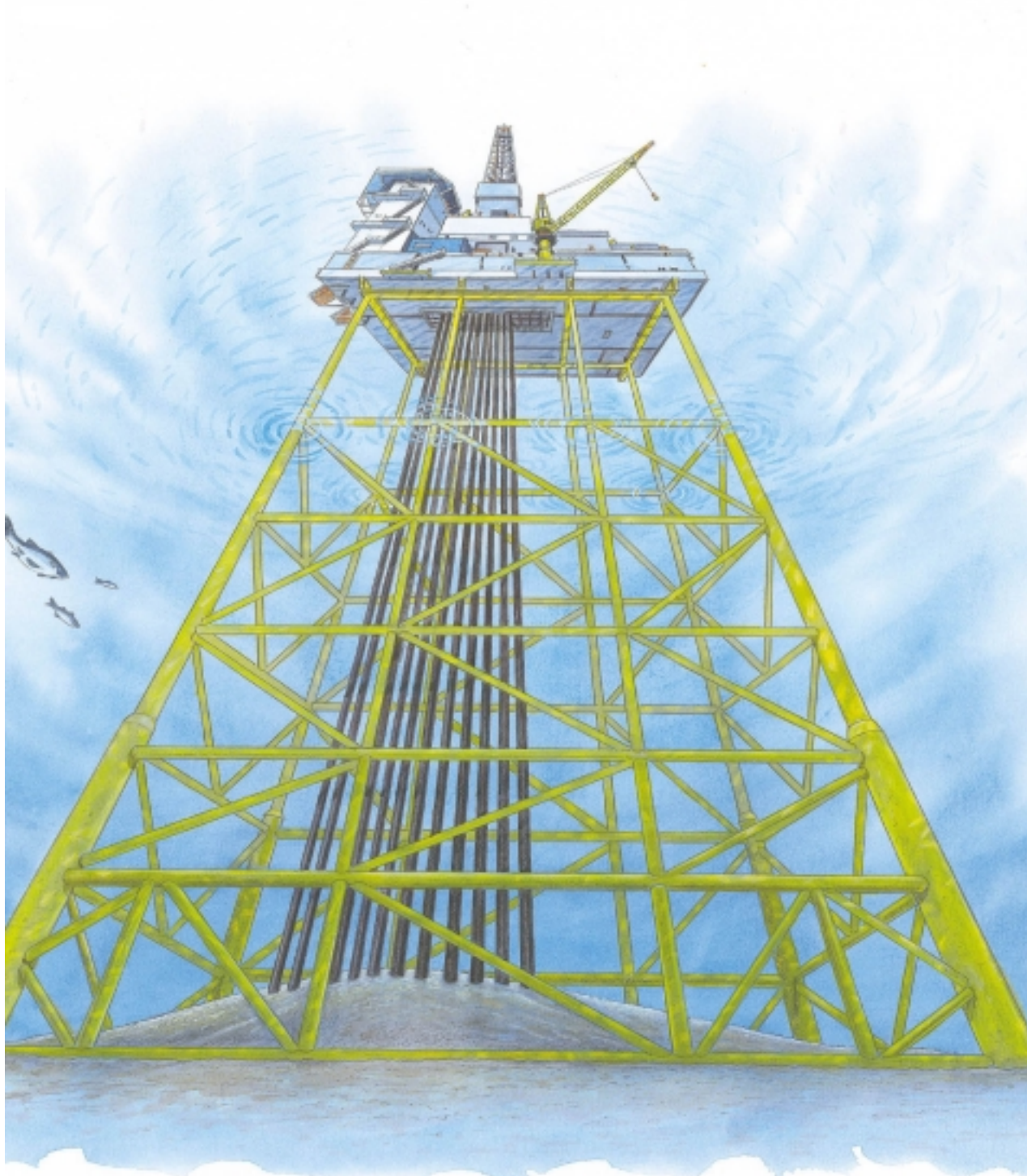


*UKOOA Drill Cuttings Initiative Research and Development
Programme*

Project 1.2: Cuttings Pile Toxicity



**UKOOA Drill Cuttings Initiative Research and
Development Programme
Project 1.2 :Cuttings Pile Toxicity**

Environment & Resource Technology Ltd
RF – Rogaland Research

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Scope:

1. Review cuttings components and available information from Cordah.
2. Review and evaluate the toxicology of components
3. Review and evaluate information on chemical bioavailability
4. Identify gaps in information.
5. Collate cuttings sample inventory.
6. Collate inventory of drilling mud types
7. Establish relationship to drilling history.
8. Identify likely toxicological effects
9. Assess strategies for future work.

Key-words:

Cuttings piles, oil-based cuttings, drilling fluids, environmental impacts, toxicity, bioavailability

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1 Introduction

Drilling activities generate large volumes of drilled rock (cuttings) to which variable amounts of drilling mud may adhere. The overboard disposal of these cuttings has led, at many platforms, to the development of waste piles in the immediate vicinity of the platforms. Although cuttings piles do not arise in all circumstances, more than 25 years of operation in the North Sea have led to the accumulation of a substantial quantity of highly localised drilling waste deposits, the fate and effects of which are an important consideration in developing environmentally responsible decommissioning strategies.

There are 420 platforms in the North Sea, of which approximately 210 are in the UK sector. The structures are fairly large and are placed in water depths ranging from 70 to 300 m. Other structures in the North Sea area (about 150) are mainly small and situated in the shallow southern North Sea. They are mostly owned by Dutch and Danish interests (Corcoran, 1995; Laver, 1992; NOU, 1993; Williams, 1995).

Only a few structures in the North Sea have stopped production, but several fields and structures are to be taken out of service in the near future. The exact cessation dates are frequently being reviewed because of changes in the requirements of the authorities, development of new decommissioning technology and enhanced exploitation of marginal fields. It is technically possible to remove most of the structures placed in the British and Norwegian sectors, but in some instances there may be considerable environmental, socio-economic, health and safety consequences to consider.

To achieve the best possible means of evaluating different abandonment strategies and methods, as many as possible of the different aspects must be identified and evaluated. One such aspect is the fate of oil-contaminated drill cuttings, previously deposited on the sea-floor as a result of exploration and production drilling operations.

Research item 1.2 is considered by UKOOA to be central to the issue of cuttings pile disposition. Its importance lies both in the potential implications of leaving piles in place and in the potential impacts which might ensue from disturbance of the piles during decommissioning and cuttings removal.

The aim of this report is to examine, summarise, and interpret ecotoxicological data which could assist in an improved understanding of the potential marine toxicity of the contents of cuttings piles. Since interpretation and assessment are the key endpoints, section 2 focuses closely on developing an understanding of the notion of 'toxicity', and of the factors which influence the meaning and utility

of practical measures of toxicity. We believe that this focus is essential, since it will permit an evaluation not only of gaps in the available data, but also of more fundamental weaknesses in the general philosophy behind oilfield chemicals testing and regulation.

The issue of cuttings toxicity can be considered in two general categories: hazard associated with undisturbed cuttings (ie, any existing and current hazard from stable piles) and hazard associated with disturbance and re-deposition of cuttings.

This report will consider both forms of interaction, although, since for practical reasons toxicity testing normally requires the physical introduction of a material to a test medium, most of the available information will relate to the second form of interaction, that associated with disturbance of cuttings piles and the potential release of contaminants into the marine environment.

2 Overview of toxicity assessment

The term 'toxicity' encompasses a wide range of chemical effects on individuals. Effects can be gross (such as mortality) or subtle (such as inhibition of growth or reproduction), and can reflect a considerable variety of mechanisms or modes of action. While a detailed investigation of mechanisms and consequences is always in principle desirable to ensure adequate understanding, the cost and practicality of such investigations is often beyond the scope of routine evaluation.

Toxicity tests are a practical approach to estimating the potential for biological harm presented by industrial chemicals and wastes. In relation to the aquatic environment, toxicity tests are predominantly exposure-related and measure acute (short-term) lethal responses in test organisms. Aquatic tests are thus an indirect measure of effect – in contrast to much mammalian toxicology, where attention focuses on the relationship between dose (the amount administered directly) and response. Aquatic ecotoxicology is therefore to a large extent dependent on the quality and detail of information available on the exposure conditions (chemical partitioning, adsorption, speciation etc). The reliability of data can be substantially reduced in cases where test exposure conditions are unknown or are poorly characterised.

A key aspect of aquatic ecotoxicology is that 'toxicity' as derived in standard exposure-response tests is not a fundamental property of materials. Toxicity values are derived by calculation and inference from relatively simple observations of response under different exposure conditions. They represent the result of responses observed under particular conditions at a particular time; since the exposure may differ for different species, the magnitude and pattern of response can also vary. This does not mean that the intrinsic biochemical effects are different between species, but it does underline that tests do not measure this intrinsic property.

A more detailed discussion of toxicity test methodology and application is presented in the Appendix. This provides the reasoning behind the evaluation of data, and the conclusions drawn from the evaluation.

3 Composition of drill cuttings

An assessment of the possible chemical constituents of drill cuttings can provide an indication of potential sources of toxicity. However, it should be recognised that there is at present no sound scientific basis for estimating the toxicity of whole cuttings from a knowledge of the composition. The complexation and speciation of individual components will influence their availability, while the physical formulation of the original drilling mud will influence interactions between components. The presence of components of low intrinsic toxicity could, for instance, have a marked effect on the availability of more toxic components (eg the effect of surfactants on availability and uptake of hydrocarbons). Toxicity tests can in fact provide useful tools to investigate and understand component interactions, but have rarely been used in this context in relation to oil industry activities.

3.1 *Cuttings inventory*

It has not been possible to complete this task yet. Responses from operators are still being received. A supplementary request has been circulated by the project managers, DNV, for information on this subject.

3.2 *Field observations*

Bell et al (1998) summarised the analytical data available from reported studies on North Sea cuttings. These are not comprehensive in terms of potentially toxic contaminants, focusing primarily on 'total hydrocarbons', cadmium, chromium, mercury and sulphide. Analytical methods are not reported, so it is difficult to determine whether the concentrations tabulated for cuttings samples from different platforms are directly comparable. Bell et al noted that metals concentrations varied with no particular pattern. One reported value for Hg (128 ug.g⁻¹) seems exceptionally high, and would merit closer examination; otherwise, the reported metals concentrations appear lie within a relatively small range.

The data collated by Bell et al indicate that it is not at present possible to compile a comprehensive description of cuttings pile composition. Most importantly, the total hydrocarbon analysis does not indicate the types of oil present, or the PAH or phenol content. Neither does there appear to have been any analysis carried out for non-hydrocarbon organics –biopolymers, biocides, surfactants etc. The reasons for the lack of such analysis are likely to be many and complex, and primarily a combination of technical and regulatory constraints. This latter question has substantial significance for any future monitoring of pile contents; unlike THC, it is likely to be necessary to 'tailor' analytical methods to the specific materials used in drilling each well, and, as part of this process, to

decide *a priori* which molecules to use as markers for each product. Decisions about the selection of analytical methods will thus depend critically on access to reliable information on

- The types and quantities of product used in drilling each well and hole section
- The volumes discharged at each stage
- Verification of the chemical composition of the batches of product used at each stage

It is recognised that there will be practical constraints on the availability of such information, and it is therefore important at an early stage to carry out practical investigation of at least some cuttings piles in order that the analytical challenges can be properly characterised and a practicable strategy devised.

3.3 Drilling muds and additives

To successfully drill a well, several conditions must be present. An important factor is the properties of the drilling mud. The main functions of a drilling mud can be described by the following (OLF 1996a):

The drilling mud must:

1. assist in removal of cuttings from the well bore;
2. control formation pressure (e.g. hydrostatic pressure proportional to the depth of the formation);
3. maintain bore hole stability (e.g. chemical stabilisation of formation types);
4. protect producing formations by minimising formation/fluid interactions;
5. control corrosion of the metal components of the drilling tools, casing and rig facilities that are exposed to a corrosive environment (e.g. dissolved O₂, CO₂, H₂S);
6. Seal the wall of the bore hole;
7. Maximise drilling penetration rates;
8. Cool and lubricate the bit and drill string;

Considering the variety of functions of a drilling mud and the great variations of wells to be drilled, successful drilling of a well needs careful selection of the right drilling mud. Factors affecting the choice of the correct drilling mud include: formation lithology; well design; the formation pressure and strength; formation temperature; logistics and rig type; as well as environmental and health considerations (OLF 1996a).

3.3.1 Base fluids

Drilling muds contain a base fluid and a mixture of chemical additives manufactured to perform a variety of functions during drilling (Davies and Kingston 1992). Depending on the type of the base fluid, three main types of drilling muds can be defined:

- water-based muds (WBM);

- synthetic/pseudo-oil based muds (SBM) (Friedheim 1997);
- oil-based muds (OBM) (Bell et al. 1998, Burke and Veil 1995, Cripps et al. 1998, Kjeilen et al. 1996, OLF 1993)

Water based muds are formulated either with fresh or sea water or with a brine (e.g. KCl). The salinity ranges from 0 to about 900 kg/m³, depending on the salt type and desired density of the mud (OLF 1996a). Oil based muds initially consisted of a fluid having a 100% oil only phase. To improve the performance, invert emulsion systems were developed, in which an internal water phase is emulsified into the continuous oil phase. These invert systems contain about 5-50% water (vol), and are also typical of SBMs (OLF 1996a).

Initially, diesel oil was used as the only oil base fluid. During the early 80s, the diesel oil was replaced by mineral oils of lower toxicity. From 1991 onwards, no discharge of oil base fluids has been allowed on the Norwegian Continental Shelf, and from this period onwards, the use of SBMs has become increasingly important.

As mentioned, a number of factors affect the choice of drilling mud to be used. Oil-based muds have certain operating advantages over WBMs. These include; low friction, high temperature stability, and low interaction with the clay of the formation drilled (OLF 1996b). From a technical point of view, the OBMs are preferable to WBMs in many applications (OLF 1993). The WBMs, due to their water content, continually disperse cuttings particles into the drilling fluid. To counteract this, the mud is often diluted and excess amounts of drilling mud are released during drilling operations. Use of WBMs hence produces larger amounts of drilling wastes than the OBMs (OLF 1996b). The drilling performance of the SBMs is basically comparable to the OBMs. The SBMs were developed to have an environmentally acceptable, good performing, alternative to the OBMs.

3.3.2 Drilling fluids additives

The types and amounts of chemical additives included in the mud formulation vary according to the needed characteristics of the mud. In general, the quantities of additives (exclusive of the base oil) for OBMs/SBMs are less than that added to WBMs (OLF 1996a).

Within the major categories, similar types of additives are generally used with different mud systems. However, some additives may be more relevant to use with specific mud types. Presented below are the functions and types of the major chemical additives used in different drilling muds:

- **Weighting materials:** added to increase the weight of the mud, so that it can properly maintain adequate well pressure. The weighting agent is normally a major component of the mud system.

Most commonly used is barite (BaSO_4), which may contain traces (up to several hundred ppm) of heavy metals, Others include calcium carbonate and hematite (iron oxide). The same types of weighting agents are used with all mud types.

