. Evaluation of the chromatographic data did not show any traces of polyalfa-olefins which has also to some extent been used as a drilling fluid. The hydrocarbons found in the lower part of the pile consist of petroleum type hydrocarbons. The source of hydrocarbons in the older parts of the cuttings pile is not drilling fluids/muds directly (no oil-based fluids were used). It may be other drilling related discharges that must be seen in relation to different working and discharge routines in the early history of North Sea drilling operations.

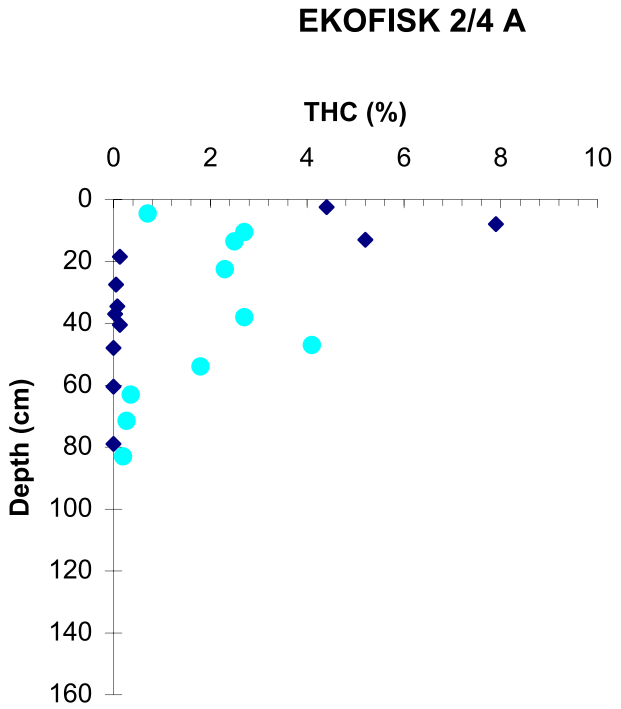


Figure 34: THC at Ekofisk 2/4 A. ♦ Vibrocore 9 NE side of platform. Cuttings depth 43 cm ● Vibrocore 1998 SW side of the platform. Cuttings depth 135 cm.

6.4.7.2 PAH

The PAH levels in the cuttings pile are above background levels, but are not dramatically high (Figure 35), which corresponds well with the fact that the pseudo oil used in the drilling process only contains traces of PAH:s.

For the larger PAH components (see discussion for Beryl in section 6.4.5.2), the B(a)P concentration is comparably low when seen in relation to sum PAH:s (Figure 36).

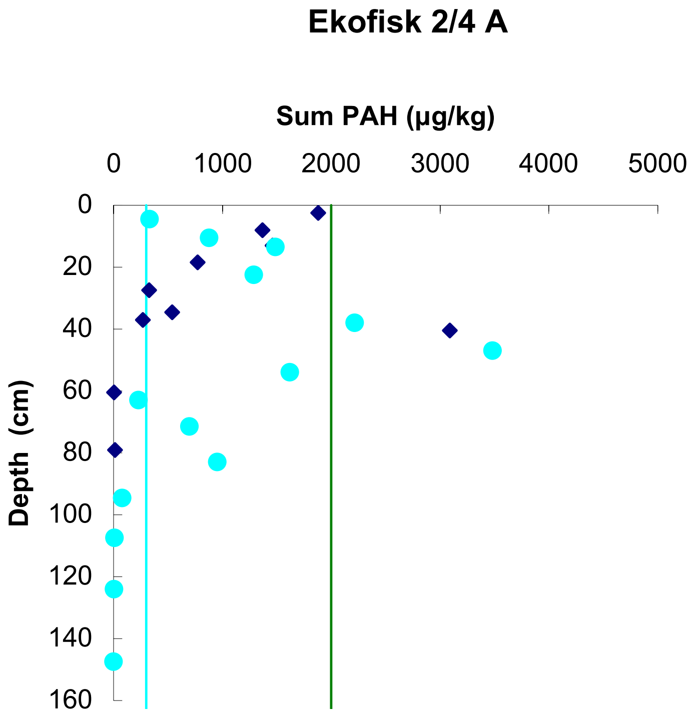


Figure 35: sum PAH-naphthalene at Ekofisk 2/4 A. ♦ Vibrocore 9 NE side of platform. Cuttings depth 43 cm ● Vibrocore 1998 SW side of the platform. Cuttings depth 135 cm.

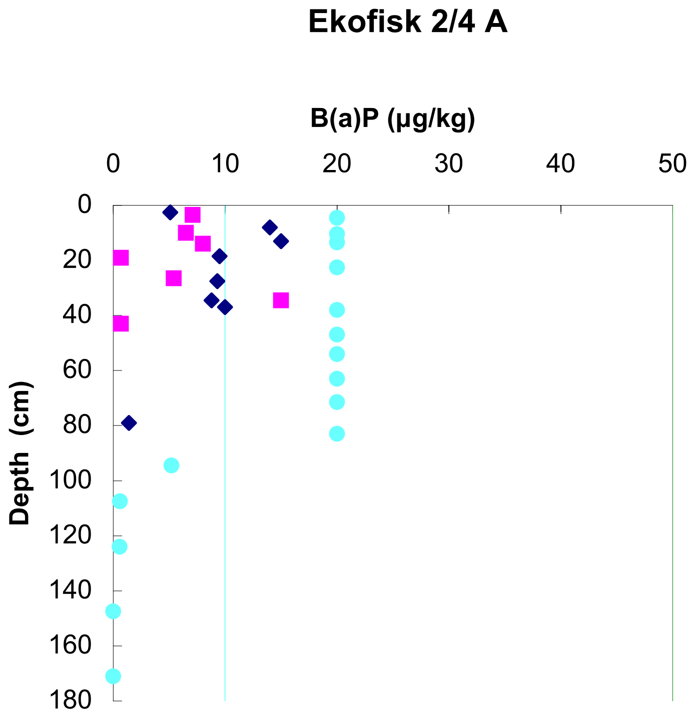


Figure 36: B(a)P at Ekofisk 2/4 A. ♦ Vibrocore 9 NE side of platform. Cuttings depth 43 cm ● Vibrocore 1998 SW side of the platform. The detection limit illustrated by the constant concentration in the top of the core from 1998 data depends on interference from the esters. Cuttings depth 135 cm.

6.4.7.3 PCB

PCB was found in elevated concentrations in the vibrocore (V9) and also in the V10 from the peripheral part of the Ekofisk pile. No PCB data exist from the 1998 survey, and the sub-core taken from a boxcorer on the SW-side of the pile did not penetrate deep enough down to the historical layer where PCB was found in the vibrocore sampled at the NE side of the platform. Hence, only two core samples have so far been found to contain PCB levels of concern. Possible origins of the PCB are e.g. paint, hydraulic oil or transformer oil. The most likely source is being the platform itself. Based on the core from the NE-side, possibly up to 20 % of the cuttings layer could be severely contaminated by PCB:s, assuming that the PCB is evenly distributed layer-wise. Measuring of PCB in the core from the SW side shoved that the PCB contamination in that side was much less (Draft report to PPCoN, 2001). That results support that PCB does not seams to be a general problem associated with cuttings piles.

The PCB pattern shown in Figure 38 shows a similar pattern of congeners in all samples in the layer with the highest concentrations.

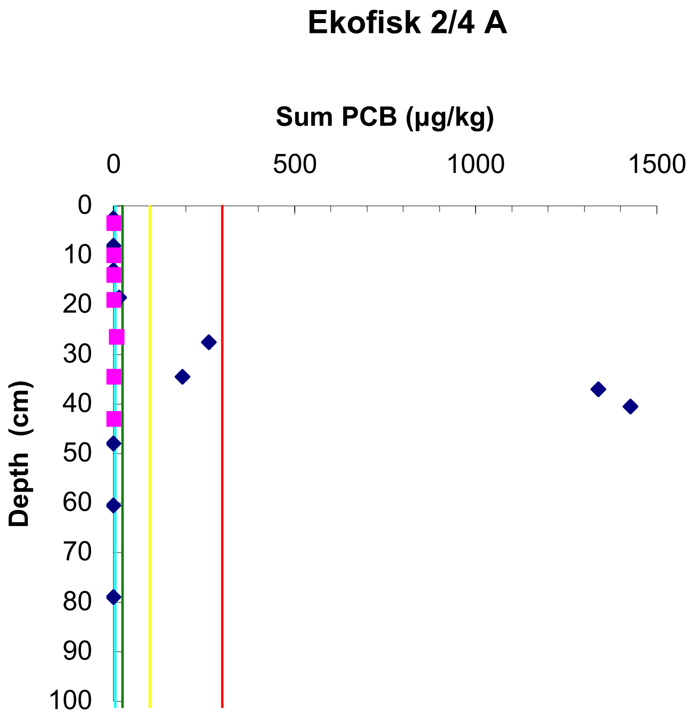


Figure 37: Sum Dutch 7 PCB: congeners at Ekofisk 2/4 A. ♦ Vibrocore 9 NE side of platform. Cuttings depth 43 cm ■ SW3 core SW side of the platform.

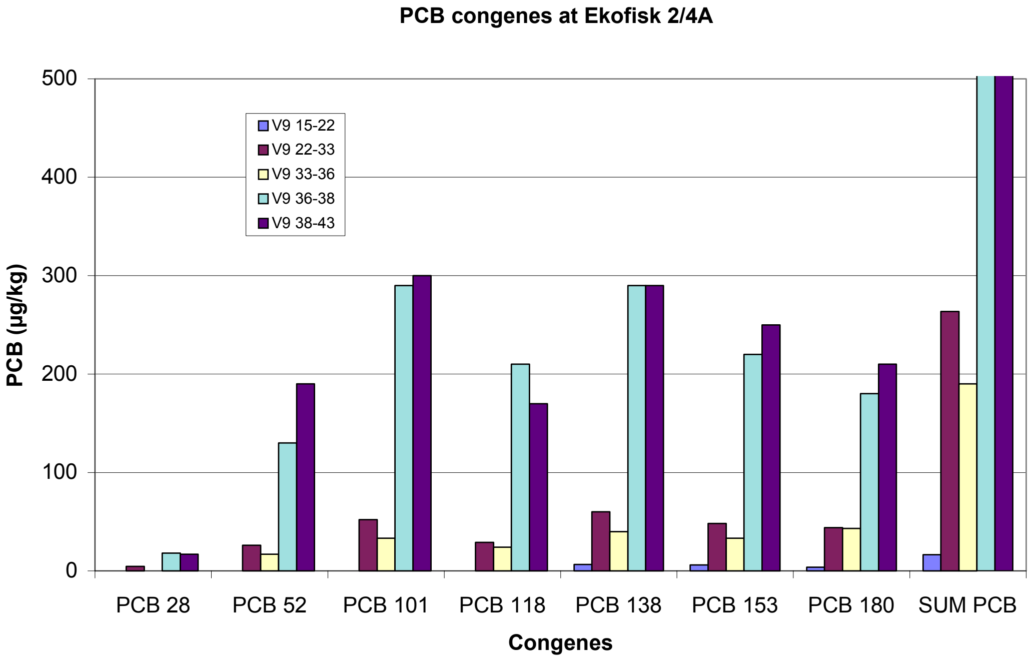


Figure 38: Illustration of the different PCP-Congenes found in the PCB contaminated layer at the Ekofisk 2/4A cuttings pile.

In order to find the possible sources for the PCB:s in the pile, a PCB profile interpretation was made based on the analysis data of the different PCB congeners (NET, 2001). Such a profile interpretation involves comparing % profiles of the environmental samples with a set of established standard or reference profiles, where the standards profiles are established on the basis of the "dutch" 7 congeners distribution in commercial PCB blends.

Data from all samples having PCB concentration above 25 µg/kg were used for this profiling. These analyses suggest that different mixtures of several commercial products could be represented in the various cuttings layers. The samples from the V9 core with the highest PCB concentrations were suggested to contain 70% Kanechlor KC 500, about 20% Aroclor 1260 and 10% Aroclor 1268. Other products and other combinations of them were also suggested for other layers, including Clophen A60 and Aroclor 1248. Some assumptions were also made about partial biodegradation of some congener in part of the V10 core, but it is not possible to make any firm conclusions based on the current work. The PCB congeners found in the V10 core sampled in the peripheral part of the pile had a more complex composition than the V9 core. This part of the cutting pile is also very thin and consequently more affected by erosion and degradation processes. Judging from this profiling interpretation, it is possible that more than one source may have contributed to the PCBs in the pile (NET, 2001), although no firm conclusion can be made.

The most likely commercial use of Kanechlor has been marine antifouling paint while the Aroclor mixtures were used in an array of different products, e.g. insulation fluid, hydraulics, joint filler, softeners and paint products. More specifically, Aroclor 1248 is likely associated with hydraulic oils and Aroclor 1262 with softeners in various products (NET, 2001). It is likely that one source of the PCB:s in the cuttings are sand blasting (i.e. paint chips) while maintaining the structure.

6.4.7.4 TON

Of the 27 total nitrogen analysis carried out, 6 were below the detection limit of 300 mg/kg TS, while the rest varied between 430 and 1800 mg/kg, with an average concentration of 813 mg/kg. Details are found in Appendix 4.

6.4.8 Metals Ekofisk 2/4 A

The measured metals data from the cuttings from Ekofisk 2/4 A is presented in Figure 39-52. Data from the 1998 investigation are also shown in the graphs where available. The selected metals include a number of metals (Fe, Mn, Co, V, Ba, Sr) that has no major concern in sense of pollution. However, these metals are of value to understand processes and the origin of components found in the cuttings.

For the elements where environmental classification is available (SFT classification), this is illustrated by colour coded lines in the respective graph (see section 6.3.2 and Figure 16). The metals found in the cuttings pile may have different origins. The most important likely metals sources are listed below, indicating which metals may originate from the different sources:

- The rock milled during the drilling process (Fe, Li)
- Drilling mud (Ba)
- Contaminants in the drilling mud (Pb, and possibly others; Hg, Zn, As)
- Produced water (Hg, Zn, As)
- Other unspecified sources not directly attributable to the oil production activities can also be envisioned

The material found in the cuttings pile has a composition that largely differs from the sandy sediments normally found on the North Sea continental shelf. Sandy sediment has a high content of quarts in contrast to clay sediment, which results in the sandy sediment having a lower concentration of most metals. As indicated below, the sediment type found in the cuttings pile is comparable with clay sediment. Presuming that the cuttings material is more comparable with clay than sediment, it is expected that the concentrations of all metals are higher than in the surrounding sand and in the sand found underneath the cuttings pile (see Figure 39-51).

6.4.8.1 Individual metals

Data from both sides of the Ekofisk 2/4 A platform, as well as from the two sampling occasions (1998 and 2000 data) show fairly good agreement for most metals.

It could be noted that the **Ba**-concentration at the NE-side is considerably lower than on the SW side. From the XRF data with total Ba this can not be seen. It is difficult to draw conclusions based on the NS4770 Ba data being dependent on the low solubility of Ba.

The information seems to be more qualitative which means that we only can use the data to state that the sediment is contaminated with drilling mud. The most likely source for the contamination of **Pb** in the cuttings pile is barite (Analysis of barite can have Pb concentrations in the range of 1000 µg/kg). However it is difficult to se any correlation between Pb and Ba in the cuttings, indicating total different kinetics and probably large variation in the Pb level in the used barite.

For the elements **Cr**, **Cu**, **Pb**, **Zn**, **Cd** and **Hg** there is a common feature found in the Ekofisk 2/4 A cuttings pile: The oldest layer close to the underlying sand contains higher concentrations of these elements. This layer coincides with the layer contaminated with PCB (see PCB section above). This layer is estimated to be up to 20% of the total cuttings pile volume at the most.

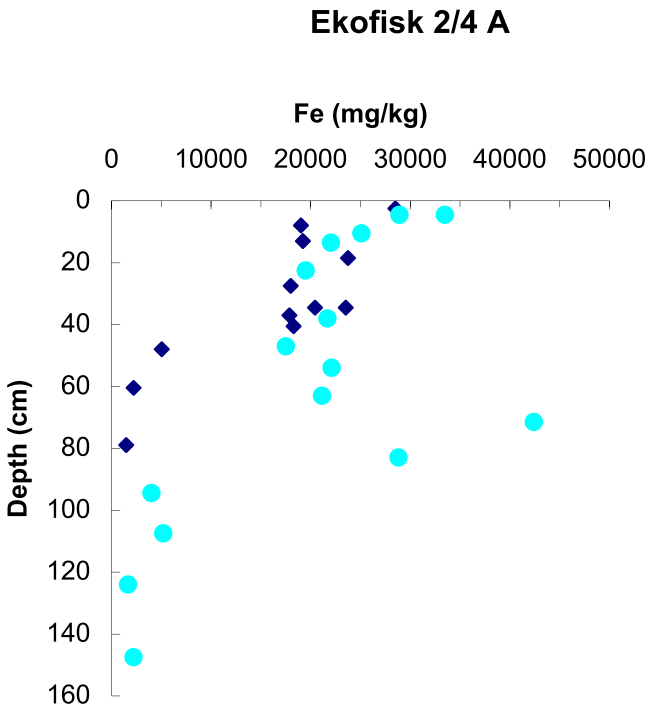


Figure 39: Fe at Ekofisk 2/4 A. ♦ Vibrocore 9 NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

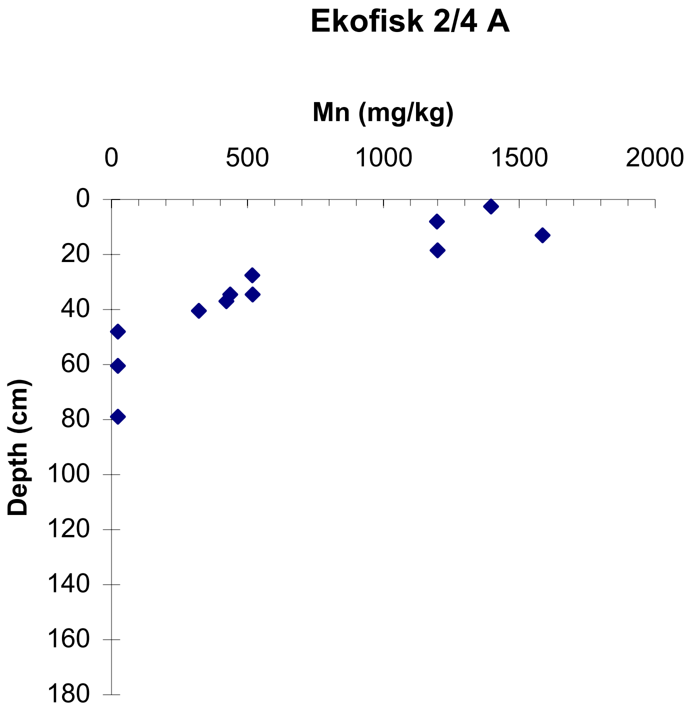


Figure 40: Mn at Ekofisk 2/4 A. ♦ Vibrocore 9 , the NE side of platform. Cuttings depth 43 cm.

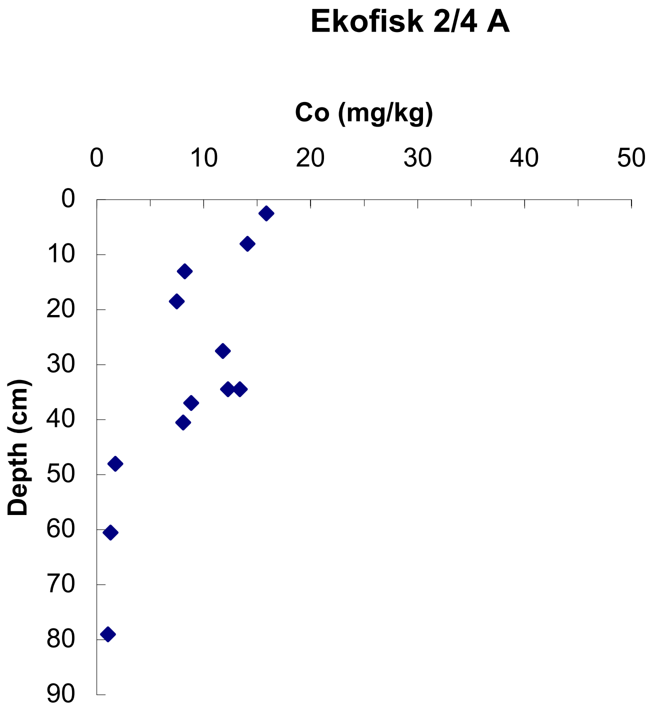


Figure 41: Co at Ekofisk 2/4 A. ♦ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm. Co was not measured during the 1998 investigation.

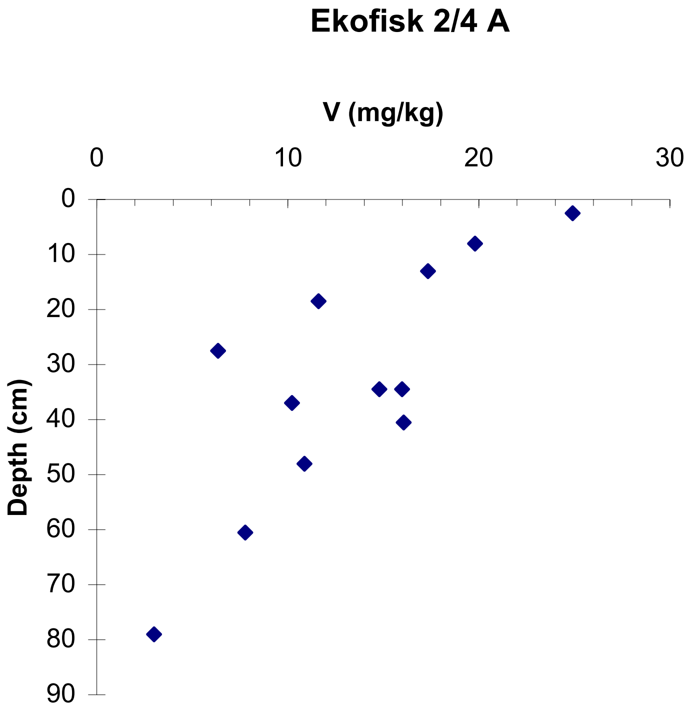


Figure 42: V at Ekofisk 2/4 A. ◆ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm. V was not measured during the 1998 investigation.

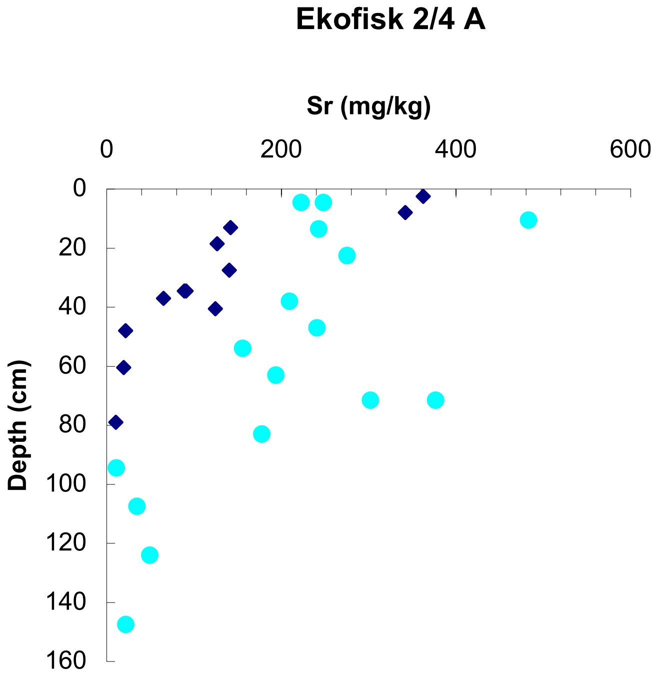


Figure 43: Sr at Ekofisk 2/4 A. ◆ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

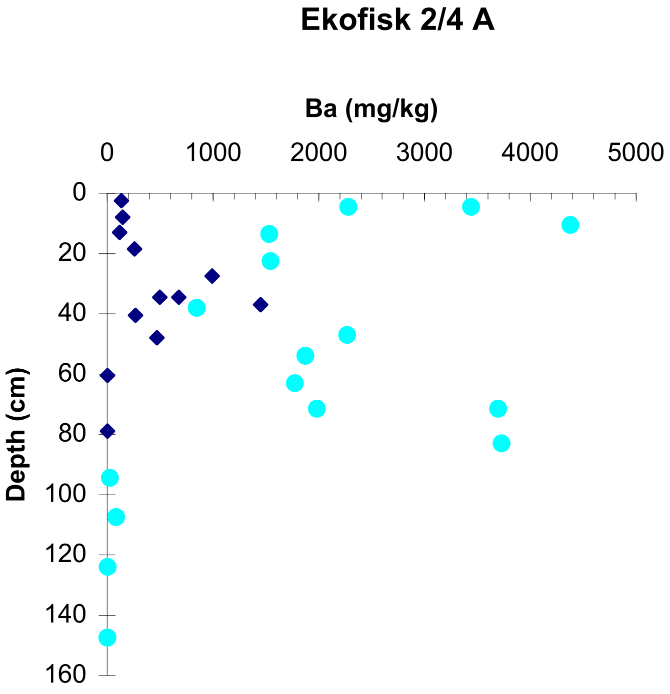


Figure 44: Ba at Ekofisk 2/4 A. ♦ *Vibrocore 9 the NE side of platform. Cuttings depth 43 cm* ● *Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.*

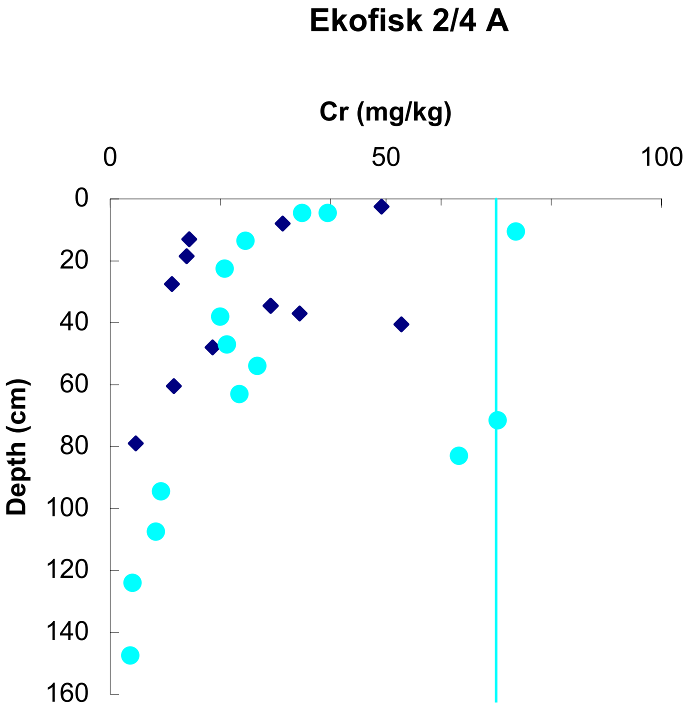


Figure 45: Cr at Ekofisk 2/4 A. ♦ *Vibrocore 9 the NE side of platform. Cuttings depth 43 cm* ● *Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.*

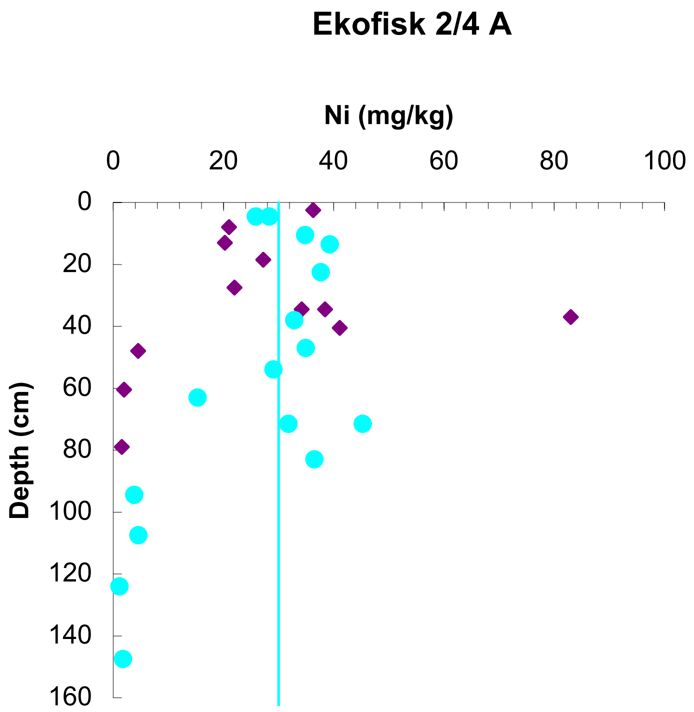


Figure 46: Ni at Ekofisk 2/4 A. ♦ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

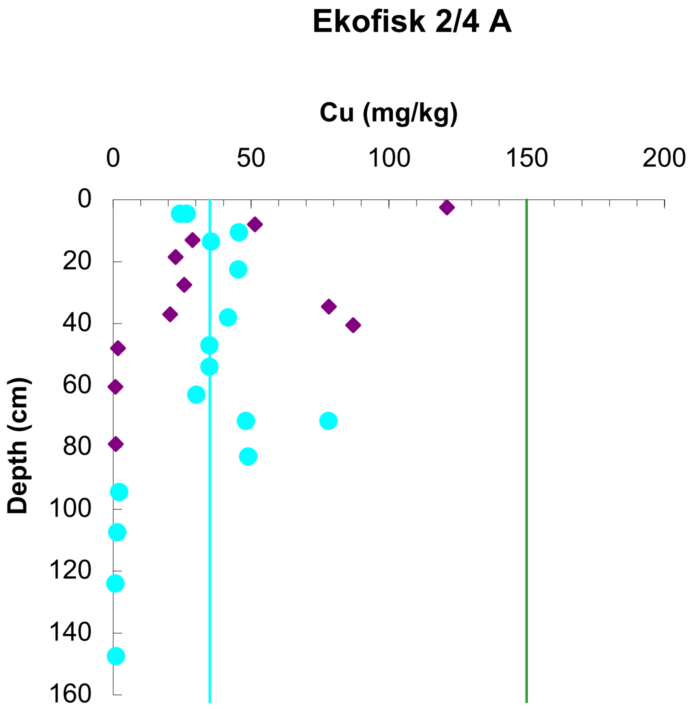


Figure 47: Cu at Ekofisk 2/4 A. ♦ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

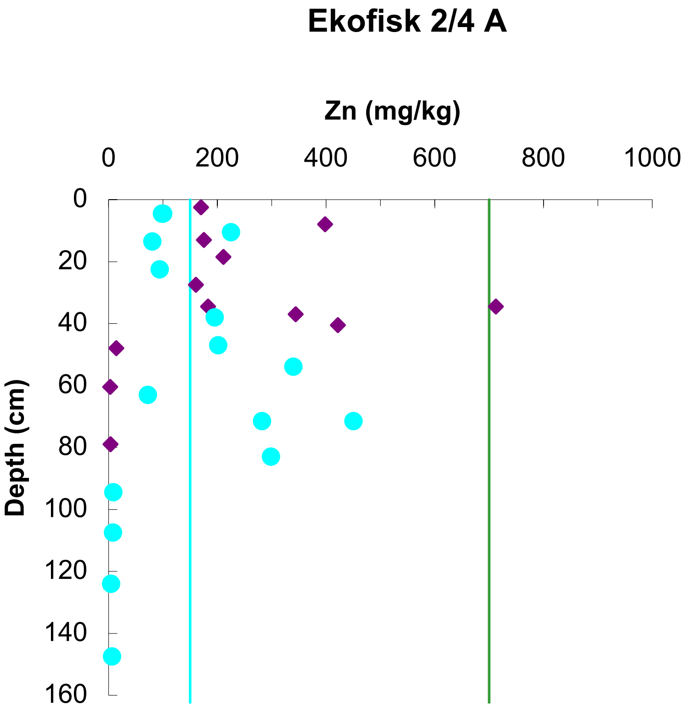


Figure 48: Zn at Ekofisk 2/4 A. ♦ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

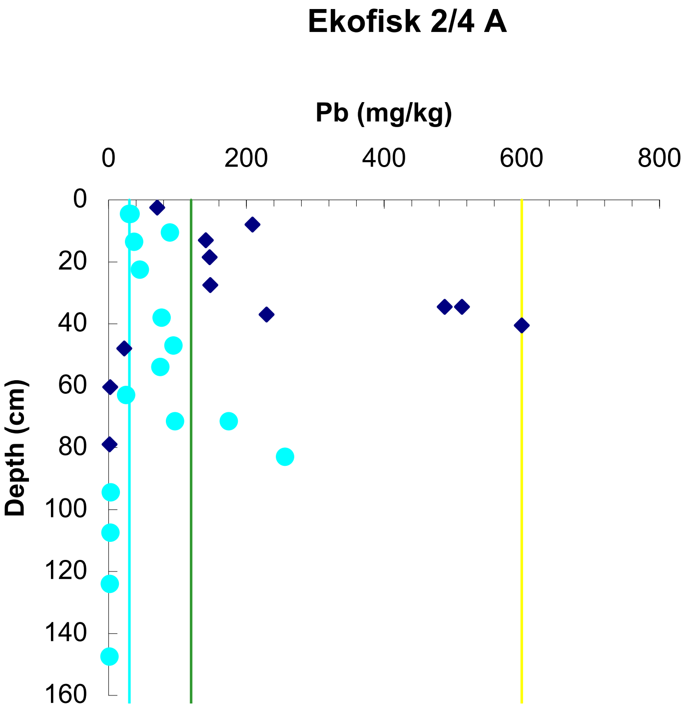


Figure 49: Pb at Ekofisk 2/4 A. ♦ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

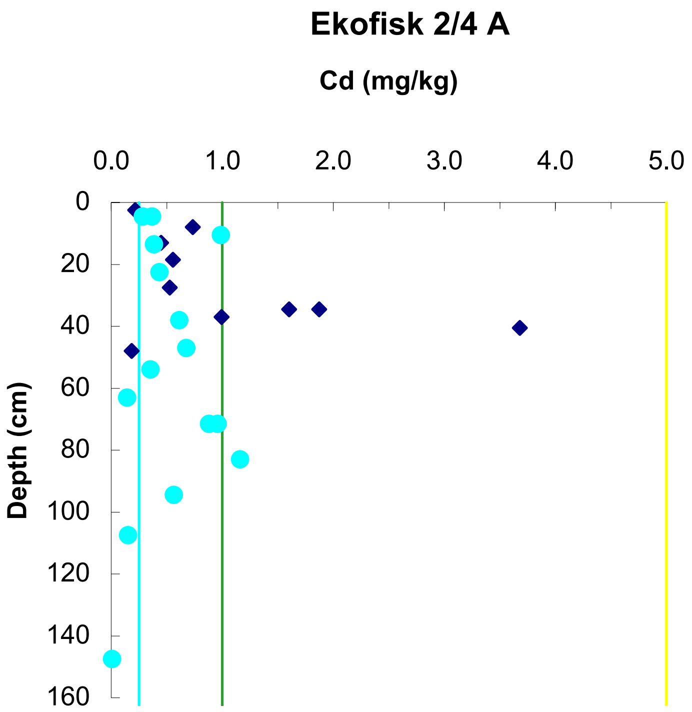


Figure 50: Cd at Ekofisk 2/4 A. ♦ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

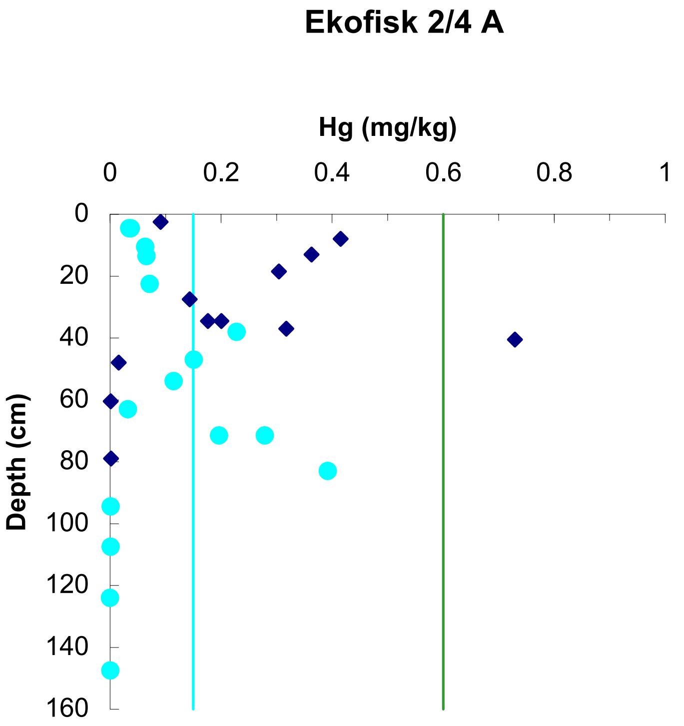


Figure 51: Hg at Ekofisk 2/4 A. ♦ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

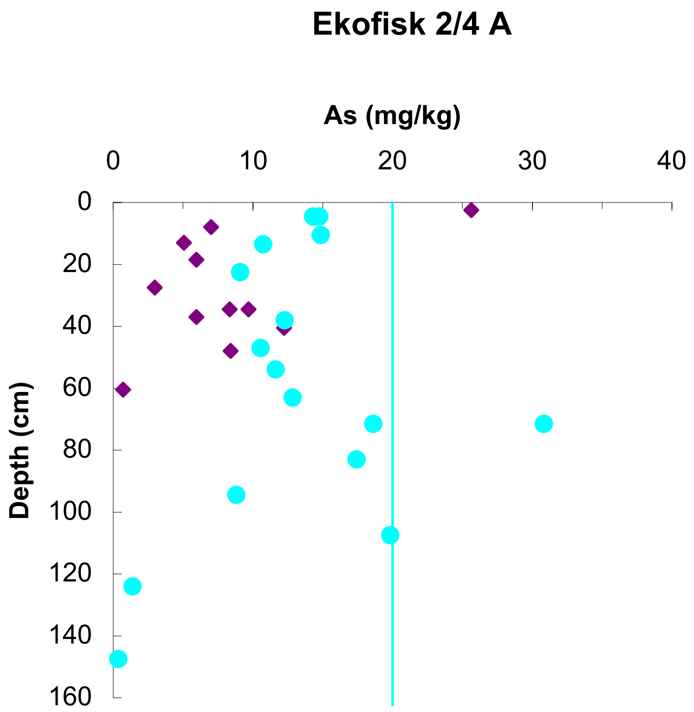


Figure 52: As at Ekofisk 2/4 A. ◆ Vibrocore 9 the NE side of platform. Cuttings depth 43 cm ● Vibro core samples from 1998 taken at the SW side of the platform. Cuttings depth 135 cm.

