NORTH WEST SHELF
JOINT ENVIRONMENTAL
MANAGEMENT STUDY

Contaminants on Australia's North West Shelf: sources, impacts, pathways and effects

NWSJEMS
TECHNICAL REPORT No. 13

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Final report

North West Shelf Joint Environmental Management Study Final Report.

List of technical reports

NWSJEMS Technical Report No. 1
Review of research and data relevant to marine environmental management of Australia’s North West Shelf.
A. Heyward, A. Revill and C. Sherwood

NWSJEMS Technical Report No. 2
Bibliography of research and data relevant to marine environmental management of Australia’s North West Shelf.
P. Jernakoff, L. Scott, A. Heyward, A. Revill and C. Sherwood

NWSJEMS Technical Report No. 3
Summary of international conventions, Commonwealth and State legislation and other instruments affecting marine resource allocation, use, conservation and environmental protection on the North West Shelf of Australia.
D. Gordon

NWSJEMS Technical Report No. 4
Information access and inquiry.
P. Brodie and M. Fuller

NWSJEMS Technical Report No. 5
Data warehouse and metadata holdings relevant to Australia’s North West Shelf.
P. Brodie, M. Fuller, T. Rees and L. Wilkes

NWSJEMS Technical Report No. 6
Modelling circulation and connectivity on Australia’s North West Shelf.
S. Condie, J. Andrewartha, J. Mansbridge and J. Waring

NWSJEMS Technical Report No. 7
Modelling suspended sediment transport on Australia’s North West Shelf.
N. Margvelashvili, J. Andrewartha, S. Condie, M. Herzfeld, J. Parslow, P. Sakov and J. Waring

NWSJEMS Technical Report No. 8
Biogeochemical modelling on Australia’s North West Shelf.
M. Herzfeld, J. Parslow, P. Sakov and J. Andrewartha

NWSJEMS Technical Report No. 9
Trophic webs and modelling of Australia’s North West Shelf.
C. Bulman

NWSJEMS Technical Report No. 10
The spatial distribution of commercial fishery production on Australia’s North West Shelf.
F. Althaus, K. Woolley, X. He, P. Stephenson and R. Little

NWSJEMS Technical Report No. 11
Benthic habitat dynamics and models on Australia’s North West Shelf.
E. Fulton, B. Hatfield, F. Althaus and K. Sainsbury

NWSJEMS Technical Report No. 12
Ecosystem characterisation of Australia’s North West Shelf.
V. Lyne, M. Fuller, P. Last, A. Butler, M. Martin and R. Scott

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NWSJEMS Technical Report No. 14
Management strategy evaluation results and discussion for Australia’s North West Shelf.
R. Little, E. Fulton, R. Gray, D. Hayes, V. Lyne, R. Scott, K. Sainsbury and D. McDonald

NWSJEMS Technical Report No. 15
Management strategy evaluation specification for Australia’s North West Shelf.
E. Fulton, K. Sainsbury, D. Hayes, V. Lyne, R. Little, M. Fuller, S. Condie, R. Gray, R. Scott, H. Webb, B. Hatfield, M. Martin, and D. McDonald

NWSJEMS Technical Report No. 16
Ecosystem model specification within an agent based framework.
R. Gray, E. Fulton, R. Little and R. Scott

NWSJEMS Technical Report No. 17
Management strategy evaluations for multiple use management of Australia’s North West Shelf – Visualisation software and user guide.
B. Hatfield, L. Thomas and R. Scott

NWSJEMS Technical Report No. 18
Background quality for coastal marine waters of the North West Shelf, Western Australia.
K. Wenziker, K. McAlpine, S. Apte, R.Masini

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ACRONYMS

ACOM	Australian Community Ocean Model
AFMA	Australian Fisheries Management Authority
AFZ	Australian Fishing Zone
AGSO	Australian Geological Survey Organisation now Geoscience Australia
AHC	Australian Heritage Commission
AIMS	Australian Institute of Marine Science
AMSA	Australian Maritime Safety Authority
ANCA	Australian Nature Conservation Agency
ANZECC	Australian and New Zealand Environment and Conservation Council
ANZLIC	Australian and New Zealand Land Information Council
APPEA	Australian Petroleum, Production and Exploration Association
AQIA	Australian Quarantine Inspection Service
ARMCANZ	Agricultural Resources Management council of Australia and New Zealand
ASIC	Australian Seafood Industry Council
ASDD	Australian Spatial Data Directory
CAAB	Codes for Australian Aquatic Biota
CAES	Catch and Effort Statistics
CALM	Department of Conservation and Land Management (WA Government)
CAMBA	China Australia Migratory Birds Agreement
CDF	Common data format
CITIES	Convention on International Trade in Endangered Species
CTD	conductivity-temperature-depth
CMAR	CSIRO Marine and Atmospheric Research
CMR	CSIRO Marine Research
COAG	Council of Australian Governments
ConnIe	Connectivity Interface
CPUE	Catch per unit effort
CSIRO	Commonwealth Science and Industrial Research Organisation
DCA	detrended correspondence analysis
DIC	Dissolved inorganic carbon
DISR	Department of Industry, Science and Resources (Commonwealth)
DEP	Department of Environmental Protection (WA Government)
DOM	Dissolved organic matter
DPIE	Department of Primary Industries and Energy
DRD	Department of Resources Development (WA Government)
EA	Environment Australia
EEZ	Exclusive Economic Zone
EIA	Environmental Impact Assessment
EPA	Environmental Protection Agency
EPP	Environmental Protection Policy
ENSO	El Nino Southern Oscillation
EQC	Environmental Quality Criteria (Western Australia)
EQO	Environmental Quality Objective (Western Australia)
ESD	Ecologically Sustainable Development
FRDC	Fisheries Research and Development Corporation
FRMA	Fish Resources Management Act
GA	Geoscience Australia formerly AGSO
GESAMP	Joint Group of Experts on Scientific Aspects of Environmental Protection
GIS	Geographic Information System
ICESD	Intergovernmental Committee on Ecologically Sustainable Development
ICS	International Chamber of Shipping
IOC	International Oceanographic Commission
IGAE	Intergovernmental Agreement on the Environment
ICOMOS	International Council for Monuments and Sites

IMO	International Maritime Organisation
IPCC	Intergovernmental Panel on Climate Change
IUNC	International Union for Conservation of Nature and Natural Resources
IWC	International Whaling Commission
JAMBA	Japan Australian Migratory Birds Agreement
LNG	Liquified natural gas
MarLIN	Marine Laboratories Information Network
MARPOL	International Convention for the Prevention of Pollution from Ships
MECO	Model of Estuaries and Coastal Oceans
MOU	Memorandum of Understanding
MPAs	Marine Protected Areas
MEMS	Marine Environmental Management Study
MSE	Management Strategy Evaluation
NCEP - NCAR	National Centre for Environmental Prediction – National Centre for Atmospheric Research
NEPC	National Environmental Protection Council
NEPM	National Environment Protection Measures
NGOs	Non government organisations
NRSMPA	National Representative System of Marine Protected Areas
NWQMS	National Water Quality Management Strategy
NWS	North West Shelf
NWSJEMS	North West Shelf Joint Environmental Management Study
NWSMEMS	North West Shelf Marine Environmental Management Study
ICIMF	Oil Company International Marine Forum
OCS	Offshore Constitutional Settlement
PFW	Produced formation water
P(SL)A	Petroleum (Submerged Lands) Act
PSU	Practical salinity units
SeaWIFS	Sea-viewing Wide Field-of-view Sensor
SOI	Southern Oscillation Index
SMCWS	Southern Metropolitan Coastal Waters Study (Western Australia)
TBT	Tributyl Tin
UNCED	United Nations Conference on Environment and Development
UNCLOS	United Nations Convention of the Law of the Sea
UNEP	United Nations Environment Program
UNESCO	United Nations Environment, Social and Cultural Organisation
UNFCCC	United Nations Framework Convention on Climate Change
WADEP	Western Australian Department of Environmental Protection
WADME	Western Australian Department of Minerals and Energy
WAEPA	Western Australian Environmental Protection Authority
WALIS	Western Australian Land Information System
WAPC	Western Australian Planning Commission
WHC	World Heritage Commission
WOD	World Ocean Database
www	world wide web

TECHNICAL SUMMARY

The North West Shelf (NWS) has been subject to inputs of contaminants (toxicants and nutrients) from a variety of point and diffuse sources over the last 35 years. The various types of contaminants behave differently and can have different effects depending on their loads to, and concentrations in, the environment. Effective environmental management relies on an understanding of the types and quantities of wastes discharged, the sources of those discharges and their environmental consequences viewed individually and from a cumulative perspective, and considering both acute and chronic effects.

An electronic database of annual loadings of point source contaminants discharged into NWS waters has been compiled for the period 1985 to 2001. The contaminants include toxicants such as heavy metals and petroleum compounds and nutrients such as nitrogen.

Concentrations of heavy metals in the waters surrounding the offshore petroleum facilities were lower than the highest level of protection specified in the ANZECC & ARMCANZ (2000) guidelines. There are significant discharges of heavy metals from the Parker Point Power Station where the annual loads in 2000 range from 252 kg/yr for cadmium to 8 145 kg/yr for zinc. There appears to be no data on the concentration levels of these metals in the waters or the sediments surrounding the discharge sites.

In 2000, 12 million tonnes of produced formation water containing 214 tonnes of oil was discharged from nine offshore petroleum facilities. This compares with an estimated 3,300 tonnes of oil naturally seeping into NWS waters. Few studies of the fates and effects of petroleum-based compounds have been undertaken on the NWS. These studies report no acute effects, but suggest that chronic and sub-lethal effects on marine plankton and bacteria have occurred in the vicinity of some of the production platforms.