- **Viscosifiers:** used with all types of mud. In invert emulsion systems (OBM/SBM), the viscosifiers builds viscosity through complex interactions with the emulsions (Fjelde 1998). Bentonite clay is often used with most water-based muds (also as organoclay: alkylamine-treated clay minerals). With WBMs, organic polymers derived from cellulose and natural biopolymers are also in general use.

- **Fluid loss control agents** are compounds added to reduce the loss of fluid from the mud into the drilled formation.

Types of agents include: bentonite clay, lignite and polymers (carboxymethyl cellulose (CMC), polyanionic cellulose (PAC), and modified starch). Bentonite clay consists of very fine particles, and is the most commonly used fluid control agent. Lignite is an important additive for WBMs. It also acts as an emulsion stabiliser. Various polymers may also be used, the types of which differs between WBMs and OBM/SBMs.

- **Emulsifiers** are added to stabilise oil-in-water emulsions (OBM/SBM) A combination of two emulsifiers is often used to ensure a homogenous composition.

Types of primary emulsifiers include fatty acids (and derivatives) and rosin acid (and derivatives), prepared from sodium soaps from paper industry, and fatty imidazoline derivatives. Types of secondary emulsifiers include amines, amides, sulfonic acids, lignosulfonates, alcohols and related co-polymers. These are used to improve emulsion stability, especially at high temperatures, and to wet the drilled solids. In OBM/SBM systems, dimeric and trimeric fatty acids may also be used to maintain the emulsion.

- **Brines**, concentrated inorganic salt solutions, are used both as the water fluid phase in WBMs, for well completion, and as the water phase emulsified into the OBM/SBM fluids. The brines are added to OBM/SBM to 1) balance the interactions of drilling fluid with clay and soluble salts in the formation, 2) because it is denser than the oil/synthetic oil phase, thereby increasing the weight significantly, and 3) because the emulsion formed has a higher viscosity than either of the two phases alone.

Typical brine salts used are:

- for WBMs: KCl, NaCl

- for completion fluids: NaCl, CaCl_2 , ZnCl_2 , CaBr_2 and ZnBr_2

- for OBM/SBMs: CaCl_2 , (NaCl). Typical use concentrations are a 20% CaCl_2 brine, added by 20-40% to the mud.

- **Alkaline chemicals** are normally added to control the pH, which is beneficial to reduce corrosion and to activate some emulsifiers. Lime ($\text{Ca}(\text{OH})_2$) is normally used with OBM/SBM,

while caustic soda, and other inorganic compounds including: NaOH, KOH, Ca(OH)₂, K₂CO₃ are, or were, used in WBMs.

- **Lost circulation materials** are added to block pores, voids or fractures (all mud types). Many types of materials are used, including; crushed nut shells, shredded vegetable fibre, mica flakes, graded sizes of calcium carbonate, shredded cellophane, diatomaceous earth etc. The concentration used varies widely.
- **Shale control additives** cover a range of different compounds used with WBMs. Most frequently used is KCl, other compounds include polyglycols and polyglycerols, polyacrylamides (with high molecular weight), Aluminium sulfate, inorganic silicates, sulfonated asphalts, and synthetic cationic polyamines.
- **Lubricants and detergents** are also used with WBMs. The most common used lubricants are modified natural esters, fatty acids or glycol esters, while the most popular detergent used is ethoxylated alcohols.

In addition to the listed chemicals, biocides and corrosion inhibitors are used, as well as wetting agents and thinners.

Some of the additives may contain toxic components, e.g. certain heavy metals that may be an environmental risk if they are present at elevated concentrations and in a toxic state. Depending on its source, barite is contaminated with variable amounts of heavy metals. Since barite is used in such large amounts in muds, it is then also the main source of heavy metals in cuttings piles. Certain oestrogenic chemicals that are known to disrupt fish reproduction, may also be present in some of the additives, such as the corrosion inhibitors. The oestrogenic compounds used are mainly alkyl-phenol ethoxylates (APEs) (ENDS, 1997). Substances recognised as having endocrine disruption potential have been progressively replaced in drilling fluids.

3.3.3 Quantities of drilling muds and additives

Presented below are the composition of “typical” water based and oil based muds (Table 1), as presented in a confidential report on oil field chemical use, issued in 1998. A more detailed description of the composition of drilling mud and mud/cuttings discharge in the North Sea is provided in Kjeilen et al (1999).

Table 1 Example drilling mud composition (from confidential report in oilfield chemical use, 1998)

Compound	WBM (% of weight)	OBM/SBM (% of weight)
Barite	57.6	69.5
Base oil		25.8
Bentonite	4.1	0.3
Calcium chloride		2.0
Caustic soda	1.2	
Emulsifiers		1.8
Oil wetting agent		0.1
Polyanionic cellulose (PAC)	1.2	
Salt	33.0	
Soda Ash	1.0	
Starch	1.2	
Xanthan	0.5	
Other	0.2	0.5

3.3.4 Historical outline

Composition of OBMs :

- Fluid used: diesel (high aromatic content) (60)-80%
brine (CaCl₂) 20-(40)%
- organophilic clay (barite + ammonium surfactants)
- barite as weighting agent
- primary emulsifiers (often oxidised form of toluol – blend of fatty acids)
- secondary emulsifiers (often ethoxylated alcohols)
- oil wetting agent (surfactant)
- fluid loss agent (latex/polymer)
- lime/caustic soda (pH control)

From approx. 1985: diesel oil replaced with mineral oils (paraffinic oils), otherwise formulations remained similar.

Composition of WBMs:

- water (sea water/brine)
- bentonite clay
- barite
- lignosulfonate (originally as Cr-compound)
- lignite (which is a low grade coal)
- CMC – carboxymethylcellulose (used as a viscosifier)
- Xanthan gum (used as a viscosifier) (biocides are/were often used together with xanthan gum – usually glutaraldehyde (water soluble))
- Starch (modified)
- Oxygen scavengers (ammonia/sodium sulphite)
- SAAP ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$)
- Detergents
- Lubricants
- Emulsifiers
- Defoamers
- Sulphide scavengers (Zn/Fe carbonates)
- From approx. 1985: Cr- lignosulfonates replaced by Fe-lignosulfonates.

1985 onwards – polymer mud (KCl):

- water/brine (KCl, up to 40kg/m^3)
- CMC/PAC (carboxymethylcellulose or poly anionic cellulose) equivalent products, but with varying degree of substitution (and price).
- PHPA (partially hydrolysed polyacrylamide) (also with partially hydrolysed polyacrylate as a co-polymer)
- Clay

Recently: KCL-muds are added Glycol (propyleneglycol/ethyleneglycol) or silicate.

Ca. 1990: introduction of SBMs:

Similar to oil based muds except base fluid which is replaced with esters, ethers or PAOs/LAOs (poly alpha olefin or linear alpha olefins). PAOs/LAOs most commonly used now.

Table 2 (after Kjeilen et al, 1999) provides an overview of the relative quantities of drilling fluid components discharged in North Sea operations.

Table 2 Quantities of drilling fluids components discharged by year

Compound	Quantity discharged per year (tonnes)									
	1996	1995	1994	1993	1992	1991	1990	1989	1988	1987
Weighting agents	73824	81795	97730	133592	154933	134056	100828	106000	86000	64698
Inorganic chemicals	28468	28764	22779	18201	14001	19320	16771	7600	2700	5012
Lost circulation chemicals	167	256	410	489	490	180	183	160	450	53
Lignosulphonates, lignite	88	153	256	10095	495	373	539	640	800	751
Polymeric viscosifiers and filtrate reducers	1893	2072	2902	3003	4348	3756	2759	2400	1200	1077
Asphalt and asphalt based prod.	0	33	9	101	267	290	485	180	190	164
Defoamers	15	15	41	51	93	53	89	100	30	45
Biocides	62	27	49	82	111	47	92	30	25	25
Corrosion inhibitors	37	40	602	2476	122	40	120	10	40	8
Scale inhibitors	20183	14174	14303	5790	4377	3224	2497	580	2360	371
Drilling lubricants	123	124	176	118	119	87	74	1	8	8
Pipe release agents	0	61	52	141	54	57	9	15	25	24
Dispersants	2	14	4	84	200	216	164	55	7	211
Oxygen scavengers	0	3	6	1	29	34	14	4	1	2
Detergents	16	34	41	31	464	386	691	340	200	142
Cutting wash fluids	0	663	4	1048	75	199	5	110		31
Emulsifiers	319	442	359	517	203	2099	16	45		10
Dope	20	34	43	28	14	181	127			
Cementing chemicals	2286	3305	2569	2419	2531					
Completion fluids	20981	11056	7654	2850	2740					
Other chemicals	753	658	190	1426	115	455		60	20	602

4 Cuttings exposure scenarios

4.1 *In situ* conditions

For cuttings piles which are left undisturbed, environmental hazard will not be associated with the cuttings *per se*, but with the toxicity of any materials which leach from the piles. The estimation of the nature and rates of leaching is beyond the scope of this report, but it is pertinent to make some comments about the possibilities. Concern at this time will primarily relate to materials which are effectively immobilised deep within piles, or those with relatively low diffusion and leaching rates, since these can in principle be the only materials still present in older piles. It is not clear whether this would restrict attention only to the less water-soluble components of cuttings, or whether the physical and chemical structure of piles would promote the retention of the more water-soluble components also. It would be reasonable to assume, though, that the chemical composition of leachate will differ substantially from the chemical composition of the cuttings (or, conversely, it would seem highly improbable that all chemical components would diffuse and leach at exactly the same rate).

Chemical releases through diffusion within and from the pile can more readily be addressed, at least in principle. For metals, for instance; there is little evidence to suggest that trace metals are ‘naturally’ released from stable adsorption states in settled sediment, especially in the presence of high concentrations of sulphide.

Hydrocarbon base fluids represent, by mass, the largest organic chemical components of the cuttings. Older fluids (diesel and early low-tox fluids) would contain varying proportions of relatively soluble low-molecular weight aromatics (benzenes, toluenes, and xylenes) which would probably be lost relatively rapidly to the water column from material close to the surface of the pile. Whether there is a possibility for continuous diffusion of these components through the pile we do not know, although other topics within the JIP will address this.

More recent mineral and ‘synthetic’ base fluids are virtually or completely free of aromatics, and are generally very poorly soluble. Very high addition rates (5-10 g.l⁻¹) in standard water-phase toxicity tests elicit little or no response, even although the fluid is equilibrated with seawater for 20-24 hours prior to testing. This suggests that leaching rates of recent base fluids are unlikely to present an acute toxicity hazard in the overlying water – it is physically improbable that sufficiently high aqueous concentrations could be achieved, and there is considerable evidence (the accumulation of reported sediment toxicity data for recent base fluids under the HOCNF scheme) that achievable concentrations would not cause acute toxicity. There is no information available to indicate whether achievable water

concentrations might cause chronic toxicity. Since (as indicated elsewhere in this document) nonpolar narcosis is considered the most likely mode of action for hydrocarbon base fluids and rates of uptake and depuration from water are high, it is unlikely that low levels of aqueous exposure would lead to sufficient accumulation in the tissue for chronic effects to arise. This has not been tested, though, and remains an area which might require clarification at a future date. Toxicokinetic modelling would be a valuable tool in addressing the issue of chronic toxicity associated with base fluids, and in particular in establishing whether or not there is a critical tissue residue for chronic effects.

There are no historically well-documented mechanisms for the release of trace metals from stable cuttings piles. It is conceivable that bioturbation could increase the rate of resuspension of surface particles, and that this could temporarily increase the potential for re-partitioning in water near the pile surface. In a high-particulate microenvironment, with concentrations of sulphide which will increase roughly in proportion to any increase in suspended metals levels, little trace metal might be solubilised. To the extent that particulate resuspension above an intact pile occurs, the most probable fate for any metals released in this way is re-deposition in sediments in the near vicinity of the cuttings pile.

4.2 Consequences of disturbance

4.2.1 Water column exposure

Disturbance of a cuttings pile will lead to the release of cuttings material to the water column. The quantity will depend on the design and efficiency of the containment system. For the majority of the mud systems used in drilling in the North Sea (both water-based and oil-based), there is a substantial quantity of acute toxicity elutriate data. If drilling mud alone had been discharged, and the deposited material had undergone no changes *in situ*, then it might be reasonable to suggest that resuspension of the deposited material would not give rise to significant releases and that re-deposition of disturbed material would occur quite rapidly. The reasoning for this would be:

- Only the denser, more rapidly-settling material would have accumulated in the pile – fines, and contaminants associated with fines, would have been transported away from the pile before settling
- Any readily-leached or soluble material in the cuttings would have desorbed during the original deposition process

However, the deposited material is approximately 90% drilled solids by weight, and for material which has been on the seabed for any significant period of time it must be assumed that some chemical changes will have taken place. Cuttings thus have the potential to contain mineral-derived toxicants (primarily trace metals, but possibly also reservoir fluids in some instances) as well as the degradation

and transformation products of the organic components of the drilling mud. While the observed persistence of cuttings piles strongly suggests that any degradation processes are not rapid, it remains a possibility that cuttings could contain (for instance):

- Alkylphenols; degradation products of some nonionic surfactants
- Intermediate degradation products of base fluids (eg, more polar, more soluble and potentially more toxic materials such as carboxylic acids – although these are also likely to be less environmentally persistent than the parent materials once released to the environment)

If cuttings are disturbed, the fates of different components (whether those originally present or their degradation, reaction or transformation products) will depend on the chemical and physical forms in which they are re-introduced to the water column.

4.2.2 Sediment exposure

Sediment exposure will occur following any event which causes re-suspension and subsequent deposition of cutting material. With earlier, single-phase mud systems, it is likely that any water-soluble material would have been released to the water column during the original process of settlement. With multi-phase systems (such as invert emulsion muds) it is possible that some more water-soluble chemicals could have been retained within the cuttings during settlement and that subsequent changes in cuttings structure might lead to their release during disturbance. It is not certain that such releases would occur, however, and it is equally possible that the fate of resuspended material could be determined by physical interactions between components. For instance, Aronstein and Alexander (1992) showed that surfactants at low concentrations enhanced the biodegradation of sorbed hydrocarbons in samples of aquifer sand and soil slurry; this raises the possibility that similar processes might occur in cuttings re-deposited on the seabed sediments. If so, the potential toxic impact of the components of the deposited material might have to be offset against the reduction in persistence afforded by the joint presence of base fluid and surfactant.

The fate of poorly-soluble materials is also of interest, since this group includes many of the chemicals of greatest concern (PAHs, alkylphenols, metal complexes). If such materials desorb from cuttings particles, they would be more likely to persist at low concentrations in the water column. Borglin et al (1996) investigated the parameters affecting the desorption of hydrophobic organic chemicals (hexachlorobenzene and PCB) from suspended sediments, and concluded that this process would take weeks to months; while not directly addressing the issue of PAH desorption from cuttings, these results are probably sufficiently apposite to suggest that no significant PAH losses would occur during the disturbance of a pile. This inference is supported by studies conducted by Phillips et al (1998), who provided evidence for long-range transport of drilling-derived sediment-sorbed PAH (low-to-

medium molecular weight); their data indicated particle-associated transport of more than 50 km with little evidence of chemical change. While this provides some assurance that losses to the water column via desorption will be limited, it raises an additional concern with respect to the physical dispersion of strongly-adsorbed chemicals; in the event that changes within the pile might have altered the effective particle-size distribution and dispersion characteristics, it is possible that sediments at a considerable distance might be subject to slight increases in the concentrations of these chemicals.