6.4.9 Metals Ekofisk 2/4A: summary

The most striking features of the metals found in the Ekofisk 2/4 A are summarised in the points below:

- The sediment type based on the content of Fe is, as with the Beryl pile, to be characterised as clay sediment, which consequently implies higher "natural" background concentrations than the surrounding sand.
- The pile seems to be fairly homogenous, -layer wise, for the metals of most concern regarding pollution.
- The deepest part of the pile contains higher concentrations of Cr, Cu, Pb, Zn Cd and Hg compared to the top layer. This deeper layer corresponds to the layer with elevated PCB concentrations.
- Most metals of environmental concern are found at elevated concentrations compared to background levels. Most metal concentrations do however fall into SFT class I or II (minor to moderately contaminated), except for Pb that has concentrations corresponding to SFT class III (markedly polluted).

6.4.10 Radioactivity

Measurements of NORM (radioactivity of natural origin) were conducted by TNO, in the three samples used for their meso-cosmos experiments (Task 2c). The samples for NORM were taken after homogenisation of bulk material. The reference sample is sand sampled from the Dutch sector of the North Sea.

The table 10 below summarises the radioactive isotopes measured. It could be notified that one of the most interesting isotopes, Ra-226, which is generated from scale and trapped into Ca CO_3, are found in the highest concentrations when compared to the reference sample.

Table 9: Radioactive isotopes in the cuttings top layer at Beryl A and Ekofisk.

Sample location	**U-238**	**Ra-226**	**Pb-210**	**Ra-228**	**Th-228**
	Bq/kg dry weight				
Background sand at TNO	>	5.3	8	5.8	4.2
Beryl A	19	57	30	23	24
Ekofisk 2/4 A	28	28	30	23	22

Overall, the radioactivity is low and there is no evidence that radioactive products seem to accumulate on the top of the cuttings pile. As comparison, measurements of some corresponding radioactive isotopes in the Maureen cuttings are shown in table 11 (Cordah, 2000).

Table 10: Data of radioactive isotopes from Maureen cuttings pile (Cordah, 2000).

Sample	**Ra-226**	**Pb-210**
	Bq/kg dry weight	
Maureen cuttings pile	76	<48
Normal background	<20	<50

6.4.11 Sources of hydrocarbons at Beryl and Ekofisk

The sources of hydrocarbons within the cuttings material can be judged from the GC chromatograms, as different components are dominating with different hydrocarbon sources.

The decalines are non-aromatic, ring structured compounds in the base oil used in the OBM drilling mud (Figure 53) illustrates what could clearly be seen in the GC-FID chromatograms, e.g. that the mineral oil component in the cuttings pile at Ekofisk is low, while a main source of organic compounds within the Beryl material is such mineral oils.

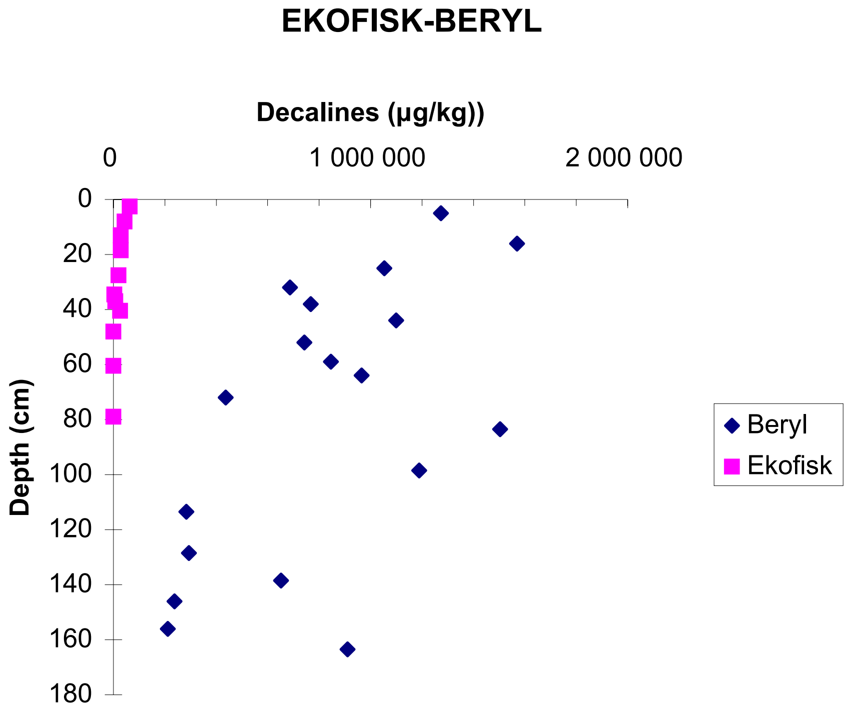


Figure 53: Decalines at Ekofisk 2/4 A and Beryl.

The NPD:s are representative of the aromatic components of the base oils. When drilling with low toxicity oils this component will be lower compared to when drilling with more diesel based oils.

The NPD:s profile clearly shows a historical record with higher concentration downwards into the in pile at Beryl A, indicating that early drilling incidents used more diesel-based oils. This corresponds well with the reported drilling fluids used over the years.

For the Ekofisk pile, most of the hydrocarbons are found in the surface layers (upper 20-60cm). Viewing the chromatograms from these surface layers of the Ekofisk samples, it is evident that the source of hydrocarbons is different. It is suggested that this hydrocarbon layer mainly represent esters. It have been reported by PPCoN that esters and some polyalphaolefines have been used at Ekofisk 2/4A during the last period of drilling activity, which then corresponds well with the observations made. There are also some hydrocarbons in the underlying layers. As only water based muds were used prior to the ester/polyalphaolefin based muds, the hydrocarbons in these layers do not originate directly from the drilling fluid. However, with the modes of operation in the early days of drilling at the Ekofisk field, there may have been associated discharges of hydrocarbons in special cases. It is assumed that such discharges are the source of the hydrocarbons in these layers.

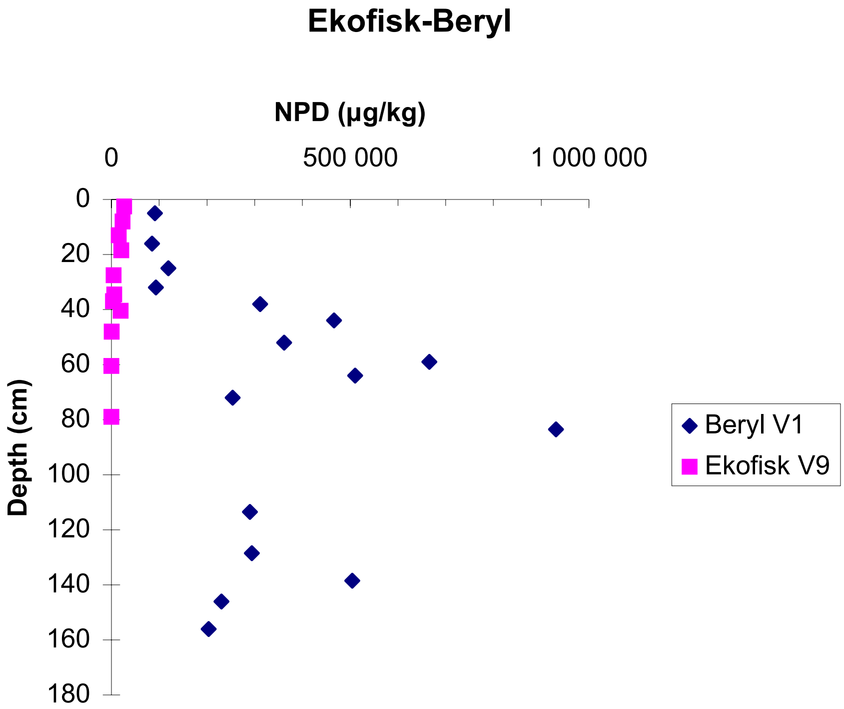


Figure 54: NPD:s in the cuttings piles at Ekofisk and Beryl.

6.4.12 Surface layers: Crust

It has been suggested several times that cuttings piles may be covered with a hard crust. It has been suggested that this could be expected mainly with OBM type piles, formed from microbial processes. The suggestions have been presented in different reports/ presentations, but with no reference to hard data, and to our knowledge, no data is available on the composition of any crust found on top of the cuttings pile. Neither has any crust formation previously been experienced on any of the cuttings piles where RF has been involved in the investigations.

A rather extensive sampling program has been carried out during this survey, at both Beryl A and Ekofisk 2/4A, with more than 50 box core samples taken at each site. A crust layer was found in some of the Ekofisk 2/4 A samples, but not at the Beryl. The limited ROV inspection that was included at these piles also confirmed that only Ekofisk 2/4 A had a crust layer. It is difficult from the ROV inspection to figure out how large an area was covered with crust, but it could be as much as 30% of the SW-part of the pile. The crust typically covered sections of a few m^2, interrupted by areas with no crust. The box-core samples confirmed this (see Figure 55-56).

The crust layer found was up to several cm thick. Within the cores from Ekofisk 2/4 A, a layer that could be old crust was also found in the box corer sub core (SW 3) about 20 cm down in the core.

Figure 55: The surface of a Box-core sample from Ekofisk 2/4A cuttings pile. The picture shows the crust and the Sea anemone vegetation on the crust. The Sea anemones need a hard substrate to grow.

To try to understand when a crust is created and where it originates from, the crust layer was examined further. The crust was found to consist of large stone-like items (0.5-1 cm^2), joined together. The crust was broken apart by placing it in hydrogen peroxide, and the grain size distribution was measured, as shown in (Figure 57).

The dominating building blocks in the crust turned out to be small ‘stones’. These stones were examined further, e.g. they were dried and dissolved in acid and analysed for content of Ca. The dissolution occurred easily, with the evolution of gas thought to be carbon dioxide. The Ca content indicates that the composition of the crust fits well with the elemental composition of limestone.

Figure 56: A closer look at a peace of the crust from the Ekofisk 2/4 A.

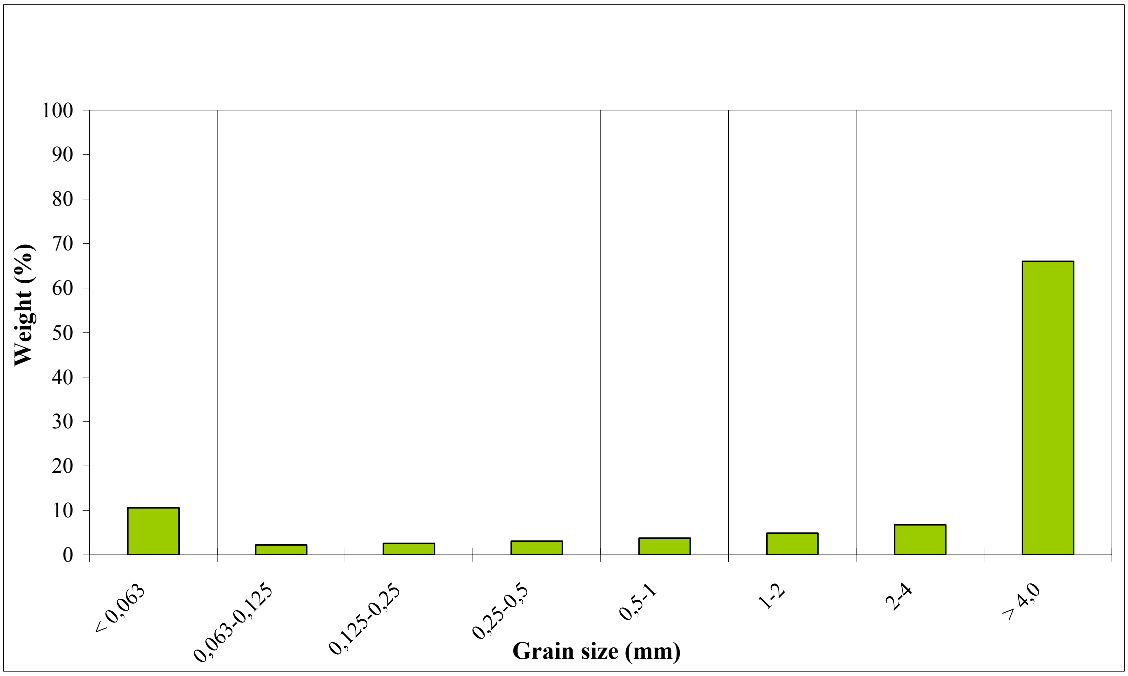


Figure 57: Grain size distribution in the crust after breaking it apart.

A major difference between the reservoir at the Beryl field, where no crust was found, and at the Ekofisk field is that the reservoir rock in the Beryl area is sandstone while the reservoir rock at Ekofisk is limestone. Assuming the crust is created of components from the reservoir rock, the building block in the crusts could originate from limestone chips from the reservoir created during the drilling process. This would also help explain the differences between the two piles. Actually, a common technique to stabilize oil containing waste is to treat with lime / cement / clay etc. Similar reactions may take place on the surface of the cutting pile on Ekofisk. Such a treatment process seems to be based on both chemical and physical reactions taking place between hydrocarbons and calcium. These reactions create a firm hard material which encapsulates and binds hydrocarbon so firmly that such waste is allowed to be disposed of safely or used for other purposes, for instance road building.

The other obvious hypothesis for the crust formation is discharged cement chemicals from well cementing operations. To examine whether any of the hypotheses could be supported, further analyses were initiated.

6.4.12.1 Methods: further analysis of crust composition

To get a better understanding of the mechanisms behind the formation of the crust, a series of more sophisticated analysis were performed:

1. X-ray diffraction analysis (XRD) on different parts of the crust. Such analysis is used to identify crystalline phases in the material, and was carried out by SGAB Analytica.
2. Thin grinding with microscopic examination was carried out on an intact crust section. This method is useful for identification of building material (like e.g. concrete).
3. Low vacuum electron microscopy with energy dispersive crystal for elemental analysis (LV-SEM/EDAX) gives additional information of structure and elemental composition.
4. Analysis of acid soluble components in the crust was carried out mainly to identify whether acid soluble silica was present. If present, that is an indication of the presence of a cement product.

The latter three tasks were carried out by SP (SP Swedish National Testing and Research Institute, Department for Building technique) using standard methods (ref. SP report BTmF105580).

6.4.12.2 Results: Further analysis of crust composition

The XRD analysis showed that the building blocks in the crust consisted of Brucit (Ca_2SiO_4), Calcite ($CaCO_3$) and Portlandic ($Ca(OH)_2$ $CaMgFe2O_6$). The other phase, the material between the building blocks, was identified to contain the same crystalline phases. SEM/EDAX analysis showed that the main components were Ca, Si and Mg.

The more extensive analysis of the crust made by SP showed several important things. First of all, two types of ballast material were found (Figure 58-59), as seen with both light and electron microscopy. This can be explained by that the ballast material originating from a special mixture of concrete, or, it can be a result of crust erosion. It can also be a result of the crust or the discharged concrete ‘picking up’ a second ballast material from the surroundings as the crust was formed.

The overall analyses showed a high concentration of acid soluble silica. This, together with the structure of the material and its composition, weigh against a natural origin of the material. The structural analysis indicates that the crust is highly eroded concrete with several side products generated from seawater. Normally, concrete would form a protective layer in seawater that prevents erosion. In this case however, it is likely that the source of the concrete is excess concrete from well cementing operations that has been discharged with the cuttings flow, and then have ended on the sea floor. This settling phase may then have resulted in a weak material with cracks and seawater pockets. Such material is then much more exposed to erosion and corrosion processes than a solid concrete structure.

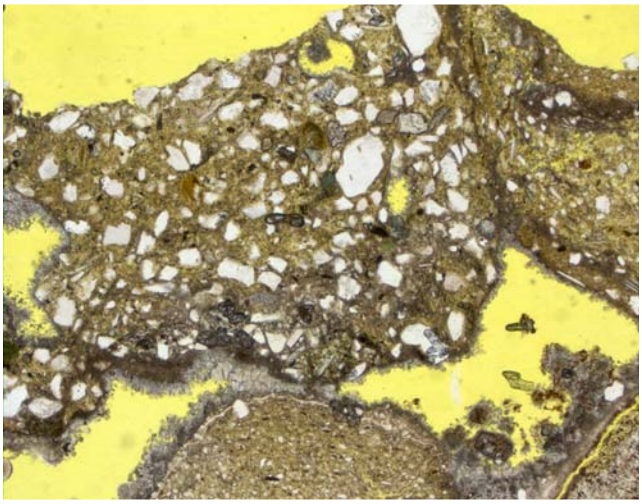


Figure 58: Microscopic picture of 1x1.5 mm of the crust. The picture shows Ballast particles consisting of quarts (White) a cement type material (Brown) and cracks (Yellow) in the material.

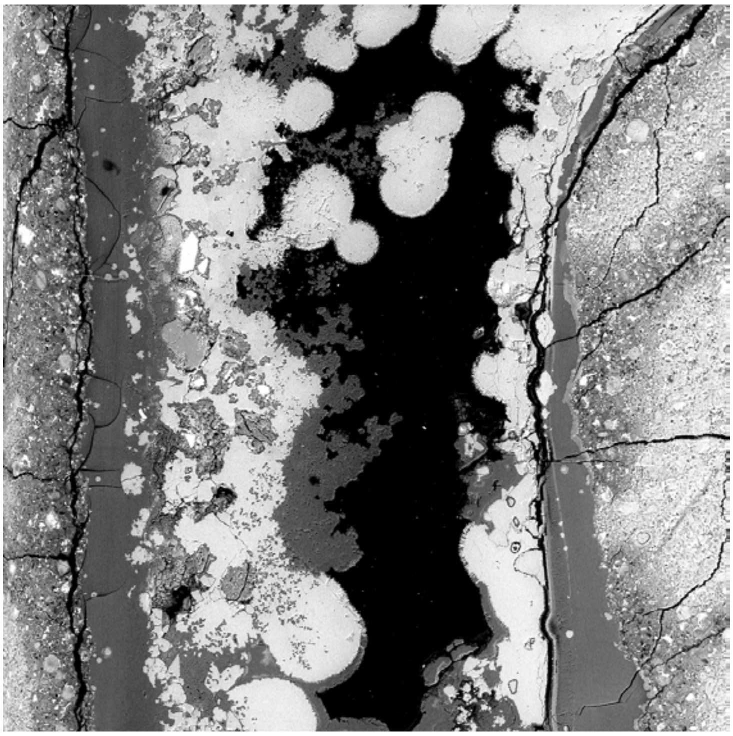


Figure 59: SEM- picture of a total converted area (Magnification 100x) between the two types of ballast material.

6.4.12.3 Conclusion: Further analysis of crust composition

The main conclusion from the analysis carried out is that the crust found at Ekofisk 2/4 A is not of natural origin. The crust is most likely formed from discharged concrete (assumingly from well cementing operations) and has settled on the sea floor. The crust as seen today is confirmed to be heavily eroded concrete. It is likely that this is an ongoing process, and as a consequence it must be expected that the crust will continue to erode. It is therefore very likely that the crust eventually will break up and expose the protected cuttings layer below the crust. However, how exposed the protected cuttings layers will become if the crust is broken will depend on whether the crust itself is covered with sediment before final break-up.

6.4.13 Load of contaminants in the cutting piles

6.4.13.1 Summary of contaminant concentration

A summary of the organic and inorganic contaminants rated in the SFT classification system can be found in table 12. For the classification the median value is used. However, using the average value would only affect Ni, which would then end up in another SFT class.

Table 11: Rating the cuttings piles within the SFT classification system.

Element	Beryl A				Ekofisk 2/4 A		
	Average mg/kg	Median mg/kg	SFT Class		Average mg/kg	Median mg/kg	SFT Class
Chromium	51	46	I		32	28	I
Nickel	32	29	I		35	33	II
Copper	67	54	II		72	48	II
Zinc	316	264	II		377	346	II
Arsenic	17	13	I		10	10	I
Cadmium	0.74	0.46	II		0.85	0.59	II
Lead	291	215	III		195	149	III
Hg	0.56	0.46	II		0.24	0.19	II
SUM PAH- naftalen	9117	6337	IV		927	869	II
Benzo(a)pyren	48	40	II		14	7	I

The contamination level in both piles is rather similar when looking at metals, with most of the metals of concern ending up in SFT class II. The exception is lead (Pb) for which the measured concentration is higher for both piles (SFT class III). The largest difference between the piles is seen for PAH and PCB. In the Beryl A pile, where oil based cuttings have been discharged the concentration of PAH is high compared to the Ekofisk 2/4 A pile. However, there are less difference between the piles when looking at the more carcinogenic PAH components, like B(a)P. PCB was not detected in the Beryl pile, while rather high levels were found in the Ekofisk pile (SFT class 5). It must be noted that the PCBs were found in a restricted layer in the historic layers of the pile.

It is not within the scope of this report to address the seriousness of, or acceptable limits of, the present components. The reference to the SFT classification can though be used as a reference to highlight those components that may be of special concern.

6.4.13.2 Load of contaminants on pile scale

The mapped cuttings pile volumes at Beryl A and Ekofisk 2/4A are presented in Table 13. Combined with the density data, it makes it possible to make a reasonable good estimation of the total load of the different contaminants found within the cuttings piles.

Table 12: Pile data used for load calculations.

Pile	Mapped volyme	Density	Dry Load
	m^3	Ton/m^3	Ton
Ekofisk 2/4A	5300	1.36	7208
Beryl A**	24624	1.58	38906

*ROV survey

**Sonar Graphic

For the calculations of total amount of contaminants, the median concentrations calculated (Table 11) from the whole data set of the measured contaminants in the respective cuttings pile were used. However, when the contaminants were found in demarcate layers like e.g. the PCB:s at Ekofisk, this has been taken into account. For components that showed large heterogeneity, this is marked in the summary table of the contaminants below (Table 13). Only data from the current study is used in these estimates. However, the data from the 1998 Ekofisk 2/4 A-survey confirmed that this pile had fairly homogenous layers, as demonstrated in Figure 39-52.

The get some perspective on what these figures means calculation is also made assuming that the cutting would contain the concentration of contaminants equivalent with maximum for SFT Class1.

Table 13: Calculated load of different contaminants in the investigated cuttings piles.

	Ekofisk 2/4A			**Beryl A**		
	Pile	**SFT Class 1**	**Factor above**	**Pile**	**SFT Class 1**	**Factor above**
	kg	**kg**	**SFT Class 1**	**kg**	**kg**	**SFT Class 1**
PCB	0.24*	0.04	6.7	N.D.		
PAH	6.3	2.2	2.9	246	12	21
Hg	1.4	1.1	1.3	18	5.8	3.1
Cu	346	252	1.4	2103	1363	1.5
Zn	2494	1081	2.3	10279	5840	1.8
Pb	1074	216	5.0	8371	1168	7.2
Cd	4.3	1.8	2.4	18	10	1.8
	Ton			**Ton**		
THC	72			1829*		

ND Not detected
*Large variatins found in the pile

6.4.14 Toxicity

Under this heading an evaluation of standard toxicity test results are presented. Examination of the endocrine disrupting potential of the drill cuttings samples has been carried out. These data are reported separately in Part 3 of this report.

6.4.14.1 Standard toxicity testing

Traditional approaches to evaluate toxicity of environmental samples are to test the effects of the samples and/or the chemical compounds found in the samples towards a set of reference species. The data presented below is based on available literature data. The toxicity of the cuttings piles are evaluated from toxicity data submitted to SFT that have been reviewed in relevance to drilling chemicals found in the respective cuttings pile. The dominating drilling chemical found at Beryl A was mineral oil. From the discharge records, a base oil type HDF 200 is the most frequently used product. At Ekofisk the discharge records is not very complete, but it seems, from these records, that the portion of the drilling mud used that were not purely water based contained mainly polyalfa-olefine and ester-based drilling mud. From the analytical date from the cuttings sampled at Ekofisk 2/4A, only, or mainly, ester types could be found. In the deeper part of the Ekofisk pile, the hydrocarbons found were mainly mineral oil types.

However, the concentrations in these layers were rather low compared to what would be expected in an OBM cuttings pile.

In the SFT report material consulted, three different tests have been performed on used drilling mud, e.g.:

- *Sceletonema costatum*
- *Balanus improvisus*
- *Mytilus edulis*

Toxicity test data from three different test occasions on such types of used drilling mud are summarised in Table 15. (The toxicity tests have been performed on cuttings material from other drilling operations, and are not directly related to any of the two piles investigated here).

Table 14: Toxicity data on drilling used mud submitted to SFT. The range represent results from three different tests.

Tested specie	**Ester based drilling mud mg/l EC50**	**Base oil HDF200 mg/l EC50**
Sceletonema costatum	23000-37000	3200->316000
Balanus improvisus	76000-135000	89000-260000
Mytilus edulis	4-126	0.7-0.8

It is obviously difficult to compare such types of tests to the realty. The rating of the chemicals was in most cases “Moderately toxic”. However, comparing these EC50 numbers with the concentrations of esters and oil found in both the Ekofisk and Beryl cuttings piles, the toxicity of the top layer must be high. The results for *Balanus improvisus* show that these organisms are more tolerant than the other test organisms. The results from the investigations of the benthic organism taxa support that in general, the environment in the cuttings pile is hostile for many organisms. The diversity indexes are low, and only the most tolerant species seems to be able to survive and proliferate in the cuttings pile.

Comparing the test results with the observations made at Beryl and Ekofisk (see section 6.4), it is somewhat surprising that e.g. *Mytilus edulis* was found at the Ekofisk 2/4 A cuttings pile (see appendix 6). There may be several explanations for this. First of all, it is debatable whether the species grow and survive at the pile at all, or whether the individuals found has recently come off the platform legs. Secondly, it may also be that the intrinsic toxicity, especially at Ekofisk may be lower due to the hard crust layer.

6.5 Benthos

6.5.1 Soft bottom macrofauna

In total 19 grab samples were collected for macrofauna analyses. Approximately 5600 specimens of polychaetes, molluscs, crustaceans were collected and identified to 135 taxa (Table 16). Polychaetes dominated the fauna numerically. The complete list of taxa from each sample / station is given in the Appendix 6.

It has long been a tradition in pollution monitoring that diversity indices are used to assess whether or not particular sites are polluted (Gray et al. 1992). Diversity combines the concepts of dominance, evenness and species richness, and is a measure of the relationship between species richness (number of species in the community) and the distribution of individuals among the species (e.g. Gray et al. 1992, Burd et al. 1990). The Shannon-Wiener diversity index (H') was used to demonstrate the distribution between species and individuals. A high value (H' > 4) indicates a species rich community and / or a good distribution of individuals among the species. A low value (H' < 4) indicates either a species poor community and / or a community which has a high abundance of one or a few species. Evenness was calculated using the Pielou's evenness index to demonstrate how evenly the individuals were distributed among the different species. The values range between 0 and 1, and will approach 0 if most of the individuals belong to one species and 1 if the individuals are evenly distributed among the species.

The species diversity and evenness were low at both the two cuttings piles (Table 15). Lowest diversity (0.83) was calculated at the 2/4 A platform at the Ekofisk field. The diversity at the Beryl platform was calculated to 1.36. The dominating fauna at both the two cuttings piles is typical of polluted areas. The opportunistic and quick growing *Capitella capitata* was the dominating species *C. capitata* is a non-selective surface deposit-feeder and is found in large numbers in polluted areas all over the world (Pearson & Rosenberg 1978). *C. capitata* was also the dominating species at the 2/4 B and 2/4 C platforms in the characterisation study by Cripps et al. (1999). At the two reference stations, diversity was higher.

Table 15: Number of individuals and taxa per 0.5 m^2 (At 2/4 A only four replicates were sampled, and the numbers are therefore weighted), Shannon-Wiener diversity index and Pielou's evenness index at each station.

Station	**Individuals Number**	**Taxa Number**	**Shannon-Wiener Index**	**Evenness**
Beryl A	1314	31	1.39	0.28
Beryl Ref*	778	80	4.95	0.78
Ekofisk 2/4 A	2188	30	0.83	0.17
Ekofisk Ref*	1428	67	2.30	0.38

*1000 m downstream the cuttings pile center line

A comparison of the Benthos found in the cuttings piles with the expected populations for the specific area can be seen in table 17 below.

The stations selected in table 17 is so called regional reference stations assumed to be unaffected by the oil activity. The stations are representative for the Ekofisk and Sleipner areas. The Sleipner area is bordering to the Beryl area. The data show that the Sleipner stations show similar indexes and taxa as the Beryl Ref station downstream the cuttings pile, while the diversity at the Ekofisk ref is lower than the regional reference station at Ekofisk. It should however be noted that the diversity index at Ekofisk in general is lower, particularly if older data is reviewed (OLF database).

Table 16: Benthos data from the North Sea (OLF data base of surveys around oil installations in the Norwegian sector).

Station	Induviduels	Taxa	Shannon - Wiener	Evenness	UTM33 N	UTM33 E	Depth	ES100
	Number	Number	Index	J			m	
Ekofisk								
1996 REG1-02	622	72	4.86	0.79	6367742	-200940	65	33
1996 REG1-04	508	87	5.23	0.81	6290261	-190276	68	41.8
1996 REG1-05	864	85	3.91	0.61	6387213	-256899	69	27.2
1996 REG1-06	605	68	4.45	0.73	6358846	-251726	70	30.3
1996 REG1-07	593	68	4.71	0.77	6329308	-251870	72	31
Sleipner								
1997 REG2-01	951	110	5.3	0.79	6755994	-196497	110	41
1997 REG2-02	2744	121	3.2	0.46	6714086	-176087	109	21
1997 REG2-03	1515	138	5.7	0.8	6677388	-182928	114	45
1997 REG2-04	774	109	5.4	0.79	6641545	-194436	114	42
1997 REG2-05	958	128	5.6	0.8	6576422	-201628	115	44
1997 REG2-06	522	80	5.1	0.8	6499240	-246044	71	38
1997 REG2-07	1065	122	5.2	0.75	6534358	-279459	98	41
1997 REG2-08	1313	135	5.5	0.77	6589330	-268350	109	42
1997 REG2-09	1726	145	5.5	0.76	6642384	-247808	114	40
1997 REG2-10	2122	158	5.8	0.79	6680828	-230406	114	46

7 Comparison between Ekofisk 2/4 A and Beryl A cuttings piles

The differences between these two cuttings piles might not be obvious. In fact, there are many similarities between the two piles, and individual differences may be “masked “ by the more obvious differences between the piles and the surrounding sediment. However, there are some apparent features in which the Beryl A and Ekofisk 2/4 A piles are clearly different.

The similarities and differences can shortly be summarised trough the following points:

- There are only minor differences between the piles considering the inorganic contaminants. The main source of the inorganic contaminants is most likely the barite in the drilling mud and/or the reservoirs. The operational difference is small, and hence the same pattern was expected with both types of cuttings piles.
- Considering the organic contaminants, there are clearly large differences between the piles. Knowing that a major source of organic contaminants is the drilling fluids, and since the drilling fluids used at the two sites have been different, this is as expected. The WBM/PBM Ekofisk pile is a complex pile where the top of the pile

have high concentrations of esters originating from the drilling fluid, while the older and largest part of the pile contains rather low concentrations of organic compounds. The Ekofisk pile has layer-wise a rather homogeneous concentration of all contaminants measured. The Beryl A pile has higher organic load, and there are large variations in the concentration within short distances in the pile. There also tend to be increasing organic load vertically into the pile, and the total load is considerably higher than for the Ekofisk pile. It is hypothesised that the organic load of the cuttings pile has considerable impact on the pile "stability", but this is not directly addressed through this work.

- The physical properties of the two piles are rather similar, with one significant exception: A hard crust layer was seen at Ekofisk only. It might prove to be an important factor determining the "lifetime" of a pile (how this affects the erodability of the pile is further examined in task 3, UKOOA phase II). Measurements of other physical properties show only minor differences between the piles.

8 Conclusions

The following conclusions can be drawn:

- **Field sampling**

The nature of the cuttings piles made traditional coring work difficult. The experience at both the cuttings piles sampled was that the coring equipment must be carefully selected to be able to retrieve samples and to reduce the number of failed attempts.

- **Physical properties**

The material found in the cuttings pile is extremely soft with very little bearing capacity. The CPT measurements could not distinguish between the material in the Beryl A and Ekofisk 2/4 A cuttings pile. Shear strength measurements on the material from the cores gave only small differences.

- **Sediment redox conditions**

Sulphide measurements directly on the cores sampled suggested ongoing anoxic processes within both cuttings piles. However, the oxic/anoxic conditions in the piles seemed to vary. There was no apparent difference between the two piles.

- **Organic contaminants**

THC: Both cutting piles contain significant amounts of hydrocarbons. The THC concentrations measured were highly variable. The total load of the Beryl pile is considerable higher than the Ekofisk pile, and, in Beryl, hydrocarbon levels are high throughout the pile, and tend to increase vertically into the pile (concentrations measured varied between 0.2 and 20%). At Beryl A, the hydrocarbon source is mainly mineral type oils. At Ekofisk, the main portion of the hydrocarbons was found in the surface layer (about 20cm), where concentrations up to 8% were measured. The THC in the Ekofisk surface layer is dominated by esters, as can be seen from the chromatograms from the THC analysis. Further down into the Ekofisk pile, THC levels decreased considerably, reflecting the use of water based muds.

PAH: The PAH concentration also differed between the piles, Beryl having the highest concentration. The concentration of the carcinogenic PAH component B(a)P were not dramatically high, and was rather low compared to the sum PAH measured. It can clearly be seen by looking at the historical layers through the pile, that lower toxicity base oils with lower aromatic content has been used in the latest drilling periods. At the Ekofisk 2/4 A, the concentration of the PAH components, including B(a)P is low. This reflects the different origin of the THC in this pile.

PCB: No PCB was detected in the Beryl pile. In the Ekofisk pile, high concentrations of PCB were found in some layers (up to 1500 µg/kg sediment in a thin layer). The PCB contaminated layer was found in the oldest part of the cutting pile and is at present covered with cuttings layers where no PCB was found.

- **Metals**

Both cuttings piles show quite similar contamination patterns for metals. According to SFT classification, Pb represents the highest contamination found. Both piles also contain concentrations of Cu, Zn, Cd and Hg indicating a moderate contaminated marine environment.

- **Crust**

A hard crust layer was found on the surface of the Ekofisk pile. No such observations were made on the Beryl pile. The crust most likely has formed from discharged concrete. The observed crust is classified as being heavily eroded concrete.

- **Toxicity**

Standard toxicity tests: Reviewing data from toxicity tests performed on used drilling mud (other sites than Beryl and Ekofisk) and comparing the EC50 values, both investigated piles have an environment highly toxic for the test organisms used in these test. It is however not obvious that such tests are directly comparable to cuttings pile conditions, as can be seen i.e. by the quite frequent findings of *Mytilus* at the Ekofisk 2/4 A pile. Different explanations can be envisioned, e.g. the toxic compounds may be poorly bioavailable at the pile surface to which the animals would become exposed.

- **Biota**

Both cuttings piles contained a rather similar pattern of the benthic fauna. The number of taxa found was in line with what could be expected in this area (i.e. when coparing with seabed surveys in relevant areas). Both cuttings piles were dominated by the species *Capitella Capitata*, which is usually one of the dominating species at contaminated sites.

9 Analysis parameters suggested to become recommended parameters of CP sampling

Within this characterisation work, new issues not investigated or measured into any detail in previous drill cuttings surveys have been included. It is clear that some of these are rather novel in nature (alt least with regard to cuttings piles), and they may therefore raise other issues than those investigated through this project. Some of these issues are already being examined further, while others could benefit from being looked into in more detail. The issues being examined further are treated separately (see part 2 and 3 of this report).

Other issues are mostly related to parameters to be included as part of the characterisation work. Some of these have been properly included in this work, but are not recommended by the OLF guideline that provided the basis for planning. Others were not sufficiently included in this work, but may be relevant to include in the future. Such issues include, but are not restricted to:

9.1.1.1.1 PCB

From the analysis data obtained through this work, it seems clear that PCB should be included as a standard parameter in characterisation studies of cutting piles. The approach often taken, analysing for the Dutch 7 congeners is suggested to be sufficient to screen and quantify PCBs as a general group of components.

9.1.1.1.2 Radioactivity (NORM)

The NORM analysis carried out by TNO was sampled only from the surface layer of Beryl. We believe it would be valuable to measure NORM (radioactive isotopes) in the cores through the whole cuttings pile in the individual layers (same set of samples as with the rest of the analysis). This would most likely sort out whether radioactivity varies between historical cuttings layers. It would also be valuable as a means to assume/verify that NORM levels measured are of little concern in drill cuttings management.

9.1.1.1.3 Mineralogy

Analysis of the mineralogy gave valuable information on main components (elements) of the cuttings material, and indirectly about processes going on in the pile. It may prove valuable to include such analysis also in future characterisation work.

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Characterisation of the cuttings piles at the Beryl A and Ekofisk 2/4 A platform - UKOOA Phase II, task 1

PART 2:

Availability of trace metals in cuttings deposits-studied by sequential extraction.

10 Summary Part 2

The presence of elevated concentrations of metals in drill cuttings deposits have been demonstrated in most pile characterisation cases (when compared to expected background levels). However, the main concern of these metals are related to what state they are in, and how accessible they are for the surroundings, especially how bioavailable they are for the biota.

To address this aspect, a sequential extraction procedure was applied to cutting deposits from the cuttings pile at Ekofisk 2/4 A and Beryl A. To obtain a more complete picture of the differences between cuttings of different types and contaminant levels, some additional samples were also included (the greater Ekofisk area and the Frigg area operated by TotalFinaElf).

The sequential extraction procedure used was a four-step procedure, where the last step matched the metals analysis previously performed on the cuttings material. The procedure was performed on wet sectioned material stored in plastic bags in a freezer. Wet material was used to avoid speciation changes during a drying process.

The metals released during the different extraction steps are not directly linked to the bioavailability. The extraction steps are selected to simulate different geochemical processes were primary release of metals from sediment occur.