Concentrations of the antifouling chemical, tributyltin (TBT), were found in coastal waters of the Dampier Archipelago to be at levels ranging from 0.003 to 0.025 μg/L. Studies have suggested that imposex and other effects, such as reduced growth, could occur at these levels.

Once contaminants are introduced to the marine environment they are subject to a range of physical, chemical and biological processes that influence their fate. In chapter 3 we review what is known about fates, pathways and potential bioavailability for the key contaminants of concern identified as part of the contaminants inventory and the review of toxicological data (chapter 4). These contaminants were identified as: six metals; barium, cadmium, chromium, copper, lead, mercury and zinc; one organometalloid: tributyltin (TBT); one nutrient: nitrogen; a waste stream; produced formation waters (PFW); and hydrocarbons (oil). The chemical behaviour of the major contaminants within each of these groups, including their transformations in the environment, the environmental pathways of effect and potential biological impacts, are reviewed.

The major gaps in understanding of contaminant behaviour, and therefore potential bioavailability, on the NWS relate to a lack of detailed understanding of the chemistry and behaviour of some of the major contaminants. Their bioavailability and the extent, severity and scale of impact will vary significantly depending on the type of contaminant. This is because the effects occur through different pathways depending on whether the contaminant is a naturally occurring toxicant (e.g. heavy metal), a synthetic toxicant (e.g. TBT, PCBs, biocides), a biostimulant (e.g. nitrogen) or other such as thermal load (e.g. cooling water discharge).

Discharges of PFW from offshore petroleum facilities and of contaminants from the power station are likely to continue for many years more than those from drill cuttings which presents a classic chronic versus acute assessment problem. However, the fact remains that much more is known, or can be inferred, about the dispersion and dilution of discharges than about the longer term fate of drill cuttings, either within the pile or once dispersed.

Based on what is currently known, it would seem desirable that management of these discharges is not performed on an annual loading basis, but that it should be performed within a structured and more holistic framework which takes into account as many factors as possible, such as contaminant speciation and water column and sediment chemistry following discharge.

The toxicity response of marine organisms may be acute or chronic and the effects can be either lethal or sub-lethal depending on the contaminant and its concentration. A review of toxicological data for the key contaminants of concern, listed above, reveals that they are fragmentary and incomplete for the NWS. In most instances, toxicity data is based on research and tests conducted overseas and based on test species not found in NWS waters. These data indicate that for the present contaminant loads on the NWS acute effects are unlikely, but where effects are detected, these are likely to be transient and/or highly localised (e.g. the effects of drill cuttings on benthic communities). Chronic effects are more difficult to predict based on the existing toxicological data. Therefore, the development of chronic and sub-lethal tests for discharges of the key contaminants should be given high priority. Development of chronic and sub-lethal tests would also enable use of the ANZECC & ARMCANZ approach of developing guidelines from multi-species tests, or from chronic and sub-lethal tests for a minimum of five species from four trophic groups.

The difficulty of identifying a sufficiently sensitive indicator species for the waters of the NWS, combined with the fact that the toxicity of the major contaminants of concern depends on a range of factors such as the concentration levels in the water and sediments, their chemical state and bioavailability, means that developing robust, reliable toxicity tests for all contaminants of concern is a huge task requiring far more resources than were available. Our approach has been pragmatic, and used as much existing data and information as was available, while bearing in mind the sources of those data.

In the past, aquatic ecosystem management has relied heavily on water quality criteria as benchmarks to assess the significance of a concentration of particular contaminant in a water body. More recently a broader ecosystem-based approach is being used and managers are looking beyond the water component of ecosystems and using the quality of the sediments and the biota as additional indicators of the status of a water body with respect to specific contaminants. Most water quality guidelines such as the ANZECC Water Quality Guidelines (2000) are generic and may need to be modified where there are site-specific considerations for particular contaminants. These could be high background levels exceeding the guideline’s threshold values for adverse impact; or the existence of particularly sensitive organisms. For this reason a site-specific water quality study has been undertaken (Wenziker et al. 2006) to quantify background levels of contaminants of concern and to identify threatened endemic organisms. This provides an estimate of background concentrations for selected metals and organics in the marine waters of the North West Shelf, to ascertain whether the guideline trigger values from ANZECC & ARMCANZ (2000) are relevant to the region.

The results of the water quality study indicate that the coastal waters of the North West Shelf are generally of very high quality. The concentrations of metals were low by world standards, with localised elevations of some metals adjacent to industrial centres and ports. No organic chemicals were detected. The reporting limits were well below the guideline trigger values recommended in ANZECC & ARMCANZ (2000) for a *very high* level of ecological protection for the five organics for which guideline values were available.

The findings of this study suggest that ANZECC & ARMCANZ (2000) 99% species protection guidelines are relevant to the region for all metals analysed, except cobalt, for which the 95% species protection guideline is recommended for use.

1. INTRODUCTION

1.1 Background

Contaminants can be separated into two broad groups: *toxicants* and *biostimulants*. *Toxicants* affect biota according to their environmental concentrations and their management is based on establishing environmental quality criteria (for water and sediments) through ecotoxicological studies. Some marine organisms will be more susceptible than others to the same contaminant and this needs to be taken into account when developing criteria based on ecotoxicological studies of single species. The toxicants can be further divided into those that are naturally occurring (e.g. heavy metals) and those that are synthetic (e.g. PCBs and TBT). Some are persistent and accumulate in the sediments and biota; others are less persistent or degrade rapidly. The fate of these substances in the environment will influence the approach used to derive environmental quality criteria and make management decisions.

Biostimulants, such as the nutrients, nitrogen and phosphorus are not toxic at normal concentrations and are often taken up rapidly by phytoplankton in the water column and by algae attached to hard substrates, stimulating their growth and causing an increase in plant biomass. These unnaturally high levels can change community structure, reduce light availability and cause a number of flow-on effects on ecosystem structure and function. Management of these substances relies on understanding the cause-effect pathways in the ecosystem in question, establishing surrogate indicators for nutrient enrichment to focus monitoring, and applying load-based management regimes based on this understanding and monitoring feedback.

One class of contaminant that enters the NWS marine environment is the toxicants. The extent to which most toxic substances affect aquatic biota is related to their bioavailable concentration in water and sediments and the extent to which they are bioaccumulated in certain organisms or biomagnified as they are passed along the food chain.

The suite of toxicants can be further subdivided into two groups; those that occur naturally, and those that are synthetic.

Most aquatic organisms have evolved a degree of resilience to the effects of toxic substances that are naturally occurring in the environment. Adverse effects do occur however when bioavailable concentrations exceed certain critical thresholds. Therefore the best approach for managing the environmental impacts of these substances is through the application of water quality guidelines which are based on toxicological studies and include appropriate safety factors. These safety factors balance the degree of uncertainty in applying laboratory-based relationships to complex ecosystems.

The development of appropriate guidelines for synthetic substances is more problematic. Aquatic biota have not had the opportunity to evolve a natural degree of tolerance to synthetic substances because they only occur in nature as a result of human activities. In addition, there is limited scientific knowledge enabling predictions to be made of the short and long-term effects of most synthetic substances at the ecosystem level. This was dramatically demonstrated by the unforeseen bioaccumulatory effects of DDT which was first documented in the early 1960s. More recently, widespread effects of very low concentrations of TBT on gastropod populations have been reported and led to the ban or reduction of use of this antifoulant in most countries.

The toxicity response of marine organisms may be acute or chronic and the effects can be either lethal or sub-lethal depending on the contaminant and its concentration. Sub-lethal toxicity is difficult to assess, quantify and monitor because it far less obvious than lethal effects and is displayed in a range of forms such as altered metabolic rates, reproductive failure and physical deformities. Such effects are usually detected only after a long period of low level exposure. A significant difficulty in assessing the toxicity of contaminants is that different marine organisms vary greatly in their sensitivity to contaminants. In most instances toxicity data is based on research and tests conducted overseas, and based on test species not found in our waters. As such the data may not be generally applicable to the marine environment of the NWS as there may be species which are more or less resilient than the test species.

1.2 Scope of Contaminants Project

Specific objectives of the contaminants component of the North West Shelf Joint Environmental Management Study were to:

1. Establish an inventory of contaminant inputs (nutrients and toxicants) from all known point and diffuse sources;
2. Review the pathways, fates and bioavailability of the contaminants of concern in the water, sediments and biota;
3. Establish environmental quality criteria to assess environmental health and provide early indications of environmental degradation; and
4. For the contaminants of concern, collate and evaluate the applicability of available toxicological data, and if necessary develop acute and chronic toxicity data using local marine indicator species.