5 Toxicity data

A substantial amount of data are available, dating from the late 1970s and early 1980s. Especially in the first half of the 1980s, there was considerable interest in the effects of drilling muds and cuttings, and a wide variety of test methods were applied or developed. These include laboratory tests on various forms of drilling mud elutriate, as well as numerous 'mesocosm' and tank tests designed to investigate the effects of muds and cuttings on community structure and sediment re-colonisation. Different standardised methods were developed in a number of European countries and in the USA, but even within Europe there was no effective intercalibration or standardisation of methodology until the early 1990s. Even when standardisation was implemented (via the agency of OSPAR), test methods initially focused on acute, water-phase tests.

The development and implementation of test methods capable of reflecting acute toxicity of poorly-soluble chemicals in sediments (solid-phase tests) has occurred only relatively recently. It was noted in 1992 (ERT, 1992) that at that time methods were still under development and had not achieved international standardisation. Since then, some progress has been achieved, with the adoption of a standard OSPAR method following a ring test in 1993 (TNO, 1994). This has facilitated a more comprehensive testing regime for more recent drilling muds. However, testing has not been retrospective; since some of the muds and components of environmental concern were used prior to this date and have been progressively phased out since then, there is still a lack of relevant solid-phase test data.

The adoption of more relevant toxicity test methods has been relatively slow, creating gaps in our understanding. This process has still not been completed; in 1999, the US EPA (Federal Register, 1999) published comment on policy in relation to the testing and discharge of SBMs, in which it was recognised that the existing EPA guidelines for mud testing were not appropriate for SBMs and recommending the adoption of a solid-phase test method. There is an element of irony in this, since the OSPAR method adopted in 1993 was closely based on an EPA/ASTM method first published in 1985.

Finally, it should be noted that chronic testing (estimating the effects of chemicals over exposure periods which represent a significant fraction of the lifespan of the test organism or life-history stage of the organism) has not been a recognised need or requirement within any national or international offshore regulatory scheme. Since it has not been required for compliance purposes, little or no such work has been commissioned or undertaken.

5.1 Toxicity of drilling muds and components

5.1.1 Formulated muds and hydrocarbon base fluids

The following figure (Thomas, 1983, cited in IOE 1986) illustrates the overall pattern obtained from extensive testing of drilling muds in the late 1970a and early 1980s, a period of time during which there was a high degree of interest in assessing the environmental impacts of drilling fluids. It is important to note that

- the range of values (LC50, ppm) is very wide for each type of mud and
- that all the tests represented below were water-phase tests –they were conducted on elutriates of drilling muds and only represent the ‘toxicity’ of readily-leached materials

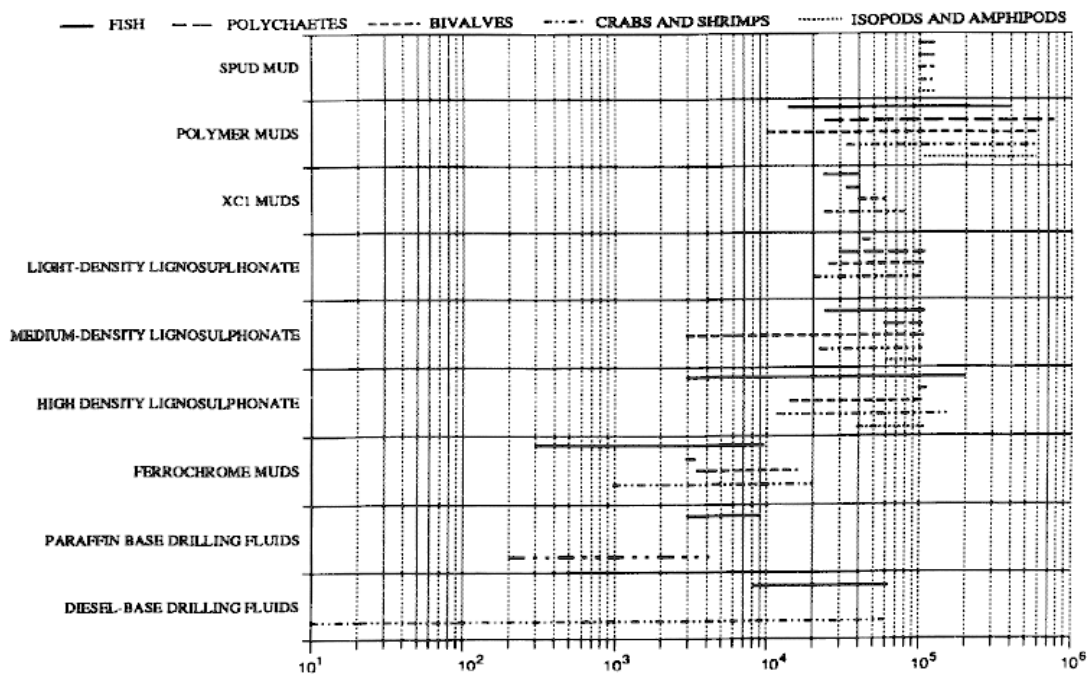


Figure 1 Summary of drilling mud test results (Thomas, 1983)

A substantial amount of testing was conducted in the first half of the 1980s. Neff (1987) reported that by 1983 some 400 tests, predominantly on sample elutriates, had been conducted on over 70 used water-based drilling muds, using some 60-plus species. Ninety percent of these tests yielded acute toxicity values (LC50s) of more than 10000 ppm, although the design of test methods means that the units of concentration are often arbitrary and difficult to compare with each other. A similar review (IOE, 1986) came to comparable conclusions, and noted that acute lethal tests (LC50s) had little

relevance to longer-term toxicity. This review also recommended the use of solid-phase assays and that tests be conducted on whole cuttings as well as muds.

While elutriate tests are valuable in assessing the magnitude of transient hazard to the water column during a relatively short period of cuttings settlement, they are of little value in evaluating the potential impact of the cuttings in sediment, or the potential impact of materials leaching from settled cuttings. It remains possible that a degree of environmental hazard could be associated with the elutriation or leaching of persistent material of relatively low acute toxicity.

In North Sea states, standardised sediment toxicity testing was introduced as part of the harmonised offshore chemicals testing process in 1995, although some form of sediment testing had been conducted in most countries for several years prior to that date. This afforded the opportunity to establish the acute toxicity of poorly-soluble chemicals, and also enabled for the first time a practicable method for testing oil- and synthetic-based drilling muds. The majority of current and recent mineral oil-based and synthetic-based muds and drilling fluids have been tested using the standard OSPAR *Corophium* test. The results of some of these tests, compiled from a variety of confidential sources, are presented below in Figures 2 and 3. Figure 2 is a frequency distribution of LC50 values for formulated muds (mg.kg^{-1} dry sediment), while Figure 3 presents a similar distribution for base fluids.

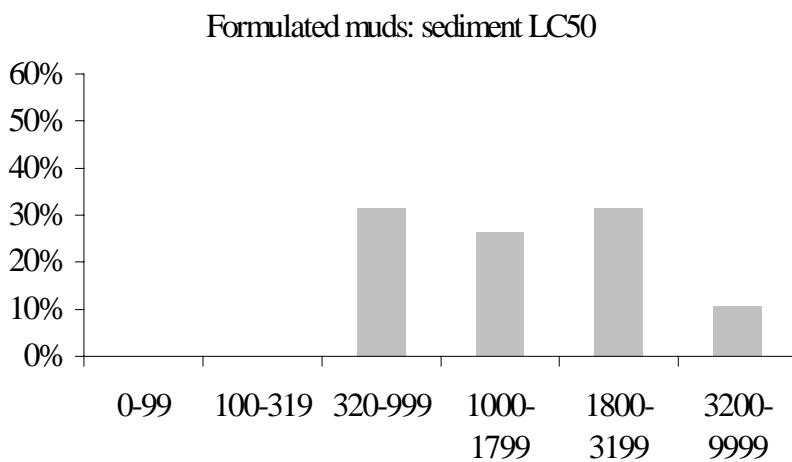


Figure 2 Frequency distribution of acute toxicity of drilling muds (LC50, mg.kg^{-1})

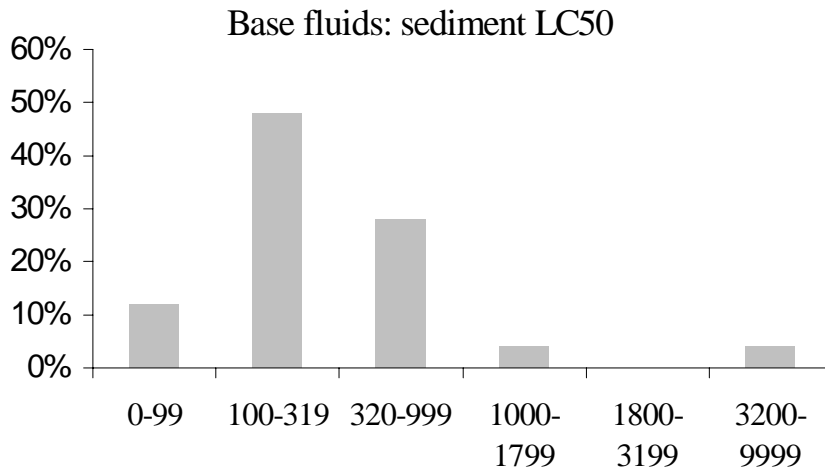


Figure 3 Frequency distribution of acute toxicity of low-tox and synthetic base fluid (LC50, mg.kg⁻¹)

Neither distribution is symmetrical, and to illustrate this the median and average values for each data set have been tabulated below:

Table 3 Median and average sediment LC50s for recent base fluids and muds

	Formulated muds	Base fluids
Median LC50	1596	219
Average LC50	2162	952

The data cover base fluids and muds tested between 1991 and 1997. It is clear that, overall, LC50s for base fluids are substantially lower than for formulated muds, but that even for base fluids only a small proportion have LC50s of less than 100 mg.kg⁻¹. If base fluids were the sole or primary source of toxicity in recent mud formulations, it would be expected that a mud LC50 would be between twice (for a 50% base fluid formulation) and five times (for a 20% base fluid formulation) higher than the corresponding base fluid LC50. The limited precision of the test method (coefficient of variation estimated at 50%) precludes definitive comparisons on the basis of individual base fluid/mud combinations. However, the table above indicates an approximate proportionality which is not inconsistent with the expectation that components other than base fluids present in muds contribute to overall toxicity.

It is possible that some of the apparent pattern in the reported sediment toxicity data is an artefact of the test duration, although there are no reports that this has been investigated. One limitation of a fixed-duration test (and especially when the frequency of response observations during the test is low)

is that it measures only the extent of the response within the fixed period. This means that chemicals which are accumulated into the test organism more rapidly are more likely to express their effects fully within the test 'window'. Chemicals which are taken up more slowly will register as less acutely toxic, but will not necessarily be so. With sediment tests, in which partitioning and uptake might be slower than in water-phase tests, the observed response could be due as much to differences in molecular size as to differences in intrinsic toxicity. This would be the case if the primary mode of action of paraffins and olefins is nonpolar narcosis, which is a reasonable expectation for these chemicals. For this mode of action, toxicity is likely to be dependent on tissue burden – the concentration of chemical in the body, and there is evidence that similar tissue burdens produce similar levels of acute effect across a range of aquatic species and chemical types (eg McCarty et al, 1992; Driscoll et al, 1997). If this is the case, then differences in acute toxicity reported by standard tests for base fluids would primarily be a reflection of differences in relative rates of uptake and depuration, and consequent differences in the tissue burden accumulated during the test period.

5.1.2 Components

As section 3 has indicated, there are a very large number of possible drilling fluid components, and an even larger number of potential formulations. An analysis of the current list of chemicals classified for use offshore (UK OCNS database, CEFAS) identified over 550 chemicals registered by four major drilling mud companies. The UK OCNS classifies products primarily by order-of-magnitude toxicity, with the classification modified to take account of persistence and bioaccumulation potential. A frequency distribution by toxicity class for these chemicals is presented in Figure 4. In individual cases, chemicals may have been assigned to a class lower than indicated by their toxicity (as measured by OSPAR test methods), so the distribution could represent an over-estimate of toxicity. What this figure indicates is that only a small proportion of notified chemicals could be considered acutely toxic, and that the overwhelming majority are of similar toxicity to, or lower toxicity than, the majority of hydrocarbon base fluids.

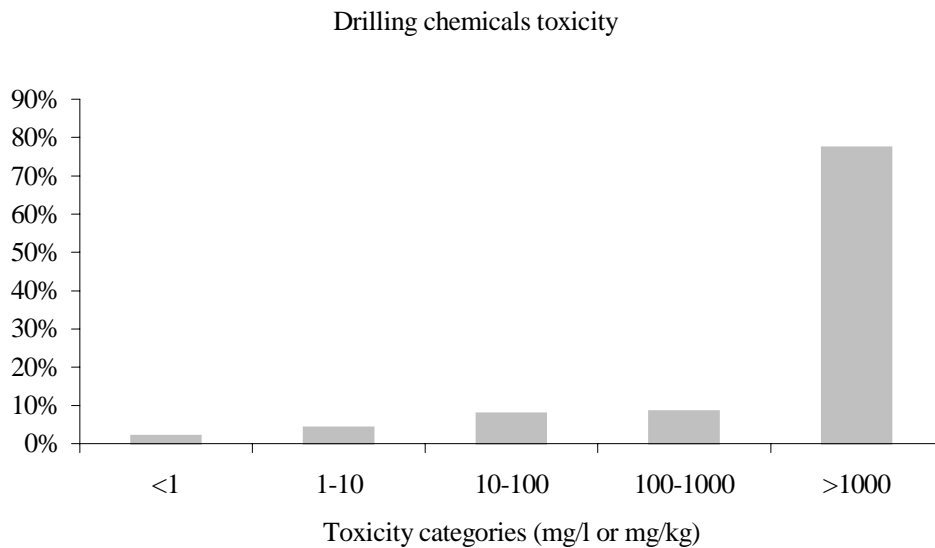


Figure 4 Frequency distribution of UK OCNS toxicity categories for drilling chemicals

5.1.2.1 Organic substances

Fe-lignosulfonates

The toxicity attributed to these substances was caused by addition of hexavalent chromium. Following the discovery of the damaging impact of Cr^{6+} , (Crawford & Gates, 1981; Carls & Rice, 1984) the use of Cr-containing Fe-lignosulfonates was progressively eliminated. The contribution to toxicity from older piles may possibly be quantified if records on drilling chemicals are available. The use of chromium containing compounds has been reduced in recent years, for lignosulfonates from ca. 1985 and onwards. The presence of this type of potential contamination from old piles should be assessed by field measurements.