The results are presented both in mass scale and percent scale to be able to compare samples with large differences in total concentration.

When investigating the mobility of the metals in the cuttings material it is shown that metals of high environmental concern (Hg, Pb and Cd) are to a considerable extent bound in fractions of high mobility in regard to geochemical processes. However, at the higher metal contamination levels, the fraction (%) of the total pool of these metals in the most bioavailable fractions are reduced. Potential impacts to the environment thus do not increase linearly with the total concentration of these metals.

The attempt to apply multivariate analysis (Principal Component Analysis - PCA) to relate the different metals to particular fractions did not enable a generalisation of the results, neither with respect to metals bound to specific fractions, location of the cuttings sample in the specific piles, or between the different piles.

11 Introduction Part 2

The availability of trace metals bound in sediment to biota is important to understand the possible effects of metals in sediment to biota. One way to achieve this information is to expose different species for contaminated sediment. The uptake of metals is then a function the biota's capacity to take and bound different metals. However metal uptake in biota occurs through membrane walls and will need the metals in some kind of dissolved state. The mobilisation of metals from the solid sediment occurs through geochemical different processes. Exposing biota of contaminated sediment is time-consuming experiment where several different species should be used with different capability for uptake of metals.

A simpler approach that is selected in this work to achieve the information on the availability of the metals in sediments (e.g. to establish how strongly the metals are bound to the sediment matrix) is to apply a sequential extraction procedure. In a sequential extraction procedure successively stronger extraction reagents are used for extracting the metals. The type of reagents used will operatively define how the metals are bound to the sediment matrix. These results can then be linked to the biogeochemical processes occurring in the sediment, or in this case, the availability of the metals in the cuttings piles to biota and possible spreading to the seawater. The drawback with this approach is that no direct information on the availability is generated. However with the knowledge of the which metals that mobilises with the different processes and the knowledge of which metals that have high uptake rate in biota's different organs the information can pinpoint the metals that is of most worries in the cuttings.

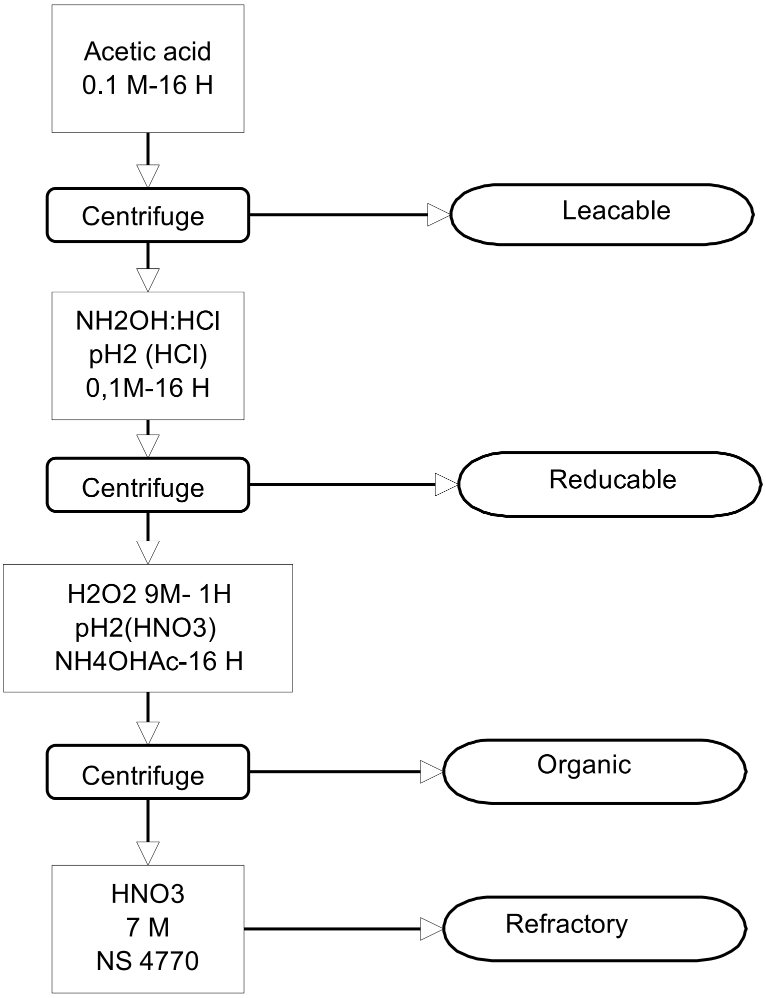
The sequential extraction procedure applied in this work was originally proposed by Tessier et al. (1979) and contained a protocol with seven different extraction steps. A more simplified four-step procedure based on the Tessier procedure was developed by Lopez-Sanches et al. (1992) on request from the Community Bureau of Reference (BCR) to be suitable for developing material for quality control.

In this work this simplified procedure was followed with the exception of the last step, which was modified to be able to compare the result of the total metal concentration with the previous analysis of the cuttings material carried out as part of the original characterisation studies. The extraction method used previously as part of the main characterisation work was defined in the OLF Guidelines (OLF, 2000) which also harmonises with SFT guidelines for surveys around oil installations (SFT, 1999).

12 Methods

12.1 Sequential procedure

The schematic diagram below shows the sequential extraction procedure used:



Schematic diagram of the extraction procedure

12.2 Extraction procedure

In the experiment cuttings material was selected from wet material stored frozen (for up to 2 years). Approximately 2 grams of the wet material was weighed in to a 50 ml polypropylene screw capped centrifuge tube. For the extraction steps performed at 20°C, the extraction was performed in a rotary shaker except for the 1-hour treatment with H_2O_2. The shaker was operated with end over shaking at a speed of 60 rpm (rotations per minutes). The 1-hour treatment with H_2O_2 was performed at 85°C in a water bath. The extraction step with nitric acid at 120°C was made in a pressurised vessel (part 1).

After every extraction step the samples were centrifuged and the supernatant was transferred to a clean tube. The solid part was rinsed with Milli-Q water and once again centrifuged. The two supernatants were combined and diluted to a total volume of 50 ml. The solid part was then added the extraction reagents of the next step and the next extraction step were started. The supernatants from the different extraction steps were stored in a refrigerator until analysed.

12.3 Analysis

After proper dilution, the extracts were analysed with ICP-MS (VG PQ2+). An ICP-MS is an inductively coupled plasma combined with a mass spectrometer. This type of instruments has multielement capacity combined with low detection limits. A peak jump procedure was selected covering the elements Ag, As, Ba, Cd, Cu, Co, Fe, Mn, Ni, Sr, V and Zn. For instrument calibration standards containing the reagents used for the different extraction procedures were used.

In addition to the ICP-MS measurements, Hg was analysed by cold vapour technique. The extraction of Hg is more complicated by the volatility of elemental Hg which make losses of Hg in the first 2 steps likely. It is also possible that loss of Hg can occur in step 3 during the 16 hours extraction period when most of the H_2O_2 had evaporated. The complicated issue with Hg is that if elemental Hg is formed the Hg can diffuse through the plastic vials used in the sequential extraction procedure.

However data from these samples analysed on the total content (NS 4770) of Hg was generated from the original characterisation study (Section 1). By comparing these original data on these samples from the main characterisation study and the results from the last extraction step, a fairly good estimate on the mineral bound fraction of Hg is obtained. This approach add more uncertainty to the Hg data, but was the most feasible way to establish some results for Hg in the cuttings samples.

13 Chemical forms of the metals

The different extraction steps mainly released metals bound to or adsorbed on the phases below

Step1: **Leachable,** mainly carbonates

Step 2: **Reducible,** phases of manganese (Mn^{4+}) or iron (Fe^{3+}) or cobalt (Co^{3+})

Step 3: **Organic,** bound and sulphides

Step 4: **Refractory,** mainly hard mineral bound metals

The highlighted text above is referred to in the legends of the figures later in the report.

The later in the extraction procedure the metals are released (e.g. the more extraction steps needed to dissolve/release the metals), the more strongly the metals are bound to the substrate. However in the interface between the sediment and water it is likely that the release from the reducible and the organic bound metals will dominate (Westerlund et al., 1986, Sundby et al.,1985).

14 Selection of samples

The samples in this study were carefully selected to contain different contamination levels from cuttings piles at the Ekofisk, Beryl and the Frigg area. The table 17 below summarises the selected samples

Table 17: Selected samples from the different cuttings piles or deposits.

Installation	Core	Layer		Installation	Core	Layer
	Id	cm			Id	cm
Beryl	V1	0-10		Ekofisk 2/4C	VC4-2	65-72
Beryl	V1	40-48		Ekofisk 2/4C	VC4-2	81-92
Beryl	V1	60-68		Ekofisk 2/4C	VC4-2	92-100
Beryl	V1	65-75		Ekofisk 2/4D	D51C	9-17
Beryl	V1	85-90		Ekofisk 2/4D	D51C	19-40
Beryl	V4	10-18		Ekofisk 2/4D	D51C	63-80
Beryl	V4	18-24		Frigg DP2	CORE 7 98	1-2
Beryl	K1	0-4		Frigg DP2	CORE 7 98	12-17
Beryl	K1	13-20		Frøy	CORE1 99	0-5
Albuskjell 1/6A	Grabb A3	0-6		Frøy	CORE1 99	5-15
Ekofisk 2/4A	V9	0-5		Frøy	CORE1 99	15-22
Ekofisk 2/4A	V9	15-22		Lille Frigg	L FR MSA 3	0-4
Ekofisk 2/4A	V9	33-36		Lille Frigg	L FR MSA 3	8-12
Ekofisk 2/4A	V10	1-10		East Frigg PSA	E FR PSA 10	0-10
Ekofisk 2/4A	VC2	0-9		East Frigg PSA	E FR PSA 3-2	2-12
Ekofisk 2/4A	VC2	15-30		East Frigg PSB	E FR PSB 3-2	0-4
Ekofisk 2/4A	VC2	68-77		East Frigg PSB	E FR PSB 3	4-10
Ekofisk 2/4B	VC6	0-3		NE Frigg	NE FR 4	8-16
Ekofisk 2/4B	VC6	65-93		NE Frigg	NE FR 11A	3-10
Ekofisk 2/4B	VC6	33-42		Sand	Ekofisk	68-90
Ekofisk 2/4C	VC4	0-8		Sand	Beryl	Ref
Ekofisk 2/4C	VC4	94-100		Sand	Frigg	0-5

15 Cuttings piles features

The selected samples represent a broad spectrum of different characteristic of cuttings. Below are the different features of the cuttings at the different location described

Definitions:

OBM-Pile Cutting deposits where oil based mud has been used and discharged in the drilling process. Concentration of oil >1000 mg/kg is found in the cuttings.

PBM-Pile Cutting deposits where pseudo oils (Esther and Olefines) has been used and discharged in the drilling process.

WBM-Pile Cutting deposits where only water based cuttings has been discharged.

Features of the different cuttings deposits

Beryl	OBM-pile
Albuskjell 1/6 A	WBM-pile
Ekofisk 2/4 A	PBM-pile in the top layer and WB pile deeper down. Oil is also found below the PBM layer, indicative of an OBM layer bordering to the WBM layer. Higher contamination of metals deeper in the pile.
Ekofisk 2/4 B	OBM-Pile (moderate concentrations of oil), possibly POB influence
Ekofisk 2/4 C	OBM-Pile (moderate concentrations of oil), higher contamination of metals deeper in the pile.
Ekofisk 2/4 D	OBM-Pile (moderate concentrations of oil)
Frigg DP2	OBM-Pile (moderate or low concentrations of oil)
Frøy	PBM-Pile (Linear alfa olefin)
Lille Frigg	WBM-Pile, low contamination of metals
East Frigg PSA	WBM-Pile, low contamination of metals except Cr
East Frigg PSB	WBM-Pile, low contamination of metals
Northeast-Frigg	WBM-Pile, low contamination of metals except Cr
Sand	Substrate layer below the cutting deposits. In grain size point of view defined is sand.

16 Results

The sample material used for this study was selected from “new”, wet material that was stored frozen since it was collected. Comparing the total concentrations obtained on these samples with the original analysis show that the total concentration (main report, Cripps et. al., 1999, Westerlund and Olsen, 2000) obtained by summarising the metals from all fractions fall within the expected concentration range. A deviation larger than the analytical error from the earlier data is expected due to less homogeneity in this type of material compared to normal sediment.

16.1 Fractionation data

To get some general idea about the partition of the metals in the different fractions a summary table is generated. The samples are divided into 3 groups (see also table 2). All data is available in the appendix 5. The sum of the four fractions is directly compatible with the results presented in Part 1. No total statistical evaluation between the two sets of data has been done However a brief examination of the data shows good agreement between the data sets based on the replicates found in the main data table in appendix 5.

1. **Beryl, Ekofisk, Frigg DP2**
   Moderate to high metal contamination of the cutting deposits
2. **Frigg**
   Low metal contamination of the cutting deposits
3. **Background**
   Background substrate. Sand under the cutting deposits with low metal concentration.

Table 18: (next page): Summary of all measurements. The result is given in both in concentration and also on percent basis. The first column with Beryl Ekofisk and Frigg DP2 represents high level contamination of metals, The second column labelled Frigg represents Frøy,Lille Frigg, East Frigg and Northeast Frigg and represents cuttings with low level contamination of metals and the sand represents the background substrate below the cuttings layer with low concentrations of metals from the North sea high silica sand. Note that the concentration in the table is in mg/kg wet weight cuttings. The results for Hg is presented in table 19 dye to different assessment of the data due to loss of Hg in the sequential procedure.

	Average				Average		
	Beryl Ekofisk DP2	Frigg	Sand		Beryl Ekofisk DP2	Frigg	Sand
Sr	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	89.17	74.97	65.44		42.7	34.4	78.1
Reducible	39.38	38.44	11.13		18.8	17.7	13.3
Organic	14.34	28.53	0.81		6.9	13.1	1.0
Refractory	66.16	75.80	6.44		31.6	34.8	7.7
Fe	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	865	306	93		5.1	4.7	2.2
Reducible	2831	1009	564		16.7	15.6	13.2
Organic	1442	49	4		8.5	0.8	0.1
Refractory	11822	5089	3605		69.7	78.9	84.5
Mn	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	405	66	9		44.0	8.4	18.8
Reducible	175	89	22		19.0	11.2	43.4
Organic	120	90	1		13.0	11.4	1.3
Refractory	221	545	18		24.0	69.0	36.5
Co	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	1.06	0.34	0.21		9.9	9.1	3.9
Reducible	0.89	0.35	1.03		8.3	9.2	18.8
Organic	3.58	1.74	0.16		33.6	46.2	2.9
Refractory	5.13	1.34	4.11		48.1	35.5	74.5
Ba	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	29.0	8.4	0.51		2.9	0.5	1.5
Reducible	42.5	36.1	5.53		4.2	2.1	15.8
Organic	9.7	32.6	3.19		1.0	1.9	9.1
Refractory	926	1651	25.72		91.9	95.5	73.6
Pb	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	10.37	0.43	0.03		4.8	4.1	0.7
Reducible	26.5	3.1	1.0		12.2	29.4	20.8
Organic	34.2	0.9	0.1		15.7	8.9	2.4
Refractory	146.6	6.1	3.6		67.4	57.7	76.2
Cr	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	2.38	10.37	0.05		6.5	26.6	1.0
Reducible	4.43	9.96	0.43		12.1	25.5	8.4
Organic	7.59	8.02	0.28		20.8	20.6	5.5
Refractory	22.15	10.66	4.42		60.6	27.3	85.1
Cd	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	0.043	0.013	0.008		4.4	10.1	18.1
Reducible	0.123	0.023	0.015		12.4	17.2	33.0
Organic	0.340	0.049	0.008		34.4	37.4	16.7
Refractory	0.484	0.046	0.015		48.9	35.3	32.2
Zn	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	19.32	1.48	7.25		5.6	5.3	22.4
Reducible	56.82	6.47	13.18		16.4	23.0	40.6
Organic	54.61	7.62	1.58		15.7	27.1	4.9
Refractory	216.69	12.59	10.41		62.4	44.7	32.1
Cu	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	0.21	0.13	0.12		0.5	1.2	1.1
Reducible	1.32	0.90	0.15		3.2	8.4	1.3
Organic	16.12	4.07	3.18		39.6	38.3	27.8
Refractory	23.1	5.5	8.0		56.7	52.1	69.8
Ag	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	0.0040	0.0032	0.0019		1.1	8.3	1.8
Reducible	0.0037	0.0044	0.0011		1.1	11.3	1.1
Organic	0.0192	0.0098	0.0906		5.5	25.3	87.1
Refractory	0.3220	0.0213	0.0104		92.3	55.1	10.0
Ni	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	8.32	3.60	3.93		28.2	30.0	40.9
Reducible	2.29	0.92	0.57		7.7	7.7	6.0
Organic	10.17	3.87	1.17		34.4	32.3	12.2
Refractory	8.77	3.60	3.93		29.7	30.0	40.9
V	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	0.15	0.11	0.14		0.9	1.4	2.9
Reducible	4.07	2.34	0.94		25.1	28.5	19.8
Organic	0.39	0.27	0.35		2.4	3.3	7.4
Refractory	11.61	5.50	3.31		71.6	66.8	70.0
As	**mg/kg**	**mg/kg**	**mg/kg**		**%**	**%**	**%**
Leachable	0.143	0.170	0.062		1.2	3.9	5.5
Reducible	0.525	0.522	0.148		4.5	12.0	13.0
Organic	0.574	0.178	0.054		4.9	4.1	4.7
Refractory	10.419	3.465	0.876		89.4	79.9	76.8

16.2 Geochemical characteristics of the measured elements

The elements determined represents elements of environmental concern and elements associated with the release processes in the sediment. The main processes of each element are summarised briefly in the following: The main source for most metals in the cuttings is most likely barite. However this does not automatically mean dissolution of barite is necessary to release metals associated with the barite.

Sr	Dissolution of carbonate
Mn, Co, Fe	Redox processes where Mn is the easiest metal to reduce
Cr	Can occur in several different oxidation states. The normal oxidation state of Cr in seawater is +VI which occur as $CrO_4^{2-.}$ During anoxic conditions Cr might occur in oxidation state +III.
As	Often found at relatively high concentrations in biota. The dominant oxidation state of As in seawater is +V which occur as $HAsO_2^{2-}$
Ba	Added as $BaSO_4$ in the drilling mud and have low solubility. Ba is always found at elevated concentrations in cuttings deposits compared to expected concentrations in sediments. The sequential extraction will indicate the kinetics for the dissolution of the $BaSO_4$
Pb	Known contaminant in $BaSO_4$ in mud used in the start of offshore activity in the North Sea. Possibly very strongly bound in the $BaSO_4$ matrix
Cd	Could be built in to the carbonate species
Ag	Low solubility of AgCl. Diagenetically generated Ag will precipitate at low concentrations
Cd, Zn, Cu	Elements with a high uptake rate in biota. Both Cd and Zn form strong soluble Cl-complexes in seawater. If sulphide is present these elements will precipitate as sulphides at low concentrations.

16.3 Results by element group

Sr The two dominating fractions are *Leachable* and the *Refractory*. It could be noted that the *Refractory* part in the sand samples (background without cuttings) is very low. The Sr in the *Leachable* fraction is believed to originate from the dissolution of biota built of carbonates. It is obvious that the cuttings contain Sr with strong bindings to the matrix.

Ba The analysis of major components in the cutting piles showed (see mineralogy section) that barite is one of the main components in the cuttings. The amount

Ba extracted in this fractionation study (called refractory fraction) is still only a small fraction of the total Ba in the cuttings. Even though the barite is the most likely source for the metal contamination in the cuttings pile it is not possible to se any direct relation onf extractable metals and extractable Ba. The barite is crystalline and has a low solubility. Of the measured elements here only Sr can be found in the barite crystals (Deer et al. 1969) while if Pb is found separate particles of $PbSO_4$. The XRF measurement (Part 1 mineralogy) of the minor components confirmed that the Sr strongly bound in the cuttings while the NS4770 digestion released most of the Pb. With this large differences between how the metals is bound in the barite it is reasonable to understand that no direct correlation between the extractable fractions of Ba and other metals can be seen.

Mn Co Fe The dominating fraction in which these three elements with well-known redox properties are found differs. The largest fraction where they are found is the *Leachable* fraction. MnO_2 in the sediment reduces to soluble species of Mn during sulphide conditions (e.g. reducing conditions). No reducing reagents were added in this extraction step. Consequently, the cuttings have a sufficient low redox potential for reduction of manganese, however not sufficiently to deduce all available reducible Mn. In contrast to this, in the samples from the sandy layers, only a minor part of the Mn is found in the *Leachable* fraction. The dominating fraction of Co is within the *Organic bound and sulphides*. The dominating form of Fe is in the *Refractory* fraction, indicating that most of the Fe is mineral bound. There are no clear trends or differences in the different cuttings material either geographically or in the different layers.

Zn Cd Cu Zn and Cd have a similar partitioning with the dominating fraction being the *Refractory*. However for Cd more than 50% is found in the other fractions. This figure is slightly lower for Zn. However it should be noted that the samples with the highest concentrations have a higher part of the metals mineral bound (*Refractory*). For Cu the dominating fraction is also the *Refractory*. For the samples with the lowest concentrations there is larger part found in the *Reducible* fraction. For all these elements there is also a fairly large fraction within the *Organic and sulphides*.

Ni Ni shows a very similar pattern in the sand and the cuttings with low contamination. In the cuttings with higher concentrations the *Organic and sulphide* fraction becomes larger. It can though be noted that a large part of the Ni is easy to mobilise.

Pb Ag For Pb there are large variations. In the samples with the lowest total concentration a large part is found in the *Leachable* fraction. The same is found for the sand (background) at two locations. For the more contaminated cuttings the variation is large, however some of the samples with highest concentration of Pb at Ekofisk show also a large *Leachable* fraction. There is no very clear pattern for where the highest concentrations within the *Organic and Sulphide* fraction are found. For Ag, the samples with low concentration have the dominating portion in the *Refractory* fraction, while in the samples with lower concentrations, the Ag can be found in other fractions. This reflects the solubility of AgCl.

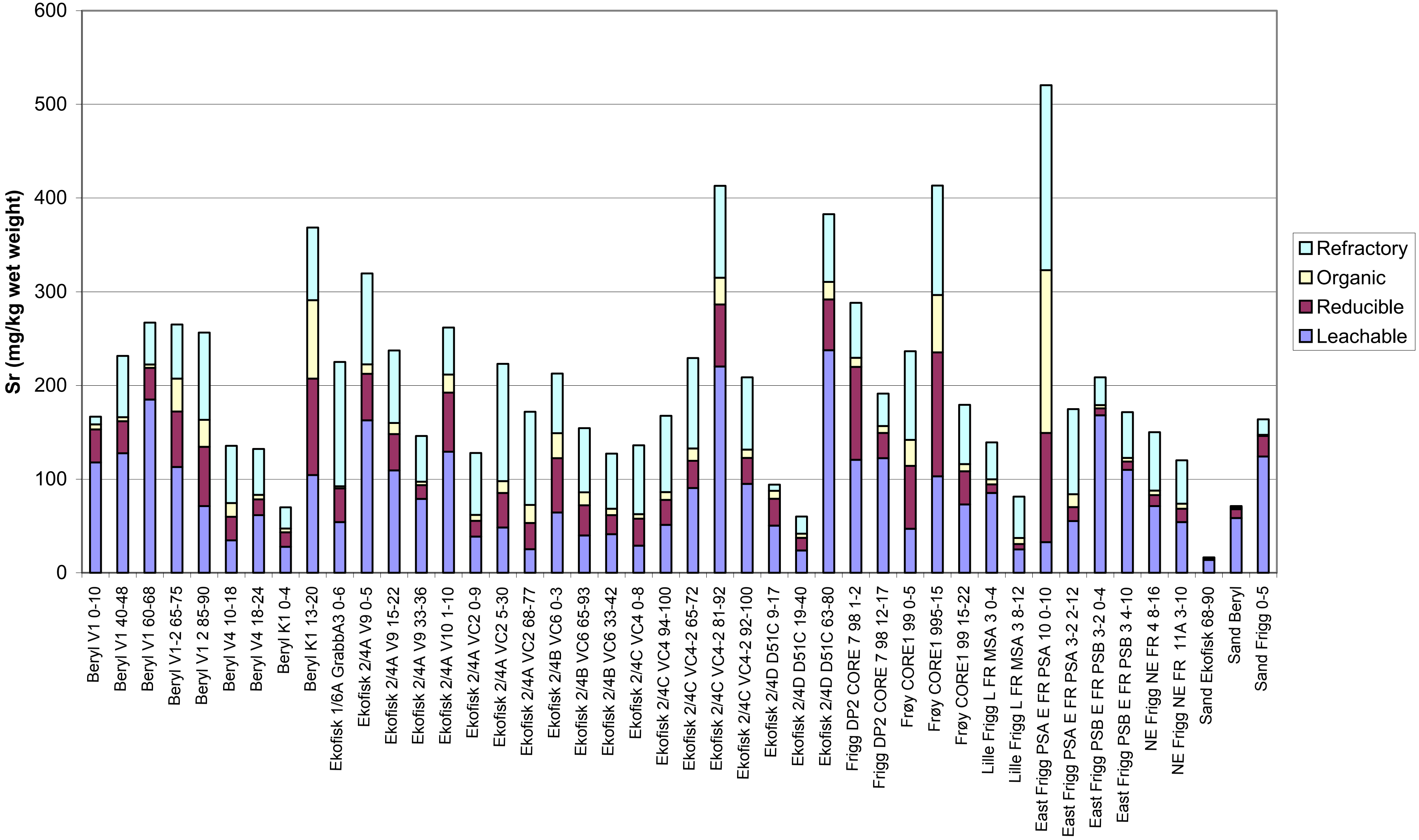
Cr As For Cr the samples with the highest concentrations also have large parts in the *Leachable* and *Reducible* fractions. For As, the samples with low total concentrations contain signifficant parts within the other fractions. The samples from Ekofisk 2/4 A that had high concentrations of Cd also contain farly large fractins of mainly *Organic* and *Reducible* bound As.

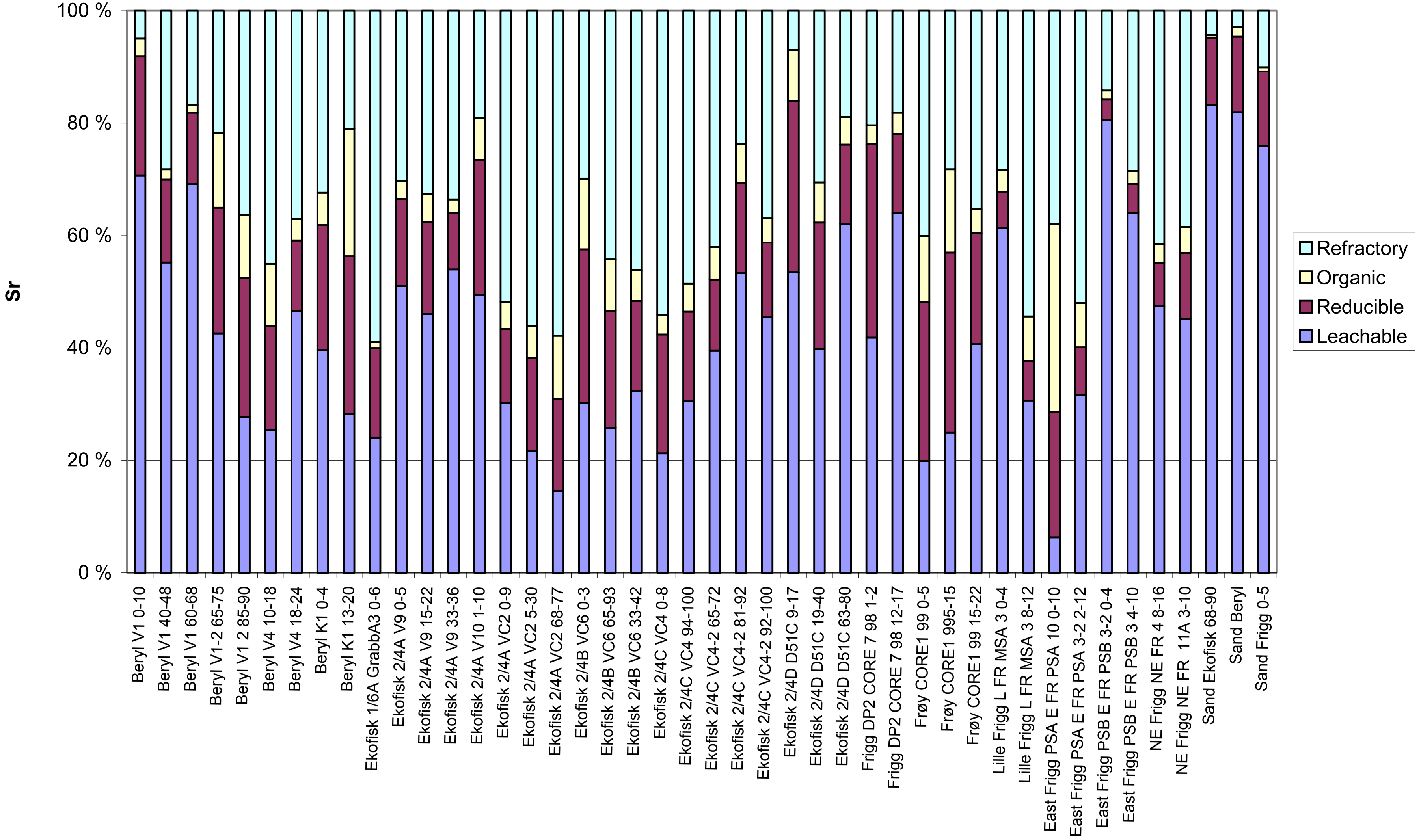
V For V the largest fraction is the *Refractory*. However for most samples there is also large fraction of *Reducible*. The size of this fraction seems to be relatively larger in the samples with low contamination.

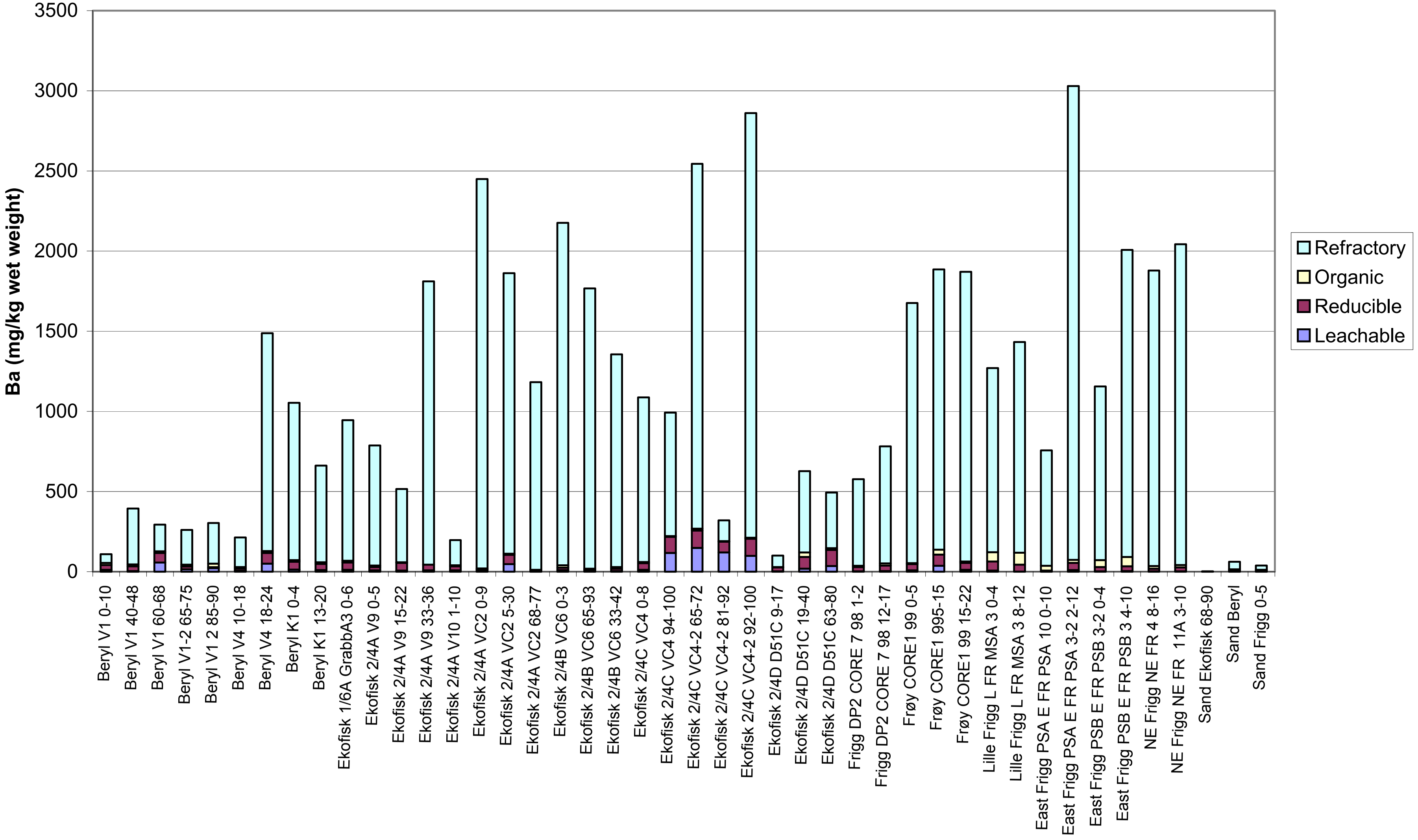
16.4 Main figures

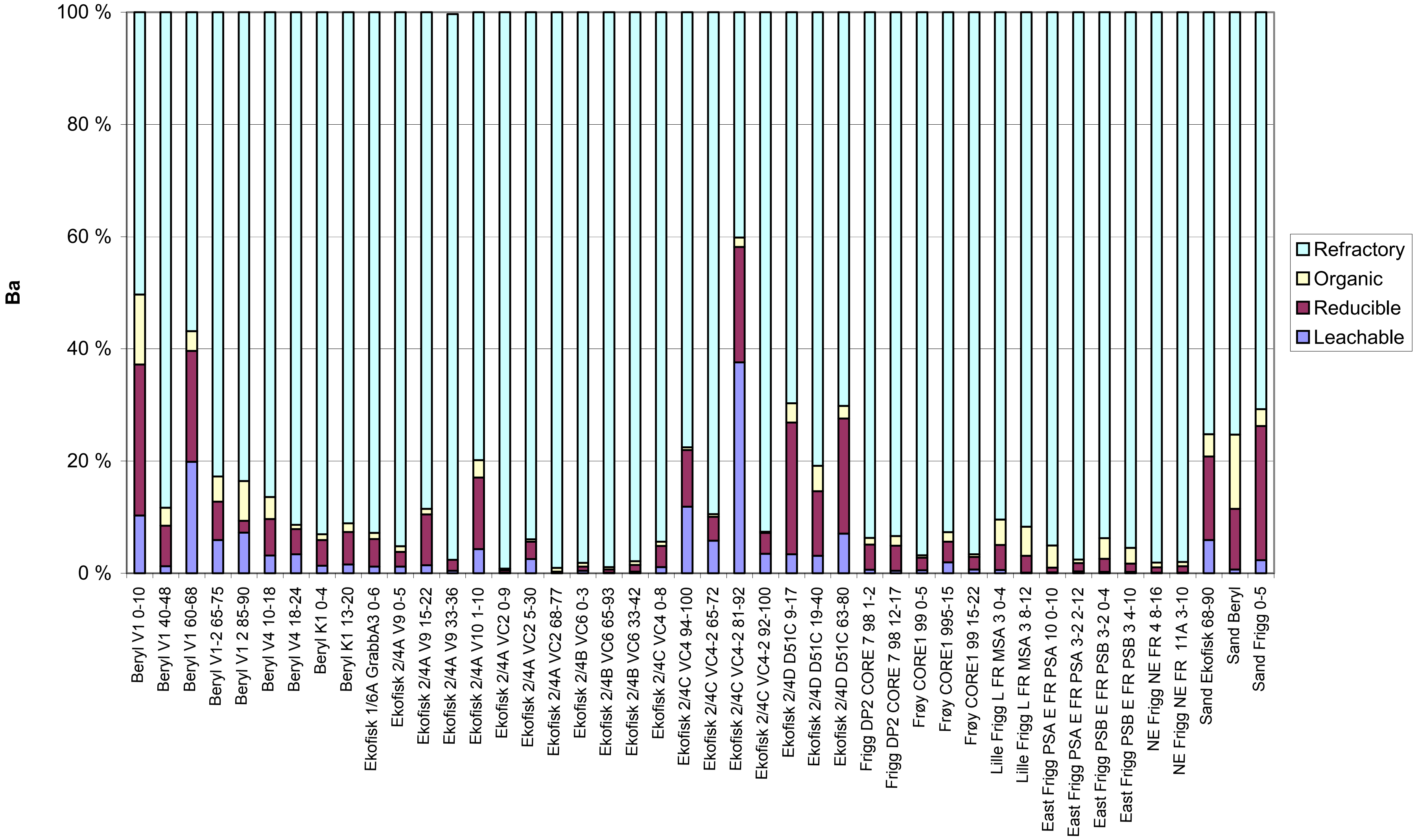
In the following, two data sets are presented. The first set presents the results in concentration scale (mg/kg wet weight), the second presents the results on % scale. All data are illustrated as a series of graphs. The legend refers to the fractions as defined in the method section (the details can be found in the method section). The sample labelling on the axes starts with the installation name and core number and finally the depth of the slice in the core. More information about the origin of the samples can be found in table 17 and Part 1.