2. CONTAMINANT INPUTS

2.1 Nutrients

The supply of nutrients in the form of nitrogen to the NWS in terms of both quantity and the processes involved remains poorly defined. Nutrient concentrations appear to be low, yet the area supports a phytoplankton population similar to other coastal areas (Furnas & Mitchell, 1999). The inference therefore is that nitrogen (N) is either being re-cycled and/or any nitrogen inputs are being utilised rapidly by the phytoplankton. Holloway et al. (1985) calculated that the amount of "new" nitrogen that needed to be supplied to the shelf is in the order of 10 to 39 kg N day^{-1} per metre of coastline, with a median of around 16 kg N day^{-1} m^{-1}. The possible sources and sinks of nitrogen on the NWS are outlined below:

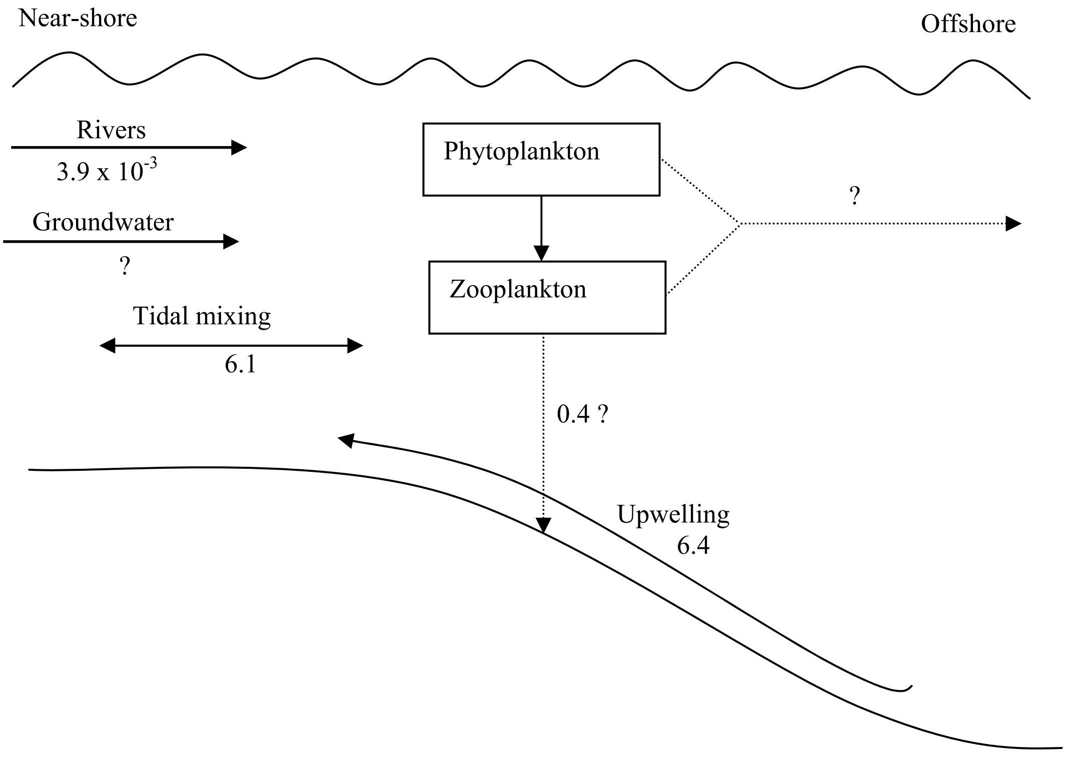


Figure 2.1.1: Data summarised from Holloway et al. (1985). Numbers are in kg N day^{-1} m^{-1}.

Figure 2.1.1 indicates that in order to supply the estimated 16 kg N day^{-1} m^{-1} required to drive the observed productivity, rivers represent only a small contribution and it is the cross shelf advective processes that are important. Tropical cyclones will also increase N flux onto the shelf and this has been estimated in an average year to account for 140 kg N m^{-1} which is the equivalent of about nine days nitrogen demand (Holloway et al. 1985). Only a small proportion of nitrogen is exported to the sediments and this is likely to be regenerated but it is unknown how much nitrogen is exported off-shelf in the form of particulates.

The major anthropogenic sources of nutrients being discharged into the NWS are from Produced Formation Waters (PFW). Furnas and Mitchell (1999) report nutrient concentrations in Harriet A discharges of PFW at around 3 mM which equates to an input of about 350 kg N day^{-1}. Using the estimated primary production requirement of 16 kg $Nday^{-1}m^{-1}$ and an estimated NWS coastline of 860 kilometres, the requirement becomes 13 x 10^6 kg N day^{-1} for the NWS. Thus the PFW input equates to about 0.002% of the total requirement.

However, it needs to be remembered that petroleum production is localised, and so therefore are the associated discharges, and indeed Furnas and Mitchell (1999) did identify increased primary production in the vicinity of platforms, though again this was very localised. The second factor to remember is that natural N flux on the NWS is in the form of NOx whereas nitrogen in PFW discharges is primarily NH_4^+ and this is often more readily utilised than nitrate (Lomas & Gilbert, 1999).

A minor source of nutrients is discharges from wastewater treatment plants at Dampier, Woodside's onshore treatment facility at Withnell Bay, and at the Dampier salt ponds. Another wastewater treatment plant at Wickham ceased discharging into the ocean in 1999. The total nitrogen loadings from these sources (table 2.1.1) are very small compared to more developed areas in Australia such as Cockburn Sound (3000 tonnes/year, Department of Environmental Protection November 1996, *Southern Metropolitan Coastal Waters Study (1991 – 1994): Final Report, Report 17*) and Port Phillip Bay (6000 tonnes/year, CSIRO 1996, *Port Phillip Bay Environmental Study: Final Report*). They are also smaller than estimates of the natural groundwater loading (13 tonnes/year per kilometre of coastline; Appleyard, 2000) and do not appear to have had any local impact. Flushing by large tidal currents should ensure rapid assimilation of these inputs through natural biogeochemical processes.

Table 2.1.1: Annual loadings of nitrogen (tonnes/year) from point source discharge locations.

	Location			
Annual loadings	**Dampier Salt**	**Woodside OTP**	**Wickham WWTP**	**Dampier WWTP**
Maximum (year)	0.229 (1999)	8.787 (1989)	3.073 (1998)	1.821(1999)
In year 2000	0.180	0.283	ceased	0.776

2.2 Toxicants

A range of toxicants including heavy metals and petroleum compounds are discharged into NWS waters from known point and diffuse sources on the NWS. These have been compiled into a contaminants input inventory to help determine the loads on the marine ecosystem and the potential for detrimental impacts. Contaminants data have been acquired from sources such as industry reports and WA government departments (WA Departments of Industry and Resources and Environment).

Table 2.2.2: Summary of contaminants and their discharge location contained in the contaminants inputs inventory for the year 2000. A blank entry means that there is no data or no discharge for these contaminants. A zero value means that discharges have occurred in previous years but are reported to be zero for this particular year. Discharge locations are shown in figure 2.2.1.

Contaminants input inventory for 2000

	Location																
Contaminant (Year 2000)	Dampier Salt Ponds	Airlie Island	Harriet A	Harriet B	Harriet C	Stag	Griffin	Vicksburg	Wandoo	Thevenard Island	Cossack Pioneer	Goodwyn	North Rankin	Woodside OTP	Wickham WWTP	Parker Pt Power St	Dampier WWTP
Arsenic (kg/yr)			6.7														
BOD (kg/yr)																	362
Cadmium (kg/yr)			13											< .8		252	
Calcium (tonnes/yr)	231																
Chlorine																	
Chromium (kg/yr)			154													1494	
COD (tonnes/yr)														7.6			
Copper (kg/yr)			31											< .8		450	2.2
Glycol (tonnes/yr)														1.6			
Iron (tonnes/yr)			2.7														
Lead (kg/yr)			62											< .8		565	
Manganese (kg/yr)			57														
Mercury (kg/yr)			.62													0	
Nickel (kg/yr)			62														
Oil (tonnes/yr)		5.6	56	0	0	5.5	35	0	93	0	1.6	5	2.5	.26			
PFW (million kl/yr)		.41	2.7	0	0	.29	1.7	0	6.0	0	.25	.24	.06				
Surfactants (kg/yr)														50			
Susp. Solids (tonnes/yr)			33											1.8			1.3
Sulfinol (kg/yr)														0			
Sulphate (tonnes/yr)	274													23			
Sulphide (kg/yr)														36			
TDS (tonnes/yr)																	34
Total N (tonnes/yr)	.18		140											.28	0		.78
Total P (kg/yr)			679											71			
Zinc (kg/yr)			31											4.3		8145	4

The petroleum industry is required to report data on discharges of oil and assess the environmental effects and risks of Produced Formation Water to the Department of Industry and Resources, while the Department of Environment licenses discharges containing a variety of contaminants in WA state waters.

The point source data consist mainly of petroleum-based compounds, heavy metals and various other chemicals associated with industrial effluents, and nutrients from sewage treatment plants (table 2.2.2). The inventory is an electronic database covering the period 1985 to 2001 and includes discharges at 17 locations (figure 2.2.1). It is linked to a GIS, which allows time series of annual contaminant loadings to be displayed (figure 2.2.2) by selecting a discharge sited on the map of the NWS.