Linear alkylbenzenes (LAB)

LAB has not been used in the Norwegian sector. For those piles in the UK sector where LAB has been used, one should be aware that the degradation is a sequential process and that the basic molecule of sulfonated LAB is among the final, most persistent and toxic degradation products (Argese et al. 1994).

Biocides

These substances have not been considered as of major concern in drill cuttings piles. Due to their high water solubility most of them will dissolve during cuttings settlement. However, some biocides might persist in cuttings in those instances where they have been used in SBM. In multiphase emulsions water micelles may remain trapped in oil micelles within the cuttings. Biocides trapped

within the structure of piles could inhibit degradation, although the likelihood of this cannot be quantified at present. It is conceivable that biocides deposited with SBM could subsequently migrate into other horizons of the pile. The extent to which this might occur, and the influence it might have on degradation processes, can only be verified by field measurements. Acute toxicity assays provide little support in this context.

During the first period of operation in the North Sea formalin (formaldehyde) was the most commonly used biocide. Due to its persistent nature, high toxicity, (including carcinogenic effects) and its high vapour pressure it presented a human health and safety risk, and has been replaced by substances such as glutaraldehyde and quarternary ammonium (alkyl ammonium chloride) compounds. Formalin is readily soluble in water and given the composition of the old muds it is to be expected that a substantial fraction dissolved in seawater as the cuttings settled to the seabed. Glutaraldehyde has been the main replacement for formaldehyde. According to OLF (1996) it has a NOEC value for fish at 10 mg/l and only near-field acute environmental effects are to be anticipated.

The reported use in drilling of biocides in the Norwegian sector range between approximately 30 and 100 tonnes per years for the last decade. The presence of biocides requires analytical verification, together with an assessment of *in situ* degradation processes and their influence on contaminant bioavailability.

Ethoxylated nonylphenols

This group of substances has been progressively phased out of use. Uncertainties or lack of information with respect to degradation rates and diffusion rates out of the cuttings pile make predictions of potential toxicity impracticable, and there is a clear requirement for quantitative analysis in this respect. Toxicological aspects of the ethoxylated nonylphenol group are summarised below. Cuttings piles in the North Sea are heterogeneous in size and in layering. In one study of North Sea cuttings pile heights, a 50% reduction in about 10 years was estimated (Figure 5, Kjeilen et al. 1999). It is therefore possible that a continuous release of nonylphenols occurs from old drill cuttings.

A range of polyethoxylated nonylphenols have been used during drilling in the North Sea until this type of surfactant was phased out in this decade. They represent a group of substances of major concern. Nonylphenols are moderately acutely toxic, have some limited bioaccumulation potential, and possess hormone-mimicking properties (Staples et al., 1998). An increasing degree of ethoxylation reduces toxicity and increases water solubility. The hydrophobic moiety of the nonylphenols plays a significant role in the contribution to toxic effects (Argese et al. 1994). During microbial degradation the ethoxy groups are removed, and the remaining alkylphenol unit may be more readily bioaccumulated (Argese et al. 1994). Recorded residence times will be variable and influenced by experimental design Liber et al. (1999). Branching, i.e., addition of methyl groups to the molecule,

increases surface activity of the molecule but it also reduces the degradation rate (Kravetz et al. 1991). The nonylphenols will therefore, in line with other persistent and hydrophobic substances, show a complex distribution in drill cuttings piles and different types and metabolic products will migrate at different rates towards the pile surface.

Nguyen (1999) reported that alkylphenols were present in cuttings samples from Fulmar A at concentrations of between 1.4 and 19.3 $\mu\text{g}\cdot\text{g}^{-1}$, and that they were strongly and preferentially associated with the particulate phase (concentrations in leachate or elutriate water were of the order of 1 $\mu\text{g}\cdot\text{L}^{-1}$).

Nonylphenols possess estrogenic effects (Ashby et al, 1997), they bioaccumulate, and they may interfere with development (Shurin & Dodson 1997) and other processes (Billingham et al. 1998, Bechmann 1999). The environmental effects of nonylphenols has recently been reviewed in: *The Science of the Total Environment* Volume 233, 1999. Biological effects following exposure to nonylphenols have been observed at ambient environmental concentrations in river, sediments and estuaries. However, these situations may not be comparable to the fate of nonylphenols in cuttings; concentrations in surface waters are likely to be maintained by constant inputs from wastewater streams, whereas drill cuttings represent a relatively fixed reservoir of such materials. The nonylphenols may represent one of the main groups of future environmental concern regarding drill cuttings piles left on the seabed. Degradation may be slow under anaerobic conditions and the distribution in the sediment may be variable (Dutka et al. 1998).

Surface active agents in general

Many surface active agents are not toxic themselves, but may by their presence alter or influence the toxicity of other substances discharged or formed by degradation in piles. There has been a general trend in the North Sea towards an increased use of more readily degradable substances of lower toxicity. However, large quantities and a wide variety of substances and products are in use. They should therefore be measured/considered as an important set of co-variables that may increase toxic effects at especially longer times of exposure. Emulsification by surfactants might render more bioavailable poorly water soluble molecules (such as higher molecular weight PAHs or low-EO nonylphenols) (Middaugh & Whiting 1995). Surface active agents are also known to increase cell membrane permeability to potential harmful contaminants.

The toxicity of surface active agents such as dispersants is generally linked to the monomers, the single molecules, and not to the micelles they form when they reach the critical micelle concentration (CMC) (Singer et al. 1995). The monomers interfere with the functioning of the proteins in the lipid bilayers of the cell membranes (Edelfors & Ravn-Jensen 1992). Below CMC there may be

antagonistic interactions between surfactant monomers and hydrocarbons that reduce overall toxicity, whilst the trend is reversed and may exceed that of their water-soluble fraction (WSF), when surfactant concentrations are increased above CMC (Poremba 1993). Although the cited studies have been conducted in water, the principles also apply to interstitial water and organisms in sediments. Among the most recalcitrant substances of this kind will probably be the nonylphenols and the largest PAH from the former use of diesel.

Cano et al (1996) investigated the effect of organic carbon on the toxicity of a highly branched alkylbenzene sulphonate (anionic surfactant) to *Hyallela azteca* in sediments. They found LC50s of between approximately 200 and 1000 mg.kg⁻¹ at sediment organic carbon contents of between 0.35 and 4.64%. This acute toxicity range is similar to that observed for low-tox and synthetic base fluids in OSPAR sediment tests.

Utsunomiya et al (1997) measured the toxicity (in water) of linear alkylbenzene sulphonate, quaternary ammonium compounds (alkylammonium chloride) and their complexes to freshwater algae. The toxicity (EC50) of these anionic and cationic surfactants, for both species and singly and in mixture, was in the range of 1-20 mg.l⁻¹, with no clear overall pattern. Dorn et al (1993) reported similar acute water-phase toxicity values (*Daphnia* and fathead minnow) for alcohol and alkylphenol ethoxylates (nonionic surfactants). Maddin (1991), in a review of persistence and toxicity of petroleum industry surfactants, indicated acute toxicity ranges of 1-10 mg.l⁻¹ for anionic and cationic, and 10-100 for nonionic, surfactants. The work of Staples et al (1998) again reported acute aquatic toxicity for alkylphenol ethoxylates in the same range, but noted that alkylphenols themselves were 10-100 times more toxic and that chronic toxicity values for nonylphenol were in the 1-10 ug.l⁻¹ range.

The evidence therefore suggests that most of the surfactants typically used by the petroleum industry are of moderate acute toxicity in both water and sediments. Both Maddin (1991) and Dorn et al (1993) reported that, in general, these surfactant types are moderately-to-readily degradable.

The potential for endocrine disruption activity in relation to cuttings is still as yet not possible to evaluate. Routledge and Sumpter (1996) examined a wide range of anionic, nonionic, cationic and amphoteric surfactants, and found none to have estrogenic properties. The only material found to be weakly estrogenic were the alkylphenols, the degradation products of alkylphenol ethoxylates. Ankley et al (1998), in an overview of a workshop on screening methods for endocrine disruptors, noted that there was limited scope for discussion on invertebrates (the group of organisms likely to be most exposed in relation to cuttings), since little was known about the role of estrogens and androgens in this context. They did, however, also note that these hormones had been found in every invertebrate group examined so far.

5.1.2.2 Metals

A number of factors are likely to be of relevance in assessing the potential contribution of metals to overall cuttings toxicity:

- Metals are not degraded
- The age of the pile (old piles may contain more heavy metal contaminated barite and similar residues from various compounds)
- The extent to which reduction/oxidation inducing agents in the pile transfer metals from a bioavailable to an unavailable form
- The factors (other substances and bacteria) that may influence dissolution of metals out of the pile, or phrased differently, the migration rates of metals in the piles
- The deployment of OBM, SBM or WBM and how organic phases may bind metal containing complexes during the process of pile accumulation
- Salinity: in comparing data from different sources it is important to recognise that most trace metals in solution are less toxic in seawater than in freshwater.

In the first half of the 1980s there was a substantial investment in research into the potential effects of trace metals associated with drilling muds. Concern focused primarily on metals present as contaminants in barites and on chromium present in chrome-lignosulfonates used as dispersants or emulsifiers. Studies were conducted to establish trace metal availability, uptake and toxicity from mud components and formulated muds. A high proportion of studies were technically rigorous, in the sense that they were supported by comprehensive chemical analysis and (frequently) by estimates of measurement precision and accuracy. A number of investigations examined sublethal endpoints, although the majority appear to have concentrated on acute lethality.

The US EPA undertook a series of more ecologically-focused studies in the late 1970s and early 1980s. Tagatz and Tobia (1978), for instance, investigated the effects of barites on the development of estuarine communities, concluding that only very large inputs (equivalent to smothering) would have a measurable effect, and citing prior evidence that barite is not acutely toxic.

Bookhout et al (1984) studied the effects of Cr-lignosulfonate elutriates on crab development, and observed no toxic effects at 5% v/v. Carr et al (1982) investigated the bioavailability of chromium from a used Cr-lignosulfonate mud to five species of marine invertebrate, and concluded that bioavailability was low overall. Similarly, Neff et al (1981) observed low acute toxicity to marine invertebrates from used Cr-lignosulfonate muds and concluded that the discharge of this material would not give rise to adverse environmental effects. Uptake and depuration studies conducted in

1981 (Espey, Huston & Associates) with worms and clams indicated very little bioaccumulation from both high- and low-metals barites. A subsequent study (Neff et al, 1985) investigated chronic effects of drilling discharges and reported that there was little risk associated with metals uptake from barites or water-based drilling fluids.

The potentially most serious sources of metal toxicity, like hexavalent chromium and very contaminated sources of barite, were identified and eliminated 10-15 years ago. The heaviest metals contamination loads are thus likely to be in the lower layers in older piles. The gap between tests, especially the lack of measurements of the bioavailable fraction of metals in piles, plus the rate of diffusion to the pile surface pose severe restrictions on interpretations of data. A few preliminary studies have indicated that the occurrence and distribution of metals and their various oxidation states may be very variable within and between piles. The lack of relevant observations from drill cuttings piles therefore preclude any conclusions.

Barium (Ba), aluminium (Al) and iron (Fe) are frequently reported as measured in large amounts (at times much larger amounts than the previously cited ones) but they are not considered as toxic. However, the drilling activity seems to have led to a 13 fold increase in Ba in cod as compared to West Atlantic specimens, but nothing is inferred about toxicity (OLF 1993). Regarding invertebrates Ba was shown to accumulate in fresh water zebra mussels (Roper et al. 1996). Whilst barium sulphate, the main constituent of barite is considered as inert, the free cationic Ba^{2+} has been reported as having the potential to be toxic (eg, Downs et al. 1995), although the validity of extrapolation from mammalian to marine invertebrates has not been tested. Developmental effects of barium exposure was found in *Mytilus californicus* larvae (Spangenberg & Cherr 1996) demonstrating that low concentrations at the levels where barium may be found soluble in seawater can be toxic and of potential environmental concern. Adverse effects were observed in the 200-900 microgram/L range, which is below the concentration at which barium salts precipitate in seawater. The findings suggest that dissolution mechanisms acting on barite in drill cuttings piles should receive increased attention.

From a precautionary point of view and in light of some recent findings, metal toxicity may be of more concern than indicated in some older reports. Edwards (1998) reported that metal leaching from drill cuttings piles may be occurring at higher rates than reported before. Future assessments will benefit from the parallel information generated in research area 2.2.

Uptake at low doses over longer time periods may induce effects other than those recorded in acute toxicity tests. Long-lived sedentary organisms should be sampled and their tissues analysed. During the first years of drilling limits on heavy metal content in barite were less strict. Some old piles may therefore be those with the highest heavy metal concentration. Chronic exposure effects would be the

most appropriate for piles if they are left undisturbed. An OLF (1993) report concluded that the use of barite in drilling operations is not likely to induce acute toxic effects, whilst the absence of appropriate data prevented evaluations of chronic effects.

Most studies on bioavailability of metals have addressed bioaccumulation and chemical evaluation, but have not addressed the relationship of these measurements with chronic biological effects. When biological effects have been recorded, it was not possible to distinguish the physical impact from particulate barite from bioavailable heavy metals in barite (OLF 1993). Between- pile variations in metal toxicity will, however, be influenced by the types and amounts of organic substances that are present (Moreau et al. 1999, Van den Hurk et al. 1998a,b).

Few piles (7) have been sampled for metal analysis (Bell et al. 1998). These studies show between pile variation in metal content as well as in the gradients downwards in the pile. With respect to barium, the sensitivity of the extraction process to saturation (Hartley, 1996) calls for future method standardisation before comparisons and assessments can be made.

Although fish possess a considerable capacity to eliminate metals following exposure at elevated concentrations, the same capacity is more variable and far less well documented for the wide range of invertebrates that occur in the North Sea (Dietz et al. 1998). It has recently been found that copper tolerance is considerably lowered for crustaceans when tests are conducted which incorporate moulting. At low temperatures (not covered by official regulations or harmonised tests), standard acute copper toxicity assays with mysids showed increased tolerance by a factor in the range of one thousand. Tolerance increased from juveniles, via females to males as consequence of lower moulting rate. This type of study illustrates how carefully results from standard assays should be applied in a seasonally variable environment like the North Sea (Eva Garnacho, Univ. of Southampton, personal communication, paper in press in Marine Biology).

There is a substantial variation in the factors which influence the bioavailability of trace metals. Chromium (Cr) (later replaced by iron (Fe) in lignosulfonates, or by using alternative surfactants), occurs in several states of oxidation, the most toxic being the Cr (VI) form. It is likely, however, that Cr will, where present, be predominantly in the less toxic Cr (III) form. As underlined in (OLF 1996), worst case scenarios for Cr (VI) may suggest adverse effects, but the theoretical approach should be treated with great caution.

Measurements of metal contents in piles have shown large quantities of metals that deserve clarification of their more general abundance as well as their bioavailability. Lead (Pb) is found at the thousand ppm level, a factor of more than a hundred above the background level. Although abundant,

lead is generally bound to barite in a unavailable form. Metals such as zinc (Zn), cadmium (Cd) and copper (Cu) occur at lower concentrations, but still elevated above background levels. For Cu and Cd in particular, which are known to be toxic, their bioavailability in cuttings piles is not well documented. Preliminary information suggests that the amounts may differ considerably between piles (Stig Westerlund, RF-Rogaland Research, personal communication).