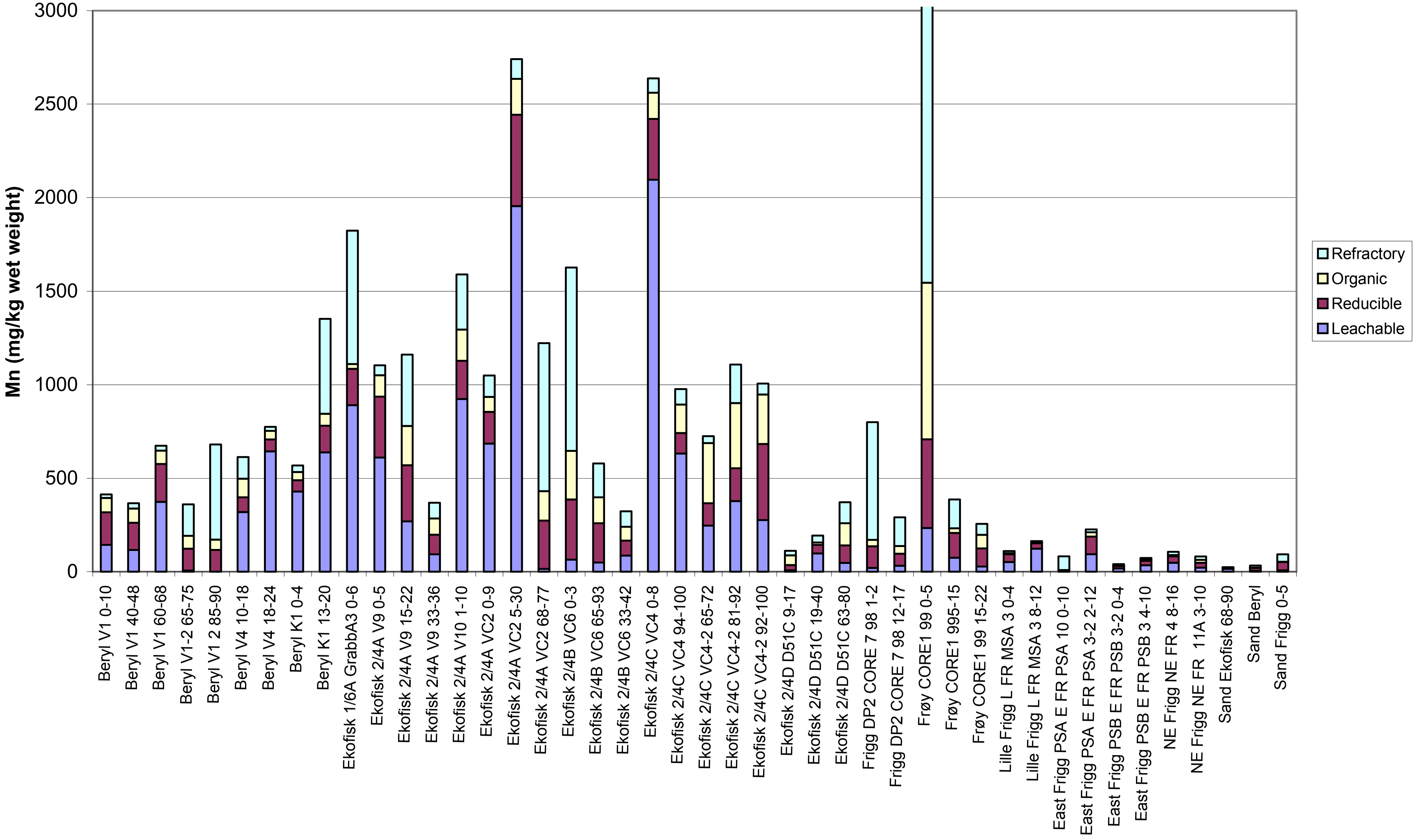
Figure 60:(Next pages) Figures with all the results for Ag, As, Ba, Cd, Cu, Co, Fe, Mn, Ni, Sr, V and Zn from the different fractions presented in mg/kg wet weight and in % of the total concentration as defined NS4770 dissolvable metals.

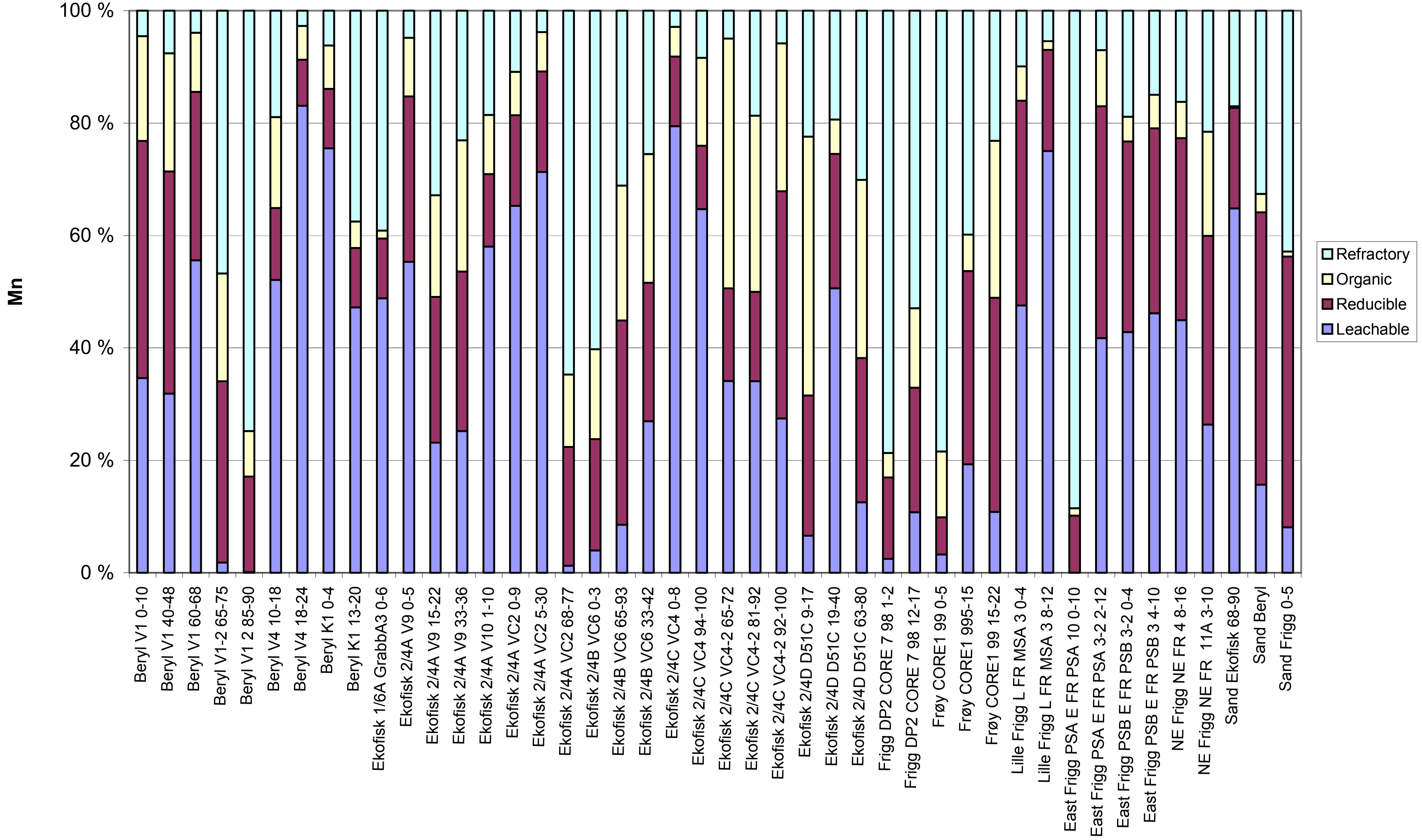

Sr (mg/kg wet weight)
0
100
200
300
400
500
600
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5

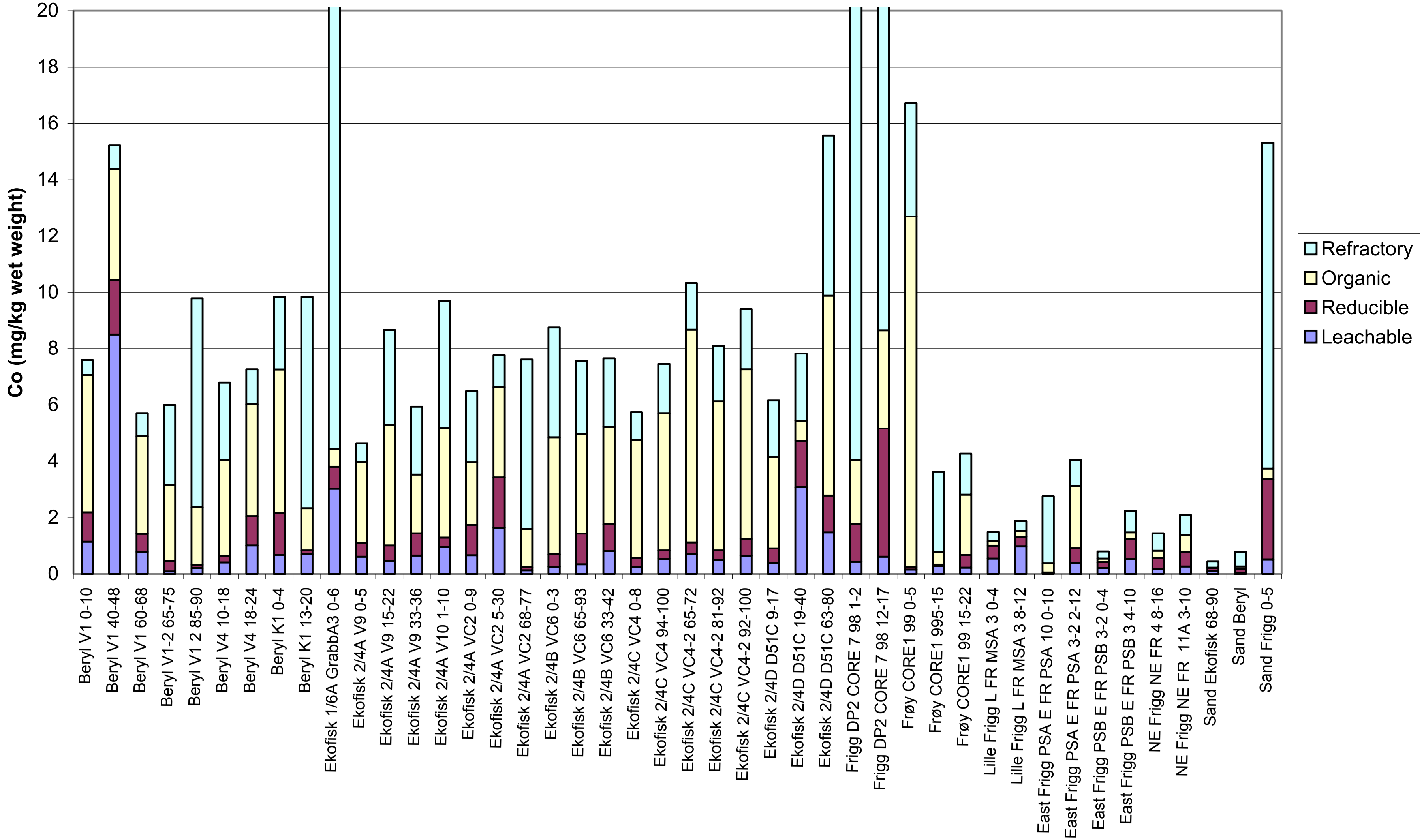

Sr
100 %
80 %
60 %
40 %
20 %
0 %
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
☐ Refractory
☐ Organic
■ Reducible
■ Leachable

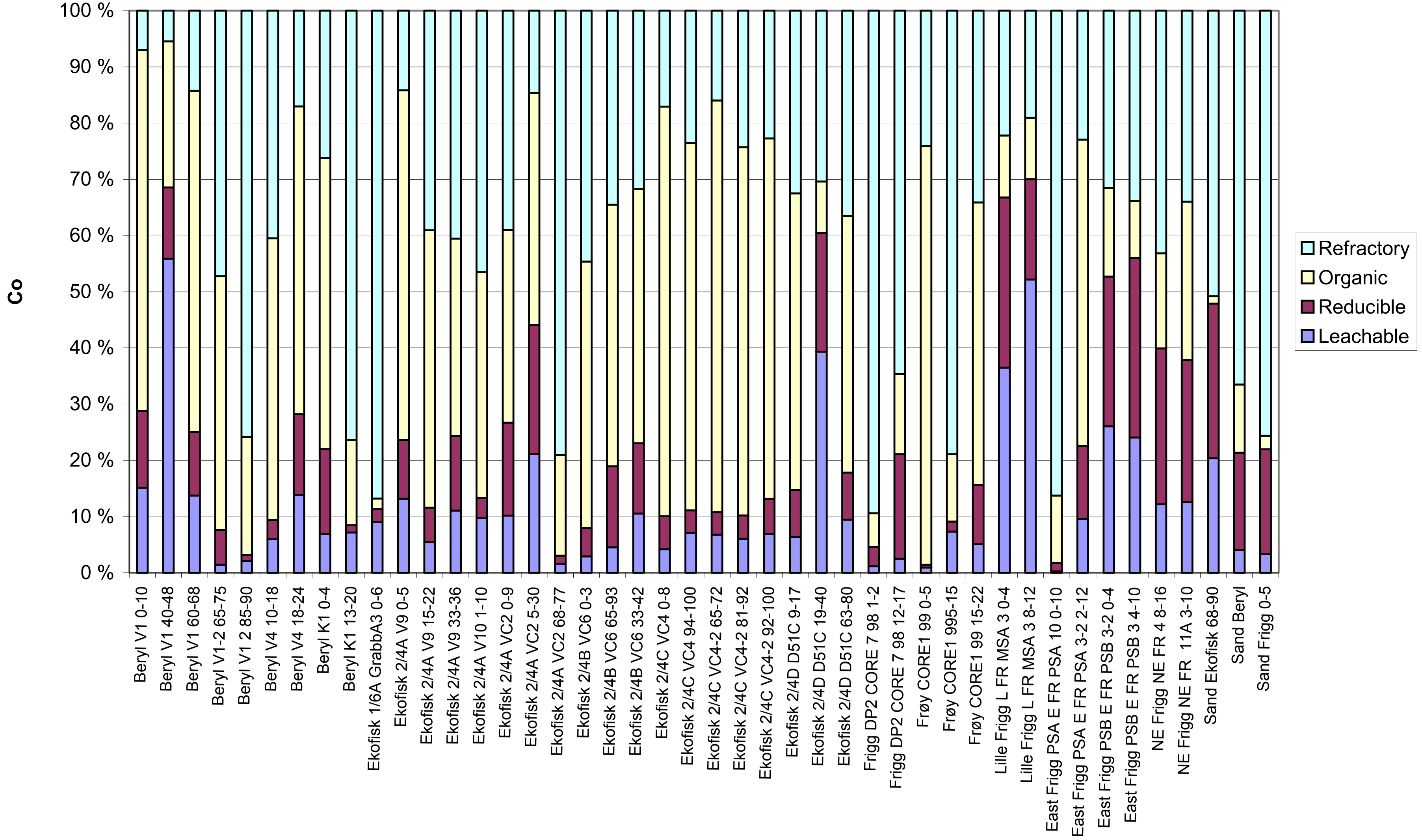

Ba (mg/kg wet weight)
3500
3000
2500
2000
1500
1000
500
0
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
☐ Refractory
☐ Organic
■ Reducible
■ Leachable

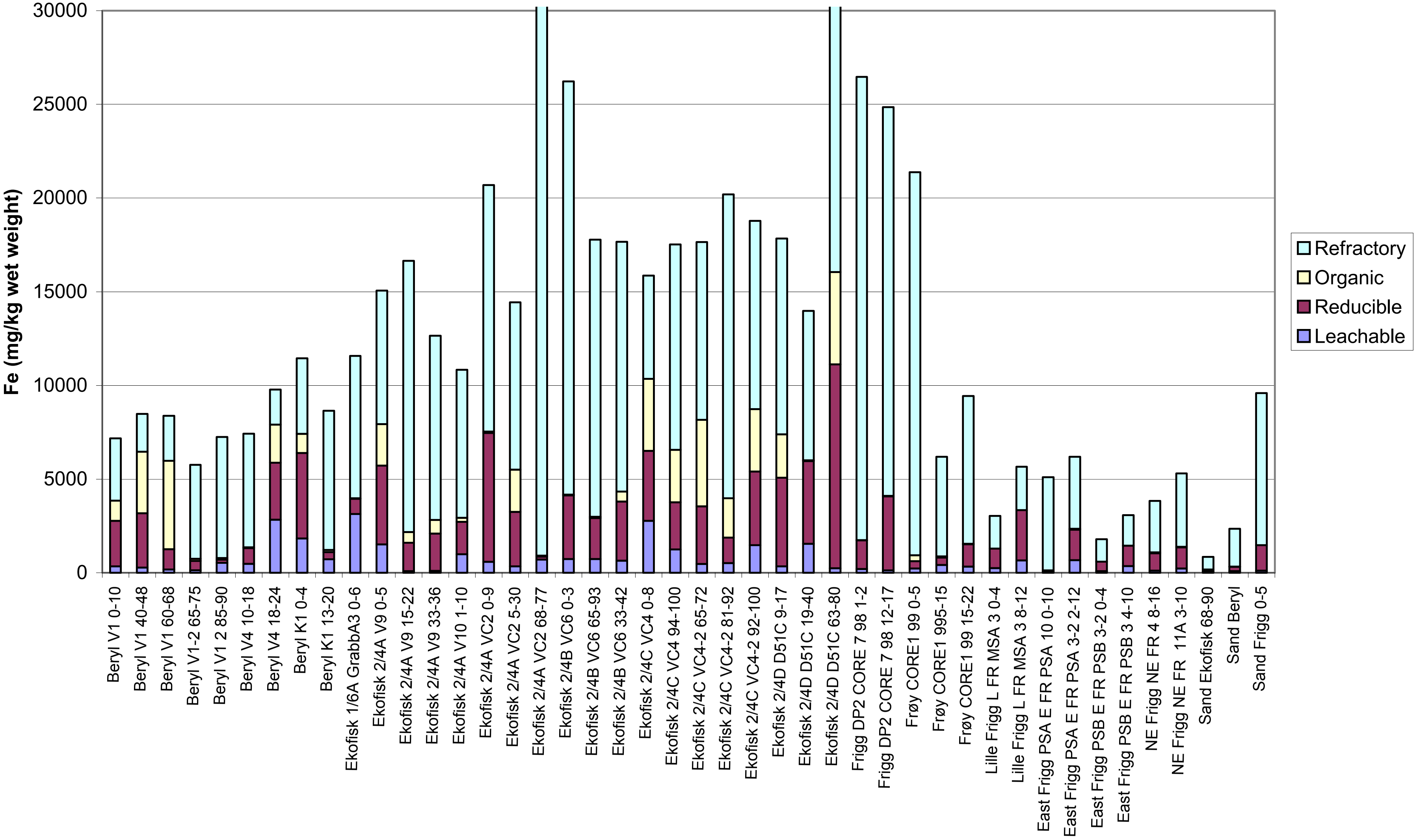

Ba
100 %
80 %
60 %
40 %
20 %
0 %
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5

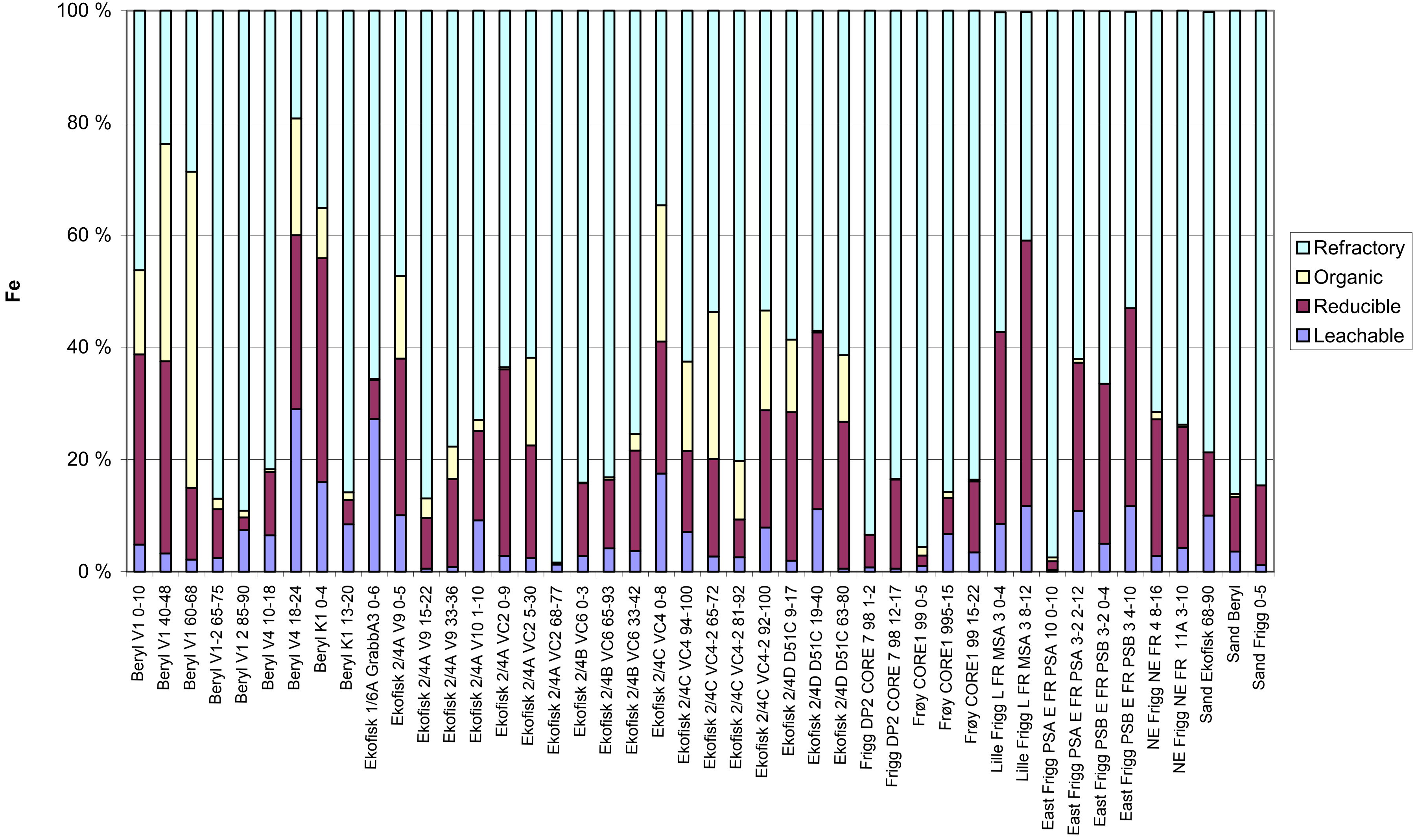

Mn (mg/kg wet weight)
3000
2500
2000
1500
1000
500
0
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


Mn
100 %
80 %
60 %
40 %
20 %
0 %
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
Refractory
Organic
Reducible
Leachable


Co (mg/kg wet weight)
0
2
4
6
8
10
12
14
16
18
20
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


Co
100 %
90 %
80 %
70 %
60 %
50 %
40 %
30 %
20 %
10 %
0 %
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
Refractory
Organic
Reducible
Leachable


Fe (mg/kg wet weight)
30000
25000
20000
15000
10000
5000
0
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
Refractory
Organic
Reducible
Leachable


Fe
100 %
80 %
60 %
40 %
20 %
0 %
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
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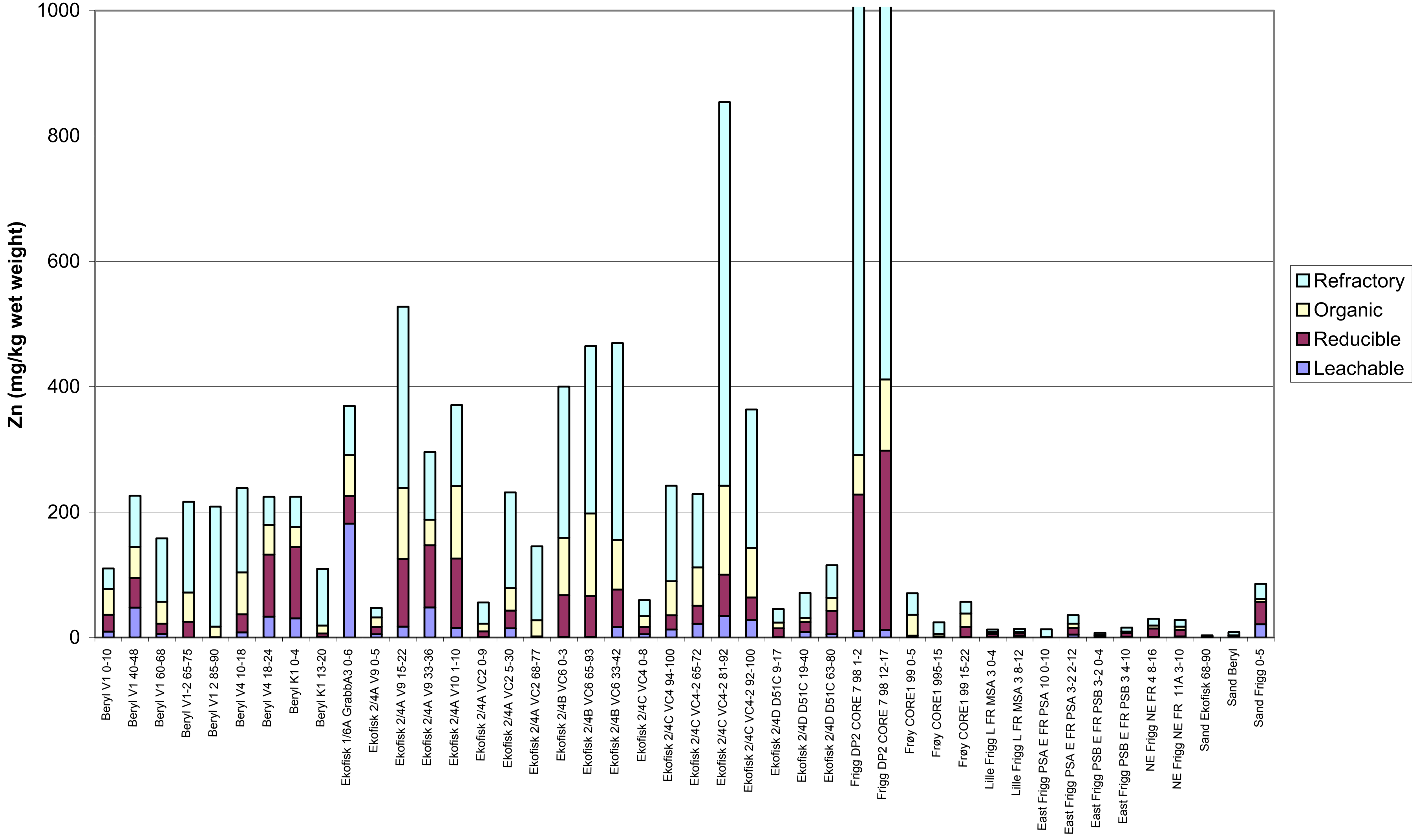
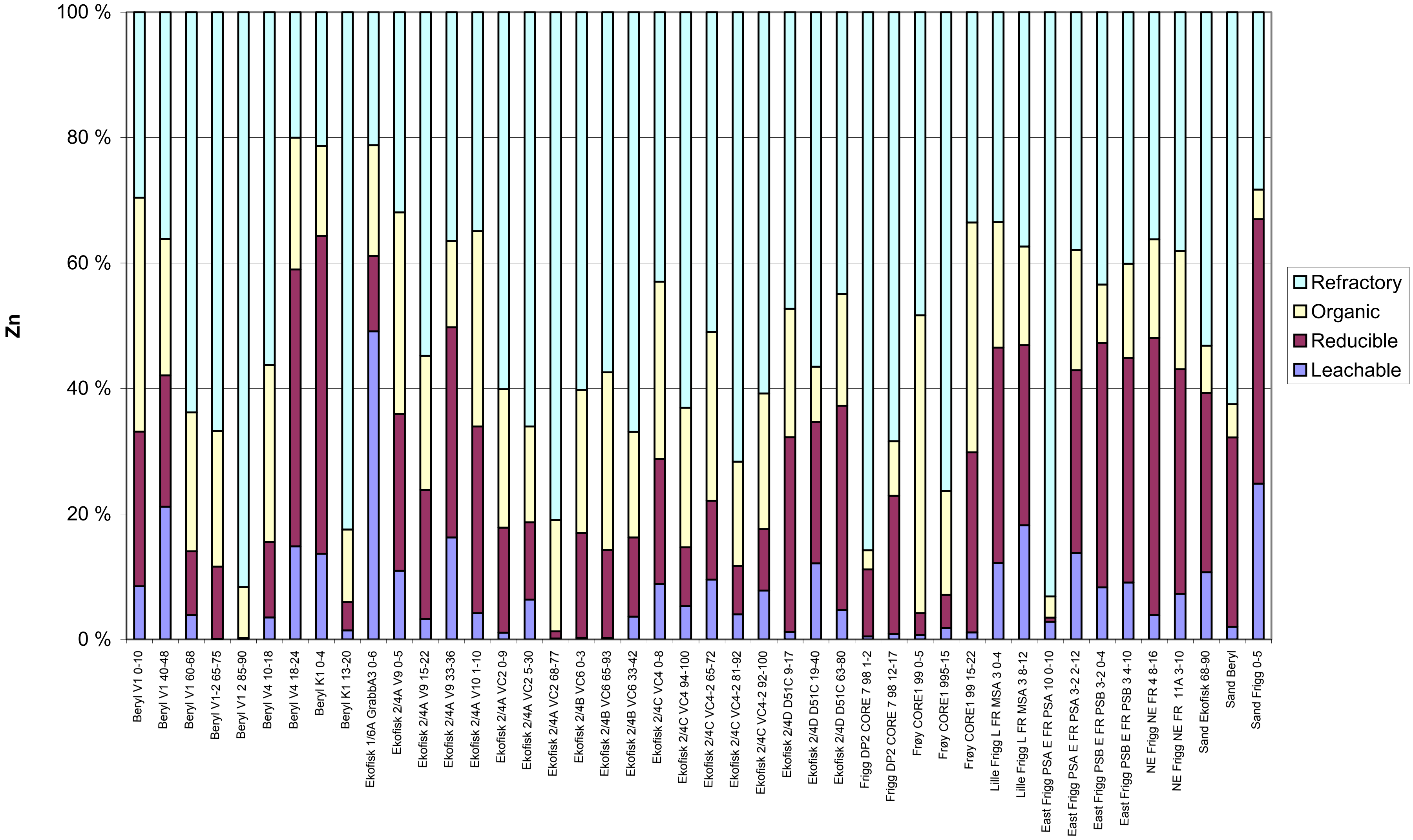
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


Zn (mg/kg wet weight)
0
200
400
600
800
1000
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5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Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
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Ekofisk 2/4A V9 0-5
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Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
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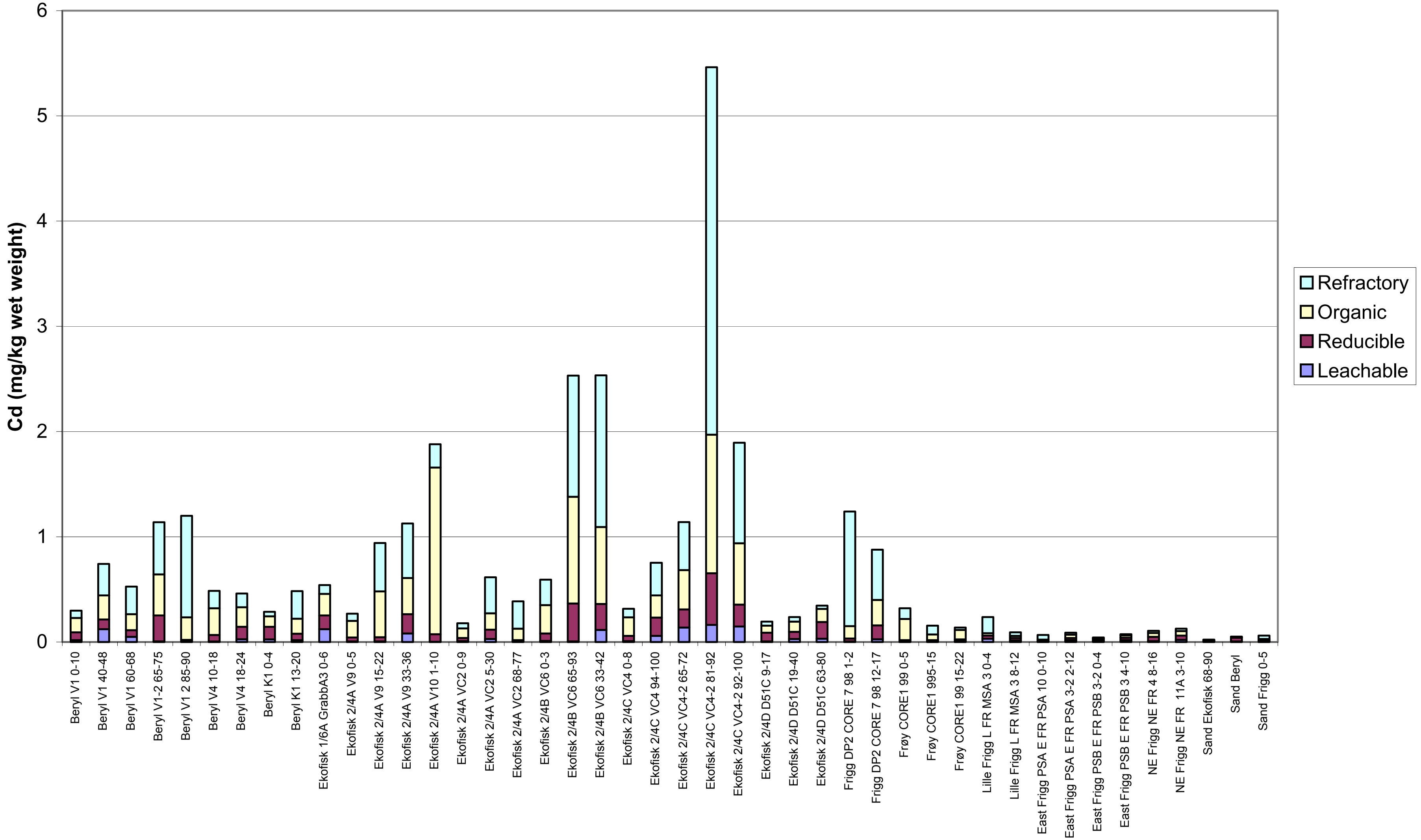
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
Refractory
Organic
Reducible
Leachable


Cd (mg/kg wet weight)
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3
4
5
6
Refractory
Organic
Reducible
Leachable
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Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
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Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
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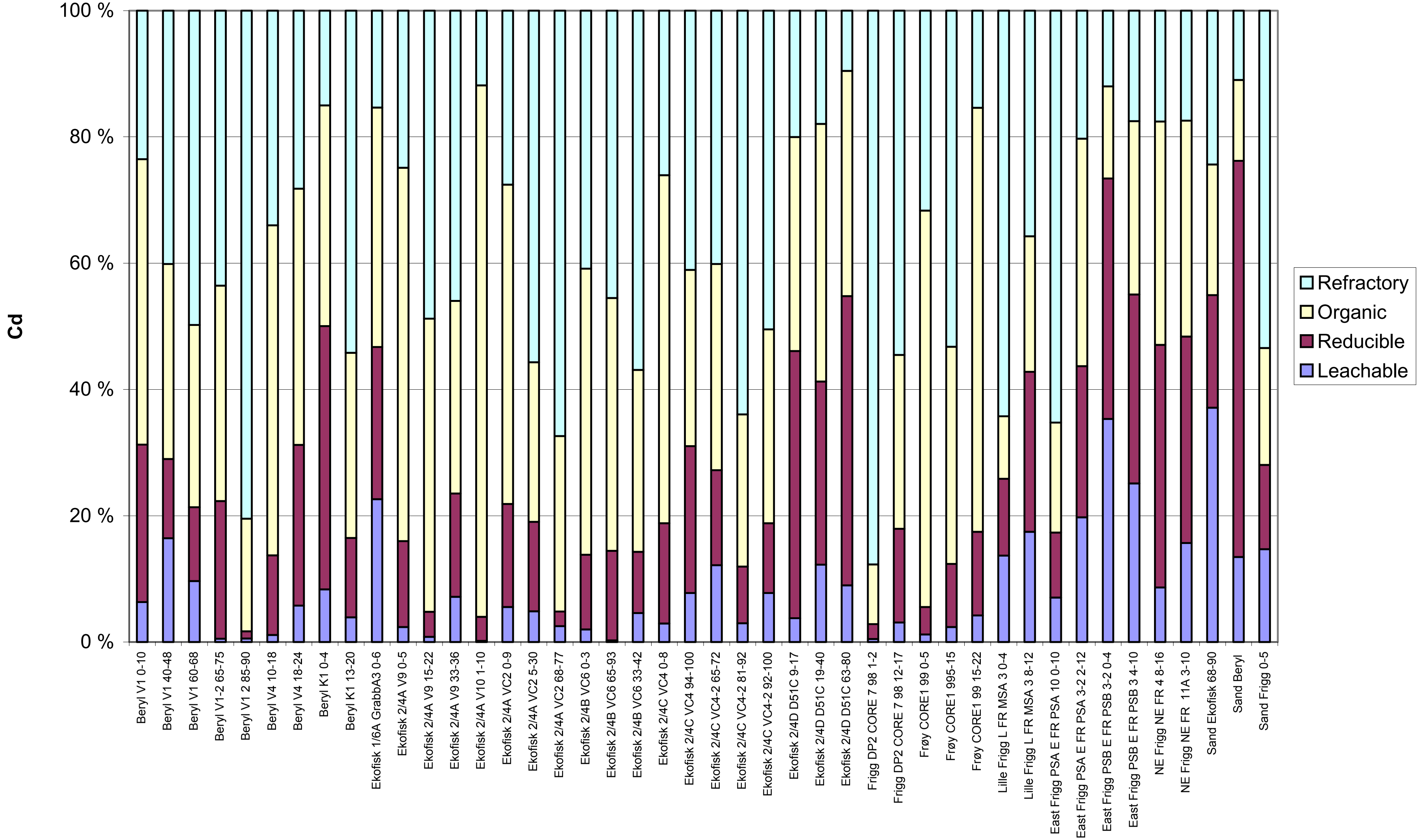
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5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60 %
40 %
20 %
0 %
Refractory
Organic
Reducible
Leachable
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Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
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Ekofisk 2/4D D51C 9-17
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Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
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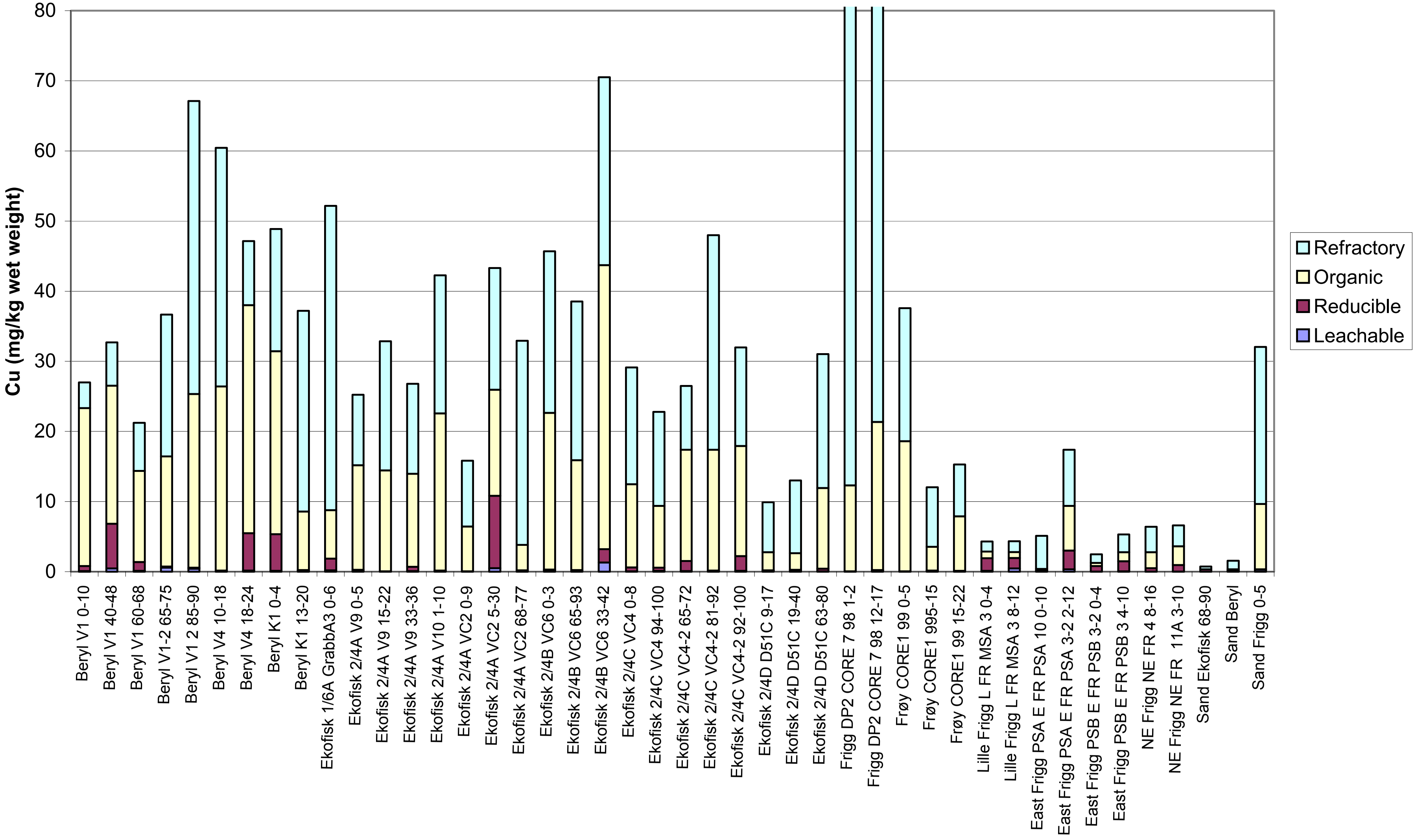
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