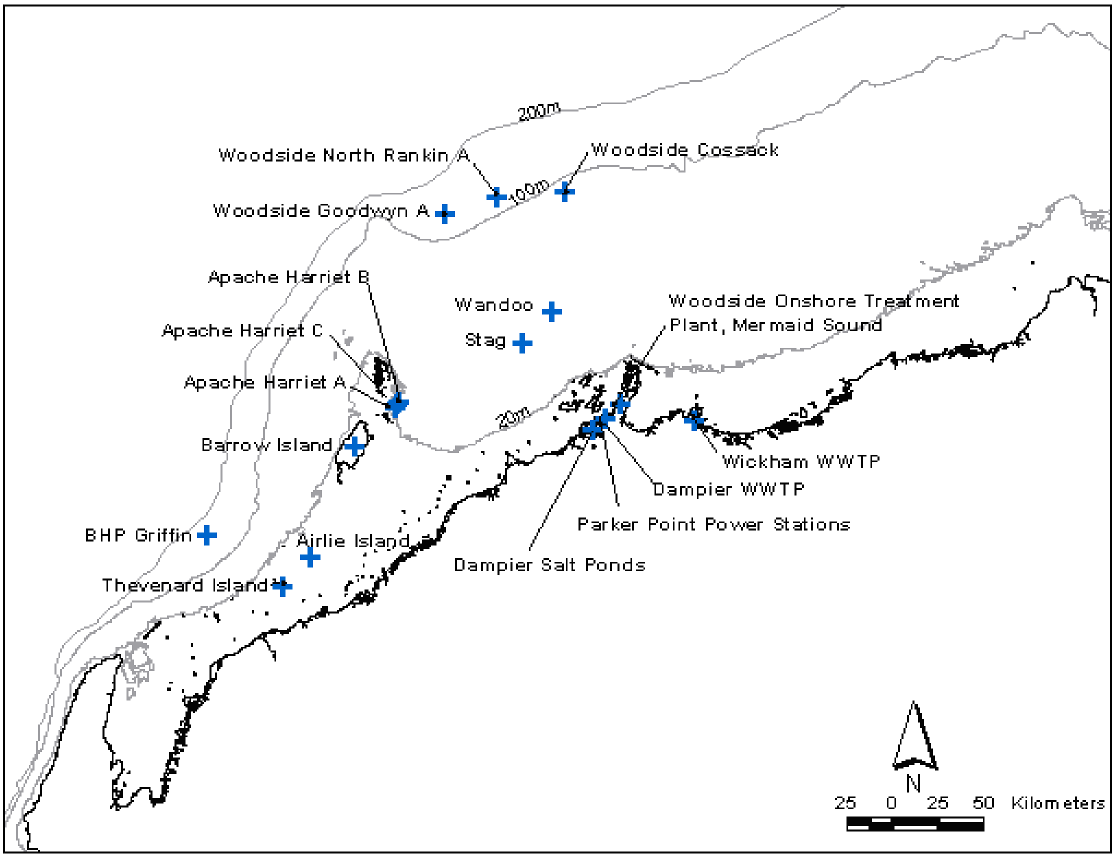


Figure 2.2.1: Contaminant discharge locations within study area.

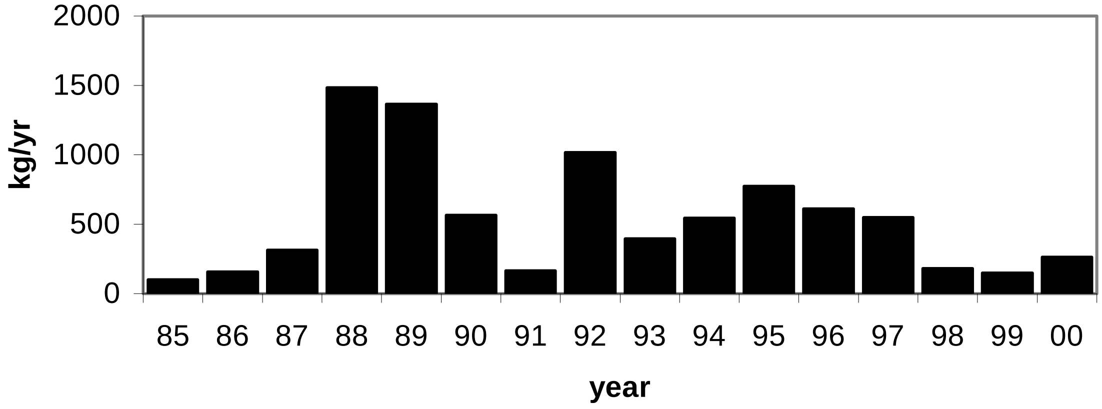


Figure 2.2.2: Example of the GIS time series display for oil discharged at Woodside's onshore treatment plant on Withnell Bay.

2.3 Produced Formation Water

Produced Formation Waters (PFW) are the subject of an extensive review by Neff (2002) and there is little point in trying to reproduce that here. However, it is worth pointing out that by the mid 1990s Australia released approximately 100 ML d^{-1} which is only about 12% the volume of PFW that the North Sea discharged, although this is likely to increase as more facilities come on line and the Australian production wells become older.

PFW containing oil is discharged from nine offshore petroleum facilities in the study area, with total annual loads increasing from 7.5 million tonnes in 1996 to over 12 million tonnes in 2000. Over the same period the component of oil discharged increased from 110 tonnes to 214 tonnes per year (figure 2.3.1). These quantities are low compared to major tanker spills such as the Kirki in 1991 (18000 tonnes). They are also most likely to be much lower than the amount of natural oil seeps, which are known to be very prevalent on the NWS. Based on geological considerations, Wilson et al. (1974) estimated that the amount of hydrocarbons from natural seeps entering the ocean on a global basis each year is about 0.6 million tonnes. They also estimated that 45% of this seepage comes from areas of high seepage, 55% from areas of moderate seepage and less than 1% from areas of low seepage. The NWS is identified as an area of moderate seepage, and probably accounts for at least one percent of the global moderate seepage areas. On this basis, natural seepage of oil on the NWS is at least 3300 tonnes annually. This is an order of magnitude larger than discharges from production platforms. However, the ecological impacts of these discharges remain largely unknown.

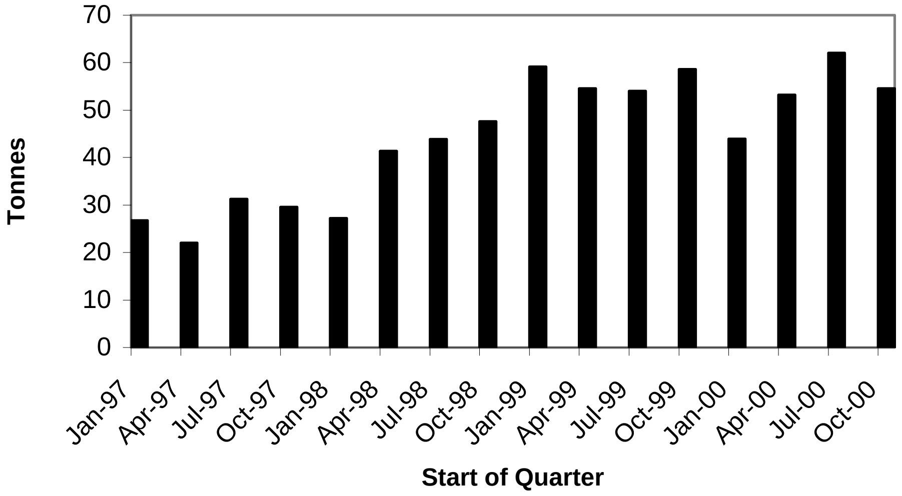


Figure 2.3.1: Quarterly discharge of oil in PFW from all production platforms in the study region.

2.4 Heavy metals

Another potentially significant component of industrial wastewaters discharged into NWS waters is heavy metals. At all but Hamersley Iron Parker Point Power Stations, the reported annual loads are small (table 2.2.2) and have decreased considerably over the past eight years. For example at Woodside's onshore treatment plant at Withnell Bay, zinc discharges have decreased from 100 kg/year in 1993 to 4.3 kg/year in 2000. Discharges of copper have not exceeded 11 kg/year (1995), while discharges of cadmium and lead were less than 5.5 kg/year (1997) and 24.4 kg/year (1995) respectively. In 2000 the discharge loads of copper and cadmium and lead were less than 0.8 kg/year.

At the Parker Point sites annual loads of cadmium, chromium, copper, lead and zinc ranged from 252 kg/yr for cadmium to 8 145 kg/yr for zinc. These are far higher than those at the other site and may be cause for concern, particularly for benthic habitats exposed to high concentrations of heavy metals that are likely to be accumulating in the bottom sediments. To determine the potential environmental impact, an investigation of heavy metals in sediments affected by the effluent discharges from the Parker Point Power Station will be required.

Apache Energy reported discharges in 2000 of cadmium, copper, lead and zinc at the Harriet A platform of 12.8, 30.9, 61.7 and 30.9 kg/year respectively. The concentration levels in surrounding waters were estimated to be less than 0.02 µg/L for cadmium and less than 0.1 µg/L for copper, lead and zinc. These levels are all much lower than the highest level of protection specified in the ANZECC & ARMCANZ (2000) guidelines, which are 0.7 µg/L for cadmium, 0.3 µg/L for copper, 2.2 µg/L for lead and 7 µg/L for zinc. Accumulated levels in sediments around Woodside's onshore facilities at Withnell Bay and King Bay were also lower than the ANZECC & ARMCANZ (2000) screening levels, except for one site where lead exceeded the guidelines by 30%. Accumulated levels in oysters in the same area were generally within National Food Authority Guidelines (NFA, 1994), with slightly higher levels for copper and zinc.

2.5 Tributyltin (TBT)

The predominant contaminant of concern in ports is the antifouling ingredient tributyltin. TBT is toxic to a wide range of organisms at concentrations as low as 0.001 to 0.1 µg/L (DA Lord Science and Engineering, 2002).

On the NWS, the main areas of concern with respect to TBT contamination are the major ports at Port Hedland and Dampier, through direct leeching from ships and from the dredging of sediment to keep access clear. Thus, the behaviour of TBT in turbid waters and anoxic sediments are those most likely to be relevant.

By estimating the potential loading of TBT into the major NWS shipping ports of Port Lambert, Port Hedland and Dampier, Crawley (2000) calculated the TBT concentration in the harbour waters to be 0.008 µg/L. This exceeds the 95% species protection level in the ANZECC & ARMCANZ (2000) guidelines of 0.006 µg/L. While this may be of concern, these calculations ignore the dynamical effects of tides and other ocean currents which would cause flushing and dilution.

Further discussion of the fates and pathways and toxicology of TBT can be found in chapters 3 and 4.

2.6 Summary

An electronic database of annual loadings of point source contaminants (Contaminants Inputs Inventory) discharged into NWS waters has been compiled for the period 1985 to 2001. The contaminants include toxicants such as heavy metals and petroleum compounds and nutrients such as nitrogen.