The fate of trace metals following marine disposal of drilling muds is not well understood. While it is often assumed that reducing conditions will decrease the availability of metals, Krantzberg (1994) has pointed to circumstances where an increased oxygenation state in sediments can reduce metal availability by promoting co-precipitation with iron and manganese hydroxides. There is a considerable amount of current research into developing methods for assessing the hazards of metals in sediments, with particular emphasis on identifying a reliable operational factor from which to estimate the bioavailable and toxic fraction of the total metal concentration. DeWitt et al (1996) examined the utility of acid-volatile sulphide (AVS) as a normalising factor in a study of bioavailability and chronic toxicity of cadmium to estuarine amphipods. This study demonstrated that the metal was not toxic at concentrations of up to 1.37 mg.g^{-1} in the presence of $1 \text{ } \mu\text{mol.g}^{-1}$ AVS. No measurements of AVS have been made in cuttings or in cuttings-contaminated sediments, and so we cannot determine whether this would be a significant factor in regulating metals availability in the vicinity of cuttings piles. The accumulation of published evidence cited above suggests that it is unlikely that trace metal contamination associated with cuttings discharge will be accompanied by significant biotic uptake or acute or chronic biological effects. However, Westerlund et al (1998) reported that recent studies on fish in have indicated a pattern of metal accumulation which appears to be related to proximity to platforms.

There remains a possibility that trace metals might re-partition into the water column following disturbance of piles; the hazard associated with this is difficult to estimate, since neither the magnitude of release or the rates of dilution are known. As with any transient event, the implications of disturbance would be difficult to assess in terms of conventional constant-exposure toxicity data, and this type of issue is best addressed by a combination of toxico-kinetic and fate modelling.

5.2 'Used' drilling muds toxicity

Until recently, and for a number of years, SFT has in the Norwegian sector required the toxicity testing of used drilling muds. These data have been examined, to determine whether they can provide additional understanding of the potential toxicity of muds immediately prior to disposal (recognising that disposal was not standard practice during this period). A range of tests was conducted, including

Skeletonema, *Balanus*, and *Mytilus*. The first two are water-phase tests, the results of which could be expected to reflect the effects of readily-desorbed components. The third employs a micro-encapsulation technique which, when used in conjunction with a filter-feeding animal, is probably better used to estimate dose-response than exposure-response. A striking feature of the SFT data is that there is little or no agreement between results from the different test methods (and often more than order-of-magnitude disagreement), and that the range encompassed by the EC20 and EC80 values was in most instances very large. The former observation underlines that conventional test methods do not measure intrinsic toxicity, while the latter observation suggests a combination of chemical and physical effects (the data indicate flat response curves indicative of poorly-soluble material).

Notwithstanding the above observations, the *Skeletonema* data have been abstracted and assessed. The most obvious feature of the data was that cationic polymer muds were, in general, associated with the lowest EC50 values (although there was, as for all mud systems overall) a very wide range of values. Accordingly, we have treated the cationic polymer muds as a separate category, and for the purposes of comparison frequency histograms were constructed for these muds and for the largest remaining class, the mineral/synthetic muds (Figures 5 and 6).

Table 4 Average and median EC50 values (mg.l^{-1}) of elutriates of used drilling muds to the marine alga *Skeletonema costatum* (source- SFT records)

	Mineral	Cationic
Median	16500	260
Mean	39776.9	15456.53

The median and average EC50 values (mg.l^{-1}) for both categories are summarised in Table 4. The large difference between the median values illustrates the substantially greater effect of cationic muds, while the average values show, in comparison to the median values, that neither data set was normally-distributed. All the results, however, illustrate the effects of water-extractable material, and are therefore of limited value in assessing the toxicity of cuttings settled on seabed sediments.

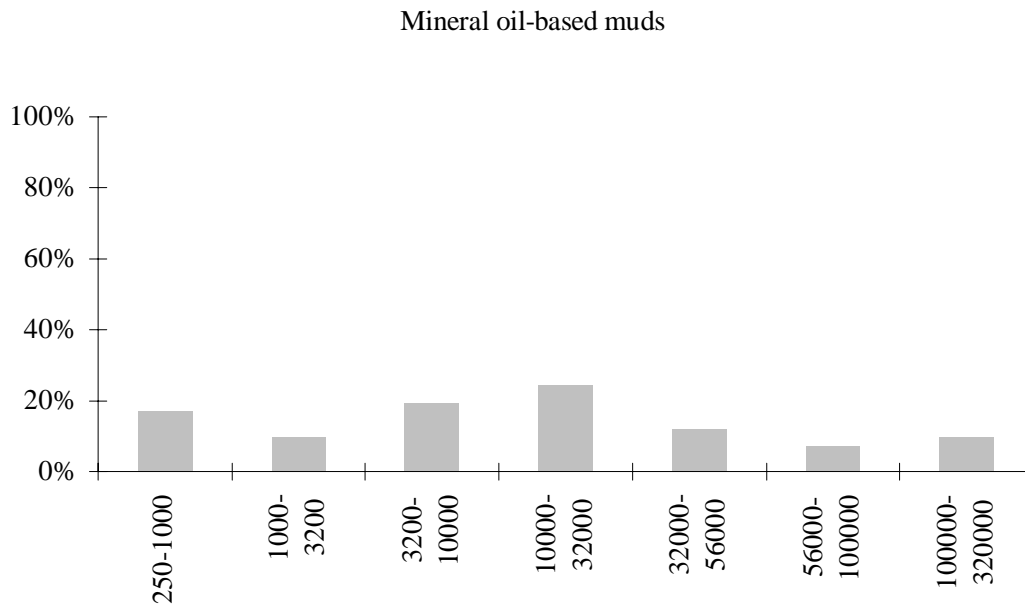


Figure 5 Frequency distribution of *Skeletonema* EC50 values (mg.l⁻¹) - SFT data, mineral oil muds

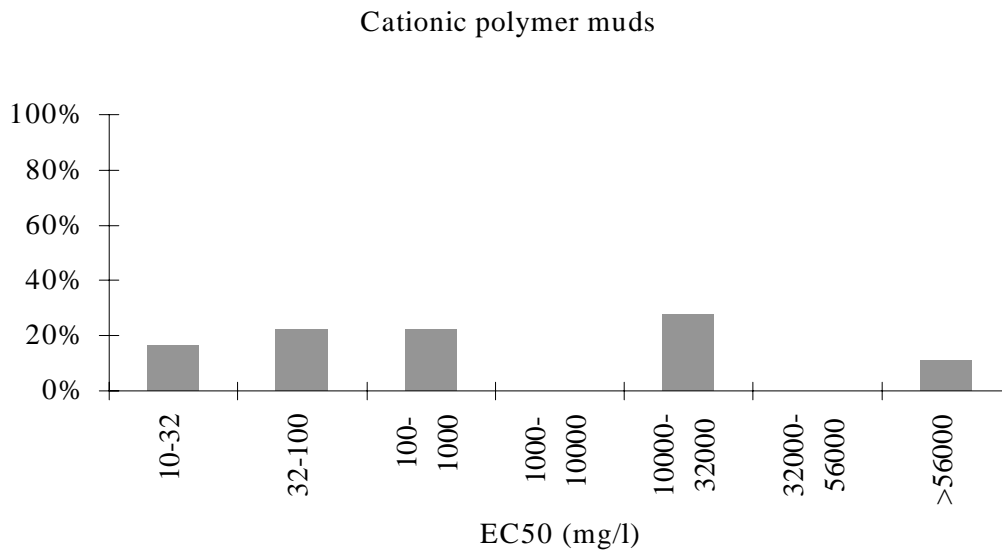


Figure 6 Frequency distribution of *Skeletonema* EC50 values (mg.l⁻¹) - SFT data, cationic polymer muds

A cursory examination of the above data would lead to the inference that cationic polymer muds presented a substantially greater environmental risk than mineral oil or synthetic-based muds, and this would be consistent with the known high aqueous toxicity of cationic polymers. However, we are

aware of one study (ERT, 1992, confidential report) in which a used cationic polymer mud was tested in a solid-phase system (*Corophium* test). The sediment LC50 in this test was greater than 60000 mg.kg⁻¹, indicating that the polymer was not biologically available in the mud/sediment mixture. Clearly, it is not safe to build conclusions on the results of a single study, but this observation underlines the concern that many of the large number of tests conducted over the past 20 years may have been inappropriately designed from the point of view of environmental hazard assessment.

5.3 Cuttings toxicity

Nguyen (1998, 1999) reported the results of a series of studies conducted on cuttings samples recovered from the vicinity of the Fulmar A platform. Toxicity tests were carried out in 1998 using the marine amphipod *Corophium*, with animals exposed both to cuttings-amended sediments and to the water overlying these sediments. Although it was not possible in this study to determine definitive LC50 values, the author concluded that the LC50 for all samples would lie at or below 1% cuttings in sediment. A marked toxic effect was observed in animals held in the overlying water; in the light of the observed 'flat' exposure response relationship and a lag in response, the author concluded that the water-phase effects were attributable to the leaching of poorly-soluble materials from the cuttings in the sediments.

Subsequent studies (Nguyen 1999) were carried out to more precisely evaluate the sediment-phase toxicity of Fulmar cuttings, and further investigate the potential toxicity of cuttings elutriates. These tests were carried out on pooled samples from a minimum of three cores, and on surface and subsurface cuttings layers. This study calculated the sediment EC50 for cuttings to be between 0.1% and 0.33%, with the top layer from the pile causing greater effect than material from deeper in the cores. The elutriate tests appeared to confirm earlier findings, that toxicity in the water phase was associated with the leaching of poorly-soluble material; LC50 values (% cuttings in water, v/v) were in the range 0.03-3%. As with the sediment-phase tests, the lower layer materials were apparently less toxic. Nguyen (1998) concluded that the toxicity data could potentially be explained by the total hydrocarbon concentrations (adverse effects were observed at THC concentrations of 43-62 mg.g⁻¹).

5.4 Cuttings-contaminated in-situ sediment toxicity

The persistence of toxicity resulting from the deposition of cuttings in the marine environment can most directly be assessed by means of sediment bioassays. The concept of the 'sediment quality triad' was introduced by Chapman (1991), and advocated field studies based on a combination of chemical, biological (usually macrofaunal) and toxicological measurements. This approach was first applied to North Sea monitoring in 1991 (Roddie et al, 1993), and has subsequently been applied on at least

seven occasions. Studies have also been carried out in which the primary focus was on sediment toxicity alone (Grant and Briggs, 1999; Neustadt, 1995).

The majority of studies have used a bioassay procedure with the marine amphipod *Corophium volutator*. This procedure is technically the same as the OSPAR toxicity test procedure (OSPAR, 1995), with the difference that the result is reported as percentage mortality in 'unknown' samples, rather than as an LC50 estimated from exposure to known concentrations of a test material.

Seven such studies were carried out by ERT between 1991 and 1997, and the toxicity and corresponding sediment hydrocarbon concentrations are summarised in plot form in Figure 7.

Percentage mortality has been plotted against total hydrocarbon concentration. The relationships depicted can only be regarded as approximate, since the analysis and testing were carried out on duplicate samples taken at each station. The precision of both measurements must also be taken into account. It is not suggested that these data demonstrate that hydrocarbons are the only source of toxicity in cuttings-contaminated sediments (and it is clear that in one case the sampling transect did not coincide with a distinct contamination gradient). There is, however, sufficient consistency in the pattern to indicate that elevated response is generally associated with hydrocarbon concentrations in excess of approximately 100 mg.kg⁻¹. Assuming an approximate average oil-on-cuttings concentration of 10%, this would correspond to a cuttings-in-sediment concentration of 0.1%. In Figures 8 and 9, all of the data points from all seven data sets have been plotted together. With the exception of a small number of samples, data fall into two general categories: >50% mortality at >100 ppm, and <50% mortality at <100 ppm. It must be emphasised that this is an approximate interpretation, but one which serves to suggest better than an order-of-magnitude convergence of data. Within each category, there is a substantial variation.

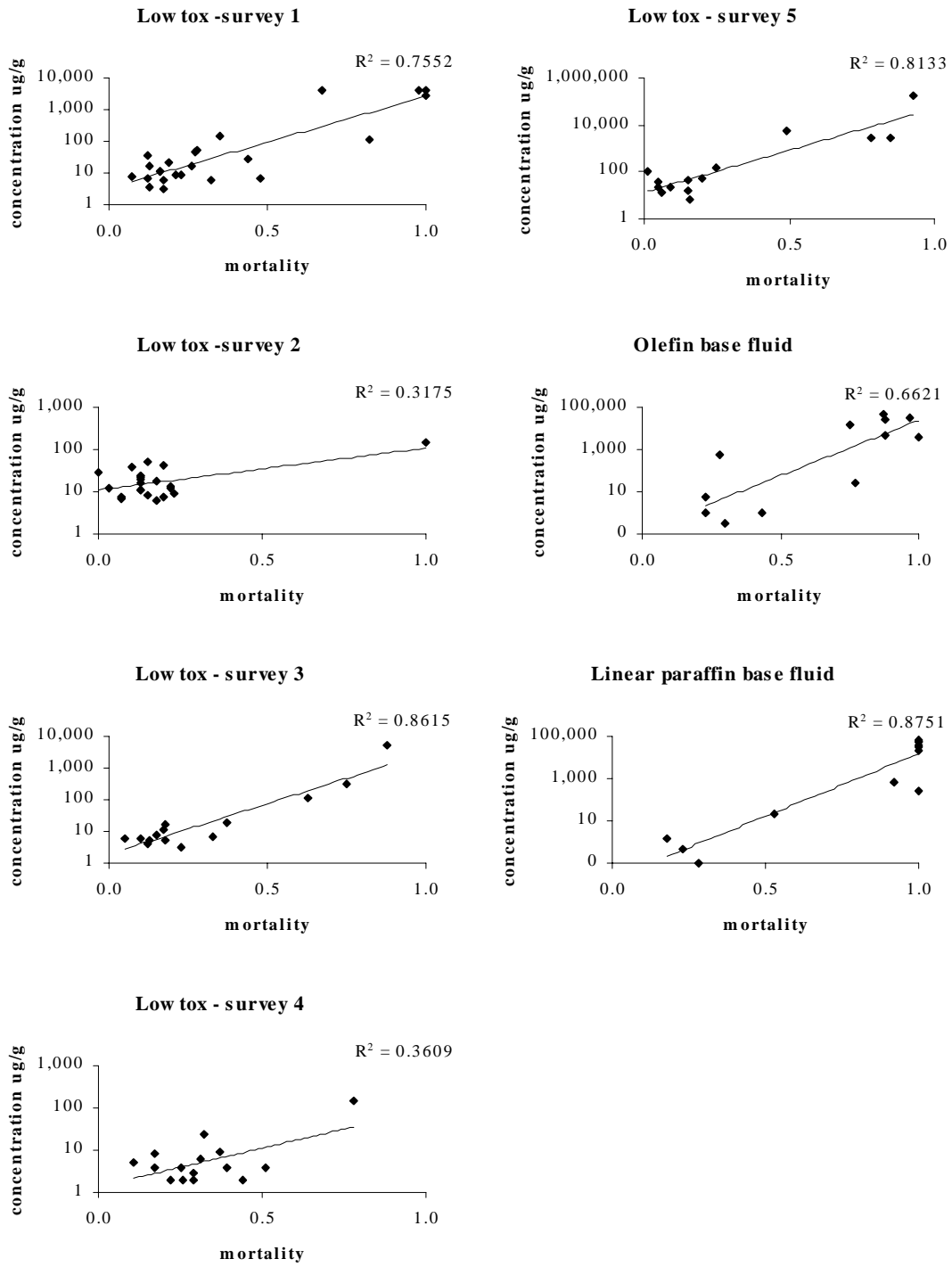


Figure 7 Offshore sediment bioassays: relationship between mortality and THC concentration