Cu (mg/kg wet weight)
0
10
20
30
40
50
60
70
80
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
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Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
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Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
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East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
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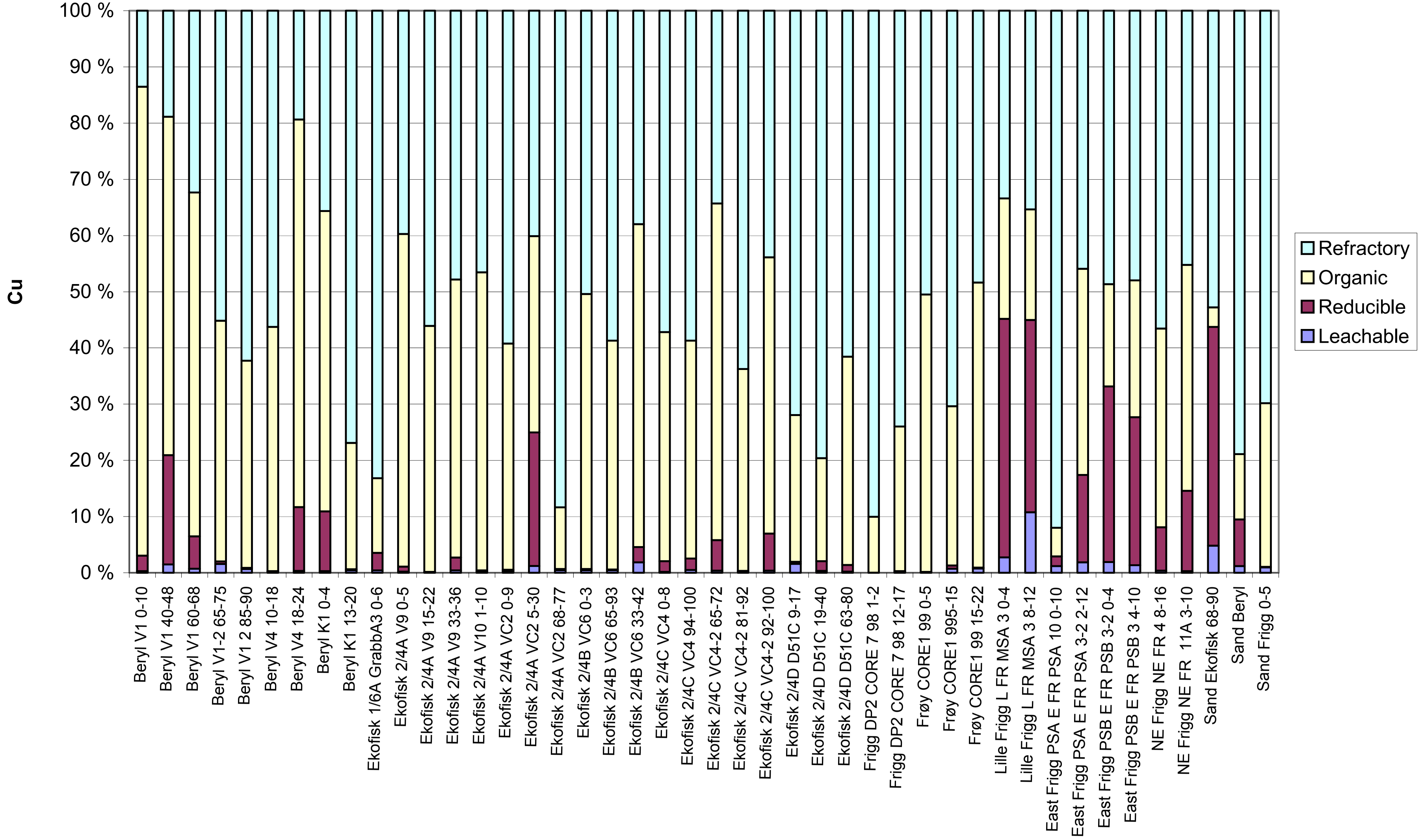
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5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10 %
0 %
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Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
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Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
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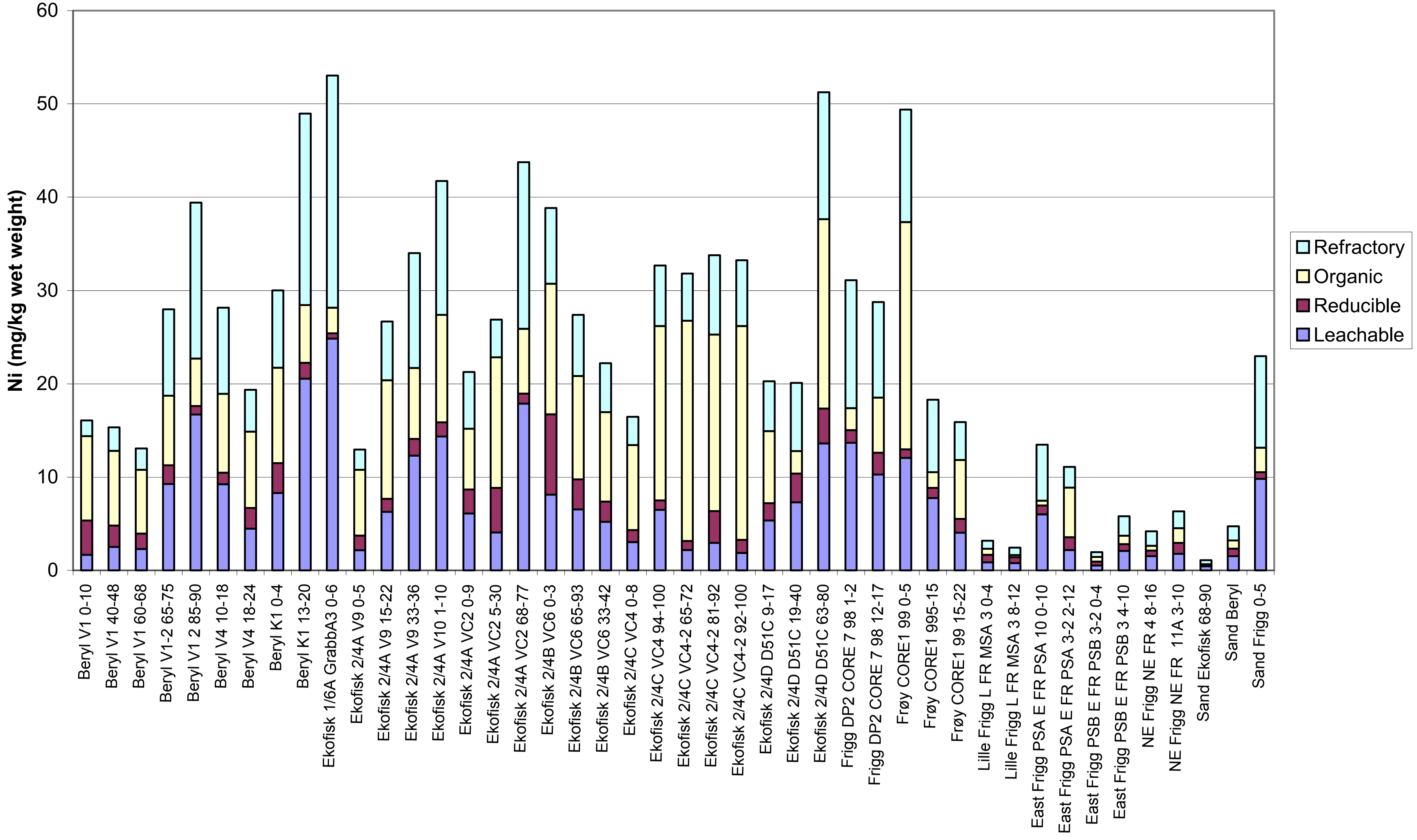
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
Refractory
Organic
Reducible
Leachable


Ni (mg/kg wet weight)
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10
20
30
40
50
60
Refractory
Organic
Reducible
Leachable
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Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
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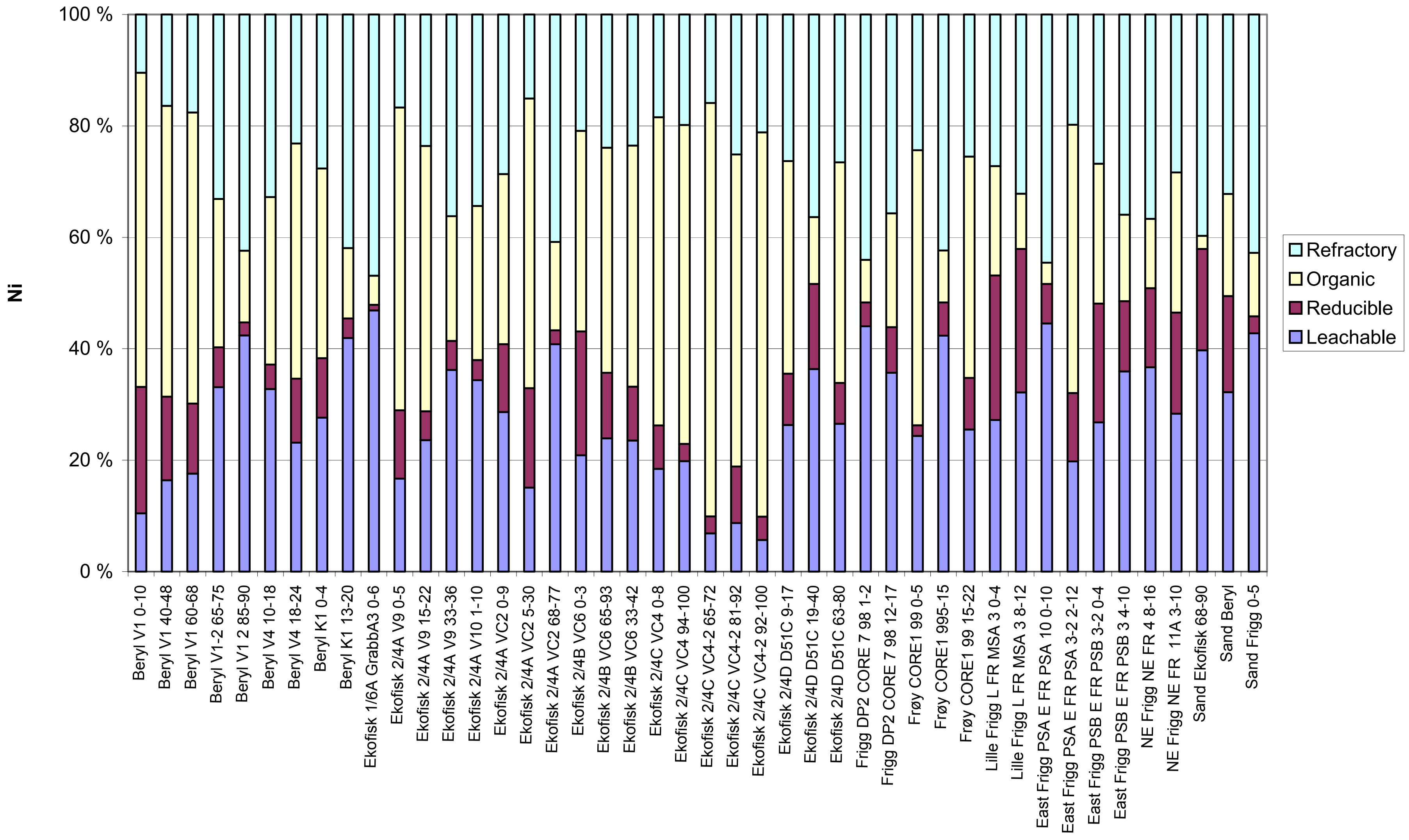
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5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60 %
40 %
20 %
0 %
Refractory
Organic
Reducible
Leachable
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Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
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Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
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Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
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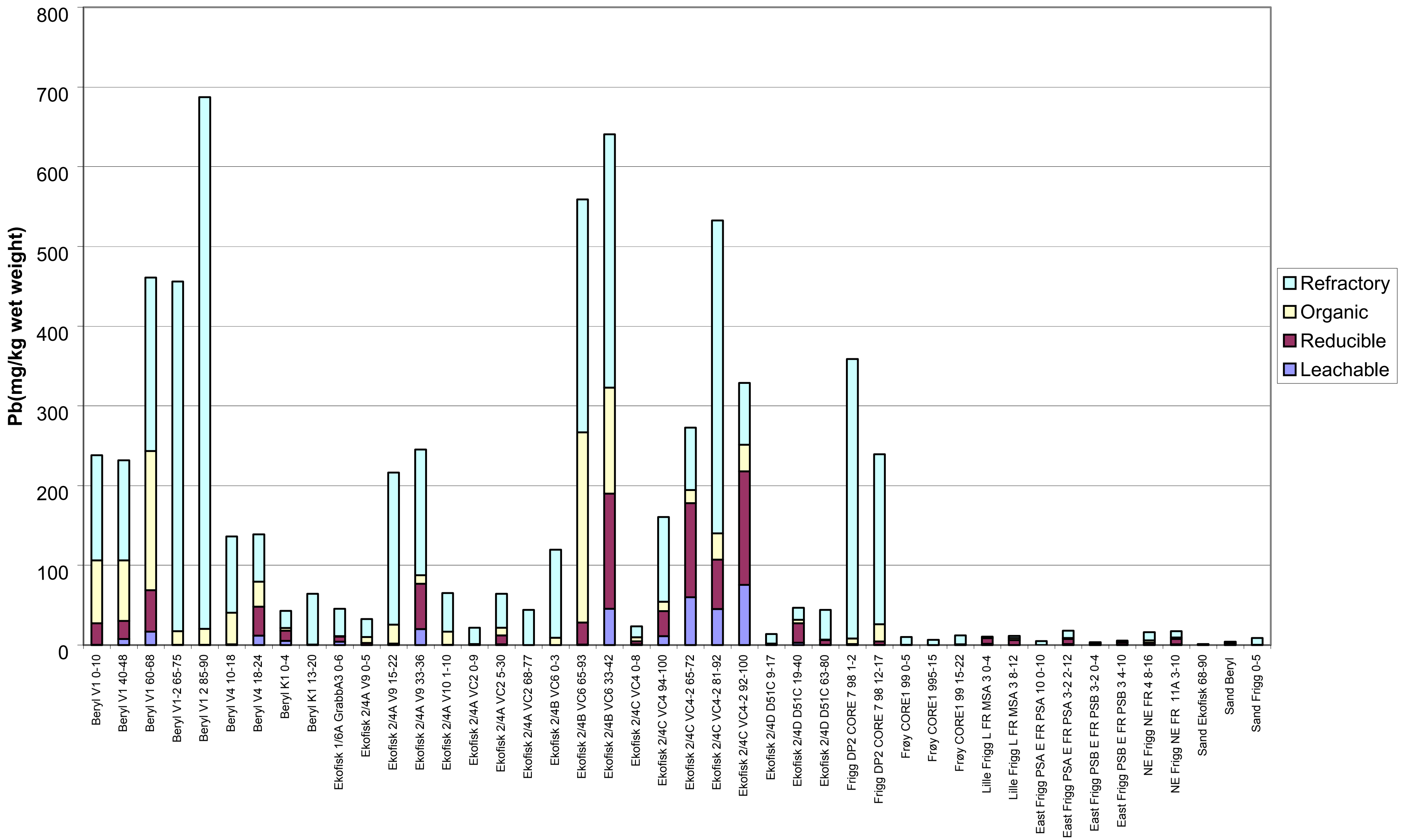
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


Pb(mg/kg wet weight)
800
700
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300
200
100
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Refractory
Organic
Reducible
Leachable
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Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
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Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
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NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
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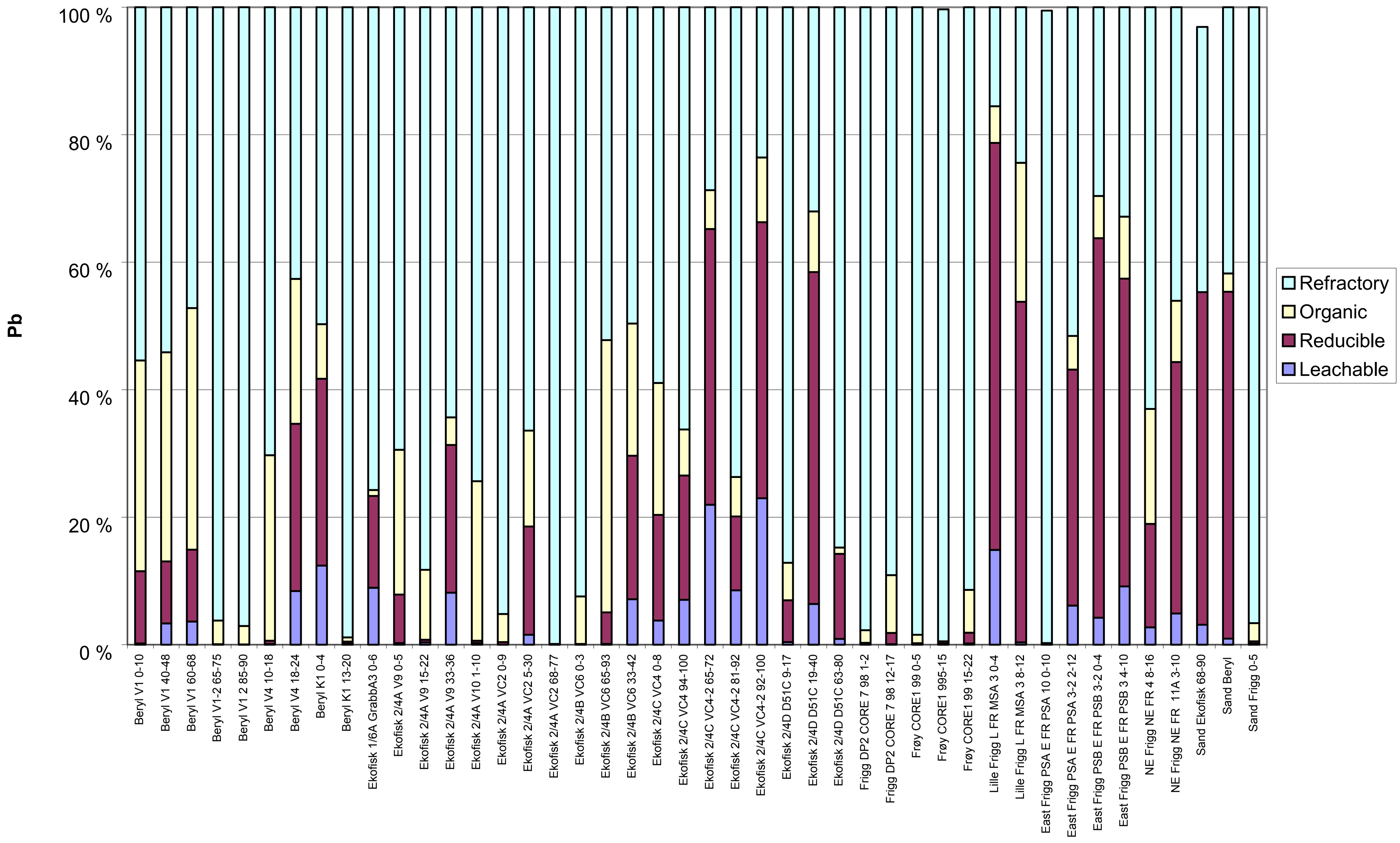
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Refractory
Organic
Reducible
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Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
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Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
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Ekofisk 2/4D D51C 63-80
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Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
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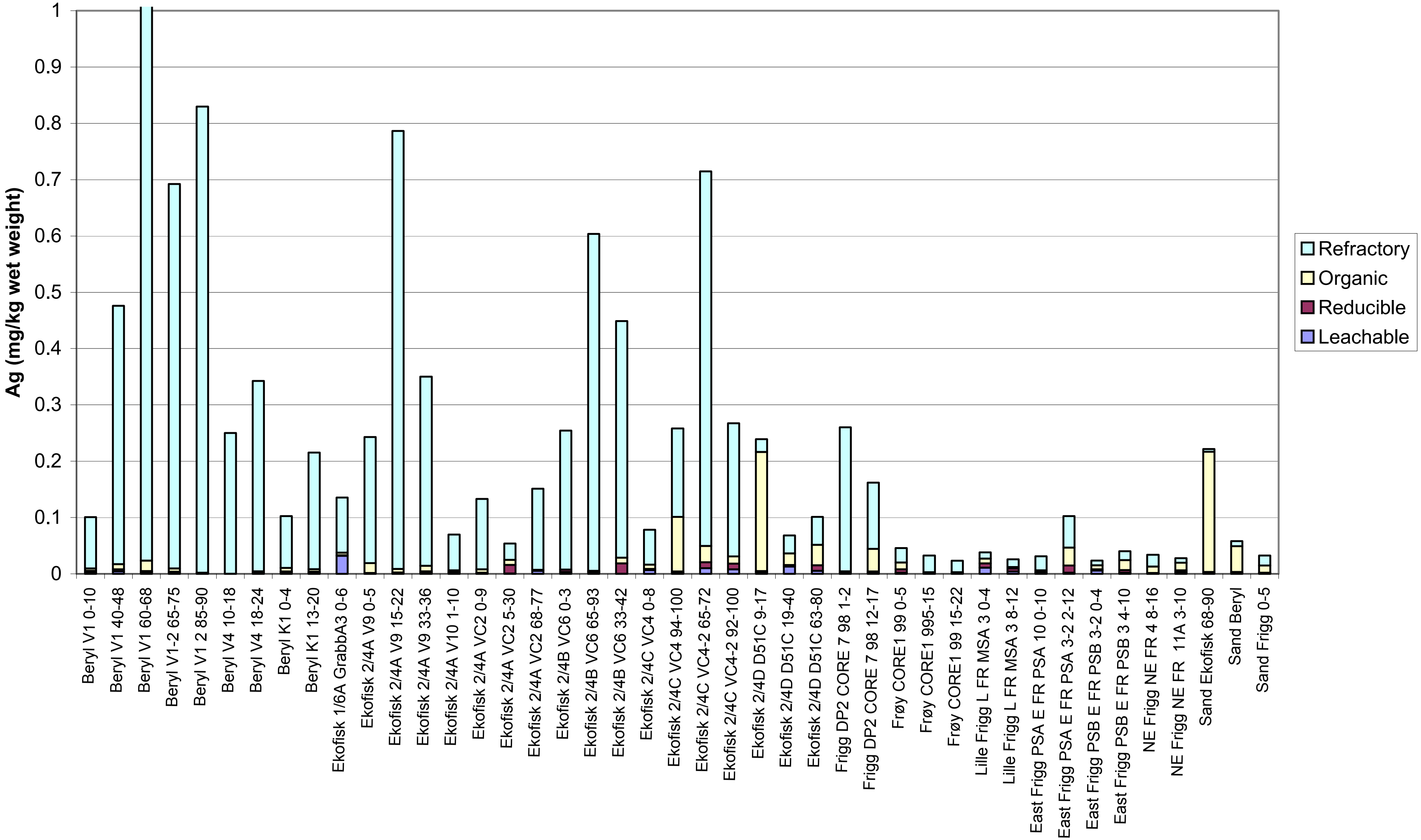
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


Ag (mg/kg wet weight)
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0.7
0.6
0.5
0.4
0.3
0.2
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0
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
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Ekofisk 2/4D D51C 9-17
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Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
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Frøy CORE1 99 15-22
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Lille Frigg L FR MSA 3 8-12
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NE Frigg NE FR 11A 3-10
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Sand Beryl
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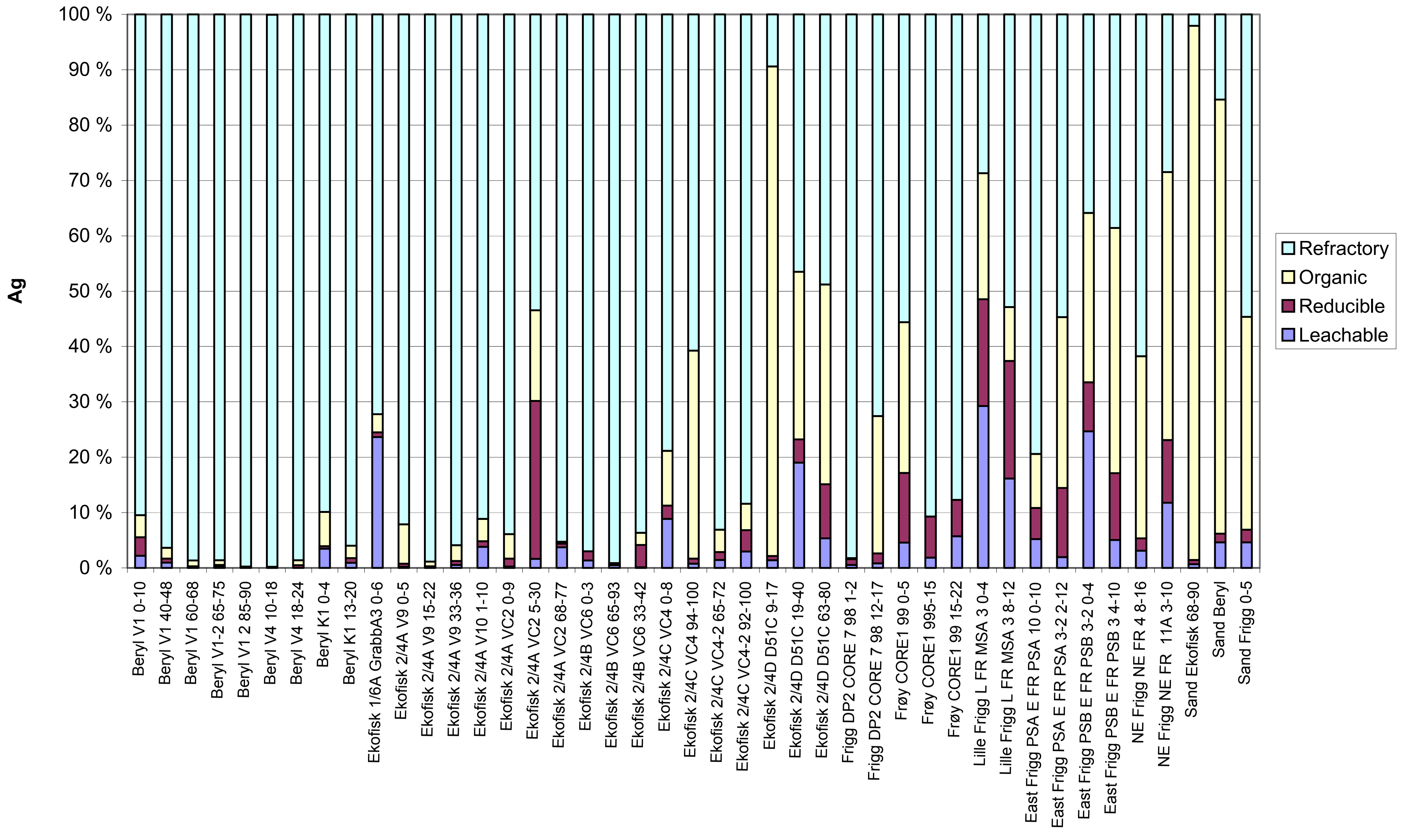
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Reducible
Leachable
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Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
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Beryl V4 18-24
Beryl K1 0-4
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Ekofisk 2/4A V9 15-22
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Ekofisk 2/4A VC2 5-30
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Ekofisk 2/4C VC4 94-100
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Ekofisk 2/4C VC4-2 92-100
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Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
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Frøy CORE1 995-15
Frøy CORE1 99 15-22
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Lille Frigg L FR MSA 3 8-12
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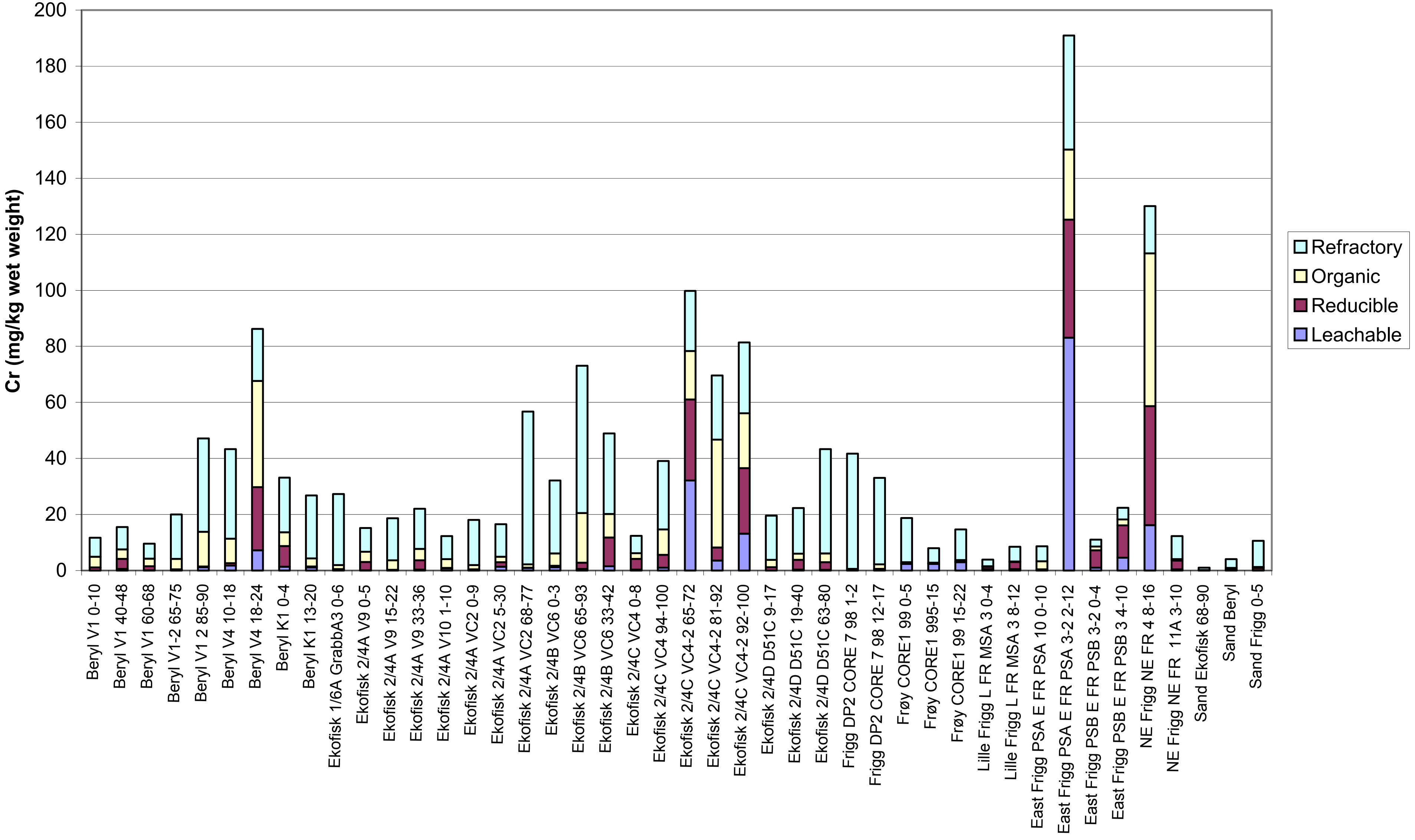
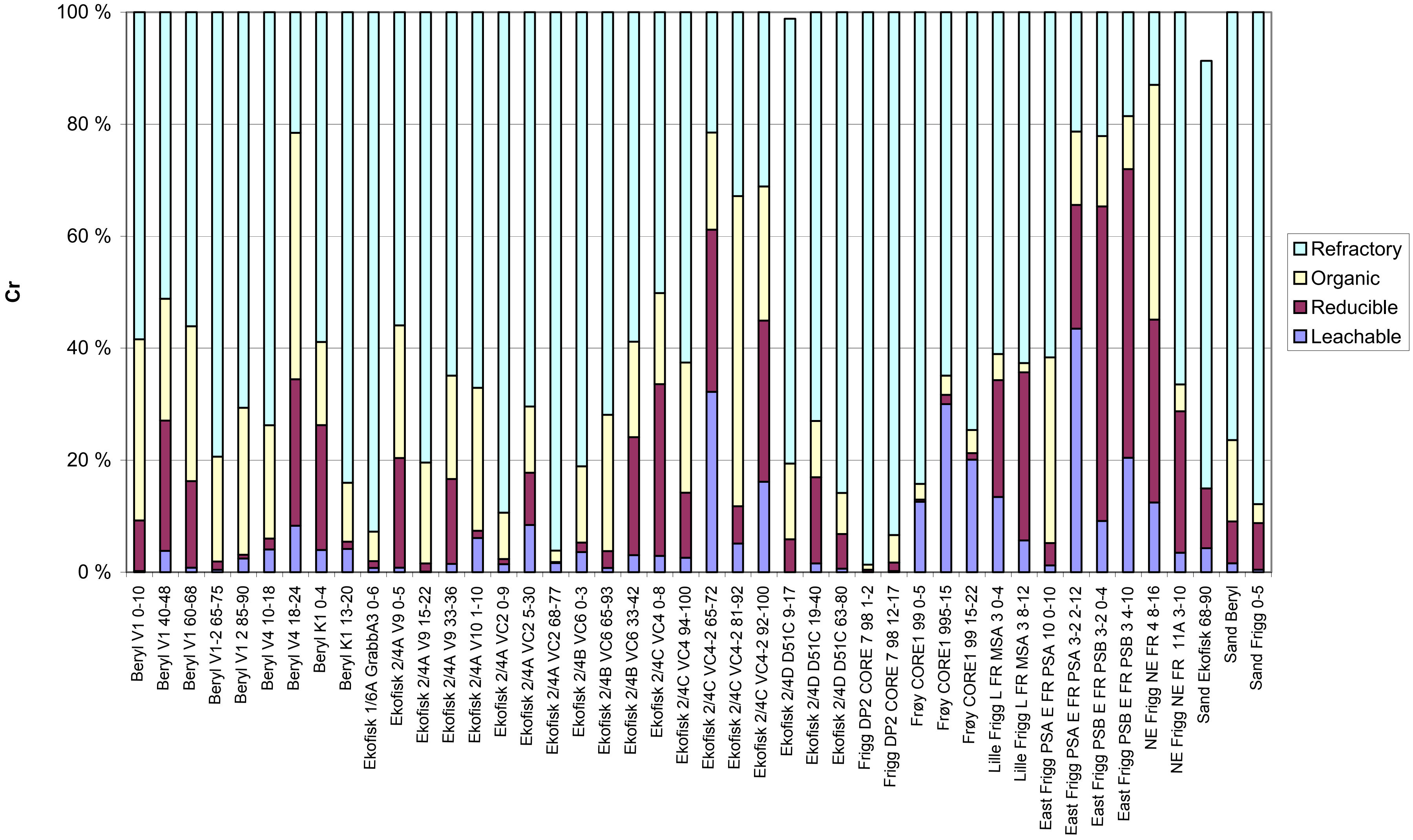
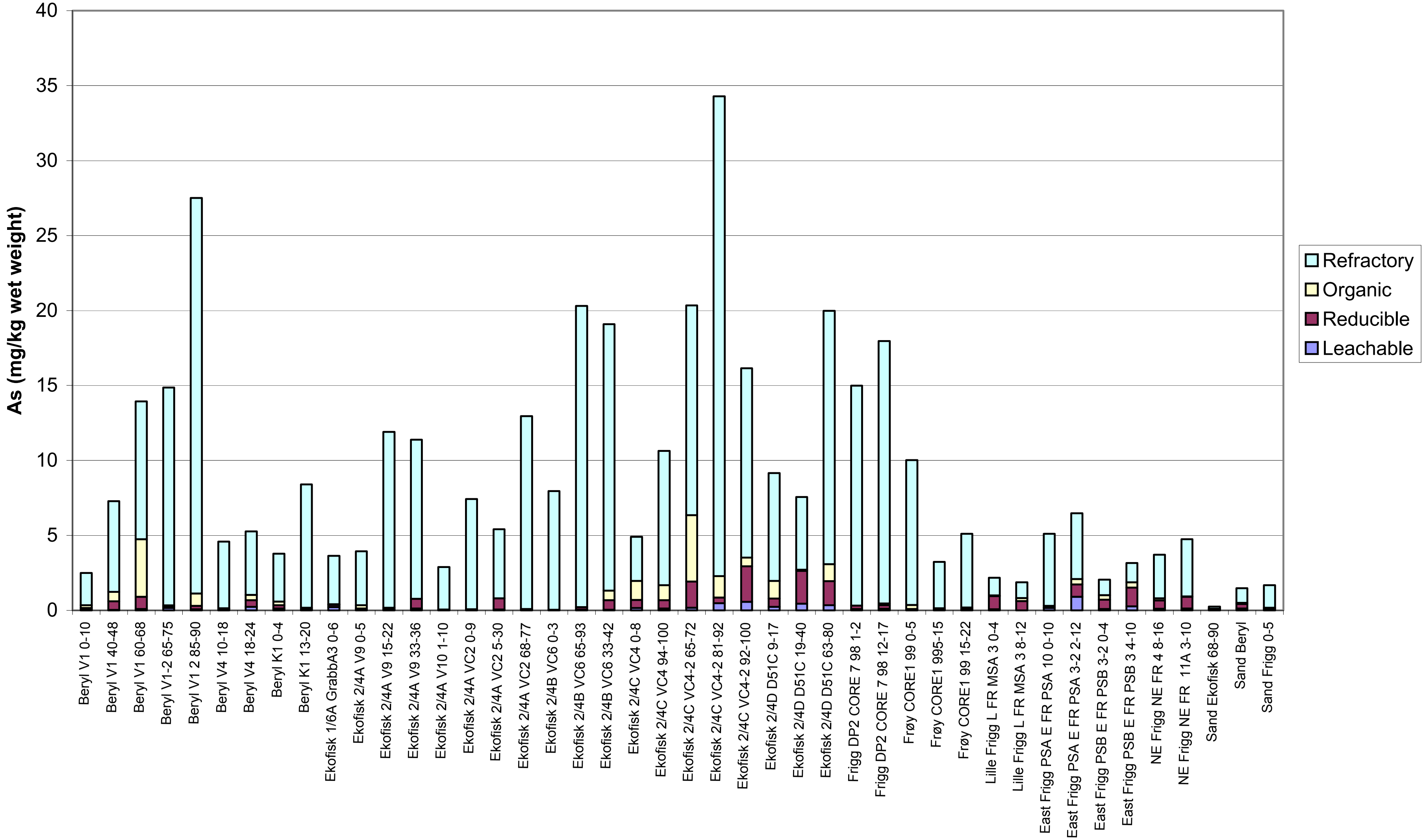
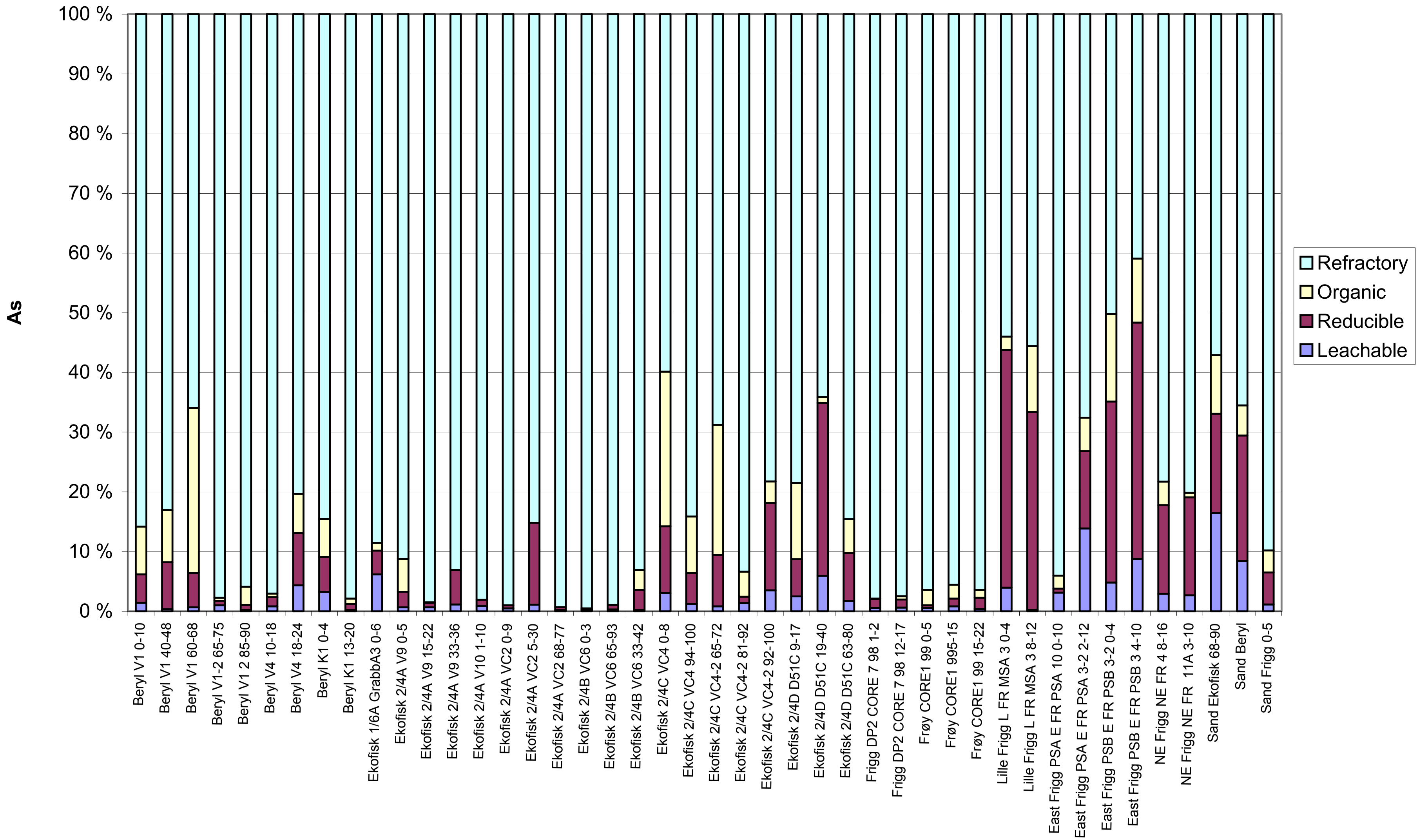
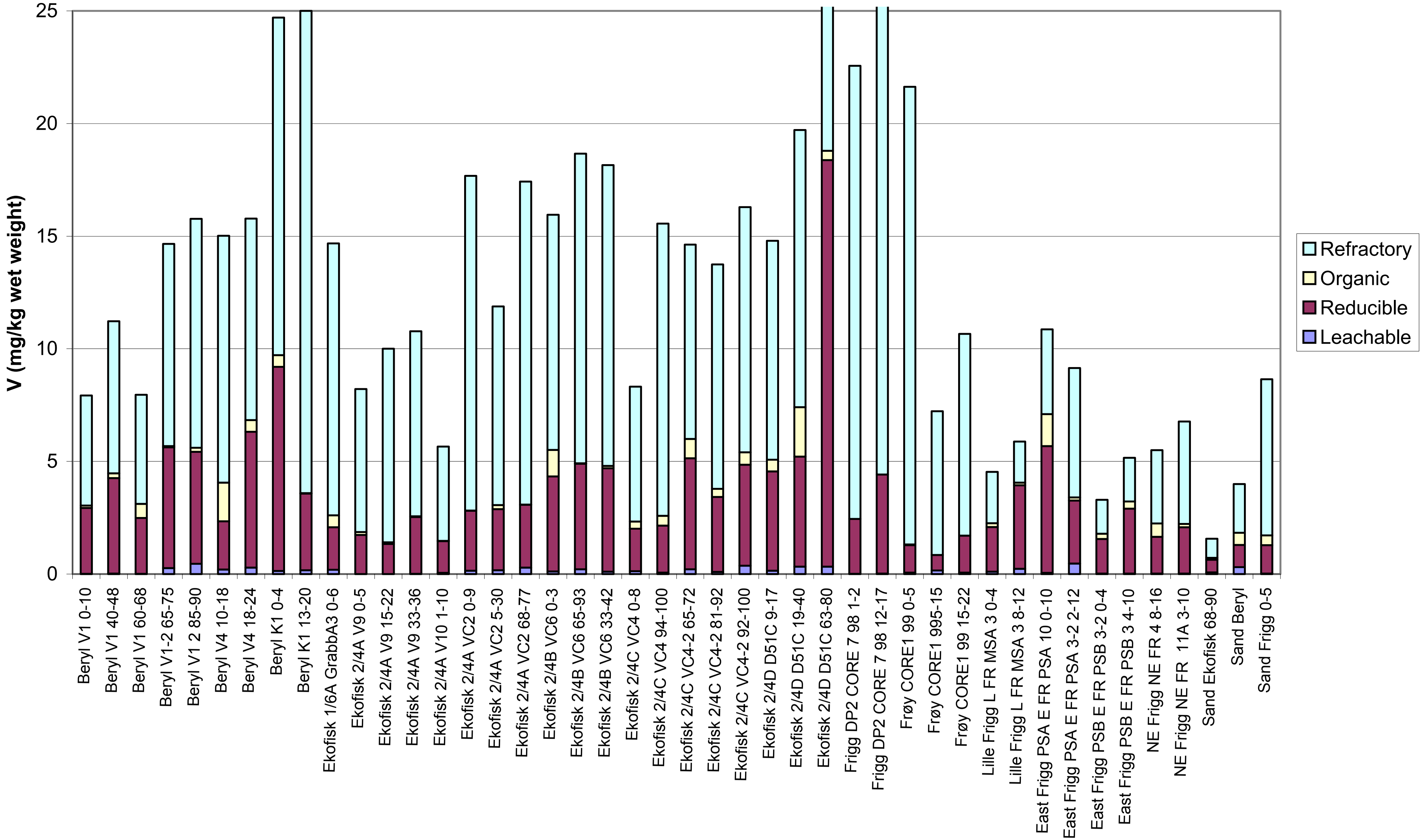
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5