The annual loads of heavy metals from the petroleum production facilities are generally less than a few kilograms per year and have been decreasing over the six year period. The resulting concentrations of heavy metals in the waters surrounding the facilities were lower than the highest level of protection specified in the ANZECC & ARMCANZ (2000) guidelines. There are significant discharges of heavy metals from the Parker Point Power Station where the annual loads in 2000 range from 252 kg/yr for cadmium to 8 145 kg/yr for zinc. There appears to be no data on the concentration levels of these metals in the waters or the sediments surrounding the discharge sites.

In 2000, 12 million tonnes of produced formation water containing 214 tonnes of oil was discharged from nine offshore petroleum facilities. This compares with an estimated 3 300 tonnes of oil naturally seeping into NWS waters. Few studies of the fates and effects of petroleum-based compounds have been undertaken on the NWS. Those studies report no acute effects, but suggest that chronic and sub-lethal effects on marine plankton and bacteria have occurred in the vicinity of some of the production platforms.

Concentrations of the antifouling chemical, tributyltin (TBT) were found in coastal waters of the Dampier Archipelago to be at levels ranging from 0.003 to 0.025 µg/L. Studies have suggested that imposex and other effects, such as reduced growth, could occur at these levels.

3. FATES AND PATHWAYS

3.1 Overview

The scope of this chapter is to review what is known about fates, pathways and potential bioavailability for the key contaminants of concern identified as part of the contaminants inventory and the review of toxicological data (chapter 4). These contaminants were identified as:

- Six metals: barium, cadmium, copper, lead, mercury and zinc;
- one organometalloid: tributyltin (TBT);
- one nutrient: nitrogen;
- a waste stream: produced formation waters (PFW); and
- hydrocarbons (oil).

Subsequent to the original list, chromium was identified as a major contaminant and was included in the review.

There is a paucity of published literature directly relevant to the North West Shelf (NWS) as outlined by Sherwood et al. (1999) and Heyward et al. (2006). A search of the bibliography by Jernakoff et al. (2006) reveals that of the 1 725 records, only 26 relate to chemistry, and of those, only 15 are in published literature. Thus any review will rely heavily on overseas data. Obviously, in some cases there will be a large amount of published data (e.g. mercury), while in others there will be a general lack of information (e.g. lead). It is not the aim of this review to evaluate all the available data, but to attempt to synthesise that which is available and may be relevant to the circumstances of the NWS. In addition, some of these contaminants have previously been the subject of detailed reviews (e.g. Swan et al. 1994) and there is little point in repeating this process. Therefore, in these cases only new data relevant to the NWS has been incorporated.

3.2 Metals

3.2.1 Barium (Ba)

In oceanic terms, barium (Ba) behaves as a bio-intermediate in an analogous way to calcium in that it is assimilated by the surface biota, exported to the deeper ocean as particles (skeletal material) where it is largely redissolved. However, more coastal environments such as the North West Shelf (NWS) are subject to a variety of sources such as aerial transport, riverine and anthropogenic inputs.

The major anthropogenic input of barium on the NWS is barite ($BaSO_4$) which is used to control hydrostatic head pressure during drilling operations. There appears to be little work globally looking directly at the fate of barite per se, though much of the barium transport from the upper ocean to the sediments has been suggested to be as a strontium enriched barite ($(Ba,Sr)SO_4$; Dehairs et al. 1980). A biological role in barium cycling appears to be almost essential as the water column is undersaturated with respect to barite at all depths (Hanor, 1969; Church & Wolgemuth, 1972) and phytoplankton have been shown to be capable of accumulating barium to relatively high levels (Fisher et al. 1991). Thus, the assumption is that barium is incorporated as barite, exported from the photic zone to the sediments, where it is redissolved to become available again for biological uptake.

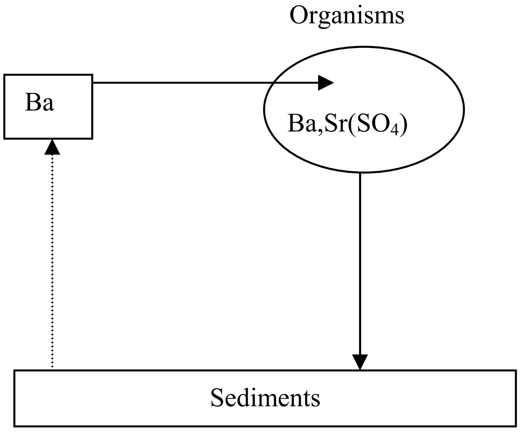


Figure 3.2.1: Schematic diagram of barium cycling.

Marine pore waters are generally saturated with respect to barite which, combined with the under saturation of sea water leads to an efflux of barium from the sediments to the overlying water. This efflux has been estimated to range from 3 to 16 nmol cm^{-2} y^{-1} (Chan et al. 1977; Fischer et al. 1986; Falkner et al. 1993). However, McManus et al. (1994) measured rates much higher than these (25 to 50 nmol cm^{-2} y^{-1}) in Californian continental margin sediments.

Relevance to the North West Shelf

Obviously barite associated with drill cuttings has the potential to feed into this cycle and to upset the natural balance. However what, if any, impact this could have is unclear. The factors controlling barium remobilisation in the sediments are poorly understood (McManus et al. 1994). One strong possibility is sulphate reduction (Church & Wolgemuth, 1972) in the oxygen minimum zone of sediments. While this process may or may not be important in unaffected marine environments, it is potentially highly important in cuttings piles which are known to be anoxic. A major microbial pathway in anoxic environments is sulphate reduction and it is therefore conceivable that Ba could be remobilised from the $BaSO_4$. Presumably, while the cuttings piles remain intact, the barium will remain, to some extent, within the sediment. However, disturbance of the pile could potentially see the release of a pulse of barium into the water column. The likely effects of this are unclear, given a range of factors will control the availability of this barium: water depth will to some extent control solubility and any "within pile" reactions which may have taken place. For example, it has been proposed that barium may be associated with iron-manganese oxyhydroxides (de Lange et al. 1990; Dymond et al. 1992; Falkner et al. 1993). Thus, depending on the other elements present within the cuttings pile, and the chemistry occurring, it is possible that some of the barium remobilised through sulphate reduction, could become associated with other elements.

Potential for bioaccumulation and toxicity

The low aqueous solubility of barium makes it an unlikely candidate for bioaccumulation.

Few data exist for organisms associated with high sedimentary concentrations, such as cuttings piles. However, studies of sediments layered with barite showed an inhibition of colonisation and altered community structure (Tagatz & Tobia, 1978; Starczak et al. 1992), but this was attributed to the change in physical structure of the sediment. The general consensus is that barium solubility is low enough that there will be insufficient barium released into the overlying waters to have any toxic effects. Similarly, ingestion of barite tends not to have any effects due to its inert nature (Neff, 2002). There is some evidence that barium incorporated into organic complexes could be more toxic (Neff, 2002) and this raises the issue of possible reactions within cuttings piles, but little is know about cuttings pile chemistry.

3.2.2 Cadmium (Cd)

Cadmium is generally regarded as one of the most toxic metals, yet there appears to be little detailed understanding of its chemistry in the marine environment. However, oceanic studies have shown a depletion of cadmium in the upper water column but more elevated levels at depth, similar to nutrient species. This is taken as being indicative of Cd being regulated by marine biogeochemical processes, i.e. uptake by phytoplankton in the surface waters, subsequent decomposition of the organic matter and re-mineralisation at depth (Abe, 2001). Indeed, there has been shown to be a linear relationship between cadmium and phosphate in the oceans. This biological role is further emphasised by the fact that cadmium concentrations are correlated with the $\delta^{13}C$ of dissolved inorganic carbon (McCorkle & Klinkhammer, 1991).

In sea water, cadmium exists as the solid species cadmium carbonate ($CdCO_3$) and the dissolved species $CdCl^+$ (56%), $CdCl_2$ (15%), $CdCl_4^{2-}$ (10%) and $CdCl_6^{4-}$ (9%) (Forstner, 1980). However, in reducing environments Cd(HS) is the dominant species.

The marine environment is the ultimate sink for cadmium, as shown by estimated residence times (Forstner, 1980).

Table 3.2.1: Cadmium residence times.

Reservoir	Mean residence Time
Soil	280 years
River water	Few days
Atmosphere	20 – 30 days
Ocean water	250 000 years
Pelagic sediment	2 to $5x10^8$ years

It would appear from these residence times that once incorporated into sediments, the cadmium becomes “locked away” and it is the biological component of its cycle that is important in the shorter term. There is in fact some speculation that Cd may be an essential element for phytoplankton (Hunter & Boyd, 1999). Regardless of whether this is case or not, it has been shown that Cd^{2+} can substitute for Zn^{2+} in the growth mechanism of the diatom *Thalassiosira weissflogii* (Price & Morel, 1990; Lee et al. 1995). This may be a mechanism to deal with times of Zn deficiency, but Cd is generally at much lower concentrations so it is not clear why this may occur. In addition, it has also been shown that coccolithophorids can accumulate Cd due to the similar ionic radius of Cd^{2+} and Ca^{2+} enabling Cd to be substituted into the $CaCO_3$ matrix. Macroalgae have also been shown to accumulate Cd, especially during seasonal cycles of excess phosphate (Walsh & Hunter, 1992), the suggestion being that the accumulation of phosphate and Cd are linked in some way. It may also be the case that this can occur in microalgae.