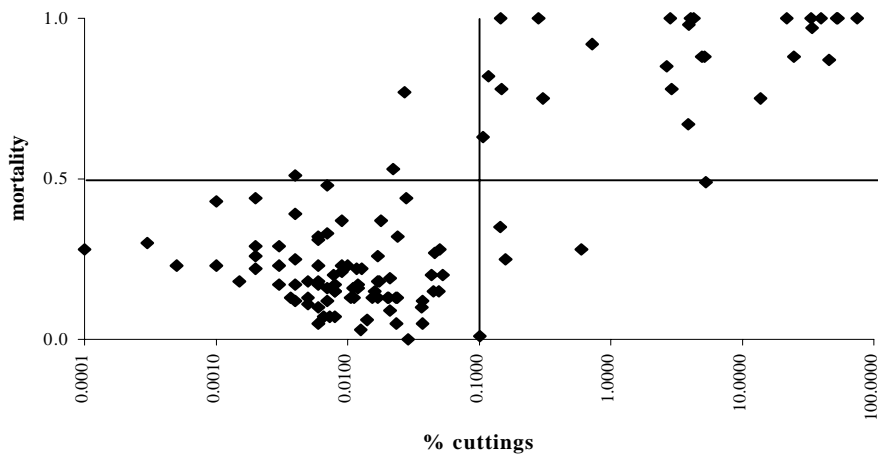


Figure 8 Offshore sediment bioassays: estimated relationship between mortality and cuttings content of sediment

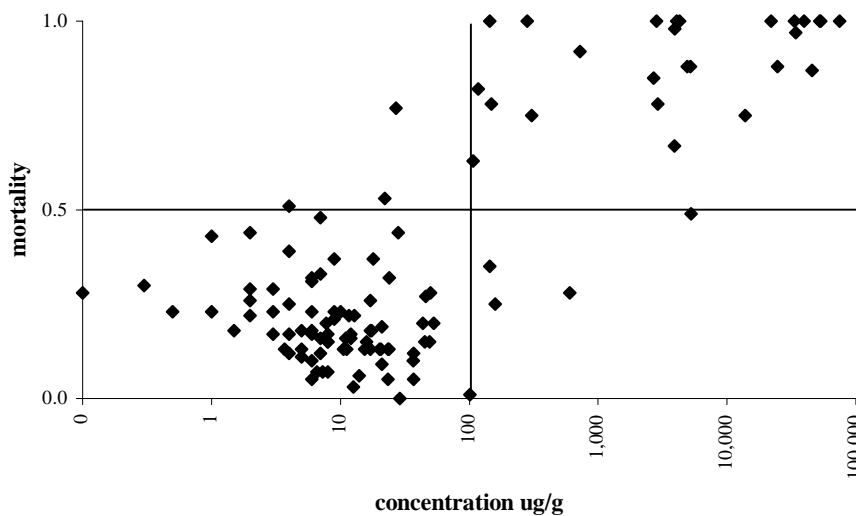


Figure 9 Offshore sediment bioassays: overall relationship between mortality and THC content

Two recent studies of cuttings-contaminated sediment have been reported by Grant and Briggs (Grant & Briggs 1999a, 1999b), using two distinct approaches in assessing the toxicity of sediment samples collected from the vicinity of NW Hutton. One of these studies used the *Corophium* bioassay in a manner similar to that described above; the other used the proprietary bacterial luminescence Microtox to measure the toxicity of dichloromethane-extracted organic contaminants in the sediment. Usefully, it was possible from this second study to infer that ammonia and sulphur did not seem to contribute significantly to the observed toxicity – although, given the obvious chemical loading in the sediment samples, this was not perhaps surprising. The Microtox study demonstrated that there was a marked

variation in the amount of extractable toxic material with depth in samples from the cuttings pile, and indicated also that, in relation to measured concentrations of hydrocarbon, that the 'intrinsic' toxicity of the extracted organics increased with depth. The use of DCM to extract the samples places a severe restriction on the interpretation of the Microtox data, since both available and non-available chemical will be extracted by this method; nevertheless, the results can be regarded as a 'bioassay' in the original sense of the word (ie, effectively an analytical measure of contaminant concentration).

The *Corophium* study of Grant and Briggs (1999b) observed a mortality-hydrocarbon concentration trend similar to that described above for a series of ERT studies. The lowest concentration observed to be associated with a significant reduction in survival was 153 mg.kg⁻¹, and interpolation on the concentration-response curve yielded an estimated 50% mortality effect concentration of about 230 mg.kg⁻¹. As with the ERT data above, the Grant and Briggs (1999b) data were relatively 'noisy', although the concentration-response regression was statistically significant.

Both field sediment-effects studies established a reasonably consistent order-of-magnitude relationship between total hydrocarbon concentration and mortality, but with substantial variability which cannot fully be accounted for. Some of the variability is undoubtedly associated with the limitation of precision of both the bioassay method and the chemical analysis; the precision of former could be of the order of 30-40% and the latter around 20% (both expressed as coefficient of variation). However, both data sets indicate substantially greater variation than could be accounted for in this way, suggesting that

- a) the actual composition of hydrocarbons could be important (Grant & Briggs suggested that PAH content might be important)
- b) other components could be contributing to the observed acute toxicity

Two questions which are therefore of importance are:

- Is there sufficient difference in the acute toxicity of aliphatic and aromatic hydrocarbons to account for apparent inconsistencies in overall toxicity?
- Do other organic components have (even in principle) sufficient acute toxicity potential in relation to their relative concentrations to account for apparent inconsistencies in overall toxicity?

The first question will be addressed in the following section. With respect to the second question, it is in principle possible that this might be the case. However, there are insufficient data to establish the probability in practice. Other organic components could represent between 5% and 20% of the total organic content of a drilling mud, and aqueous phase toxicity data indicate that many surfactants, for

instance, have acute LC50 values in the 1-10 mg.l⁻¹ range. If this level of toxicity is expressed in the solid phase, then non-base fluid organic components could in principle account for approximately the same 'amount' of acute toxicity in drilling fluids as current paraffinic and olefinic base fluids. However, the effect of chemical mixture and adsorption on the expression of toxicity is unknown and a reliable conclusion is not possible.

Interestingly, the ERT survey data indicated a consistent, monotonic relationship between mortality and distance from platform, irrespective of the degree of agreement with chemical data. This was also observed in a study conducted in 1990 as part of the Bremerhaven Workshop (Chapman et al, 1992), one of two reported studies which provide some indication of the potential impact of cuttings on overlying sediment.

The Bremerhaven Workshop study included the use of a variety of bioassays on a transect in the vicinity of an abandoned drilling site in the Dutch sector of the North Sea. A clear trend of diminishing mortality was observed in bioassays of samples collected along the transect, although there was evidence that storm events since the cessation of drilling had deposited 10-15cm of sediment on top of the cuttings. Analysis for parent HC compounds did not reveal any comparable trend in concentration. A similar pattern was observed in an experimental study (ERT, 1995) which investigated the effects of capping cuttings with clean sediment. In this 6-month study, sediment layers of different thickness were applied to cuttings, and the biological quality of the sediment layers was assessed at intervals. Bioassays carried out (*Corophium* OSPAR procedure) after three months indicated 50% mortality in sediment from an 8 cm layer, 50% mortality in sediment from a 5 cm layer, and 100% mortality in sediment from a 2 cm layer. No cuttings were present in any of the samples, and analysis did not show significant concentrations of the parent base fluid (a lox-tox mineral oil) in any of the sediment samples. As with the Bremerhaven study, analysis was not carried out for sulphide or for any more polar intermediate degradation products of the base fluid, nor for any other organic components of the cuttings.

These two studies suggest that components other than the original base fluid have the potential to influence the quality of sediments associated with cuttings. Neither, however, provides sufficient information to hazard an explanation.

The data presented above display a moderate level of agreement in respect of the acute effects associated with cuttings (or cuttings-derived material). An E&P Forum study published in 1993 (Minton et al, 1993) generated somewhat different conclusions. This study investigated the physical and biological effects of treated cuttings (ie, cuttings treated to remove some or all of the associated oil). The biological effects study concluded that an oil concentration of 1000 mg.kg⁻¹ in sediment

represented a threshold for effects. This threshold is at least one, and probably two, orders of magnitude above the concentrations suggested by the studies reported above.

5.5 Petroleum hydrocarbon toxicity

The primary purpose of this section is to attempt to establish whether petroleum hydrocarbons are sufficiently similar in terms of reported sediment toxicity to enable a 'total hydrocarbon' concentration to be used as a predictor of toxicity, or whether the variation in toxicity between hydrocarbons is sufficient to be a major source of variation in toxicity estimates.

In 1993, OSPAR organised a ring-test of sediment toxicity test methods, with the aim of identifying and selecting a method for incorporation into the harmonised suite of methods proposed for North Sea oilfield chemicals testing and regulation (TNO, 1994). One of the reference chemicals tested as part of this process was the aromatic hydrocarbon fluoranthene, and the results of the ring test provide

- a) A useful, replicated estimate of PAH toxicity in sediments
- b) a valuable reference point with respect to the precision and accuracy of standard test methods and a measure of the performance standard which can be expected of expert laboratories carrying out standardised test methods

The data from eight laboratories which tested the *Corophium* procedure (since adopted by OSPAR as a standard method) are summarised below:

Table 5 OSPAR *Corophium* ring test results

	Bioban (biocide)	Servo CK337 (corrosion inhibitor)	Fluoranthene
Mean LC50 (mg.kg ⁻¹)	72.9	313.8	19.9
Coefficient of variation (SD/mean)*100	38.5	42.8	51.9
Upper 95% limit	148.4	577	40
Lower 95% limit	-2.6	50.5	-0.33

The average LC50 for fluoranthene was 19.9 mg.kg⁻¹, a value substantially lower than the median value for recent mineral and synthetic base fluids, and one which suggests that PAHs in sediments could make a significant contribution to overall toxicity if they represent more than a few percent of the total hydrocarbon content. It is important to note, however, that the coefficient of variation for all

three ring test chemicals was large (between 38 and 52%), and that in two instances the 95% confidence interval included zero. This degree of variability is quite characteristic of standard acute toxicity tests (Parrish and Duke, 1988; Whitehouse et al, 1996), and places a severe constraint on the precision with which results can be used.

Polycyclic aromatic hydrocarbons contained in diesel and reservoir fluid

These molecules may possibly constitute the largest challenge related to contaminants in drill cuttings piles and to the environmental impact associated with attempts to remediate them.

The use of diesel as a lubricant in early oil-based drilling muds is the main source for contamination of the cuttings piles. Polycyclic aromatic hydrocarbons are a group of molecules that has received considerable attention and for which a wide range of damage has been documented (Neff et al. 1976, Rice et al. 1977, Black et al. 1983). In recent years, studies on fish have documented reproductive damage at concentrations to less than 1 ppb (nanogram/gram) of PAH in the water phase (Carls et al 1999, Heintz et al 1999, White et al. 1999) and it is believed eggs and fish larvae are particularly vulnerable.

The studies on fish and fish eggs cited above may serve as models for marine invertebrate larvae that settle on the seabed. Uptake is rapid and depuration is relatively limited. PAHs are preferentially accumulated in lipid tissue, and growth, morphological changes, and depletion of lipid stores can influence the expression of toxic effects.

The toxic effects of greatest concern occur as a result of metabolism. The initial intermediate metabolites are extremely reactive, and can damage many organic molecules including enzymes and DNA (Varanasi 1989, Decaprio 1997, Myers 1998). Damage is therefore expressed over a variety of levels of organisation, from disturbed enzyme functions to developmental damage during growth, to accumulation of genetic damage in populations. Induction of cancer is a possible outcome of such exposure. For fish, birds and mammals monitoring has, to a large extent, to rely on effects measurements because they metabolise PAH too rapidly to exhibit significant bioconcentration; the effects of metabolism are frequently more severe than the initial effects of accumulation (Neff & Sauer 1996).

In aerobic conditions the microbial degradation rate decreases as molecular size increases (Mackay et al 1992), but this relationship does not hold in anaerobic conditions (see separate section in UKOOA reports). Measurements have shown that PAC may remain at high concentrations at depth in drill cuttings piles (Kjeilen et al. 1999).

The metabolic toxicity of PAHs increase with size of the molecules. Acute toxicity assays are not sensitive to the range of types of effects for several reasons.

The rates at which hydrocarbons enter the water phase decrease with increasing molecular size (Mackay et al. 1992, Short & Heintz 1997). The OSPAR assays are therefore strongly biased towards recording effects from the smallest and most water-soluble molecules whose effects are of a more acute nature than effects observed for larger molecules. We have observed that when the OSPAR procedure for making water accommodated fraction (WAF) is followed, the oil particle size increases as oil load is increased. This adds to the bias towards the smallest and most water soluble molecules in OSPAR acute toxicity tests (Skadsheim et al 1996). Larger PAH require longer exposure times and their most marked effects are of a more chronic nature (consequences of long-term low dose exposures) than covered by the OSPAR test regime.

Swartz et al (1995) developed a model to predict the toxicity of PAH mixtures in sediments, using the equilibrium partitioning hypothesis (EqP). Although this paper did not cite any sediment toxicity values directly, the results suggested that it is practicable to construct an acute toxicity assessment from information on the physical and chemical properties of sediment and PAHs.

Driscoll et al (1997) investigated accumulation and toxicokinetics of fluoranthene in sediment bioassays with two species of amphipod (*Diporeia* and *Hyallela*). This study demonstrated differences in the equilibrium tissue burdens in the two species (<1 and 2-4 $\mu\text{mol.g}^{-1}$ respectively) which were proportional to measured toxicity responses. Driscoll et al cited 2-8 $\mu\text{mol.g}^{-1}$ as the PAH tissue concentration range within which toxic responses were apparent in other studies. The responses observed in this study were somewhat higher than predicted by equilibrium partitioning theory, and the authors concluded that tissue burden was a better predictor of acute toxicity. This study used exposure concentrations selected to bracket known LC50 values for the species used; these were in the range of 100-200 $\text{nmol.g dry weight}^{-1}$, approximately equivalent to 20-40 $\mu\text{g.g}^{-1}$ (and thus within the range for *Corophium* LC50 reported by the OSPAR ring test in 1993).