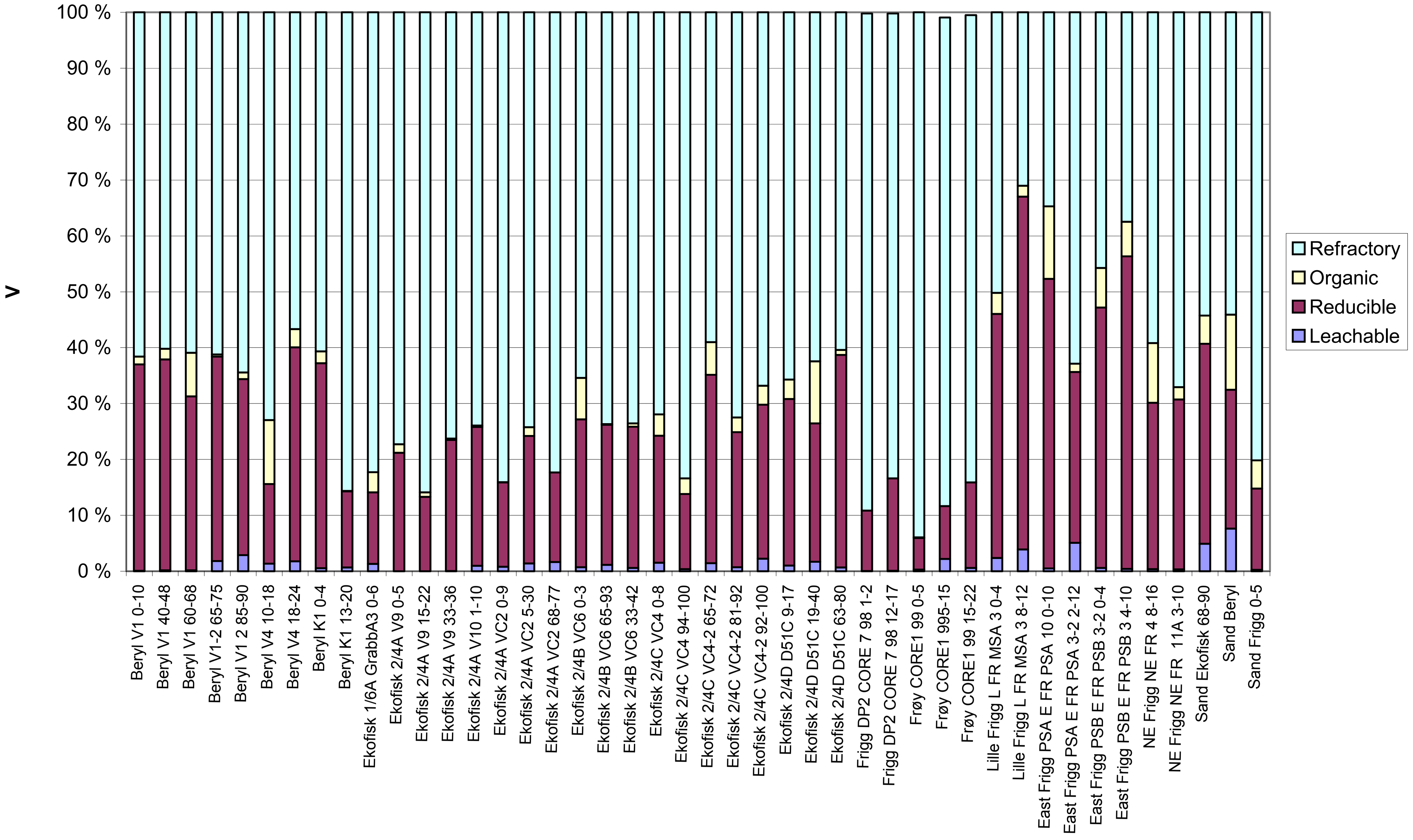

Cr (mg/kg wet weight)
200
180
160
140
120
100
80
60
40
20
0
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


Cr
100 %
80 %
60 %
40 %
20 %
0 %
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
Refractory
Organic
Reducible
Leachable


As (mg/kg wet weight)
0
5
10
15
20
25
30
35
40
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


As
100 %
90 %
80 %
70 %
60 %
50 %
40 %
30 %
20 %
10 %
0 %
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
Refractory
Organic
Reducible
Leachable


V (mg/kg wet weight)
0
5
10
15
20
25
Refractory
Organic
Reducible
Leachable
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5


V
100 %
90 %
80 %
70 %
60 %
50 %
40 %
30 %
20 %
10 %
0 %
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10
Sand Ekofisk 68-90
Sand Beryl
Sand Frigg 0-5
Refractory
Organic
Reducible
Leachable

16.5 Fractionation data for Hg

Hg has several volatile forms. If Hg bound to the sediment is reduced to elemental Hg(0) the Hg will become volatile. The fractionation performed was not designed to handle species of the highly volatile elements like Hg(0) or $Hg(CH_3)_2$. In selection of laboratory ware polypropylene tubes with polyethylene screw capped was selected because it was most preferable for all the other elements in this study. However elemental Hg will easy go through the plastic walls if formed. (Based on the results for the Mn, reducing condition is prevalent in step 1-2 and (leachable and reducing)). If volatile Hg is formed during the extraction procedure used, these species will be lost. However in step 3 (Organic and sulphides) the conditions are strongly oxidative during the extraction phase with H_2O_2 and would keep the extracted Hg in a non-volatile form. However there is still a possibility that the volatile Hg get lost during the final extraction in step 3.

Because of this, the Hg results are treated differently. In contrast to the other elements, the fractionation study for Hg only shows what is left in the refractory part and possibly organic bound metals. The total amount of Hg is however known from the characterisation study (Part 1 and Reports from the Frigg area investigations) and can be used to calculate the amount of volatile Hg lost in step 1 and 2. Measurements of Hg in the samples from Step1 and 2 confirmed that no Hg was present in these samples.

Table 19: Summary of the Hg results. The result is given in both in mg/kg dry weight and also on percent basis. The samples is divided in similar way as for the other metals with samples from Beryl Ekofisk and Frigg DP2 represents high level contamination of metals, The second group represents low contaminated cuttings with samples fro Frøy, Lille Frigg,East Frigg and NorthEast Frigg. The sand represents the background substrate below the cuttings layer with low concentrations of metals from the North sea high silica sand.

	Hg		
	Volatile	**Organic**	**Refractory**
	mg/kg	**mg/kg**	**mg/kg**
Average Beryl Ekofisk DP2	0.22	<0.001	0.29
Average Frigg	0.024	<0.001	0.030
Sand	<0.001	<0.001	0.002
	%		**%**
Average Beryl Ekofisk DP2	43		57
Average Frigg	44		56

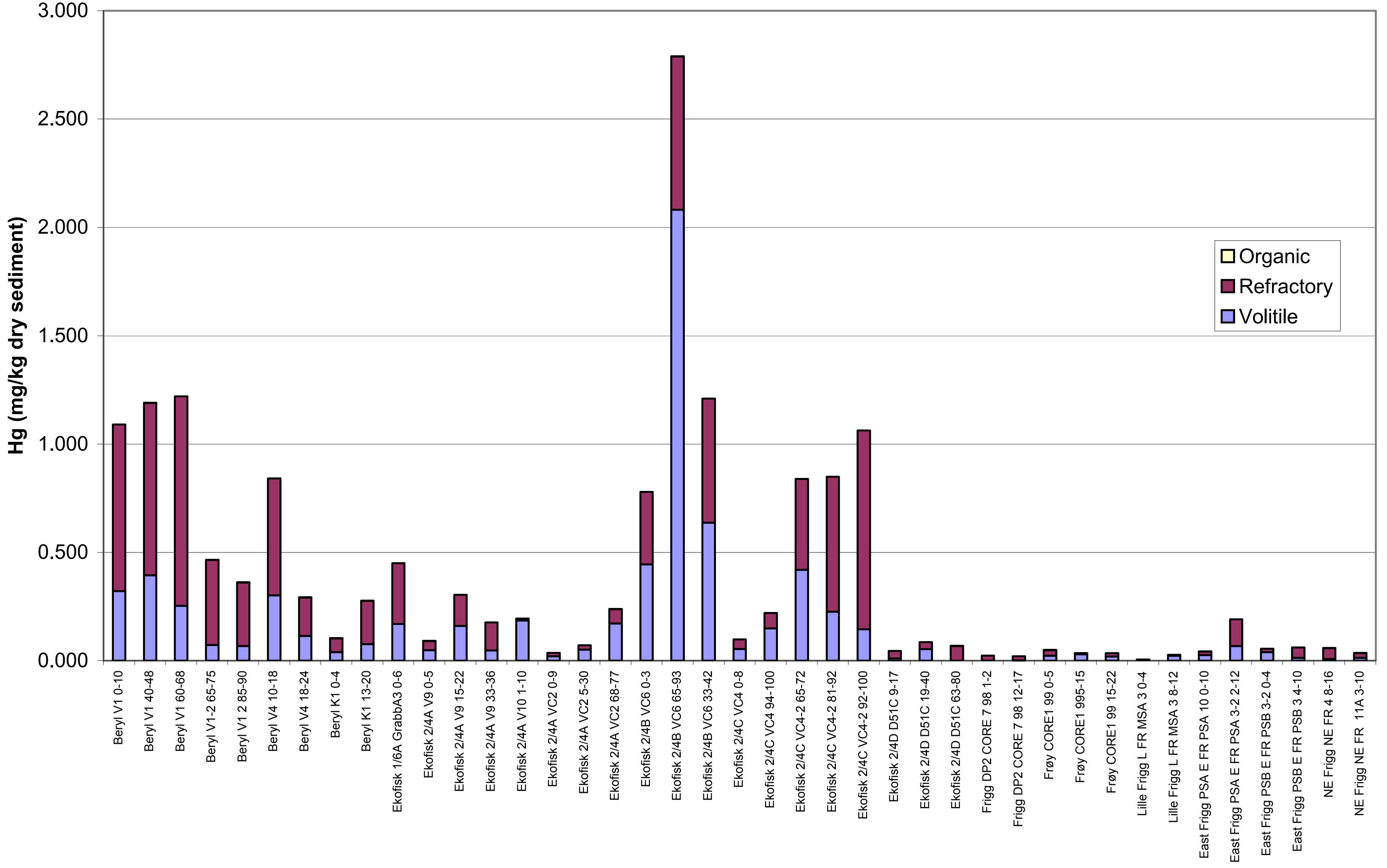
Volatile: Leachable+Reducible + possibly Organic bound

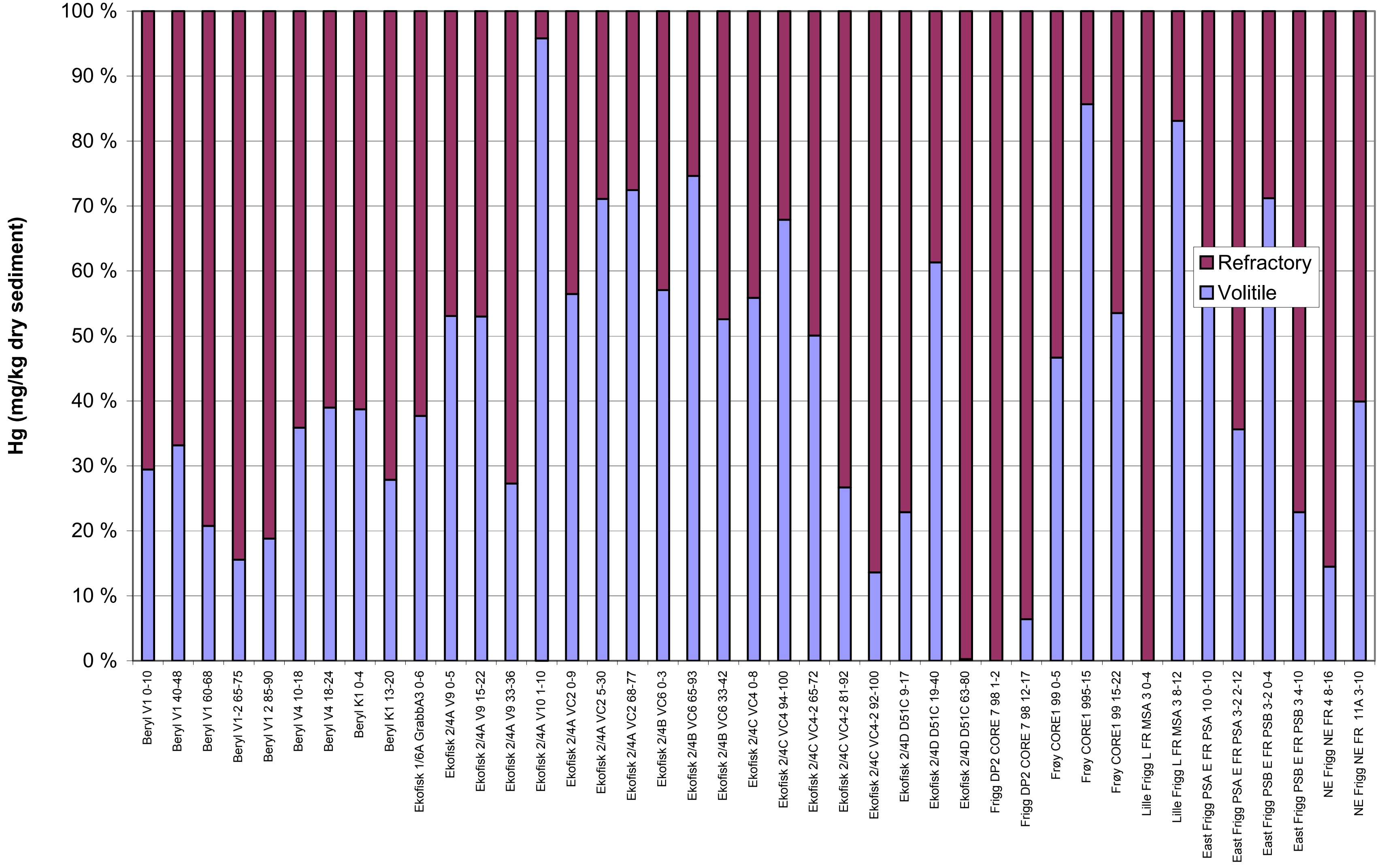
The fraction labelled organic fraction will also contain sulphides. Hg form strong sulphide-complexes. However this study does not indicate the existence of sulphide bound Hg in the cuttings.

16.6 Figures Hg

In the following two data sets for Hg is presented. The first set presents the results in concentration scale, the second presents the results on % scale. The legend refers to the fractions defined in the method section. Description on the chemical nature of the different fractions can also be found in the method section. The sample labelling in the axes starts with the installation name and core number and finally the depth of the slice in the core. More information of the origin of the samples can be found in table 19 and in Part 1.

Figure 61 :(Next pages) Figures with the results for Hg in mg/kg dry weight and in % of the total concentration as defined NS4770 dissolvable metals.


Hg (mg/kg dry sediment)
3.000
2.500
2.000
1.500
1.000
0.500
0.000
Organic
Refractory
Volitile
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10


Hg (mg/kg dry sediment)
100 %
90 %
80 %
70 %
60 %
50 %
40 %
30 %
20 %
10 %
0 %
Refractory
Volitile
Beryl V1 0-10
Beryl V1 40-48
Beryl V1 60-68
Beryl V1-2 65-75
Beryl V1 2 85-90
Beryl V4 10-18
Beryl V4 18-24
Beryl K1 0-4
Beryl K1 13-20
Ekofisk 1/6A GrabbA3 0-6
Ekofisk 2/4A V9 0-5
Ekofisk 2/4A V9 15-22
Ekofisk 2/4A V9 33-36
Ekofisk 2/4A V10 1-10
Ekofisk 2/4A VC2 0-9
Ekofisk 2/4A VC2 5-30
Ekofisk 2/4A VC2 68-77
Ekofisk 2/4B VC6 0-3
Ekofisk 2/4B VC6 65-93
Ekofisk 2/4B VC6 33-42
Ekofisk 2/4C VC4 0-8
Ekofisk 2/4C VC4 94-100
Ekofisk 2/4C VC4-2 65-72
Ekofisk 2/4C VC4-2 81-92
Ekofisk 2/4C VC4-2 92-100
Ekofisk 2/4D D51C 9-17
Ekofisk 2/4D D51C 19-40
Ekofisk 2/4D D51C 63-80
Frigg DP2 CORE 7 98 1-2
Frigg DP2 CORE 7 98 12-17
Frøy CORE1 99 0-5
Frøy CORE1 995-15
Frøy CORE1 99 15-22
Lille Frigg L FR MSA 3 0-4
Lille Frigg L FR MSA 3 8-12
East Frigg PSA E FR PSA 10 0-10
East Frigg PSA E FR PSA 3-2 2-12
East Frigg PSB E FR PSB 3-2 0-4
East Frigg PSB E FR PSB 3 4-10
NE Frigg NE FR 4 8-16
NE Frigg NE FR 11A 3-10

17 Discussion

A strongly anoxic sediment can be characterised by the dominating state of Fe being sulphides (Rule and Alden, 1996). With the stepwise extraction procedure used in this work, the Fe-sulphides would end up in the *organic* fraction. The mineralogy identified a significant fraction of pyrite (FeS_2). A further evaluation of the main components showed (Part 1) that it is possible that a large portion of the Fe in the cuttings at Beryl and Ekofisk 2/4 A is bound as sulphides. This is not confirmed by this sequential extraction procedure, which implies that large parts of the Fe are stronger bound in the minerals.

Based on the evaluation of the mineralogy data, most of the cuttings samples have a considerably lower than expected content of Fe in the *organic* and *sulphide* fractions. During the deposition of the cuttings the environment is oxic. At oxic conditions, metal sulphides may be bioavailable to the biota. Generation of sulphides may take place during drilling. To generate a large sulphidic phase in the cuttings deposits the mineral bound metals have to be released and react with sulphide. If the generation of the sulphidic phase occurred within the cuttings pile, differences in the sulphidic phases reflecting the ongoing processes in the piles would be expected in the samples analysed. From the current results, it seems more likely that the major partitioning of the metals already existed when the cuttings were discharged.

The absence of strong sulfidogenic phases could be an indication that the processes in the cuttings piles are slow and that the environment is not strongly sulphidic, which can also be seen from the direct measurements of sulphide in the cuttings (Part 1). The generation of the metal sulphide phase in the cutting deposits can have happened in a very early stage during the drilling or in the storage tanks before discharging of the mud.

The cuttings samples selected in this work showed large variation in total concentration of the examined metals. The partitioning between the different fractions in the cuttings calculated on the %-basis, generally is more similar. This is to a large extent independent of the fraction. The general consequence of this is that when high concentrations are found in the cuttings, more metal can be mobilised through diagenetic processes and be made available for biota. However there is not a linear relationship between the total metal concentration and the portions in each fraction. There seems to be a tendency that samples containing higher concentration of total metals have a slightly lower percentage of the metals in the most available fractions, however there will still be more metals easy mobilised.

A wide range of metals form strong sulphide complexes (Dyrssen, 1985). Most sulphides formed from the ions are in the 2+valens state, and most sulphide complexes have a low solubility. Evidence of rapid transfer of metals to strong sulphide compounds of low solubility is seen in the low concentrations normally found of Cu, Cd, Pb and Zn in the water of permanent anoxic basins (Haraldson and Westerlund, 1988). In sediments where sulphide is present or is generated, free metals will rapidly form solid sulphide complexes (Westerlund et al., 1986). It is likely that in cuttings piles where anaerobic degradation processes takes place, a sulphide fraction of metals could be generated from released metals that immediately precipitates as insoluble sulphides. However the anaerobic activity within the piles are expected to be low, and this mechanism will only trap the metals in the pile until they reach the surface where an oxic environment is likely to prevail. The results from the characterisation work (Part 1) also indicated that the Ekofisk 2/4 A and Beryl A did not have strong sulphidic environments. A fairly large portion of the metals that can form strong sulphide complexes (Cd, Cu, Zn) is found in the *organic* (sulphide or organic bound metals) fraction. However, there is no clear trend that these metals show a different pattern deep down in the pile compared to the surface. As a consequence of this, release of metals in the most available fraction and transformation into to sulphides does not seem to be an ongoing process. A more likely scenario is that this mobilisation of metals takes place at the top surface layer.

Cd and Zn are metals that have a high uptake rate in biota. Looking at the *Leachable* and *Reducible* fractions that represents the most available metals there is a trend that the cuttings with lower total concentration have a larger part of their Cd in these fractions. Judging from this, it is not evident that the available part of the Cd is proportional to the total concentration of Cd. On the contrary, is seems that an increase in the concentration of total Cd in the cuttings pile not directly suggests a corresponding linear increase in bioavailability.

17.1 Metal partitioning in different pile types

The attempt to apply multivariate data analysis (PCA) did not results in any interpretable pattern. One reason for this is most likely that the results have rather large spans in concentration. Simple normalisation is not sufficient to achieve a data material suitable for multivariate analysis. The contamination pattern found at the different sites is also quite complex.

As an example of the complexity, the sample from Albuskjell 1/6 A was selected as a representative for a small WBM pile, but it has a large fraction of Zn and Cd. The sample from 1/6 A is taken from the peripheral part of the pile. The pattern seen with these two metals may be a result of increased bioavailability due to mineralisation processes when the cuttings layer becomes thinner.

The unsuccessful attempt to apply PCA on the data set probably indicate the there is no particular pattern of the distribution of the different metal species associated to the different cuttings pile types or layers in the pile.

The drilling history varies at the different locations. The drilling records from Beryl A show that the drilling took place between 1975 and 2000 while the drilling at Ekofisk 2/4 A took place between 1964 and 1994. A possible scenario is that a speciation change will occur in the cuttings pile from ongoing diagenetic processes. A longer dormancy period of the cuttings pile would possibly give the result that different layers in the piles degrade differently. Based on the results seen here (both between piles and in the cuttings layers) it is not possible to see any speciation changes directly linked to this time perspective with the dormancy or historical records in these investigated cuttings piles.

17.2 Metal partitioning and bioavailability

The data generated from this sequential extraction is primary a way to estimate the release of metals during different conditions defined in the extraction procedure. The bentic species are filter feeders and access of metals increases when they are available in dissolved form. Measurements of metal in blue mussels (*Mytilus edulis*) collected on different cuttings piles in the Ekofisk area (Cripps et al., 1999) have shown that enhanced levels of many metals could be found compared to expected levels in clean North Sea environments. Measuring metals in natural collected species is difficult to compare as the exposure time and dosage is impossible to estimate. However, this observation fits quite well with the results from the sequential extraction that generally shows that most metals interacting with biota are weakly bound to the cuttings even though the dominating fraction of the element might be refractory.

The sequential extraction techniques have previously been applied in different experiments where biota has been added in meso-cosmos studies with sediments enriched with metals in different fractions. Rule and Alden (1990) used sediment with different grain-size enriched with Cd in the organic fraction. Some results from this experiment in relation to the cuttings piles would be that mussels (*Mytilus edulis*) showed an enrichment of Cd particularly from the sand sediment, however, even mussels from a clay sediment showed an increase in concentration. The same type of experiment exposing a shrimp (*Palaemonetes pugio*) showed no or little effect. The sediment in the cuttings pile contain large portions of small particles (Clay) and the cadmium would consequently be less available for mussels than Cd in the surrounding sand, if a direct comparison is feasible. Considering sediment feeders, adsorption in the gut may be different, digestive fluids possible playing a role in metals partitioning and hence bioavailability.

It is not obvious to link the results from the sequential extraction results to the bioavailability of the metals in the cuttings material. However, there is a clear indication that the elevated concentrations of metals found in the cuttings material also will result in increased load of available metals locally for biota close to the cutting deposits.

18 Conclusion

No clear trend between the partitioning of the metals in different piles and layers can be seen. The degradation of material releasing metals down in the pile has to be low. Using multivariate analysis with pattern recognition did not link the partitioning to either specific layer or metal. This approach presented no clear pattern that partitioning of the metals in the cuttings exists.

A general trend seen is that cuttings containing higher concentrations of metals have a smaller portion of the metal in the most available forms. However cutting with higher concentration of metals still contains more metals in total in those more available forms. A linear relation of metals partitioning based on concentration can thus not be used to evaluate the possible bioavailable contribution of the metals in the cuttings.

Data from other studies linked to these indicate that Cd in the cuttings will potentially be available for biota.

All metals generally associated with uptake by different biota, e.i. Zn, Cu, Cd, Hg, can be found in available fractions.

There are some discreancy in the behaviour of Cr in separate piles: At some sites with high Cr concentrations, the Cr in the cuttings appears to be in highly available forms, while at most other sites the Cr appears to be strongly bound.

Ba is strongly bound in the cuttings while large part of the Pb is found in more available fractions. Even though the Pb contamination most likely originates from the barite, significant portions of the Pb is not strongly bound in the barite fraction.

There is no data from this study that directly point at the source for the elevated metals concentrations sometimes seen in the cutting deposits. There is no correlation between Ba and any metals in this study. Even though the original source for most of the metals found at elevated concentrations is most likely barite, the solution chemistry of barite is too complex and different from the single metals to reflect the release of metals from the cuttings.

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Characterisation of the cuttings piles at the Beryl A and Ekofisk 2/4 A platform - UKOOA Phase II, task 1

Part 3:

Endocrine Disruption from drill cuttings material

GLOSSARY

Androgen receptor: A structure in a cell, which in combination with an androgen results in a specific change in cell function.

DNA (Deoxyribonucleic acid): A complex nucleic acid molecule found in the chromosomes of almost all organisms, which acts as the primary genetic material, controlling the structure of proteins and hence influencing all enzyme-driven reactions.

Endocrine Disrupter: A man-made or natural chemical that mimics a hormone and in turn can cause alterations in normal growth, development and/or reproduction.

Genome: The complete complement of genetic material in a cell.

Estrogenic Chemical: A chemical, man-made or natural, that mimics the action of the natural female steroid, oestradiol-17β.

Estrogen receptor: A structure in a cell, which in combination with an oestrogen results in a specific change in cell function.

Plasmid: A naturally occurring circle of DNA or RNA that is capable of replicating independently of the host chromosome.

Reporter Gene: A gene with ability to react to specific genetic signals by activating a measurable response.

20 Summary-Part 3

In the present study, signs of estrogenic, anti-estrogenic, androgenic and anti-androgenic activities were detected in drill cuttings piles samples from various oilfields in the North Sea. Generally however, the effects found were weak and variable, and the overall volume of results is limited. The study is therefore not conclusive with regard to the environmental risk linked to the eventual occurrence of endocrine acting substances in the cuttings piles waste material.

The present investigation form a first step into the very complex issue of evaluating endocrine disruption (ED) activities of chemicals occurring in the numerous drill cuttings piles in the North Sea. This task is a challenge due to the fact that the piles typically vary a lot in composition and texture not only between piles but also within each one of them. Identification of chemicals present in the cuttings piles being evaluated is important as a basis for selection of ED related test parameters and for interpretation of results. However, due to the chemical complexity and heterogeneous nature of the piles, this task could not be fully accomplished in the present study.