Association with phytoplankton and their grazers is the most likely route to sedimentary deposition. Indeed a relationship has been shown between organic carbon flux and Cd concentration in bottom waters (Boyle et al. 1976). Once associated with sediments, there appears to be a number of factors which can control the fate of Cd. McCorkle and Klinkhammer (1991) have shown an enrichment of Cd into oxic sedimentary pore waters of up to three orders of magnitude, but that this pore water enrichment rapidly decreases in the anoxic zone, suggesting that the cadmium has become less soluble. Cadmium sulphide (CdS) is one of the least soluble metal sulphides (after HgS and CuS) (Forstner, 1980), and this would seem to be a likely mechanism for the “removal” of Cd from bottom waters into sediments. However, this is also probably the least “stable” sulphide when compared to Hg or Cu.

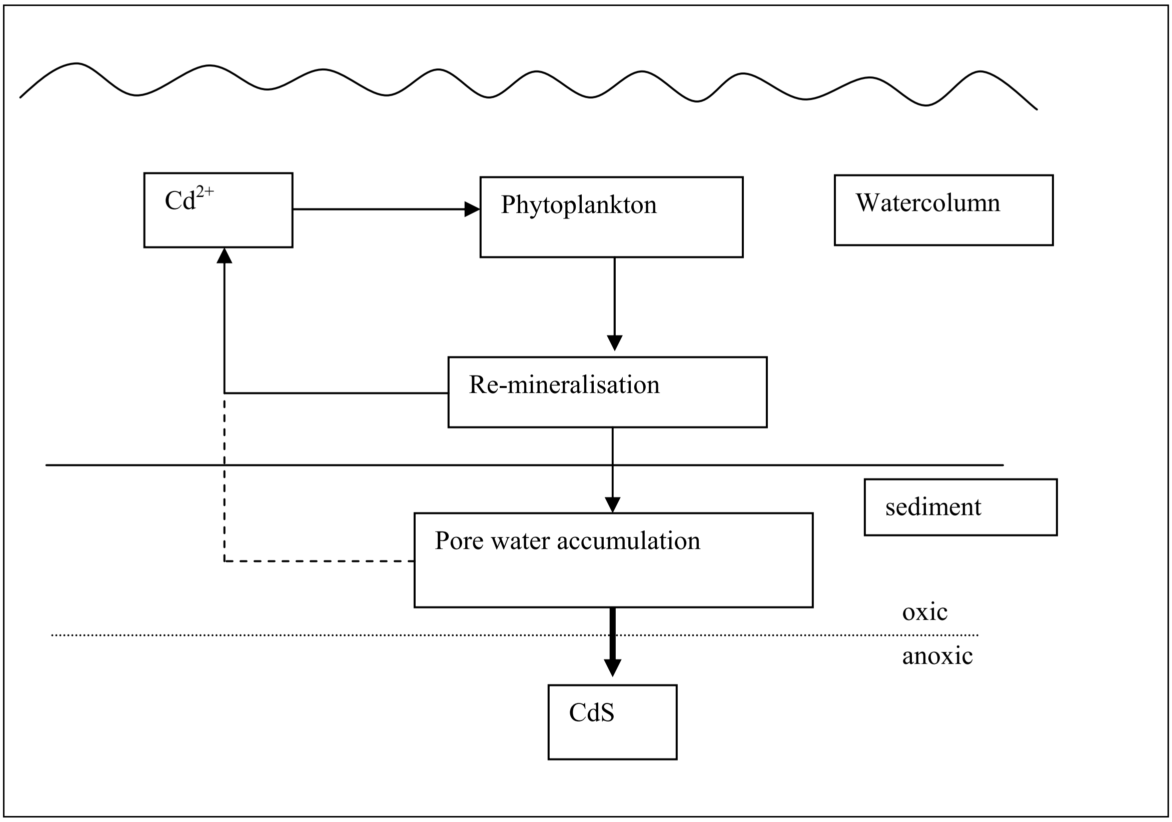


Figure 3.2.2: A potential (simplistic) schematic for Cadmium cycling.

In terms of trying to model Cd cycling, there appears to be little data, though given the Cd profile follows the phosphate profile so closely it would seem plausible that water column Cd can be modelled as a nutrient. With respect to sediments, Thomson et al. (2001) applied Fick's Law in an attempt to model pore water accumulation, though this provided poorly correlated data, probably due to the importance of organic carbon deposition as opposed to a straight diffusion relationship. The flux of cadmium from oxidised surface layers of marine sediments has been estimated to range between 1.1 and 160 pg/cm^2/hour (Zago et al. 2000).

Relevance to the North West Shelf

With respect to the NWS, Cd contamination so far identified is primarily associated with the Parker Point Power Station and to a lesser extent Produced Formation Water (PFW). Cadmium is also present in drill cuttings as an impurity in barite, though at what concentrations (on the NWS) is unknown. The effects of Cd in the Power Station discharge and PFW will be primarily determined by dispersion and water chemistry, while cuttings piles will be more complex. Since these are known to become anoxic relatively quickly, the majority of Cd may well be present as CdS and so immobilised. However, when these piles are disturbed and so become oxic, the sulphides will revert to more soluble species, causing a localised release of Cd. The effect of this on the local ecosystem is unclear as several factors including dispersion rates, the presence of other ligands and species composition will play a role.

Potential for bioaccumulation and toxicity

Although cadmium is one of the more toxic substances, its toxicity decreases with increasing salinity, due to the formation of the chloride. Unlike barium, there appears to be no consistent trend of cadmium concentration with trophic level.

The lack of any obvious increase in concentration through food webs suggests that this aspect of cadmium accumulation is less important than direct exposure/toxicity. There is a wide range of toxicity data (reviewed by Neff, 2002) relating to cadmium, but it appears few studies take into account the chemical speciation involved, such as the presence of organic ligands etc., and again, since the chemistry of cuttings piles is poorly understood, it is difficult to make a detailed assessment of the likely impacts. For example, one interesting observation from Western Australia has been the accumulation of cadmium by bivalves in Shark Bay (McConchie & Lawrance, 1991). This study showed that Cd concentrations in the molluscs were not directly related to ambient concentration, and tissue concentrations exceeded that which would be expected. Accumulation was due to the ingestion of particles of haematite (iron oxide) eroded from nearby cliffs, which chelated and concentrated the Cd. Thus the molluscs were exposed to artificially high levels.

3.2.3 Chromium

Chromium in the environment occurs in nine oxidation states from -2 to +6. However in seawater this tends to be limited to primarily two valence states Cr(III) and Cr(VI). Cr(VI) tends to be more soluble in seawater, with Cr(III) therefore more generally associated with particles. In waters which are well oxygenated, hexavalent chromium should predominate although kinetic effects allow Cr(III) species to exist as hydrolysis products $Cr(OH)_2^+$ and $Cr(OH)_3$ (Bruland, 1983). However, in near-shore or sub-oxic environments, the proportion of the trivalent species will increase.

Chromium(VI) can be readily reduced to chromium(III) by marine organisms, dissolved organic material and potentially by reactive iron (Fe(II)). The reverse oxidation of chromium(III) to the hexavalent form is relatively slow. However the presence of particulate manganese oxides may speed up this reaction.

In oceanic water chromium generally has a nutrient like profile and surface waters range from 0.1 to 0.55 µg/L, however not all of this may be bioavailable.

Relevance to the North West Shelf

Inputs of chromium to the North West Shelf are primarily associated with the Parker Point Power Station, discharging into Mermaid Sound, with smaller discharges associated with produced formation waters. Chromium entering the relatively shallow and potentially turbid Mermaid Sound obviously has an increased potential to become associated with sediments. The degree to which chromium will become incorporated will depend upon factors including the oceanographic conditions, the presence of potential binding agents and sediment chemistry.

Uncontaminated marine and estuarine sediments tend to contain chromium in the range 50 to 100 µg/g dry weight (Mayer, 1988), for example some Antarctic sediments contain 4.1 to 55 µg/g dry weight (Giordano et al. 1999) with the majority of this in the <63 µm fraction. There is good agreement between the concentrations of aluminium and chromium in some sediments, indicating that chromium is associated with the clay fraction.

Sediments receiving effluent from industries can contain total chromium at levels as high as 3000 µg/g (Johnson et al. 1981). The fate of chromium in sediments appears to depend on the source of the chromium and the presence of possible fractions within the receiving sediments. Chromium is not known to form sulphides and so much of the chromium in sediments appears to be bound to organic matter or present as the insoluble hydroxide. A small proportion may be associated with iron or manganese hydrous oxides (Neff, 2002).

Potential for bioaccumulation and toxicity

Chromium is an essential micronutrient and as such organisms are able to concentrate and regulate chromium. However, there is little information on the potential for bioaccumulation of chromium (Neff, 2002). It does appear that in general there is no clear relationship between the chromium concentration of an organism and its trophic level. In fact, in some studies chromium concentration was the highest in organisms at the base of the food web (Neff, 2002 and references therein). Chromium concentrations in soft tissues of animals are rarely greater than µg/g dry weight (Neff, 2002) but some detrital feeders (e.g. polychaetes and crabs) may show elevated levels.

The toxicity of chromium depends very much on its valence state. Hexavalent chromium is moderately toxic, while trivalent chromium, due to a low solubility in water, is in practical terms non-toxic to marine organisms. Hexavalent chromium, especially when present as a heavy metal chromate, is a known carcinogen in humans, however, when ingested with food (e.g. seafood) this is rapidly reduced in the gut to trivalent chromium, which is poorly absorbed through cell membranes. Although some organic complexes of Cr(III) can penetrate cell membranes it is thought that small quantities of hexavalent and trivalent chromium ingested this way pose no threat to humans (Neff, 2002).