Massie et al (1981), in a report on hydrocarbon concentrations and effects in the North Sea, cited Armstrong et al (1981) as reporting that naphthalenes at concentrations of greater than 2 $\mu\text{g.g}^{-1}$ wet sediment had a detrimental effect on the benthos.

Roddie et al (1991) investigated the toxicity of sediments impacted by a coastal oil spill. The study included historically impacted sediments from the vicinity of a marina. Sand contaminated with beached oil (356 $\mu\text{g.g}^{-1}$ total hydrocarbons) caused 51% mortality in *Corophium*, while marina sediments (153 $\mu\text{g.g}^{-1}$ total hydrocarbons) caused approximately 32% mortality. These effects

occurred at slightly higher concentrations than the 'threshold' value indicated from offshore sediment bioassays reported above, but are similar to lethal effects concentrations reported for base fluids. This suggests that hydrocarbons have, in a broad sense (notwithstanding any additional chronic toxic effects of PAHs in mixtures), a general narcotic mode of action which can be described by a relationship between total concentration and acute lethality.

Narcosis and the residue-based approach to toxicity and bioconcentration

McCarty et al (1992) attributed many of the problems encountered in addressing aquatic toxicity issues to a poor understanding of the relevant physical, chemical, biochemical and physiological processes. This is clearly true in relation to cuttings toxicity. McCarty et al suggested that relating tissue concentrations of contaminants to specified response endpoints would make an essential link between the well-established study of pharmaco-kinetics and requirements of aquatic toxicology. The critical body residue (CBR) has since been increasingly recognised as a valuable tool in improving our ability to understand the consequences of exposure. McCarty et al proposed, using broadly-based evidence for a wide range of chemicals, that

- a) for water-soluble chemicals, the CBR should be similar to the LC/EC50
- b) for hydrophobic chemicals (log Pow 1.5-6) the acute CBR would be relatively constant but increase slightly with increasing log Pow – averaging about 4 mM (millimoles per kilogram, comparable to the values in $\mu\text{mol/g}$ reported above)

The estimates held good for a wide range of hydrophobic chemicals (phthalates, esters, benzenes, pesticides, halogenated hydrocarbons), but were less satisfactory for alcohols and ketones, which are readily metabolised. The authors concluded that therefore a preliminary common theoretical basis for interpreting aquatic toxicity of hydrocarbons had been established. Donkin et al (1996) made a similar case for the use of tissue residues, also adducing evidence for a fairly uniform critical tissue residue for a wide range of hydrophobic organic chemicals.

Broderius et al (1995) provide an excellent discussion of polar and nonpolar narcosis, but comment that the phenomenon is still poorly understood. Polar narcosis is exemplified by phenol, while nonpolar narcosis is exemplified by 1-octanol. Slightly greater toxicity is associated with the former than with the latter. The latter, in particular, is characteristic of a very wide range of chemicals. They comment that there is a general shift towards narcotic action as hydrophobicity increases. Narcosis can most simply be defined in terms of the 'Ferguson principle' of equal potency resulting from equal concentrations at the site of action. This is a possible explanation of the general agreement with respect to similar critical tissue residues across species and chemicals – that, to the extent that the availability of sites of action (effectively, lipid concentration) is similar, the critical tissue residues in different species will also be similar.

Alkylated phenols in oil

Alkylated phenols in oil are mainly C1-C4 alkyl homologues and they may induce the same types of toxic effects as PAHs (Cronin & Dearden 1995, Cronin & Schultz 1996, Hermens & Verhaar 1997); studies on this subject are very limited, however. They may partition between water, biota and sediments in a manner similar to PAHs of comparable molecular size. Alkylated phenols may act as endocrine disruptors; combined with high bioaccumulation factors for some substances this could imply that they might exert damage at very low concentrations.

5.6 Drilled solids toxicity

No information is available on the toxicity of drilled solids alone. Clearly, there is a potential contribution of trace metals, together with (in some instances) oil contamination from the reservoir. The biological availability of trace metals from drilled solids is not known, either in an absolute sense or relative to the potential availability of trace metals from the drilling mud.

5.7 LSA scale toxicity

The Upper Jurassic Draupne Formation (= Kimmeridge Clay Formation) dominates the North Sea as well as onshore from the English Channel to Yorkshire and in the Oslofjord area, and is the main potential source of weakly radioactive shale. Coastal and river-bound erosion transport large amounts of this radioactive shale to the sea, but no adverse influence on marine life has been reported. In comparison drill cuttings piles constitute a minor addition and they do not differ from local scale aggregations caused by water transport (OLF 1993).

No information could be found on the toxicity of LSA scale. Since this type of material is, by definition, an insoluble precipitate, it is unlikely that the components would be biologically available, and it is therefore also unlikely that any acute or chronic toxicity would ensue from the association of this material with deposited drill cuttings. However, the precipitate forms under saturation conditions, and no studies have been conducted to determine the extent to which solubilisation might occur after discharge to the environment. The low levels of activity present would not be expected to give rise to any observable biological effects on the invertebrate benthos, since the lifespan of the majority of organisms is too short for the effects of low-level radioactivity to be expressed in the individual.

6 Evaluation of toxicity data

6.1 Contributions to toxicity

In considering the relative contributions of different materials to the actual or potential toxicity of cuttings, it is essential to maintain a distinction between intrinsic toxicity, toxicity as reported by standard test methods, and the expression of toxicity in a complex mixture. For instance, in water-phase tests it is to be expected that much of any observed effect will be attributable to the more water-soluble components of the mixture. This does not mean that these components are the most 'toxic', simply that their relative abundance in the test phase is higher than other components. Also, not all components of drilling fluids or cuttings would be expected to express their toxicity in all environmental compartments. More polar and soluble materials are most likely to be released to the aqueous phase during initial deposition or resuspension during disturbance of the cuttings pile. Less soluble materials will remain associated with solids, and their effects will be expressed in the sediments on which the cuttings settle. The impact of toxicity will also differ between environmental compartments; material released to the water column will be released episodically, and will disperse and dilute, while material deposited on the seabed is more likely to persist for longer periods of time. This difference has implications for the interpretation and use of toxicity data, since the majority of data represents the effects of constant exposure, and is therefore most useful in the regulation of contaminants which are continuously replenished in the environment. The persistence of toxicity arising from an episodic event can be very different in the water column and sediments, and any attempt to infer hazard should take this into account.

6.1.1 Water column

To accurately estimate releases to the water column during resuspension and deposition, it would be necessary to have knowledge of the degradation and transformation processes to which the components of the cuttings had been subject whilst in the pile. If no transformation occurred, then the aqueous availability of the components would be expected to no greater than that at the time of original settlement, and the acute toxicity of resuspended cuttings would be adequately predicted by existing elutriate toxicity tests. The data from such tests indicate (with the exception of some cationic polymer muds and diesel-based muds) that acute water column toxicity would be limited. Although we have pointed out the limitations of acute lethal tests elsewhere, the data are possibly more relevant in this type of situation, in which an episodic discharge occurs – concentrations at which even chronic effects might occur will be sustained for only a short period of time following discharge.

6.1.2 Sediments

The data presented previously indicate, in a number of ways, that hydrocarbons make a major contribution to toxicity associated with cuttings in the sediment compartment. Other organic components of drilling muds generally represent less than 20% of the organic phase by mass, and the majority of these components are of similar or lower toxicity compared to low-tox and synthetic base fluids (the main hydrocarbon content in recent and current muds). A number of studies have indicated toxic effects of cuttings in sediments at similar approximate concentrations in the region of 0.1%. These data suggest an order-of-magnitude convergence on a value of around 100 mg.kg^{-1} for acute lethal effects of hydrocarbons. This is towards the low end of values reported for recent base fluids, but well within the known error of the test methods. A significant contribution of other components to acute toxicity cannot be precluded, since it would be difficult to detect with confidence any contribution which influenced LC50s by less than a factor of 2-3. There are no data from which to estimate the potential consequences of chronic toxicity related to components such as the higher molecular weight PAHs, nor sufficient evidence to indicate whether it would be defensible to adopt a 'safety' or 'application' factor for acute toxicity data in this respect. While it is highly probable that nonpolar narcosis is the primary mode of action for the majority of components at acute lethal concentrations, the modes of action of the potentially most harmful components (alkylphenols and PAHs) are sufficiently different to suggest caution in the use of standard factors.

The variability of trace metals concentrations is too large, both in an absolute sense and in relation to other cuttings markers such as hydrocarbons and barium, to be able to attribute a specific toxicity contribution to this class of contaminant. The literature does not provide consistent guidance on the potential for metals to become biologically-available within cuttings piles or impacted sediments. There is evidence to suggest that relatively high total trace metals concentrations can be tolerated with little harm under circumstances where binding or precipitation with sediment fractions (sulphide, acid-volatile sulphide, Fe, and Mn hydroxides) is possible.

There is a paucity of quantitative observations on the presence and concentration of alkylphenol ethoxylates and their degradation products in cuttings. The availability of these materials in complex mixtures in cuttings and sediments is unknown. The literature on endocrine disruptors has focused (understandably at this stage) on the effects of constant chronic exposure on fish, and there are no comparable data for invertebrates (which would be the primary 'target' for EDs in sediments).

The available data do not suggest that organic components such as ethoxylated alcohols, biocides (such as glutaraldehyde) or the majority of anionic or cationic surfactants present a significant risk. None are highly toxic, and they are generally fairly readily degradable. None (other than alkylphenol

ethoxylates) appear to have specific modes of action which would give rise to concern with respect to chronic toxicity. It is possible, but has not been verified, that the presence of surfactants could potentially increase the biological availability and uptake of hydrocarbons. However, if this did occur, it is not known whether the surfactants would persist for sufficiently long to have a major influence on the these processes.

6.2 Adequacy of data

A primary limitation is lack of knowledge on what is present and, moreover, what fraction of which substances that occur in a form (chemical state) that is bioavailable. In summary, the main limitations are:

- Lack of specific information on which substances have been used
- Lack of description of what is present in piles and how it is distributed within piles
- Lack of descriptions of contaminating substances in drilling products and variations caused by batch production and shifts between suppliers
- Lack of measurements and criteria defining which substances or molecules are bioavailable
- Acute toxicity assays have a range of limitations (dealt with in more detail elsewhere)
- Acute toxicity tests are still most suitable for readily water dissolved substances, and fail to reflect the most important effects of the more poorly soluble substances
- A lack of methods, and hence knowledge, to assess potential effects from chronic exposures (long term at low doses)
- Lack of knowledge about degradation processes and rates
- Lack of knowledge about diffusion rates of substances in cuttings piles
- Pulses of use of diesel or other special chemicals when special problems occur that have not been reported

- Quality assurance
 - Exposure characterisation: tests on field samples tend to have more consistent confirmation of exposure concentrations than do laboratory tests. The overwhelming majority of laboratory tests on drilling muds and components are not supported by chemical analysis; with poorly-soluble chemicals and mixtures in particular, this creates substantial uncertainty with respect to the actual exposure, or even the units in which the results are reported. The majority of data should therefore be treated with a degree of caution in respect of acute toxicity, and with extreme caution in respect of any extrapolation from acute effects to chronic effects.

- Metals
 - The quantities, speciation, and partitioning of trace metals have not been adequately investigated in relation to cuttings or to species chronically exposed to cuttings. Total metal concentrations in cuttings or contaminated sediments do not provide any useful guide to their potential or actual effects on biota.
 - Although the research community is beginning to develop more effective approaches to assessing metal toxicity in sediments, these have not yet been translated into effective sediment quality criteria/standards

6.3 Summary

The quality and relevance of the data accumulated over the past 20 years has largely been determined by the objectives of various regulatory schemes. With an increasing and more effective degree of control over usage of drilling chemicals, the risks associated with new products appear to have diminished. Pre-screening procedures have been developed, which attempt to eliminate persistent, accumulative chemicals and to identify and eliminate those with very specific modes of action. This approach increases confidence that acute, lethal toxicity tests can provide useful information and enable more effective regulation of chemical use. The corollary of this is that there has been a corresponding decrease in more basic research, especially in respect of chronic and sublethal effects and effects at the community level. Improvements in available methodology, such as the introduction of solid-phase tests, have not been applied retrospectively to assess the impacts of earlier activities, and the data associated with those earlier activities are, as has been indicated, of limited relevance and use. Current regulatory schemes have achieved a good degree of control over the use of chemicals, and have been effective in

- Identifying and eliminating many chemicals of major concern
- Constraining the use of many potentially harmful chemicals
- Making informed selection of less harmful chemicals for use in existing and new products

However, the schemes (and the methods on which they rely) have not been designed to facilitate the acquisition of data from which environmental processes can easily be inferred, and there is consequently a significant gap in our knowledge of the potential impacts associated with historical cuttings deposits.

7 Conclusions

7.1 *Gaps in data*

Cuttings and contaminated sediment (complex mixtures)

Some data are available which indicates a general trend in acute toxicity of 'whole' samples. This covers very few platforms/occasions, and is insufficient to draw anything but the most general conclusions. A substantially greater quantity of similar studies would be required in order to characterise the range of variation and to provide a basis for determining whether there are consistent features in terms of toxicity. No information is available on the actual biological availability of contaminants from cuttings, especially in terms of the ways in which the composition might influence or bias availability.

Hydrocarbons

Existing data exhibit reasonable order-of-magnitude agreement with respect to acute effects, but these data can only be roughly extrapolated to estimates of chronic effects for the simplest modes of chemical toxic action (eg, nonpolar narcosis). Insufficient data are available to determine the relative importance of other chronic effects mechanisms (especially in relation to PAHs).

Metals

Few data are available on a comprehensive range of metals in cuttings. Existing data are highly variable, and patterns are difficult to explain. Better data are required, and it is important that both sampling and analysis attempt to measure sufficient additional variables to allow an assessment of speciation and availability. No direct information on metals uptake and toxicity in relation to North Sea cuttings is available.

Surfactants

With the exception of APEs, these do not appear to present a significant direct hazard. However, their interactions with other potential cuttings components is unknown. A better understanding of their persistence in sediments would be required in order to assess the potential for chronic effects.

Endocrine disruptors

No data are available on the presence and concentrations of APEs and APs in cuttings. Data are also required on the fate of these components if transferred from cuttings to sediments (the most probable route by which an effect might be expressed), and on the rates of uptake and consequent tissue burdens of these materials

Toxico-kinetics

There exist published data on toxico-kinetics of some potential components, but there are no recent studies for cuttings piles. Early studies on metals in barites did not indicate significant uptake or toxicity, but physico-chemical processes in cuttings piles might have the potential to alter the speciation and availability of metals. There has been no directly applicable research in this area in recent years. The 'black box' nature of existing toxicity test methodology does not enable an identification of the relative importance of different components.

Toxico-kinetic studies, by relating exposure to uptake, uptake to tissue concentration, and tissue concentration to toxicity, can help remove some of the 'black box' element of toxicity testing, and can generate knowledge which can more easily be translated from one set of circumstances to another. Unsupported, current test methodologies will not enable us to determine if the same factors drive toxicity in all cuttings.

The chemistry of cuttings piles is undoubtedly complex, but is poorly understood. Basic toxico-kinetic studies would provide valuable information on the biological availability of contaminants from cuttings under different environmental conditions.