In testing impact of complex mixtures, it is favourable to use some sort of integrative effect parameters that are capable of assessing the sum-effect of compounds, i.e. within one effect category (e.g. estrogenic compounds). This approach was selected in the present investigation, by the use of several cell-culture tests each indicating estrogenic, androgenic and dioxin related effects of the cuttings piles extracts.

Even though the outcome of these pilot measurements was hampered by the presence of cytotoxic components in many of the cuttings samples, the results may still be considered as important since signs of ED effects of various cuttings were recorded. The ED responses observed were relatively weak though, and further studies are needed to establish clear evidence with regard to the significance of the ED issue in cuttings. A central aspect in that respect is also the limitations of the methods used, especially with regard to extraction procedures and concentration factors. Obviously the tested extracts differ considerably from what can be expected in the nature, and issues like bioavailability may be central.

Due to the complex chemistry of the cuttings extracts, it was in this study not possible to correlate observed ED effects to specific contaminant groups chemically analysed. The study demonstrate however that the occurrence of dioxin type toxicity in cuttings can be related to high levels of PCBs, and that the cell-culture based DR-CALUX assay is able to estimate the potency of such toxicity, even in complex samples such as cuttings. Additionally, a partly correlation of high BaP levels and anti-estrogenic effects was indicated in an *in vitro* assay based on yeast cells. BaP, and similar compounds, may therefore be considered as a relevant parameter to consider in future ED studies of cuttings piles.

Obviously, the present study was hampered significantly by the acute cytotoxicity stress that many of the cuttings piles samples caused to the test cells. This was in particular the case with the yeast-based YES/YAS assays. As stated previously, it has proven difficult to find the right compromise between sufficient dilution of tested sample extracts to avoid cytotoxicity and not diluting the potential EDCs out of solution. This must be better characterised prior to further studies.

When a sample is found to be cytotoxic that basically means that the level of some chemical compound within the extracted sample prevents cell growth or induce cell-death. When such a cytotoxic response is seen it is normally not possible to see any additional effects, e.g. endocrine related responses. Such effects might therefore mask the presence of endocrine acting substances in the exposure solution (or exposure material). Later studies must put considerable emphasise in carefully designing the test scheme in order to minimise the influence of acute intoxication conditions. This involves both selecting appropriate test organisms and using exposure doses in the sublethal dose range. Higher organisms, both represented by certain invertebrates and by various fish species, may be considerably more robust towards stress caused by toxic compounds, but still responsive with respect to endocrine effects. Larger organisms are also better suited for more long-term studies that are necessary when addressing low-dose (and chronic) effects of endocrine acting substances.

21 Introduction-Part 3

There is a concern of possible environmental long-term impacts on marine organisms in the North Sea resulting from the oil industry. This is also an issue related to decommissioning and particularly drill cuttings, and relates to the debate on how to best handle the existing drill cuttings piles during the decommissioning phase at North Sea oil fields.

Generally, cuttings piles are extremely heterogeneous. There is a considerable variation in texture and chemical composition, both between piles but also within each pile. Residual fractions of oil hydrocarbons and various kinds of additive chemicals, that have served operational needs during the drilling, occur in the piles. In particular, cuttings from fields that have used oil-based drilling muds contain significant amounts of residual oil hydrocarbons. The toxicity of cuttings piles materials depend much on what kind of mud that has been used at the particular drilling site. In particular diesel based muds, and cuttings piles dominated by this type of muds, have been shown to contain toxic chemicals (Plantecuny, Salenpicard et al. 1993).

Environmental toxicity evaluations of cuttings piles may be conducted as measurements of acute toxicity in standard toxicity tests (e.g. corophium test). However, acute tests of cytotoxicity or lethality of test organisms may not give full insight in possible long-term effects that might occur in impacted areas. A supplemental approach is to establish whether chemicals that eventually may leach out from drill cuttings piles could cause any disturbance related to the endocrine (hormonal) system. Such hormone-related impacts, or endocrine disruption (ED) effects, of environmental pollutants have gained increased attention in recent years. National and international regulations have recently been implemented by the North Sea countries that prohibits discharge of known ED substances from offshore E&P activity.

Polychlorinated biphenyls (PCBs) are a group of compounds given little attention in drill cuttings characterisation and impact assessments earlier. With this UKOOA work, PCB's were measured and found to be abundant in one of the two piles investigated. The implication of this finding has been investigated further and is presented in this report. Effects of PCBs and endocrine disrupting chemicals (EDC) are closely linked since a major concern, although not the only concern, of PCBs are related to the dioxin-like behaviour of some PCB congeners. It was therefore natural to combine these issues in one report. The actual ED contribution from chemicals in the historical discharged cuttings has yet not been answered, although it is the focus of the present study to address this. Better knowledge in such matters can prove important in order to establish environmentally optimal procedures for managing the cutting piles issue in decommissioning.

22 Objectives

The objectives of this study are to:

- provide pilot screening data on the occurrence of potentially endocrine disruptive chemicals in drill cuttings from the North Sea, and to put this into context of EDs in general, and further
- examine potential impacts of PCBs known to be present in the piles investigated, also by a screening approach, and likewise put this into context of PCBs in general, and particularly their relation to ED effects.

The work presented in this Part 3 of the UKKOA Task 1 report has been carried out as a sub-task to the task 1 characterisation work. Samples were obtained from the Beryl and Ekofisk cutting piles and examined by selected screening tests. Extracts of the samples were analysed for estrogenicity and androgenicity (agonistic and antagonistic effects) by the use of screening assays based on transformed yeast cells (YES & YAS assays) and genetically modified cancer cells (ER-CALUX and AR-LUX assays). Additionally, the occurrence of dioxin related toxicity in selected samples was evaluated by the use of a DR-CALUX assay. This last type of assay was used to establish the effects of PCBs in particular, if possible. Overall cytotoxicity was also indicated by the assays. The assay results are discussed against a set of chemical contaminant parameters (THC, PAHs, metals, PCBs, nonylphenol, 4-tert octylphenol and alkylphenol ethoxylates) that have been examined in the same samples.

23 Relevant background reviews

To connect the present pilot study of ED and PCBs in drill cuttings to the known aspects of these components, some background information is presented. A section on historical data of used and discharged chemicals at the Beryl field is also included in order to evaluate the correlation between the known discharges, the measured chemicals of the cuttings pile material and the potential effects related to ED.

23.1 Endocrine disruption (ED)

The endocrine system in higher organisms consists of a set of glands and the signal chemicals (hormones) they produce that regulate the development, growth, reproduction, and behaviour of animals. The endocrine glands include such as the pituitary, thyroid, adrenal glands, the female ovaries, male testes and others depending of the organism in question. Hormones, produced by the endocrine glands, travel through the bloodstream and cause responses in target tissues and cells in other parts of the body. Examples of hormones include adrenaline, which stimulate physical activity, and estrogen, which regulate the female reproductive development. Hormones may up-regulate and down-regulate the biotic processes in the target tissues and target cells.

Chemicals that interfere with this normal functioning of the endocrine system are known as "endocrine disruptors" or “endocrine disrupting chemicals”, abbreviated ED and EDCs, respectively. Several definitions of environmental endocrine disruptors have been presented. A functional variant is to define a potential endocrine disruptor as “a substance that possesses properties that might be expected to lead to endocrine disruption in an intact organism” (Menditto and TurrioBaldassarri 1999). The EDCs exert their effects by affecting the hormonal control of biological processes in the exposed organism. They may act through a wide variety of direct or indirect effect mechanisms, such as by imitating (mimic) natural hormones, stimulating to overproduction of hormones, blocking hormone action, inhibit hormone production and by accelerating the breakdown of hormone molecules. Birth control pills may be regarded as an example of an intentionally use of ED effects.

The available information about EDCs in the environment is already extensive and it is rapidly increasing. Effects on the population level due to EDC contamination are currently a cause for concern in a number of wildlife species, in particular for top predators (Wiig, Derocher et al. 1998; Chiu, Chiu et al. 2000; Colborn and Thayer 2000), but also for certain marine invertebrates (Depledge and Billinghurst 1999). However, it is still considerable uncertainty related to the actual environmental risk of EDCs pollutants, whether they pose a real threat to the health condition, reproduction and survival in wildlife organisms, populations and communities. Several scientists even consider the EDC concern of persistent pollutants to be overestimated, e.g. Safe, Connor et al. (1998).

Chemicals that in some way inflict the steroid hormone system have gained much attention. This is especially the case for the so-called estrogenic EDCs (or xenoestrogens), chemicals that bind and activate the estrogen receptor. Estrogenic pollutants are normally less powerful signal molecules than the real estrogens, but it has been found that when several xenoestrogenic chemicals occur together, their effects may be additive. The androgenic ECDs might have a different effect. These chemicals may bind but not activate the estrogen receptor (thus directly acting as anti-estrogens) or they may effect the metabolic pathway of estrogens e.g. by speeding up the metabolism of the estrogens (acting as indirect anti-estrogens). Androgenic ECDs may also bind directly to androgen receptors for male hormones and either activate or inactivate these. Unfortunately, the term “endocrine disruption” is often used as synonymous with estrogen or androgen related effects. This simplification easily makes confusion. “Endocrine disruption” covers all kinds of hormonal disruption phenomena. A chemical tested and eventually shown to be non-estrogenic (and -androgenic) may still influence other important hormonal regulatory systems, such as the regulation mediated by the thyroid hormones. It is therefore important to be precise in terms of which endocrine system being addressed when testing for ED effects of chemicals and chemical mixtures.

Monitoring endocrine disrupting effects of environmental samples is a complex issue. For one, a whole range of different types of endocrine disturbances can be foreseen.

Secondly, the type of chemicals known to have endocrine disrupting effects is a very large and heterogeneous group, with hundreds and thousands of variable chemical formulas. Both organic and inorganic substances are known to possess endocrine disrupting properties. Some examples are chlorinated hydrocarbons (including PCBs), organophosporous esters, metallorganic compounds (including such containing tin, zinc and manganese), nitrogen heterocyclic compounds, nitrocompounds, nitrogen bases, thioethers, carboxylic esters etc. A common trait in many of them, and especially the organohalogen compounds, is that they are persistent, lipophilic and tend to bioaccumulate (Menditto and TurrioBaldassarri 1999).

23.2 Polychlorinated biphenyls (PCBs) in cutting piles

The background for addressing PCBs in cuttings piles was findings of high PCB concentrations in the Ekofisk 2/4A pile. The PCB could not be related directly to discharges from drilling operations, so the finding initiated a further examination of other Ekofisk piles. PCBs were found in the other Ekofisk piles investigated as well, but at lower concentration than in the 2/4 A pile (Westerlund and Kjeilen, 2001). Attempts were also made to identify the actual PCB mixtures that could have ended up in the 2/4 A pile, and to indicate the possible sources for these. Additionally, the possible effects of the PCBs in organisms are presently being addressed.

Virtually all PCBs that occur in the environment are of anthropogenic origin. Normally, commercial PCBs are synthesised by a bulk chlorine substitution process of a backbone biphenyl molecule. The biphenyl molecule contains two merged benzene rings. Including all possible chlorine substitutions, 209 different PCB congeners can be formed. With few exceptions, manufactured PCB blends contain a complex mixture of congeners. PCB mixtures may be in a solid or a liquid state, depending on the overall amount of substituted chlorine in the mixture. PCBs are generally lipophilic, non-reactive and very stable. Due to their unique chemical stability and their resistance to chemical oxidation, photodegradation, thermal changes, most chemical agents, acid-base reactions and hydrolysis, they are very poorly metabolised by biological systems.

PCB pollution is since long considered as one of the most significant ecotoxicological issues, with relevance both to humans and wildlife. Due to their extreme solubility in oils and fats, the PCBs are easily taken up by biota, and have a great potential for being bioaccumulated in organisms and biomagnified through the food chains. Mechanisms by which the PCBs interfere with the normal processes in humans and wildlife are fairly well described.

The PCB congeners of most concern are those that show toxic responses resembling those caused by TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) and related halogenated aromatic hydrocarbons, which act through the aryl hydrocarbon (Ah)-receptor signal transduction pathway. Such PCB congeners found to be “dioxin-like” include the coplanar PCBs which are Ah-receptor agonists and hence contribute significantly to the toxicity of the PCB mixtures. Studies with TCDD and structurally related compounds have led to the establishment of a system to base risk and hazard assessment upon, based on Toxic Equivalence Factors (TEFs). These factors are based on toxicity of single components relative to the toxicity of TCDD.

TEF and TEQ (Toxic EQuivalence) can be defined as:

- **TEF** (Toxic equivalence factor) values are established based on literature proven toxic effects, where the relative toxicity of a compound is compared to the toxicity of dioxin (TCDD). The toxicitiy of a component (based on the TEF value) is obtained by multiplying the concentration of the component with its TEF value.
- **TEQ** (Toxic equivalence) is defined as the sum of TEFs for all components in a mixture. Hence TEQ is normally calculated from the TEF values for each single component.

Due to the chemical complexity and unknown content of "dioxin-like" components in the cuttings piles, a calculation of TEQ values of pile materials based on chemical analyses is difficult. However, a comparative TEQ value for such mixed samples may be obtained by measuring the total toxicity related to Ah receptor-binding chemicals in the sample. For this purpose, Ah-receptor based binding assays and cell-culture techniques, such as DR-CALUX®, can be used. In the DR-CALUX assay, all components that have a dioxin-like behaviour (i.e. binding to the Ah receptor) will contribute to the eventual response measured.

23.3 Historical discharge data at Beryl A

Discharge records from offshore drilling sites may give an indication of which chemicals that may occur in the respective cuttings piles. However, these data records are sometimes very inaccurate, in particular those prior to 1990. For example, many of the chemical products used may be termed by their operative function or their trade names and not by their actual chemical content. Since 1990, the quality of the discharge records has improved and may in some situations contribute with valuable information. At the Beryl A field, the OBM drilling related discharged during the period 1990-2000 are reasonably well documented. A synopsis of these data is therefore included to illustrate the complexity still. As judged from this overview, large quantities of oil, barite, emulsifiers, polymers and others substances have been discharged (Table 1).

Table 20: Data records of used and discharged chemicals at Beryl A

Drilling chemicals used for drilling 21 wells at Beryl A during 1990-2000
The list contains 88% of the discharged chemicals during this period

Chemicals	Use	Used	Discharged	Used	Discharged	Used	Discharged
				On listed chemicals		On all used chemicals	
		Ton	Ton	% Tot	% Dis	% Tot	% Dis
Barite	Mud	16054	9725	49,2	61,7	42,1	54,8
Bentonite	Mud	2666	2366	8,2	15,0	7,0	13,3
Chlorides and carbonates	Cement ,Mud	4110	1889	12,6	12,0	10,8	10,6
Cement	Casing	5041	274	15,4	1,74	13,2	1,54
Cement additive	Casing	233	34	0,71	0,22	0,61	0,19
Silicalite	Cement additive	61	16	0,19	0,10	0,16	0,09
Oil	Oil mud	2214	794	6,78	5,04	5,81	4,47
Lime	Oil mud additive	244	77	0,75	0,49	0,64	0,43
Emulvis	Oil mud additive	123	23	0,38	0,15	0,32	0,13
Kleemul	Oil mud additive	500	108	1,53	0,69	1,31	0,61
Sipp drill	Oil mud additive	835	0	2,56	0,00	2,19	0,00
Ecotech	Oil mud additive	75	3	0,23	0,02	0,20	0,02
Polymer	Oil mud additive	54	48	0,16	0,30	0,14	0,27
Rheocoat Rheacap	Mud	387	354	1,19	2,25	1,01	1,99
Envirowash	Oil mud additive,Rigwash	57	44	0,18	0,28	0,15	0,25
Total		32654	15756				

The chemical products used for drilling are bulk products. Often their composition is fairly generally described. Reviewing the data-sheets with the safety information supplied with the chemical gives limited information. E.g. the datasheet of a polyalphaolefine used at Ekofisk 2/4 A state that the product contain:

- Polyalfaolefin 60-100%
- Fatty acids mixture 10-30%

Similar datasheets providing quite rough information of the main constituents can be found for the majority of drilling chemicals. Additional information that is possible to extract is information on heavy metal content and toxicity data of products that have been tested. However typical chemicals that are expected to give endocrine effects are not included in the list of chemicals analysed for in drilling chemicals.

It is possible that in the large array of chemicals used during drilling operations, low-level contamination of substances with endocrine potency may be present in some of the chemicals used. Potential ED chemicals may be present as impurities in the trade products that are used in large quantities. Since EDCs may be “active” at very low concentrations, even low levels in trade products may be significant if the trade product has been used excessively.

24 Methods and analytical approach

Prior to the characterisation of the Beryl A and Ekofisk 2/4 A piles, no information was available on potential ED related effects of cuttings materials. In the former characterisation of the Ekofisk pile, no chemicals presumed to have potential ED effects (e.g. PCBs, dioxins, octyl- and nonylphenols) were analysed for. No other reports with such chemical documentation of cuttings piles seem to be available. Hence the starting point for looking at the ED potential of cuttings piles was indeed a black box.

The chosen approach for looking at ED issues was to use simple screening tests developed and implemented for use with less complicated environmental systems. The practical implications of this approach is that the ED potential could be examined on the same sample fractions that were analysed for other chemical and physical parameters included in the characterisation work. Furthermore, the sample quantity needed was low, and no additional sampling was included for this purpose during the offshore survey. Further planning and adaptation of the ED effort as the initial results were produced was later limited by the availability of sample material. Also, possibly alternative options would have required more time and effort than feasible within the time window of this project.

24.1 General about ED screening assays

The scientific basis of the environmental endocrine disruption issue is rather new, as is the regulation framework for managing these issues. As our insight in this increase, it is apparent that a battery of test parameters will be needed for including all possible endocrine effect endpoints. Optimally, these tests should also be internationally harmonised and properly validated to ensure good quality and comparability of test results. As a part of this process several significant regulatory bodies have outlined recommendable batteries of test methods for the screening and testing of ED related effects. One example is the US EPA - Endocrine Disruptor Methods Validation Subcommittee (EDMVS) that provide technical advice and recommendations regarding validation of the Tier 1 Screening and Tier 2 Testing methods (see table 2) for the EPA - Endocrine Disruptor Screening Program (EDSP).

Table 21: Prioritised test methods identified for developing and validation by the US EPA - Endocrine Disruptor Methods Validation Subcommittee (EDMVS) concerning evaluation of endocrine disruption related effects of chemicals (info from: http://www.epa.gov/).

Tier 1 Screening Battery Methods
- Estrogen (ER) and androgen receptor (AR) binding assays
- ER and AR assays w/transcriptional activation
- Steroidogenesis assay
- Uterotrophic assay
- Hershberger assay
- Pubertal female assay w/thyroid endpoints
- Frog metamorphosis
- Fish reproductive screening assay

Tier 1 Screening Battery Alternate Methods
- Pubertal male assay w/thyroid endpoints
- Aromatase assay
- Rodent in utero through lactation assay

Tier 2 Testing Battery Methods
- Two-generation mammalian reproductive toxicity study with endocrine endpoints
- Two-generation avian reproductive toxicity study with endocrine endpoints
- Two-generation fish reproductive study with endocrine endpoints
- Two-generation mysid shrimp reproductive study with endocrine endpoints

24.2 YES and YAS assays

Several cell-culture based techniques are developed to provide information about the endocrine disruptive potency of single chemicals or chemical mixtures. The YES and YAS assays are examples of such screening tests. These two methods are based on the work by Routledge and Sumpter (1996), and Sohoni and Sumpter (1998). The assays involve the use of recombinant yeast containing plasmids encoding the human estrogen receptor (hER) or the human androgen receptor (hAR) and an estrogen or androgen responsive promoter linked to a reporter gene, lac-Z (encoding the enzyme β-galactosidase). In the presence of estrogenic or androgenic compounds β-galactosidase is synthesised and secreted into the medium where it causes a colour change from yellow to red (measured at 540 nm on a microplate spectrophotometer). The results are then compared to the yeast response to positive reference chemicals.

In cases where the chemical exposure conditions are acute toxic to the yeast cells, depression of cell growth or increased cell mortality can be recorded. As yeast grows it forms a turbid layer over the base of the plate wells, which may interfere with the light path of the spectrophotometer. This growth is not always uniform and may be positively or negatively influenced in the presence of a chemical. The plates are therefore read at an absorbance of 620nm (A_{620}) to measure the turbidity of the yeast in each well, allowing a comparison between the test chemical and the controls (blanks). Reduction in turbidity is considered to be an indication of possible cytotoxicity to the yeast.

YES/YAS assays have been conducted by Brixham environmental laboratories, AstraZeneca UK Limited.

24.3 CALUX assays

These tests are based on genetically modified cancer cells comprising genes for expression of firefly enzyme luciferase. Expression of luciferase enzymes makes the cell capable of producing light when the appropriate luciferase substrate is added. The luciferase gene is used as a reporter gene and is coupled to other genes that are expressed when the cell is exposed to certain xenobiotic chemicals. The amount of light produced is proportional to the amount of ligand-receptor binding. The signal is then recalculated to equivalents of positive reference chemical, e.g. estradiol (EEQs), dihydrotestosterone (androgen) or the dioxin reference chemical TCDD (TCDD TEQ).

24.3.1 ER-CALUX and AR-LUX

In the Estrogen Responsive – CALUX (CALUX = Chemically Activated LUciferase eXpression) assay a genetically modified T47D human breast adenocarcinoma cell-line is used and the luciferase gene is coupled to genes responsive to the presence of estrogenic substances (Legler, Van den Brink et al. 1999). Chemicals that bind to the estrogen receptor make the test cells start producing light. Similar with the Androgen Responsive AR-LUX assay, the modified cells are responsive to the presence of androgenic substances (androgens are male steroid hormones).

ER-CALUX and AR-LUX assays have been carried out by TNO Nutrition and Food Research and sub-contractors.

24.3.2 DR-CALUX

The DR-CALUX® (Dioxin Responsive-CALUX) is rather similar to the other CALUX assays, but uses a genetically modified rat-hepatoma H4IIE cell-line. The firefly luciferase gene is coupled to the Ah receptor gene battery that is expressed depending on the concentration present of dioxin and dioxin-like compounds (Murk, Legler et al. 1996). Normally, 2,3,7,8 TCDD is used as the positive reference compound

(*Figure 62*), but the assay is responsive towards toxic polyhalogenated aromatic hydrocarbons (PHAHs) and coplanar PCBs. These dioxin responsive genes are often termed as dioxin responsive elements (DREs). All chemicals that bind to the Ah receptor, and trigger the expression of the dioxin-responsive elements, makes the cells start producing light. In addition, a plasmid (pGudluc 1.1) has been incorporated in the cells containing mouse DREs coupled to firefly luciferase genes.

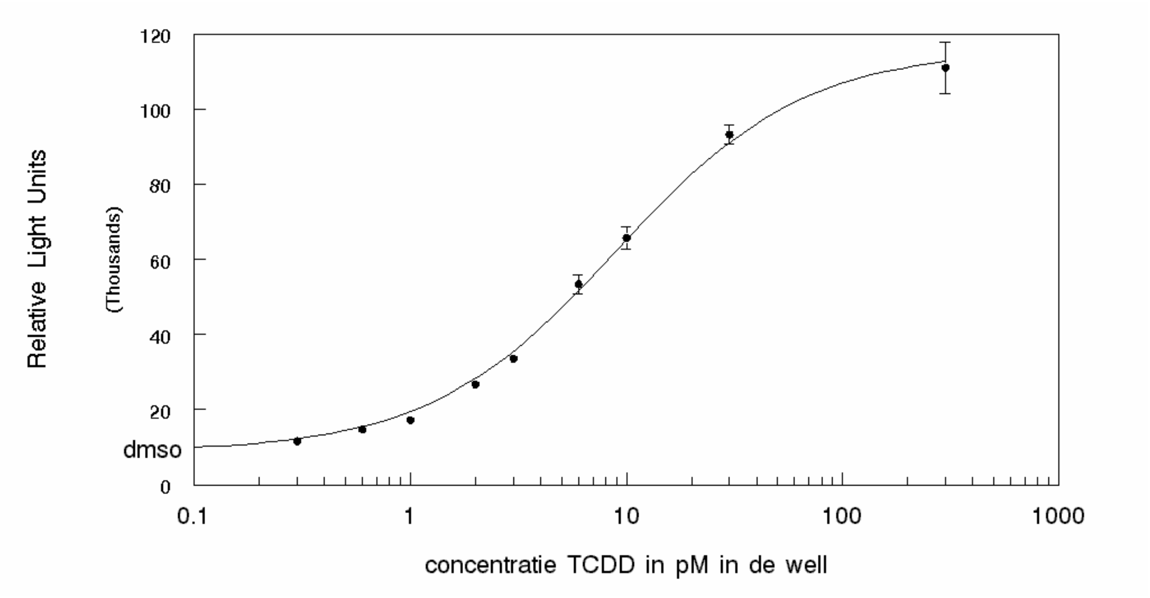

Figure 62: The dose-response curve of the DR-CALUX® cells exposed to the positive reference compound 2,3,7,8 TCDD.

The DR-CALUX assay was carried out by Biodetection Systems bv (BDS).

24.4 Selection of samples and extraction procedures

The samples to be analysed by the ED assays were selected to represent different pile fractions, and were therefore selected based on their chemical content as analysed within this task 1 work. They were selected to represent a variety of cuttings layers (old and newer ones) and concentrations of chemical groups, with special focus on the THC, PAH, PCB and metals fractions. Both Beryl and Ekofisk samples were included, and the sample fractions used corresponded directly to the fractions analysed for the other parameters indicated. The number of samples analysed using the YES and YAS assays were larger than with the corresponding CALUX assays. The DR-CALUX was focused at the influence of PCB's, and hence only Ekofisk samples were analysed with this assay.

24.4.1 Sample preparation and extraction procedures

None of the ED assays have been used with environmental samples similar to the cuttings material investigated here. Appropriate extraction procedures and sample processing has therefore been an issue of concern. Based on discussions with the labs performing the assays, it was decided to use methanol extraction with all tests (except the DR-CALUX assay). Methanol extraction is standard procedure at least with some of the assays, and was experienced to be similarly efficient to other alternatives.

Methanol extraction will favour extraction of partly water-soluble components. Based on knowledge of the more "common" EDCs, this was considered to be feasible. Other extraction agents may favour other fractions, and no single extraction method is assumed to extract all relevant EDCs equally. Not knowing what compounds to look for, it was considered to be of little value to optimise extraction methods. It was considered to be rather more important to be able to compare the findings of the different assays.

Based on this, the following extraction methods were used:

- YES/YAS Assay (both phases): 25ml methanol was added to approx. 1g sample, mixed thoroughly and left for one hour. 20ml supernatant was then removed and filtered through 0.22∝m filter. The filtered sample was then blown to dryness over night and redissolved in 1 or 4ml ethanol (phase I and phase II assays respectively). All preparations were carried out in pre-sterilised glassware.
- ER/AR-CALUX Assay: Same as above except the sample was shaken for 1 hour after the methanol was added before left to stand still, filters were pre-washed in methanol, and all glassware was washed with methanol and dried before use.

The DR-CALUX samples were processed using ASE-extraction and clean-up of freeze-dried samples (see appendix 10 for details). A different method was selected based on the standard method most often used by the lab. Since this assay was more directly focused at a target compound or group of compounds, the standard method was considered to be most useful in this case.

All assay reports are included in full in Appendix 10.

25 Results

25.1 Phase 1: YES/YAS screening and pollutant chemicals

The results of the analyses from phase 1 of the present study are presented in Table 3. The results are compared to the levels of main contaminants measured in the same cuttings piles fractions. A total of 32 cuttings pile samples were analysed using the YES and YAS assays (analysis report is added as Appendix 10). The samples originated from the Beryl cuttings pile (18 samples), the Ekofisk 2/4A cuttings pile (11 samples) and one sample each of Ekofisk 2/4C, Frøy and Lille-Frigg (which are all included in the Task 3 studies). Concentrated methanol extracts (20-fold) of the cuttings samples were used for the YES and YAS assays. No concentration gradients were tested. The samples were tested with regard to estrogenic and androgenic activity. The results obtained indicated whether they either were cytotoxic, estrogen agonist, estrogen antagonist, androgen agonist, androgen antagonist or neither at the concentrations tested.

In two batch samples of surface material (obtained by means of a box corer) from the Beryl cuttings pile, nonylphenol, 4-tert.octylphenol and alkylphenol ethoxylates were analysed, by TNO. In that study, no levels were found above the detection limit initially (20, 20 and 200 µg/kg DW, respectively). Chemical analyses of these compounds were not performed with samples from the Ekofisk cuttings material.

Table 22: Summary of data from the YES and YAS assays conducted during phase 1 and levels of selected chemicals measured in the same samples (see part 1). The samples analysed with the YES-assay are from the same fractions used for the particle analysis, and consequently cover slightly thicker layers. The presented values are average of the chemical analysis results of the merged sections. B.s = background sand (i.e. no cuttings).

BEL sample ref				Cytotoxic	Oestrogen agonist	Oestrogen antagonist	Androgen agonist	Androgen antagonist	THC	Sum EPA 16 PAH	B(a)P	Naphtanenes	PCB	Comments
									mg/kg	µg/kg	µg/kg	µg/kg	µg/kg	
Beryl	Core	Slice	REF Nr											
25	**V1-1**	0-20	423-1	x					90000	9800	53	70000	<	
31		30-40	423-2	x					98000	74000	33	132000	<	
26		40-48	423-3	x					150000	35000	40	310000	<	
24		48-68	423-4	x					69000	16000	12	250000	<	
23		68-76	423-5			x		x	190000	33000	48	410000	<	
29	**V1-2**	0-30	423-6			x			180000	43000	150	1045000	<	
30		30-60	423-7						40500	17000	42	230000	<	
28		60-65	423-8			x		x	75000	30000	170	350000	<	
27		65-90	423-9	x		x			64000	30000	40	115000	<	
2	**V3-G**	0-25	423-10	x					17000	4100	41	25000	<	
3		25-39	423-11	x					37000	5100	56	35000	<	
5		39-48	423-12						72000	7300	50	73000	<	
1		48-60	423-13		x			x	96000	525	5,5	5700	<	
6	**V4**	0-18	423-14		x				61500	5700	10	27000	<	
4		18-24	423-15	x					27000	4600	<10	28000	<	
7		24-40	423-16	x					200	180	6,5	1050	<	B.s
8	**K1**	0-10	423-17	x					12400	1250	8	6000	<	
11		10-20	423-18		x				300	500	8	9100	<	
Ekofisk	Core	Slice	REF Nr											
10	**V9**	0-15	423-19	x					48000	1700	12	8900	<	
9		15-33	423-20	x					850	750	9,4	8000	162	
17		33-43	423-21	x					706	1360	56	4623	964	
16		43-53	423-22		x				12	200	16	560	150	B.s
18		53-68	423-23		x				<	6,2	<	9,2	<	B.s
19		68-90	423-24	x					<	16	1,4	4,3	<	B.s
15	**SW3**	0-15	423-25		x			x	55000	1600	7	7000	<	
20		15-23	423-26	x					470	220	0,7	5300	<	
21		23-30	423-27	x					740	650	5,4	7800	<	
22		30-39	423-28		x				2400	1400	15	25000	<	
12		2/4C		x					7000	9000	<20	120000	NA	
14		LF				x			80	70	2,5	50	NA	
13		Frøy		x					7077	575	12	80	10	
34		*methanol*												
33		*Al-Foil*												
32		*Plastic*			x									

B.s.: Samples representing mainly background sand, i.a. the sediment layer below the cuttings material.

There was no obvious correlation between the general contamination levels (as measured) in the cuttings piles samples and the endocrine test responses. The cytotoxicity, that was apparent in 18 out of 32 samples, was perhaps the most obvious response indicated by this first screening. The cytotoxic response appeared to be randomly distributed among cores and depths. Both Beryl samples and Ekofisk samples were cytotoxic. The cytotoxic response appear to be distributed among samples with a large variety of contaminant concentrations, possibly indicating that not all toxic components were covered by the chemical groups analysed for.

Basically, judgement of endocrine effects is only relevant in samples not dominated by cytotoxicity. In the samples not suffering from cytotoxic impact, various effects were observed:

- Estrogenic effects were found in 7 samples.
- Anti-estrogenic effects (estrogen antagonism) were found in 5 samples.
- Anti-androgenic effects were observed in 4 samples.

The chemical parameters analysed clearly indicate the difference in chemical composition between the Beryl pile (OBM) and the Ekofisk (PBM/WBM), and also how unevenly the chemical pollutants are distributed with the depth in each core. Very high PAH levels were measured in many of the Beryl pile samples.

There appeared not to be any clear and obvious correlation of the ED-test responses observed and the concentrations of contaminants analysed. However, the estrogen antagonistic activity found seemed to occur preferably (beside LilleFrigg) in samples with high levels of BaP, which have a toxic action much resembling TCDD. None of the samples with estrogenic activity belonged to the high BaP category.

Cytotoxic and estrogenic responses were also observed in samples that contained significant influence of original seabed material, i.e. samples taken from below the cutting piles. In these samples the contaminant concentrations were considerably lower than in the samples dominated by the cuttings material.

Two samples showed no responses with any of the parameters examined. These were both Beryl samples and the contaminant levels did not significantly differ from the 16 other Beryl samples.

One sample stands out because it is reported to be both cytotoxic and estrogen antagonistic. This sample showed signs of cytotoxicity, but this trait was not expressed to the degree that β-galactosidase was not produced (Hutchings, pers.comm). Since no quantitative measures are given in this test, the response could be reported as seen.

25.2 Phase 2: YES/YAS, ER/AR-CALUX and DR-CALUX screening for estrogen, androgen and dioxin-like effects

The second phase of the ED work in this project was initiated as a result of the findings in phase I, where positive ED responses were observed in most samples not being cytotoxic. These observations suggested that EDC related effects of cuttings piles were an area of concern that should be pursued further.

25.2.1 YES / YAS results phase 2, dose response study

The results from the recombinant yeast assays in the second phase of the study are shown in Table 23. Eight selected samples from cuttings piles and one reference sediment sample were analysed. The result for each sample is presented as the percentage of the maximum response indicated by the positive reference chemicals in the two assays (i.e. estrogen or dihydrotestosterone). No clear effects related to estrogenicity and androgenicity were found. The negative response values observed for many of the cuttings samples indicate that the exposure solution is cytotoxic to the yeast culture. Figure 63 and Figure 64 show the concentration-response curves for the reference chemicals and the solvent extracts from the drill cuttings sediments, along with the relevant controls. Dose-response curves below the blank again suggest a cytotoxic effect of the exposure concentration. The same extraction procedure was used as in phase 1, except a 5-fold dilution was used as the starting concentration rather than the 20-fold dilution of phase 1.

As illustrated by Table 23 and Figure 63 the reference sediment (RF 3 RED SED) appear to show some estrogenic response at the highest doses, while all other samples either

Table 23: Estrogenic, androgenic responses and cytotoxicity effects in recombinant yeast to samples from drill cuttings piles. All results presented as percentage of estrogen or dihydrotestosterone maximum assay response. Data approximately zero indicate no estrogenic or androgenic effects. Cytotoxic responses are indicated by negative values.

	Beryl A			Frøy	Ekofisk 2/4A				Regoinal ref*	
Conc	V1-1 68-76	K2 4-10	K2 13-20	6A 2-6	V9 33-43**	SW2 0-7	SW2 40-50	V9 68-90	REF SED	BLANK
%	% Oestrogen yeast assay									
50	4	-20	-4	-20	-15	-31	2	-13	14	0
25	3	-19	-5	-19	-14	-29	2	-12	12	0
12	3	-13	1	-22	-15	-23	2	-3	8	1
6,25	2	-5	1	-5	-7	-18	2	-1	6	1
3,13	2	-3	-1	10	-17	-17	3	-1	-9	3

	Beryl A			Frøy	Ekofisk 2/4A				Regoinal ref*	
Conc	V1-1 68-76	K2 4-10	K2 13-20	6A 2-6	V9 33-43**	SW2 0-7	SW2 40-50	V9 68-90	REF SED	BLANK
%	% Androgen yeast assay									
50	-18	-46	-10	-45	-42	-46	-4	-3	10	-2
25	-20	-46	-6	-36	-43	-42	0	0	-2	0
12	-15	-38	1	-46	-40	-44	1	1	-2	2
6,25	-12	-20	3	-45	-21	-44	3	1	-3	2
3,13	-6	-8	7	-40	-10	-32	8	5	-2	7

Conc % reflects the exposure dose in incubation solution relative to the cuttings material weight
SW2 core similare position as SW3 core, material stored in Al-Foil
K2 core similare position as K1 core, material stored in Al-Foil
All results presented as percentage of estrogen or dihydrotestosterone maximum assay response
*Selected as a regional reference station, supposed to be unffacted by oil activity
** Sample containing enhanced levels of PCB

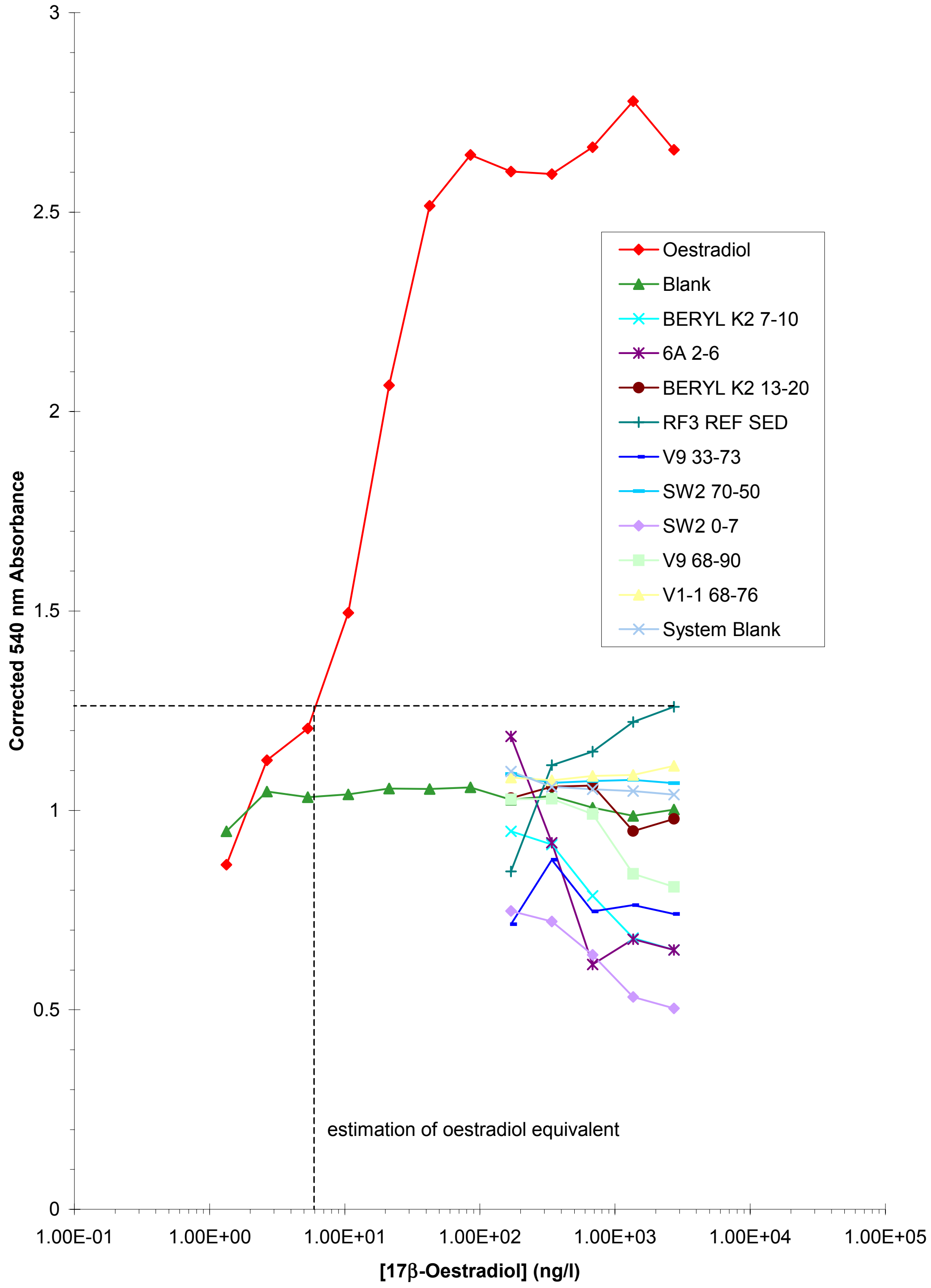

Figure 63: Dose-response curves of recombinant yeast estrogen assay (YES) of extracts from drill cuttings piles samples and reference chemical (estrogen).

appear to be cytotoxic (negative values) or they exhibit no response. There is also a trend that the cytotoxicity decreases with falling concentrations.