3.2.4 Copper (Cu)

The major species of copper (Cu) in sea water are $CuCO_3$, Cu(OH) and free hydrated Cu^{2+} (Bruland, 1983). The profile of Cu in oceanic water is unusual as it is intermediate between the nutrient type (eg Cd, Zn) and lead (Pb), exhibiting a relatively linear increase with depth. Its concentration ranges between 0.5 and 6 nmol kg^{-1}. The profile appears to be dominated by scavenging (Bruland, 1983) with regeneration at the sediment water interface.

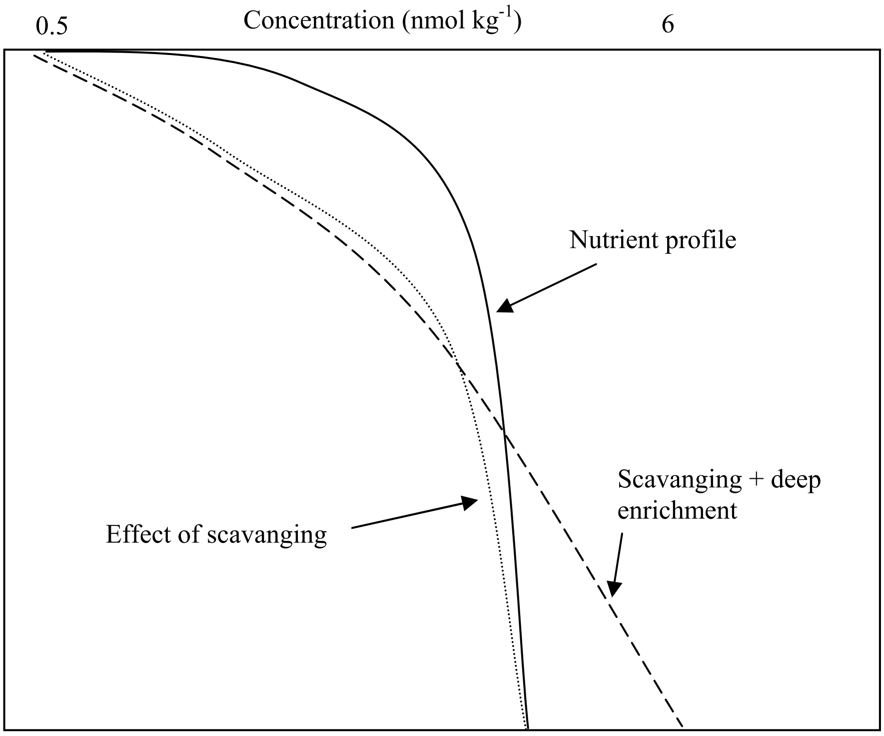


Figure 3.2.3: Profile of copper in sea water.

Copper is sorbed rapidly onto sediments, but the rate of sorption varies with sediment type. Copper will complex with humic and fulvic acids, important in some coastal areas, but also with Fe-Mn oxides, potentially more important in the deeper ocean. However, Banat et al. (1974) did show that this sorption was reversible in the presence of even low concentrations of strong chelators, but in general copper complexes are quite stable in oxidising environments.

Relevance to the North West Shelf

With respect to the NWS, the primary sources of copper, as with most of the metals, appears to be associated with the Parker Point Power Station and to a lesser extent, petroleum activities, more specifically as a contaminant in barite, although again there is no local data on this source. As with the other metals, this means that the sediment chemistry of copper needs to be considered both within the context of sorbtion/desorbtion in coastal environments and potentially anoxic sediments such as those found in cuttings piles. Without knowing the exact form of the copper in the barite, it is only possible to assume that the primary sorption mechanism is in the form of Fe-Mn complexes. In anoxic environments the Fe would be reduced to Fe^{2+} and Mn to Mn^{2+} thus causing the dissolution of the complex and release of copper into the surrounding waters. However, at the same time sulphides are being produced, which could see the formation of a variety of copper sulphide species, which are relatively stable and insoluble (Moore & Ramamoorthy, 1984). However, if elemental sulphur is present, polysulphides ($CuS(S_5)^{-2}$) can be formed, and these are soluble. Thus it is clear that more detailed knowledge of cuttings pile chemistry is required to fully understand these questions.

Potential for bioaccumulation and toxicity

Copper is an essential element for organisms and thus they have mechanisms to regulate the body burden. However, at high concentrations this mechanism can become swamped. There appears to be no evidence of food web magnification, but the filter feeders and benthic detritivores appear to be most susceptible to accumulation.

Crecelius et al. (1982) showed that 50% of Cu^{2+} added to a sediment became associated with the organic fraction and thus became unavailable to the suspension feeders, but much more available to deposit feeders. Similarly, polychaete worms have been shown to successfully regulate copper at natural levels in sediments but cannot do so at higher concentrations (Amiard et al. 1985). The toxicity of copper is very much related to the form and availability in which it exists but many ecotoxicological studies in the field have found it difficult to directly assess Cu toxicity because high levels of copper are often associated with high levels of other contaminants, and laboratory studies often cannot reproduce the complex chemistry involved.

3.2.5 Lead (Pb)

The concentration of lead in the ocean ranges from 5 to 175 pmol kg^{-1} (Bruland, 1983) with a depth profile which is the mirror image of the nutrients. That is, the maximum concentration occurs at the surface, falling away rapidly with depth to achieve a relatively constant concentration. This is due to the large impact that anthropogenic lead has on the cycle of this element, with a significant aerial deposition component.

At the pH and salinities seen in sea water, soluble lead will exist as a variety of species (Sadiq et al. 1992).

Table 3.2.2: Soluble lead as a variety of species in sea water.

Species	% of Total
Pb^{2+}	0.8 - 4.5
$Pb(OH)_n$	1.5 - 30
$PbCl_n$	13 - 74
$PbSO_4$	0.5 - 1.3
$PbCO_3$	1.8 - 83

Lead enters the sediments primarily by scavenging on particles, though in the near-shore environment organic matter will play a role in complexing the lead. One gross scale lead cycle has been outlined by Garrels et al. 1975.

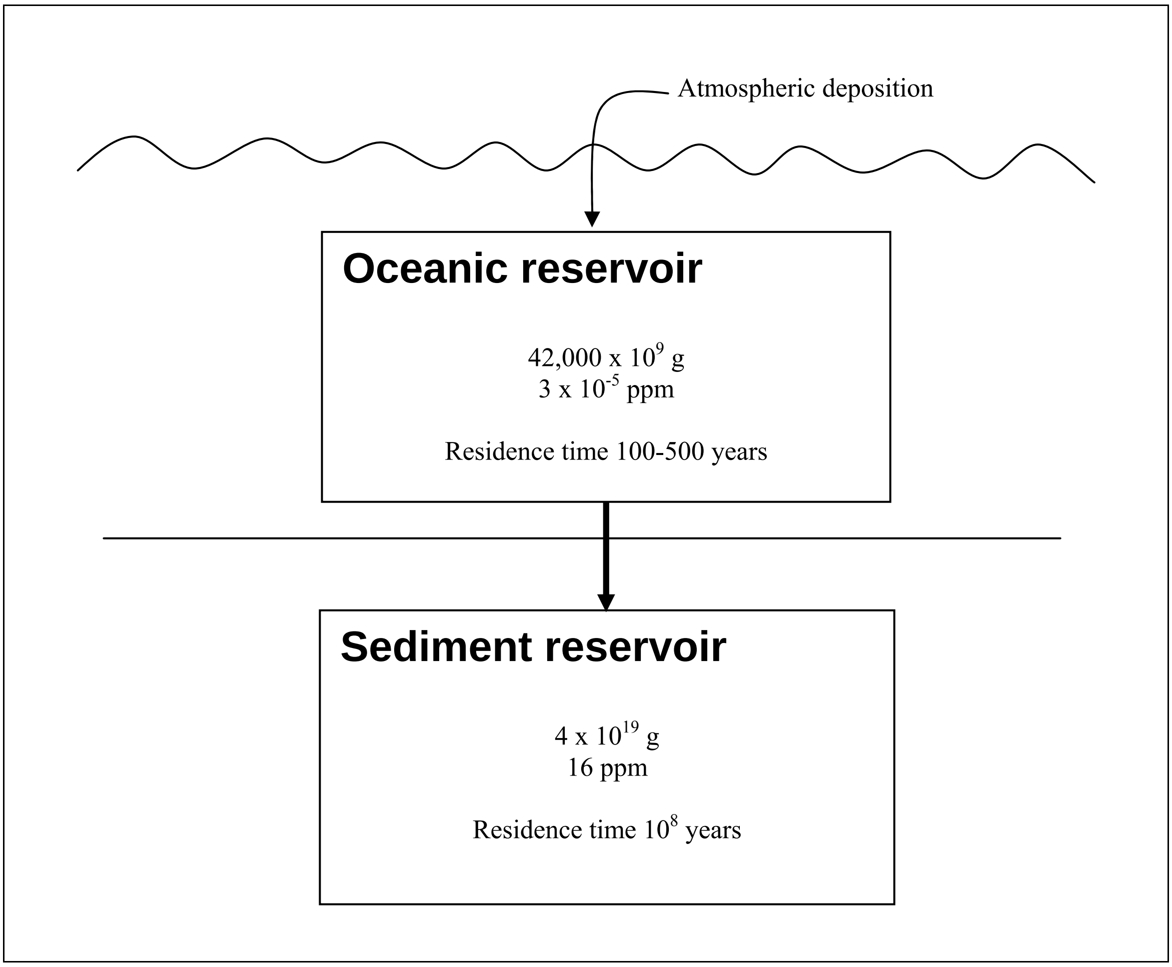


Figure 3.2.4: Gross scale lead cycle.

The actual mechanism for the transfer of lead from the ocean to the sediments isn't clear, though lead will form moderately strong chelates with organic matter containing sulphur, but how these chelates might react under different sediment chemistries appears to be unclear.