7.2 Summary of state of knowledge

The available information from field and laboratory measurements indicates that hydrocarbons play a significant role in determining the acute toxicity of cuttings. Our best estimate is that 'total' HC LC50s lie in the range 50-200 mg.kg⁻¹, corresponding roughly to cuttings-in-sediment concentrations of the order of 0.1%. It is clear that this does not account for all of the actual or potential toxicity, and that there is a need for a better understanding of the factors governing partitioning and availability of metals, PAHs and APs. At best, hydrocarbon concentration can at present be considered a 'marker' for approximate toxicity.

It is also clear that we do not have sufficient information with which to make inferences about chronic toxicity. On the basis of apparent hydrocarbon toxicity alone, the threshold for chronic effects might be expected to lie in the region of 10 mg.kg⁻¹, and the no-effect concentration to be in the 1-10 mg.kg⁻¹ range. These values provide only an approximate empirical indication, though, and are at present only a general inductive conclusion. However, this estimated threshold for effects corresponds to that estimated from ecological studies to be the threshold for observable community disturbance. This raises the possibility that the mid-field effects observed from numerous offshore surveys might be

attributable to chemical effects rather than to organic enrichment. It is not, of course, possible to attribute such mid-field effects unambiguously to drilling operations; sediment hydrocarbon concentrations could, in principle, be sustained in part by other, more recent, inputs.

Although cuttings do elicit a measurable response in laboratory toxicity tests, it is also certain that cuttings are too complex and variable to permit numerically precise extrapolation from the limited data available. Different mixtures of components could have similar effects, and the hazards posed by some components will not be usefully reflected by standard test methods. It is therefore considered important to establish the actual biological availability of cuttings components in different environmental compartments. By identifying the components which are accumulated, it will be more feasible to identify the risks, and to select the most appropriate methods for quantifying the risks.

Current regulatory schemes have made substantial progress in eliminating from use most, if not all, of the most potentially harmful chemicals. However, the methods most appropriate for effective regulation of use are generally not applicable to the process of risk and hazard assessment. Acute toxicity measurements provide little useful information on the hazards associated with the more persistent historical contaminants in cuttings, or with contaminant which have very specific modes of action. While there is no conclusive evidence that such materials are either at critical concentrations in cuttings, or that they do in fact currently cause chronic effects, there is equally no conclusive evidence that they do not present some degree of long-term hazard.

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9 Appendix

9.1 *Environmental compartments and exposure mechanisms*

The term ‘toxicity’ is widely used, but is applied with variable meaning. In general terms, the word denotes the potential of a substance to cause biological harm. However, toxicity is not an inherent property of substances – that is, there is no single, unambiguous referent for the term. It can be defined in a number of different ways, and each definition has a specific, but clearly limited, applicability. Elements of definition include:

- The *dose* of a substance required to cause a defined biological response
 - This is often expressed in units of $\text{mg}\cdot\text{kg}^{-1}$ body weight
 - The dose can be expressed in total terms, or in rate terms
- The environmental *exposure concentration* required to cause a defined biological response
 - The units depend on the environmental compartment (air, water, soil, sediment)
 - The reliability of a concentration value is often constrained by limited knowledge of the fate, partitioning behaviour or speciation of the substance in question
- The nature of the biological response
 - Many different biological responses can be measured; these differ in terms of environmental relevance, precision, accuracy (in general terms, there is an inverse relationship between precision and relevance)

Hazard, in the context of this review, can occur within two general environmental compartments – water and sediments. Hazard can also occur via exposure or dose – that is, in response to uptake from the ambient matrix (water or sediment) or via ingestion (of contaminated sediment or biota).

In the context of this report, it is also important to realise that ‘ecotoxicity’ does not become important until some form of environmental exposure occurs. Thus, although we cannot talk about the toxicity of cuttings *per se*, it is useful to consider the potential impact of cuttings when introduced to particular environmental compartments. This is a consequence of the exposure-driven nature of ecotoxicological testing noted above. This type of testing can report the concentration of a material in a given medium required to cause a defined effect on individuals –it less often seeks to determine the internal dose of a material required to elicit an effect. Thus, when toxicity data are reported or

reviewed, it is predominantly in relation to concentrations in compartments such as water and sediment.

The foregoing must be always be borne in mind when evaluating ecotoxicity data. A further constraint is that the details of exposure are often unknown or poorly understood, especially when dealing with chemical mixtures. This is a particular problem with oilfield chemicals, where it is extremely unusual for toxicity tests to incorporate any assessment of the chemistry of the test system. We are thus generally limited to a knowledge of the quantity of whole material added to the test system, and do not have reliable information on the distribution or form of chemicals within the system.

Whether exposure is well-characterised or not, the mechanisms leading to an observed effect may not be clear. Although it is common practice to compare test results in terms of sensitivity (species x is more sensitive to a chemical than species y, on the basis of comparative LC50s), this is equally commonly a misleading practice. What we can observe is that the response of one test species differs from another – but this could be due to

- ‘real’ difference in sensitivity
- differences in exposure to the chemical related to morphology or behaviour
- differences in uptake of chemical related to physiology

It is commonly the case that (due to the ‘black box’ nature of most tests) the ‘underlying’ toxicity of a material is not clearly reflected in the test results, and that results can in reality represent a wide spectrum of physical, chemical and biological processes. It is therefore necessary to be cautious in the comparison of toxicity data if the physico-chemical conditions of the tests are not thoroughly understood.

9.2 *Types of toxicity test and endpoint*

Toxicity tests are not direct measurements of a property, but rather are designed (and usually standardised) experiments from which a property is inferred. The purpose of standardisation is to provide some justification for the use of inductive reasoning in comparison between experiments – ie, to try to justify the comparison of the results of one toxicity test with another, a process which is a keystone of regulatory decision-making. The reliability of comparisons depends therefore on the degree of standardisation and the rigour and thoroughness with which tests are conducted. This means that a simple numerical comparison of existing data is limited both in usefulness and defensibility.

While standardisation is intended to provide a 'level playing field' for comparison, it is generally difficult to demonstrate that standardised procedures actually or adequately control critical test variables. For this reason, many regulatory schemes incorporate a requirement for the use of 'reference' toxicants, which are broadly the equivalent of external standards in chemical analysis. Whilst these can be of value in demonstrating consistency in the quality of test populations and experimental conditions, they are of direct relevance only in relation to tests on chemically-similar materials. This places a limit on the precision and interpretability of data for materials such as production chemicals and drilling fluids, which are often a mixture of substances with very different solubility and partitioning characteristics.

Although there are a wide variety of ecotoxicological test methods reported in the literature, the overwhelming majority of reported results are derived from acute (short-duration) lethal tests (>95%, Maltby, 1993). Studies investigating the potential effects of drill cuttings have ranged from standardised tests on drilling fluids and components to 'mesocosm' studies on cuttings in sediment (in which factors such as community structure and re-colonisation of impacted sediments are examined). The complexity and ecological relevance of assessment methods is inversely related to the precision and ease-of-use of results. The more complex and 'realistic' the method is, the greater is the number of factors and processes reflected in the results. Thus, the relative influence of different factors is often less clear. Single-species laboratory toxicity tests are usually of limited ecological relevance, but are widely used because the results are perceived to be less ambiguous – that is, they are intended to focus primarily on one aspect of ecological impact only – chemical toxicity. Chemical toxicity does not provide a single comprehensive measure of the impact of contaminants, but it does provide a relatively uniform basis for comparative assessment.

Toxicity assessment is most appropriately used in the evaluation of hazard – that is, the potential for harm. It does not, in itself, provide sufficient information to predict actual environmental harm; this is the function of risk assessment, in which a variety of approaches are taken to translate laboratory data into predictions of environmental effects. Risk assessment methods are not within the remit of this report, and will not be discussed in detail.

It is worth noting, however, that

- a) there is no general consensus on the validity or practicability of extrapolating from laboratory data to field effects and
- b) the majority of risk assessment methods employ arbitrary calculation methods which are in most instances difficult to defend scientifically (ie, they are merely convenient administrative tools developed to implement a regulatory process)

As indicated above, water and sediments are the two primary environmental compartments of concern with respect to the potential toxicity of drill cuttings and their components. Generic approaches have been developed for assessing toxicity in both media, and are reflected in a range of standardised methods published or approved by a number of national and international bodies (OSPAR, OECD, US EPA, ISO, etc). In general, water-phase tests are considered most appropriate for soluble materials, and sediment-phase tests most appropriate for insoluble or poorly-soluble materials. Since, by definition, cuttings deposited on the seabed comprise those components which do not readily dissolve in seawater, the most relevant toxicity data will be those generated in sediment toxicity tests (sometimes referred to as solid-phase tests).

OECD (for instance) has developed a comprehensive, tiered system of toxicity tests for risk assessment of pure chemicals, which incorporates a progression from acute lethal tests to more sensitive chronic lethal and chronic sublethal tests. The cost of these more sensitive tests is sufficiently high that they are rarely, if ever, employed to test industrial wastes. Consequently, available data on drilling fluids and wastes are largely confined to acute lethal test results.

Typically, water-phase tests are of 48-96 hours duration, and use phytoplankton, zooplankton and fish. Sediment-phase tests are less numerous, and are usually of 10 days' duration; the most commonly-employed methods use amphipod species. Sediment-phase tests have been available in standardised form for only a few years in Europe, with the effect that data are available only for relatively recent studies and products. A standard sediment method for testing oil industry chemicals was adopted in 1995 (OSPAR, 1995), following the recognition that existing water-phase methods were not appropriate for testing poorly-soluble materials (eg, OECD 1984). Prior to this, virtually all tests on drilling and production chemicals were conducted using a variety of water-phase preparations (elutriates, water-accommodated fractions, emulsions, and undefined mixtures). The lack of standardisation of preparation methods, together with an absence of supporting analytical data, led to the reporting of a very wide range of toxicity values, as well as creating substantial uncertainty with respect to the units in which test results were reported. This has led to invalid comparisons and erroneous conclusions. Stromgren and Reiersen (1987), for instance, compared sensitivities of different test methods in arbitrary concentration units which failed to recognise that the methods differed fundamentally in terms of exposure (in fact, one method regulated dose rather than exposure).

The duration of tests can also be an important factor in determining apparent and relative magnitude of effect. Absolute duration is of less importance if effect observations are made frequently during a test; however, there has been a steady trend towards fixed-duration tests with fewer observations which has contributed to a reduction in the discriminatory power of such tests. Recently (Crane, 1998), there has been a recognition that this trend has led to a substantial loss of information and considerable bias in

toxicity assessment, and the value of time-to-effect studies has been re-affirmed. This type of information is not routinely used in oilfield chemicals testing and regulation at present, with the consequence that acute test results have the potential to suggest differences in toxicity which might not be reflected in longer-term lethal responses (ie, short-term LC50s could differ, but the Median Lethal Threshold Concentrations could be similar). This raises the possibility that regulatory decisions might sometimes be made on the basis of apparent rather than real differences in toxicity. In the context of this report, it means that reported toxicity values cannot be regarded as in any sense absolute unless it is quite clear that potential bias can be identified and allowed for.

It remains the case, however, that although increasing standardisation in test methodology (especially in respect of oilfield chemicals) has improved the comparability of results in a technical sense, the accompanying simplification of design has certainly impaired comparability in a toxicological sense. This has not presented a major problem in terms of the primary objective of standardised tests, which is to provide an approximate tool for relative hazard classification of acutely toxic chemicals. It does, however, present a problem when any attempt is made to use the results of such tests for more sophisticated purposes (such as mixture toxicity modelling, risk assessment). OSPAR tests, for instance, lack both the necessary design features *and* the essential quality control measures to be reliably used for any purpose beyond basic hazard classification. Given the complexity of many oilfield chemical formulations, it would in fact be impossible to implement appropriate QC within any acceptable technical framework (the development and routine use of analytical methods for the majority of substances known to be present in formulations would present a major technical challenge).

9.3 Application and interpretation

Summarising the above observations:

- Standard toxicity tests have limited precision
- Exposure is rarely characterised and
 - The choice of test method is not always appropriate to the characteristics of the test material or to the primary environmental fate compartment for the material
- Test data are frequently reported in arbitrary concentration units, and this places a constraint on the confidence with which toxicity values from different sources and for different materials can be compared
- The majority of standard test designs focus on acute lethal effects, and are intended for, or have been adapted from, the assessment of relatively soluble pure chemicals – their application to complex mixtures containing less soluble materials is often of uncertain validity

9.3.1 Relevance and quality of data

Data will be assessed, as far as possible, in terms of both relevance and quality. The foregoing discussion has established that ecotoxicity tests are neither precise nor accurate, and that they are subject to a substantial range of uncertainties. While standardisation can help to increase consistency in bias (it is not possible to assert that this is equal to an improvement in accuracy), there is no direct evidence (contrary to common belief) that it can be assumed to deliver better precision. Coefficients of variation for standardised tests commonly range from 30-60% (OSPAR 1992, 1993; Whitehouse et al, 1996), and this implies repeatability within a factor of roughly two. Between laboratories, reproducibility within a factor of three is a reasonable expectation, and four is not unusual (Parrish and Duke, 1988).

It is very important to recognise also that the above constraints on interpretation apply to a relatively ideal situation, in which as much of the testing process as possible is standardised, and in which therefore there is a reasonable degree of consistency in the reported concentration units. Since there has been only gradual convergence in the approaches taken to testing, there is correspondingly a potentially wide but undefined variation in the meaning of such units. In consequence, it is not possible to assume that (for instance), effects concentrations of ppm or mg.l⁻¹ can be directly and quantitatively compared between tests conducted in different laboratories, or on different materials or species.

There are substantial uncertainties associated with the methods used to generate much of the available toxicity data, together with considerable variation in QA/QC and a general absence of supporting data providing quantitative confirmation of exposure conditions. For these reasons, few of the available data would, conventionally, be regarded as suitable for the purposes of risk assessment.

9.3.2 Chronic and sublethal effects

It has been noted above that the overwhelming majority of tests relate to acute lethal effects. It is widely recognised that standard lethal tests are not adequate to assess the hazard of substances which are highly persistent but of low acute toxicity, which have highly specific but sublethal modes of action, or which are bioaccumulative but not lethally toxic. Acute lethal tests are often most useful in performing comparative assessments of metals and organic substances which have similar gross modes of action but which are not persistent or highly bioaccumulative.

The importance of chronic effects is widely recognised, and for this reason many regulatory hazard assessment schemes incorporate the use of application factors to convert acute lethal toxicity data to estimates of chronic toxicity. These factors are either acute-to-chronic lethal conversion factors (ACR ratios) or are an attempt to convert acute or chronic lethal values to estimates of chronic sublethal

effects. This type of estimate relies on the assumptions that ACR values are reasonably consistent across a wide range of chemicals (not supported) and that modes of action at the acute, chronic and sublethal levels are similar for most chemicals (again, there is no evidence to support this – nonylphenols, for instance, can be acutely toxic at one range of concentrations and be potential endocrine disruptors at another range). Furthermore, it is very difficult to defend the application of this approach to chemical mixtures.