The reference sediment is assumed to be relatively uncontaminated (see Part 1), although it has not been examined in the current work. The finding of estrogenic responses is therefore unexpected.

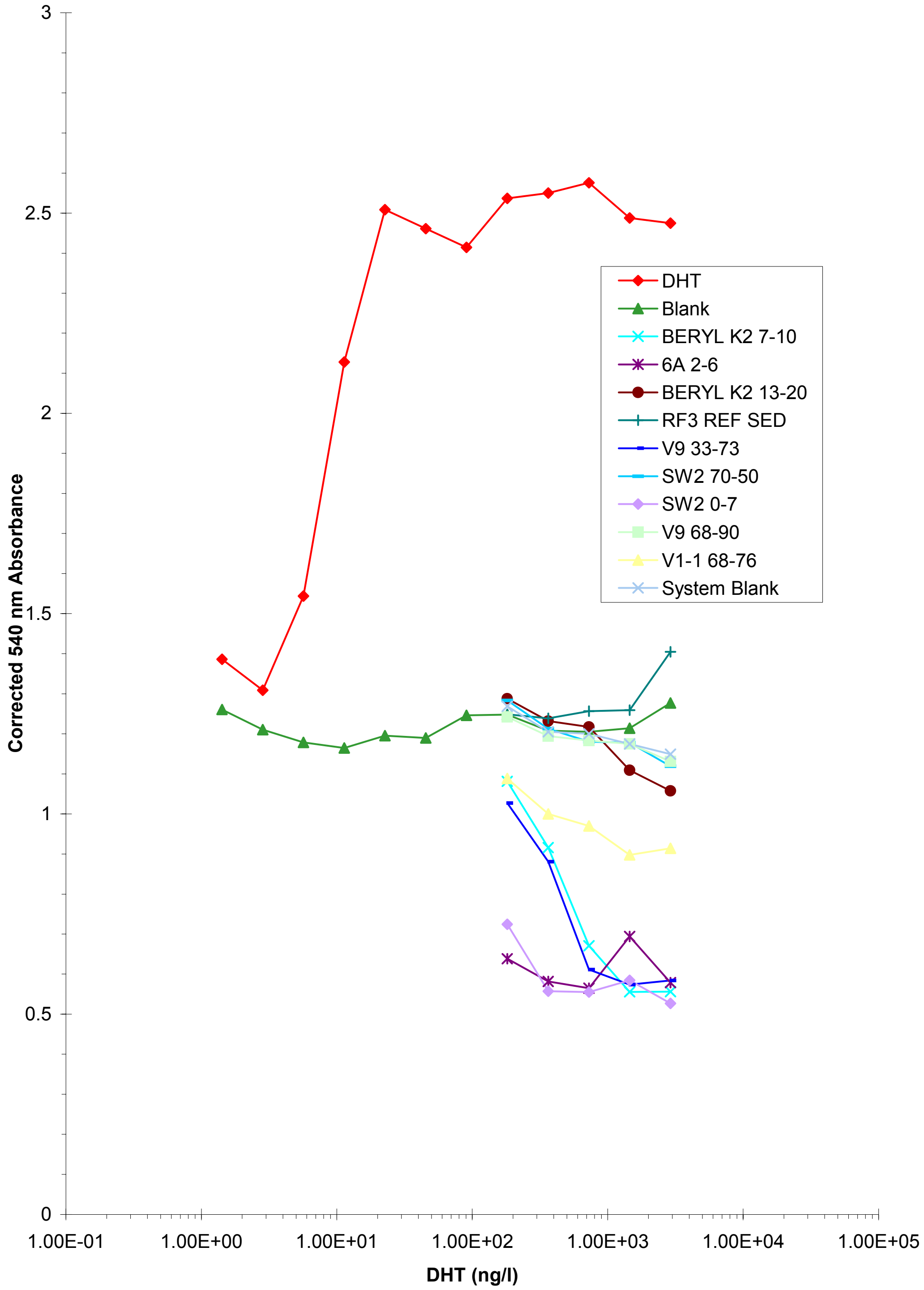

Figure 64: Dose-response curves of recombinant yeast androgen assay (YAS) of extracts from drill cuttings piles samples and reference chemical (dihydrotestosterone).

Similarly, for the androgenic responses there appear to be two groups of samples, one being clearly cytotoxic, again with decreasing cytotoxicity as the concentration is reduced, the other being close to the blank. One sample showing high cytotoxicity (Ekofisk V9 33-43) was also reported cytotoxic in phase 1. The V9 68-90 sample apparently was neither cytotoxic nor androgenic in phase 2, but was reported cytotoxic in phase 1. The V9 68-90 sample apparently is less toxic (Table 23), and hence the observations are as expected.

25.2.2 ER-CALUX and AR-LUX

The results of CALUX based estrogenicity and androgenicity testing of three selected samples from cuttings piles are shown inTable 25. The full report is included in Appendix 10.

In the ER-CALUX assay, all three samples of cuttings were found to show a slight estrogenic activity at the highest dosages used although maximum values of the assay were not reached. Using higher concentrations was only possible to a limited extent due to cytotoxicity. Only in the sample *Beryl-slice 68-76, code V1-1* a quantifiable signal of 1.3 nmol EEQ/liter undiluted extract was found. In samples *Beryl-k2 (core) slice 4-10* and Ekofisk *core SW2, slice 0-7, 654815,* a response was present but not quantifiable in the undiluted samples. However upon using higher dosages a response value could be calculated (see also Appendix 10).

Also in the AR-LUX assay, all cuttings piles samples were found to show a slight androgenic activity at the highest dosages used although maximum values of the assay were not reached. Using higher concentrations was only possible to a limited extent due to cytotoxicity. Developing a more extensive extraction procedure might be a solution to this problem. The dose response relationship for sediment [R1] was not linear, suggesting the presence of anti-androgens or other compounds interfering with the androgen pathway. Furthermore, when measuring the samples six weeks (AR-LUX-2) after the first measurement (AR-LUX-1) androgenic activity in sample [R1] and [R2] had virtually disappeared while [R3] remained constant, suggesting the presence of unstable (androgenic) compounds in [R1] and [R2].

Table 24: Estrogenic and androgenic responses in selected samples evaluated with the ER-CALUX and AR-LUX assays, respectively.

Rogaland code	*TNO code*	*AR-LUX-1 (ng R1881/ gram)*	*AR-LUX-2 (ng R1881/ gram)*	*ER-CALUX (ng 17β-estradiol/gram)*
Beryl-slice 68-76, code V1-1	[R1]	38.81 (+/- 6.94)	X	0.46
Beryl-k2 (core) slice 4-10	[R2]	21.46 (+/- 5.36)	X	0.21
Ekofisk 2/4 A SW2, slice 0-7, 654815	[R3]	35.61 (+/- 3.81)	37.13 (+/- 9.65)	0.28 (+/- 0.04)

25.2.3 DR-CALUX

The results of the DR-CALUX assay of two selected Ekofisk cuttings piles samples are shown inTable 26. One of the two cuttings samples analysed (Ekofisk V9 33-43) contained high PCB concentrations, namely 964 ng/g ΣPCB. The other Ekofisk sample

(SW2 40-50) has not been analysed directly. The sample was however taken within 15cm from the SW3 sample, both sub-sampled in a large box-corer sample. Since no PCB was detected in the corresponding SW3 layer, this is believed to be representative also for the SW2 sample.

As judged from the DR-CALUX results, considerably higher TCDD toxicity was found in the cuttings piles sample with high PCB content, possibly indicating the presence of toxic PCB congeners. The TCDD-TEQ value for this sample was 59 pg/g TCDD equivalents. In the DR-CALUX assay a sample is measured after initial degradation of less stable components, like e.g. PAH. It is therefore not likely that the response observed is due to an eventual presence of larger PAHs, such as benzo[a]pyrene, but may rather be attributed to toxic PCBs or eventually other persistent dioxin-like components.

The BDS reference material reported is the results measured of an extract of TCDD spiked sediment. The other samples are measured relative to the dose-response curve produced using this sample.

Table 25: Dioxin like toxicity evaluated in selected samples of drill cuttings material evaluated with the DR-CALUX assay. The data are expressed as picogram 2,3,7,8-TCDD-TEQs per gram dried sediment (24 hour) after correction for procedure blank.

Sample	**24 hour exposure TCDD-TEQ**	
	pg/g dry cuttings	**S.D.**
Ekofisk V9 33-43*	59	1,2
Ekofisk SW2 40-50	9,2	0,3
Reference material BDS	113,8	7,3

*Sample containing elevated concentration of PCB
n.d. Not detected
S.D. Standard deviation

26 Discussion

The discussion section has been split into two main sections. The first deals with the cuttings specific constraints and how this can be related to the more general literature findings of relevant ED work. The second section discusses the findings of the assays carried out in this project. The implications of these results are further discussed against the general findings of the first section.

26.1 General discussion of cuttings piles

26.1.1 Possible sources of EDCs in drill cuttings piles

A number of the chemicals used in offshore E&P activity and that eventually may occur in cuttings piles may potentially act as endocrine disruptors. However, the type of chemicals known to have endocrine disrupting effects is a very large and heterogeneous group, including both organic and inorganic compounds, see Menditto and TurrioBaldassarri (1999) for overview. Among compounds known to act as EDCs are the break down products of alkylphenol ethoxylates (APnEO), chlorinated hydrocarbons (including PCBs), certain trace metals, metallorganic compounds (e.g. tin containing compounds), nitrogen heterocyclic compounds, nitrocompounds, nitrogen bases, thioethers, carboxylic esters, and others. Few studies have in details addressed the occurrence of chemicals with potential endocrine impact in discharges from the oil and gas industry.

A large amount of alkylphenol ethoxylates (APnEO) has been used in several offshore oil and gas production applications in the North Sea oil fields. The largest inputs were from rig washes, which contained up to 50% APnEO, and were used in large quantities, up to 2 tons per day per site. APnEO mixtures have also been used extensively (more than 100 tons per year per installation) as cutting cleaners emulsifiers and wetting agents (Blackburn, Kirby et al. 1999; Lye 2000). Concern over the possible environmental effects of APnEOs has led to PARCOM recommendation 92/8 to phase out use of nonyl- and octylphenol ethoxylates in household (by 1995) and industrial (by 2000) detergents. In Norway, this has led to a ban of all use of nonyl- and octylphenol ethoxylates offshore. In the UK sector a phase out of all use of APnEO is initiated.

As exemplified by the discharge data from Beryl A, given in the background section of the present study, there is such an array of chemicals used and discharged in connection with the drilling process that it is difficult to pinpoint one chemical possibly responsible for the effect. Possible synergistic effects from a complex mixture of the chemicals that can have endocrine disruptive effects will make the situation more complex. If the chemicals directly used in the mud were responsible for the observed effects there could be a pattern that the samples with high concentration of THC would be the samples showing endocrine disruptive effects. The first screening with the Yeast screen method (see below) did not show any clear relation of the effects to THC levels. Furthermore the fist attempt showed that more than 50% of the samples showed to be cytotoxic. If the samples show cytotoxic responses the method can not be used at that concentration. The work done here is an attempt to use simple screening methods to find endocrine disruptive effects of the cuttings. Linking to chemicals present in the material will require extensive analytical protocols to analysis for the active chemicals responsible for the effects.

26.1.2 Studies of cuttings piles toxicity

One striking feature of cuttings piles is the variability related to chemical content and texture. Hence, in toxicity testing it is difficult to link the eventual responses observed to specific single compounds. One way of dealing with this complexity is to use integrative effect parameters, such as mortality rate, growth rate or community changes in exposed organisms. Beside rock fragments, the drilling mud is the major constituent of the cuttings piles. Evaluation of toxicity of drilling muds is based on the use of standardised acute tests. No reported study has measured endocrine related effects of bulk material or extracts of drill cuttings piles.

Examples of relevant toxicity studies includes:

- Neustadt, Marr et al. (1995) used the luminescent bacterium *Photobacterium phosphoreum* exposed to samples of oily drilling cuttings. Samples of cuttings from different depths (representing different ages, up to 15 years) showed similar toxicity (depression of bioluminescence) from the aqueous and the mixed-solvent extracts. They assumed therefore that the toxic component did not originate from the drilling mud used, but from additive chemicals which has a rather higher solubility in water than the hydrocarbons.
- Plantecuny, Salenpicard et al. (1993) studied effects of diesel oil-based cuttings (and other contaminated sediments related to oil exploration) on microphyto- and macrozoobenthic communities in situ over a 1 year period. They observed strongest toxicity responses in the experimental group exposed to cuttings, where significant impact (a decreased number of grazers and consequently lower grazing rates of animals) was apparent also after one year.
- Daan, Booij et al. (1996) conducted a comparative macrofauna community study of discharge sites of oil-based drilling muds (OBM) and water-based muds (WBM). Even 8 years after termination of OBM discharges, they found significant impact on thew macrofauna within 500 m downstream of the discharge area, whereas adverse effects on the benthic community were not observed in the case of WBM discharges.
- Cranford and Gordon (1991) found increased mortalities, cessation of reproductive and somatic tissue growth, decreased body component condition indices, and failure to accumulate lipid reserve in sea scallops (*Placopecten magellanicus*) exposed to OBM cuttings.
- Payne, Fancey et al. (1995) studied dose-response relationships for a variety of indices in a chronic toxicity study with winter flounder (*Pleuronectes americanus*) exposed to sediments contaminated with drill cuttings enriched in aliphatic hydrocarbons. By looking at organ and body condition indices, muscle and liver energy reserves, mixed-function oxygenase detoxification enzymes, blood parameters, and liver and gill histopathology they found no evidence of dose-response relationships, indicating the aliphatic component of complex hydrocarbon mixtures to be relatively nontoxic.

26.1.3 Aquatic endocrine effect studies

Obviously, mortality, growth-rate and community changes are not appropriate effect parameters for detection of endocrine related impacts of contaminants. Indeed, in effect studies where for example the mortality rate of the study animals is significantly increased, the *in vivo* levels of endocrine related parameters may be severely influenced due to general intoxication, and not due to endocrine related effect phenomena. Eventual direct cytotoxicity of chemicals occurring together with ED compounds may mask the endocrine effect. Thus, in order to detect endocrine related effects sublethal exposure concentrations must be used.

One good example of endocrine disruption is the action of the biocide TBT (tributyltin) that at very low concentrations induce the imposex condition (pseudohermaphroditism) in females of certain marine gastropods. The effect is due to an inhibition of the aromatase mediated biotransformation of testosterone (Bettin, Oehlmann et al. 1996). In the ultimate stage the imposex condition causes female sterility and this phenomenon has been linked to the long-term decline of populations of certain snail species at impacted coastal locations. The TBT-imposex effect is fairly well described from the molecular level and up to changes of population size. The discovery of this effect has also resulted in a phase out process of TBT use in antifouling paint for ships.

Another pollutant effect phenomenon that presumably is linked to pollutant-induced endocrine disruption is the occurrence of disturbed male gonad development in fish in certain British rivers and estuaries. It was discovered that wild male fish had abnormal testis histology as well as high levels of the protein vitellogenin in their blood (Jobling, Nolan et al. 1998; Allen, Scott et al. 1999). Vitellogenin (VTG) is a yolk precursor protein and is normally related to the development and maturation of eggs in the female fish. In other words, the male fish in the impacted waters seemed to be in a condition of disturbed sexual development, and it was subsequently found that this effect was attributed to the occurrence of pollutants in the water. Beside vitellogenin (VTG), also other proteins related to the female egg development can be used as biomarkers for evaluating xenoestrogenic impact in exposed specimens, one example is zona radiata protein, ZRP, also called eggshell-proteins. Soon after the discovery of abnormal VTG levels in male and juvenile fish in the British rivers, extensively exploited chemical formulations such as some species of nonylphenol, octylphenol and phthalate plasticizers were found to be estrogenic (White, Jobling et al. 1994; Jobling, Reynolds et al. 1995; Routledge, Sheahan et al. 1998). In the laboratory, induction of VTG and/or ZRP by nonylphenol has been verified in a number of studies, see review by Servos (1999). These findings have been key factors for the initiation of a phase out process for the use of nonylphenols and octylphenols from various industries, also from the E&P sector. Presently, other alkylphenols are being investigated with regard to their xenoestrogenic potency.

Another likely endocrine disruption phenomenon is the reproductive failure of alligators in several contaminated lakes in Florida, USA. The earliest observation was at Lake Apopka in central Florida where the alligator population declined dramatically between 1980 and 1987 (Guillette, Gross et al. 1994; Guillette, Woodward et al. 1999). Endocrine-disrupting chemicals, specifically the DDT metabolites p,p-DDE and p,p-DDD, are suspected as causal agents. But more recently, attention has also been focussed at to two nematocides that are established reproductive toxins in humans, dibromochloropropane (DBCP) and ethylene dibromide (EDB), which could also have played a role in the reproductive failure observed (Semenza, Tolbert et al. 1997). Crain, Guillette et al. (1998) showed that both the levels of sex-steroid hormones and thyroid hormones are influenced in impacted alligators and the endocrine alterations reported are hypothesized to be a response to embryonic exposure to endocrine disrupting contaminants.

In turtles, Willingham and Crews (1999) and Willingham, Rhen et al. (2000) have examined the endocrine disruption potential of PCB aroclor 1242 and the pesticides toxaphene, dieldrin, p,p'-DDD, cis-Nonachlor, trans-Nonachlor, p,p'-DDE, and chlordane. They found that at environmentally relevant concentrations detected in alligator eggs from Lake Apopka, trans-Nonachlor, cis-Nonachlor, aroclor 1242, p,p'-DDE, and chlordane overrided a male-producing incubation temperature and result in female hatchlings in the red-eared slider (*Trachemys scripta elegans*), a turtle with temperature-dependent sex determination (Willingham and Crews 1999). In was also observed that treated male turtles exposed to Aroclor 1242 or chlordane exhibited significantly lower testosterone concentrations than controls, whereas chlordane-treated females had significantly lower progesterone, testosterone, and 5 alpha-dihydrotestosterone concentrations relative to controls (Willingham, Rhen et al. 2000). Thus, the effects of these endocrine disruptors extend beyond embryonic development, altering sex-steroid physiology in exposed animals.

A considerable number of mammalian studies of EDC effects are conducted, most with rodents (rat mostly) as model organisms. Rodent studies are necessary since many mammalian species are highly vulnerable. Wildlife populations of several mammalian species are hypothesized to be in treat due to EDCs action. In particular this includes carnivores such as the otters, Baltic gray and ringed seals, and harbor seals (Holland), polar bear (at Svalbard), various whale species, and others (Gray, Ostby et al. 1998; Chiu, Chiu et al. 2000; Vos, Dybing et al. 2000).

The question of whether human health is influenced by low-dose long-term exposure to endocrine disrupting chemicals has attracted the attention of a considerable number of scientists worldwide, see reviews by Baccarelli, Pesatori et al. (2000) and Foster (2001). Many of these studies have been focused on the exposure to chemicals mimicking estrogenic or androgenic actions, but also other hormonal pathways such as the hypothalamus-pituitary unit, pineal gland, parathyroid and calcium metabolism and adrenal glands are being studied. A substantial body of evidence has accumulated that human semen quality may be deteriorating, a trend suggested to be due to estrogenic EDCs, e.g. (Irvine 2000). However, although there is now a large quantity of data indicating that this is a plausible hypothesis, the outcome of these studies is not conclusive about this effect nor about other possible endocrine related effects of EDCs in humans. Still, the weight of evidence available provides cause for concern and reason for further research.

To summarise, studies of endocrine disrupting effects of contaminant chemicals are conducted with a broad range of aquatic species, ranging from invertebrates to mammals. Many new studies on this subject are ongoing. New endocrine effect parameters in various species emerge as investigations in this field of environmental science proceeds. Critical evaluation of the relevance of discovered cause-effect relationships is necessary in order to ensure the proper basis for decisions related to pollutant discharge and pollution control situations.

A set of relevant effect parameters is needed for estimating the actual risks of a contamination to cause eventual impaired health condition of organisms and populations. Some of these effect endpoints have already been simplified into screening techniques with use of in vitro effect detection kits and recombinant/modified cell based assays. The outcome of this process in the long run will be the establishment of a set of certain effect endpoints in defined species (and/or in defined screening tests). Effect parameters should be investigated in order to estimate the risk of long-term endocrine pollution impact in the environment.

26.2 Discussion of results from present study

26.2.1 Study design and selection of samples

The present investigation is a pilot study of the eventual presence of endocrine acting substances in North Sea cuttings piles. As a first step screening the study have used cell-culture tests based on recombinant yeast cells and genetically modified cancer cells. These tests are designed for screening estrogenicity and androgenicity related effects. A test of dioxin-like toxicity in cuttings containing high levels of PCB was also conducted since this kind of effect may also be relevant for endocrine effect endpoints. Cuttings piles from two fields were included in the study, the oil-based pile at Beryl and the part water-based/pseudooil-based pile at Ekofisk 2/4A. A few samples from other piles have also been included initially.

In order to keep down the analytical costs, much of the analytical work in this study was conducted with a few selected samples only. The sample numbers and selection of specific samples to be analysed with the various assays were based firstly on the responses seen in the phase I YES/YAS assay, and on the contamination type and concentration of the samples. Consequently, the ER-CALUX/AR-LUX assays were used to analyse three samples. The DR-CALUX was used only with two samples, but these samples were carefully selected to represent samples from the Ekofisk pile with high and low concentrations of PCB, but otherwise seemingly similar. As far as possible the prioritised samples were selected on the basis of their chemical content.

26.2.2 YES/YAS study

In the first phase of this pilot project recombinant yeast assays were used to screen cutting piles extracts for endocrine activities. Estrogenicity, anti-estrogenicity, anti-androgenicity were measured in a number of the cuttings piles samples analysed (as seen in results Table 22). However, the effect picture recorded was highly complex and not straightforward to interpret. Based on the chemical data available a correlation between the observed ED effects and the overall contamination level cold not be identified. It was also apparent from the results that many of the cuttings piles samples contain toxic components that significantly influenced and hampered the outcome of the analyses.

In the second phase of the study, with dose-response YES/YAS assays, similar observations were made. Again, cytotoxicity of the cuttings was a dominating effect. In several of the cytotoxic samples, the observed toxicity did not show any clear dose-responsive pattern. In several samples cytotoxicity was seen even at the lowest test concentration. A few of the cuttings piles samples were found to have lower toxicity. In these however, there was no clear effects related to estrogenicity or androgenicity. In the reference sediment (RF3-REF SED) a weak response in the estrogenicity assay and a possible weak response at the top concentration in the androgen assay were observed.

Generally, yeast cells being in a condition of cytotoxic stress are likely to have limited value as test cells for endocrine effects. The primary aim of the present study was to assess endocrine activity of the cuttings piles materials. Thus, as for the YES/YAS assays, the cytotoxicity occurring in the test runs has reduced the opportunity for achieving the main objective of the study. The dilution range chosen was intended to be a compromise between diluting enough to reduce/avoid cytotoxicity, and to not dilute the potential EDC activities out of solution. However, based on the yeast assays results the samples were not sufficiently diluted. It is difficult to speculate whether it is possible, with the current test conditions, to find a suitable testing range, as the cytotoxicity possibly may be shadowing any potential ED effects. The observed cytotoxicity in the exposed yeast may have been caused by any of a number of chemicals present in the sediment. Hence, without extensive chemical analysis it is not possible to indicate a likely causative agent.

Some EDCs may induce effects even when present in very low concentrations. It is possibly that the yeast assays could have produced better clarity of ED effects if the cells had been exposed to lower, and more environmentally realistic, exposure concentrations. However, it is also possible that the yeast cells are more sensitive towards toxic action of compounds being present in cuttings, making them less suited for testing such samples. This should be tested prior to further use of the yeast based ED assays in future studies on cuttings. Alternative exposure designs, ED tests approach, test parameters and test organisms may possibly be better for such studies. This is briefly discussed in the future studies section.

26.2.3 ER-CALUX/AR-LUX

Only a few cuttings piles samples were analysed with the luciferase modified cancer cells which are assaying estrogenicity and androgenicity. It is interesting though that evidence of weak hormonal activity (estrogenicity and androgenicity) was found in all cutting piles samples analysed in these test-runs. However, no full dose response curves could be made from these data, again, this was due to cytotoxicity and/or compounds interfering with or antagonising the steroid receptor pathways. Thus, and similar as for the YES/YAS tests, an optimisation of the cuttings piles exposure criteria seem to be needed. Improved extraction procedures might prove useful in this respect. Such as fractionating samples in for instance an oil-fraction, a precipitate fraction and a soluble fraction. This might also provide valuable extra insights into the characteristics of the compounds involved.

From the few LUX-based results recorded in the present study it was apparent that the estrogenic activity occurred at significantly lower extract concentration than the androgenic effect. However, when comparing the data for androgens and estrogens one has to keep in mind that the concentrations needed for an estrogenic effect generally are lower than for androgens in these assays. Thus, having a hundred times more androgens than estrogens don't necessarily mean that the potential risks involving androgens are a hundred times higher. However, no risk assessment regarding these subjects has been carried out so far.

In the present pilot study, only few LUX based test measurements were carried out. The samples analysed were selected based on their response in the phase 1 yeast assays and based on their contaminant level. E.g. the Beryl V1 68-76 sample reported estrogen and androgen antagonistic in phase 1. In this assay, unstable androgenic activity was seen and some estrogenic activity. The second Beryl sample was not analysed directly in phase 1, but corresponds to the Beryl K1 1-10 sample of phase 1, that then reported cytotoxic, but at lower contaminant levels than the above mentioned sample. Likewise, the Ekofisk sample (SW2 0-7) corresponds to the SW3 0-15 from phase 1. In the first phase estrogenic and androgen antagonistic activity was seen. In this phase 2, more stable androgenic and some estrogenic activity was observed.

As can be seen, the data from the two tests are not highly comparable. Considering also the low number of samples analysed by this test, well-considered judgements regarding the levels of steroid-like activity in cuttings piles can thus hardly be made based on these data. Additionally, cytotoxicity of exposure solutions was a problem also for these tests. However, the assays did indicate that estrogenicity and androgenicity related effects occurred in the samples considered. This may indicate a potential for further studies. However, the problems with cytotoxicity have to be avoided in eventual new studies.

26.2.4 PCBs and DR-CALUX

High concentrations of PCB were detected in some samples of cuttings material in phase one of the present study. The work conducted in the second phase has aimed at identifying and possibly quantifying the impacts that this presence of PCBs may have. One major concern of PCBs is the congeners that structurally resemble dioxin (i.e. 2,3,7,8 TCDD), and that hence are capable of binding to the Ah-receptor of cells.

For the purpose of quantifying the effects of such PCB congeners, the DR-CALUX assay was used on two selected cuttings samples, one high and one low in PCB content. The test results revealed a considerably higher DR-CALUX response signal in the PCB containing sample. This observation indicates a significant difference between the two samples, the sample containing the highest PCB level also having the highest dioxin-like toxicity.

The use of DR-CALUX assay was intended above all to indicate a difference in TCDD toxicity in the two samples. The assay does not distinguish PCB from other dioxin-like compounds. However, the thought behind this approach was that if the responses differed much between samples that were similar (in the large picture) with respect to the chemical groups except PCB, this would indicate the relative contribution coming from the PCB fraction of the sample.

A fingerprinting exercise based on the “Dutch 7 PCB congeners” measured in the sample was carried out to eventually identify the PCB mixture(s) present in the cuttings material (NET, 2001). The fingerprinting suggested that part (about 20%) of the PCB congener profile recorded in the relevant cuttings sample is the PCB mixture Aroclor 1260. Such PCB identification based on the content of only 7 congeners is perhaps suggestive, but as an example, Table 26 shows comparative calculations based on given TEF values for the congeners present in this PCB mixture. A theoretical calculation of TEQ was conducted, basing the relative concentration of each single congener that has a TEF value attached to it on its suggested ratio in such a defined Aroclor 1260 mixture. This information can be obtained from EPA (www.epa.gov). When relating the suggested relative abundance of the different congeners to the measured PCB concentration in the sample and multiplying this value with the given TEF value for each congener, the calculated TEQ value is about 100pg/g (Table 26). This value corresponds fairly well with the measured TEQ of 59pg/g, which was estimated from the DR-CALUX assay results, even though the calculated 100pg/g accounts for parts of the PCBs present only. However, this may substantiate an assumption that the PCBs have a major influence on the total response seen.

Though it is not suggested that the findings of the DR-CALUX support the PCB mixture identification, the relatively coinciding results of the measured and calculated TEQ values supports the assumption that PCB (as a group) causes a significant portion of the TCDD related effects observed in the present cuttings sample.

Table 26: Calculated TEFs and TEQ (sum TEF) based on the composition of the PCB mixture Aroclor 1260, and the relative abundance of congeners, together with total PCB concentration in the present cuttings piles sample. The percentage abundance in Aroclor 1260 is from EPA. The calculated concentration of each presented congener in the V9 core is based on the measured concentration of the Dutch 7 congeners and the relative abundance of these, also taking into account that about 20% of the PCBs in the sample is Aroclor 1260. These numbers come from the NET report (NET, 2001).

Congener	**TEF**	**Calculated**	**Abundance in Aroclor 1260**	**TEF**
		V9 36-43		
		µg/kg	**%**	**pg/g**
105	0,0001	26,4	0,22	2,64
118	0,0001	57,6	0,48	5,76
156	0,0005	60	0,5	30
167	0,00001	22,8	0,19	0,228
170	0,0001	480	4	48
180	0,00001	1320	11	13,2
Sum TEF from PCB:S				99,8

27 Future studies

The biological relevance of the data presented in this work has not been discussed to any extent. There has been no attempt to relate the few “numbers” measured to effect observations of higher organisms. In addition, parameters like the extraction methods used distances the observed results from the natural conditions. It is therefore impossible to know whether ED effects and presence of EDC really is a concern of cuttings piles or not. However, based on the fact that some responses actually are seen, future studies are suggested.

27.1 Cell-culture assays

Based on the present pilot-study, the use of cell-culture tests of endocrine action in cuttings piles is clearly feasible. However, in follow-up studies with this approach the exposure regimes must be significantly adjusted in order to avoid cytotoxicity in the test cells. Less concentrated test solutions (lower dose-range) seem to be a obvious necessity, but the adjustment could also involve the use of improved extraction procedures such as fractionating samples in for instance an oil-fraction, a precipitate fraction and a soluble fraction. These fractions may then be used separately and eventual combined for the effect test. This kind of separated exposure approach might also provide valuable extra insights into the characteristics of the compounds involved in eventual effects recorded. Alternatively, the use of seawater-based extraction procedures could give an exposure solution that was less chemically complex, and possibly less acute toxic as well. Interestingly, an exposure solution made by this approach could be considered to reflect more realistically the process of compounds leaching out from cuttings piles in the field. In task 2c, leaching and direct uptake from the cuttings piles sediments has already been addressed.

27.2 Low-dose, long-term tests and higher organisms

Further research addressing endocrine activity of cuttings piles components should emphasis on the use of sublethal and long-term exposure conditions as well as using environmentally realistic pathways for contaminant exposure and uptake. In such studies, higher organisms, such as crustaceans and vertebrates (fish), should be used. Like in the task 2c exposure system, several species should be exposed simultaneously. The selected species should have different behaviour and metabolic pathways, thereby showing distinct responses to the exposure. In a simplified mesocosm approach it would be wise to blend the various cuttings pile layers obtained from a pile into one bulk sample. By doing this, only one artificial cuttings piles sample (but eventually in several parallels) is tested from each site. This greatly reduces the extent of the study, and hence, more resources can be used for detailed analyses of effects in the study animals exposed to the sample. The blended cuttings piles material to be tested should be carefully analysed for general and more specific chemicals. The eventual presence of nonylphenol and octylphenol related compounds as well as other known EDCs should be considered in more details. Exposure to various contaminant concentrations should be included, either by testing artificial (blended) pile material from several locations, or by testing various dilutions of the cuttings sample in inert reference sediments, or both.

The actual exposure of test animals may be performed through several techniques. By spiking an inert sediment with various amounts of the blended cuttings pile sample, a dose response model can be constructed. Such spiked sediments used in an exposure facility may either be left stable during the study, or it may be mixed either temporarily (e.g. by physically disturbance, slurrying) or semi-continuously (e.g. by bioturbation).

The use of bioturbation organisms, e.g. sediment digging polychaetes, in low-dose sediment studies would be in particular be interesting, since this allow the establishment of a simplified food-chain approach in the test model (e.g. annelid-fish). Such biological factors would also contribute to the environmentally realism of the exposure-uptake-effect chain. The task 2c of the UKOOA phase II projects has already addressed this approach, focusing mostly on chemical uptake and food chain impacts from the water column. Effect studies specifically addressing ED effects could rely on some of the issues of the task 2c, but should include other sets of biomonitoring and effect parameters.

By using higher organisms such as fish, a range of relevant effect parameters may be included in cuttings pile effect studies. Beside the endocrine effect endpoints addressed in the present investigation (steroid receptor agonism and antagonism) other endocrine systems, such as thyroid hormone related endpoints, can be addressed. In particular for cuttings piles found to have high content of PCBs the thyroid related effects should be considered. Estrogenic and androgenic related effects are easily measurable in fish, and kits for detecting such parameters are commercially available. Several species of fish may be feasible for such studies, depending on the study approach (with or without bioturbation organisms, etc) and the design of the exposure facility (size of tanks, etc).

Even though the primary aim of an eventual follow-up study with fish will be on endocrine disruption effects there are good reasons for including certain other biological effect parameters. Examples of such are biliary PAH metabolites, PAH related DNA adducts and histological examination of various internal organs (i.e. gonads, certain endocrine glands), the latter especially in long-term studies. Without going into details, non-endocrine effect parameters contribute with information about the general health condition of the test organism. This information is valuable also for the interpretation of eventual ED-related effects (or absence of such) in the cuttings piles exposed organisms.

28 Conclusions

- Signs of endocrine related activities (estrogenicity, anti-estrogenicity and anti-androgenicity) were detected in methanol extracts of drill cuttings piles originating from North Sea oil fields when tested with cellular assays based on recombinant yeast cells and genetically modified cancer cells. The responses seen were rather weak.
- Dioxin-like activity as measured with the DR-CALUX assay was found in one cuttings pile sample that contained high concentrations of PCB, indicating a possible presence of adverse PCB congeners in this cuttings pile.
- Based on the available chemical and biological data in the present study, it was not possible to see clear correlation between the observed endocrine effects and specific

chemicals detected in the cutting piles, or between the observed endocrine effects and the overall contamination level in the cuttings pile evaluated.

- There was, however, some indication that elevated BaP levels in the cuttings piles correlated with anti-estrogenic (estrogen antagonist) activity, but this need to be further evaluated.
- Cytotoxic responses in many of the cuttings pile extracts hampered the use of the cellular assays, especially the recombinant yeast based estrogenicity and androgenicity assays, and this may have masked any eventual sublethal ED activity in these cuttings pile samples.
- Due to the rather limited volume of the present effect results, test-related obstacles (Cuttings pile cytotoxicity) and the obvious chemical complexity of cuttins piles, the present study is not conclusive on whether or not endocrine acting substances in North Sea cuttings piles are a significant environmental problem.
- Further research addressing these issues is needed and these studies should emphasis on the use of long term exposures of higher and intact organisms (e.g. fish) to more realistic cuttings pile exposure regimes (e.g. mesocosm). Such studies should be conducted at clearly sublethal exposure concentrations (and dose-ranges) and they should also include endocrine related activities other than those linked to estrogenicity and androgenicity (e.g. thyroid related effect endpoints). Such studies should also characterise sufficiently both the chemical composition of the cuttings pile exposure agent used, the eventual bioaccumulation of causal agents in the test organisms, as well as including other relevant indicators of pollution stress in the exposed test organisms.

29 References

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