Relevance to the North West Shelf

On the NWS, again the primary concern with respect to lead contamination appears to be associated with the Parker Point Power Station and, to a lesser degree, petroleum production and drilling activities and hence PFW and cuttings piles which, as previously stated, tend to be anoxic until disturbed. It is reactions which may take place under these conditions that are of concern. Lead is a group IVb element, as are carbon and silicon, thus Pb can be methylated, though organoleads tend to be less stable due to the weakness of the Pb-C bond. Schmidt and Huber (1976) observed biomethylation of Pb^{2+} in anaerobic culture to produce tetramethyllead. However, Jarvie et al. (1975) suggested chemical methylation in anoxic sediments without microbial action and it should be noted that biomethylation has only been identified in culture. For methylation to occur it would seem reasonable that S concentrations would need to be low or precipitation of PbS will occur, though in the presence of high sulphide concentrations, lead may form a soluble bisulphide complex leading to an efflux from the sediment. In relatively uncontaminated sediments, porewater concentrations tend to be less than those of the overlying water column and there is no net efflux. Interestingly, oxidation of anoxic sediments did not increase the availability of lead to resident worms (Howell, 1985) which suggests PbS is oxidised relatively slowly (Neff, 2002).

Potential for bioaccumulation and toxicity

Lead in general is not readily available to marine organisms (Neff, 2002) though most organisms will accumulate it to some degree. Marine invertebrates and fish will accumulate lead in direct proportion to ambient concentrations (Neff, 2002). There is little evidence for magnification through the food chain with the highest concentrations tending to be found at the lowest trophic levels. Inorganic lead is moderately toxic to marine organisms, though it is not generally in a readily bioavailable form. Lead in sediments tends to be present in a variety of precipitated/bound forms and is therefore not available. However, alkylated lead species are generally considered to be much more toxic (Neff, 2002) compared to the inorganic forms and if conditions exist for bioalkylation, this could be of concern.

3.2.6 Mercury (Hg)

Mercury is another so-called heavy metal, with a natural global cycle and this is dominated by the exchange between the aquatic environment and the atmosphere although other sources such as rivers can be important. Release of mercury to the atmosphere relies on the formation of elemental mercury (Hg^{o}) which can then volatilise. However, a competing reaction, that of methylation, leads to retention of mercury within the marine environment, with the potential for bioaccumulation. This cycling can be illustrated schematically as follows:

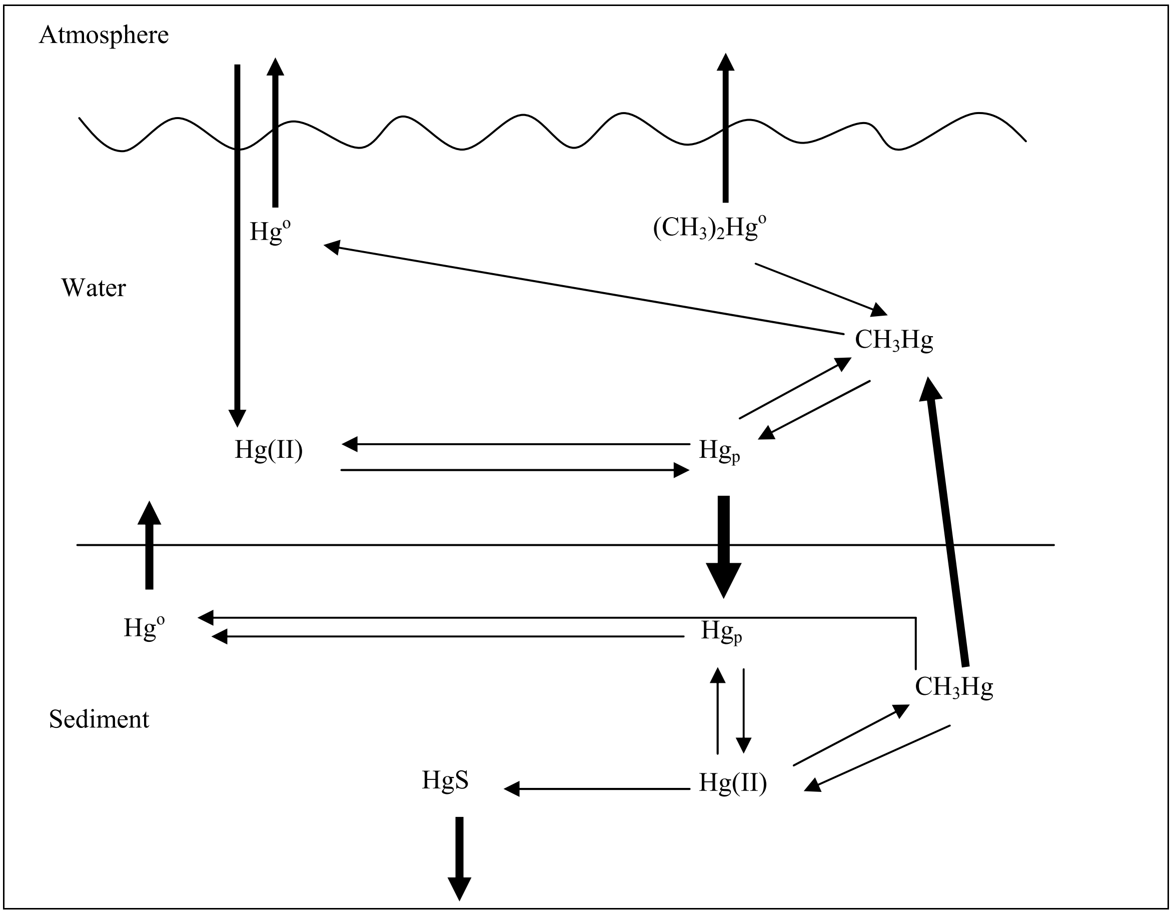
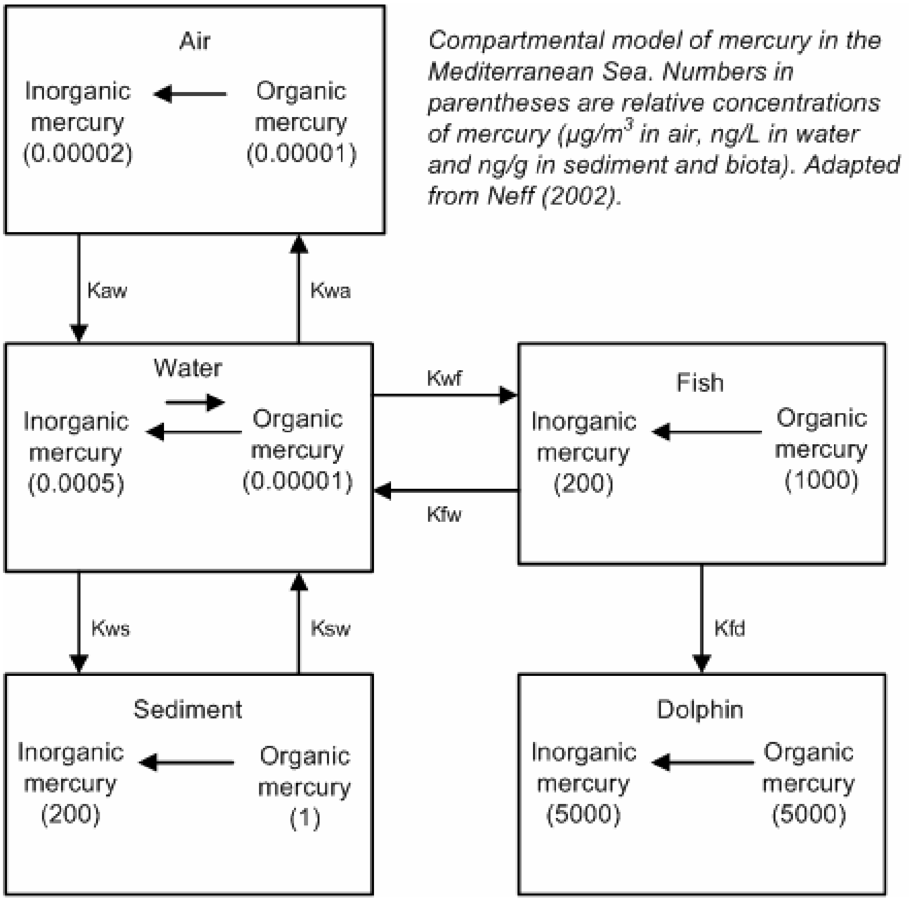


Figure 3.2.5: Mercury cycling.

Factors that control these transformations in both the water column and sediments are not clearly understood. It has been shown in laboratory studies that the reduction of Hg(II) can be biologically mediated (Mason et al. 1994 and therein). However, it is thought that an increase in anoxic conditions can reduce the formation of Hg^o while possibly enhancing the formation of methylated species (Sirca et al. 1999). There appears to have been few attempts to model mercury cycling in marine sediments. One such attempt is that by Sirca et al. (1999) in the Northern Adriatic, using a 2D model. Interestingly, while the model did appear to give quite a good agreement with the measured spatial extent of the mercury and the general trends, there were some marked differences in the relative quantities of some of the different species. This is undoubtedly due to the fact that the factors controlling this environmental partitioning are relatively poorly understood. Relative partitioning of mercury into the different compartments of the marine environment has been summarised by Neff (2002) in figure 3.2.6. This also illustrates the potential for bioaccumulation and food chain concentration.



Compartmental model of mercury in the Mediterranean Sea. Numbers in parentheses are relative concentrations of mercury (μg/m^3 in air, ng/L in water and ng/g in sediment and biota). Adapted from Neff (2002).

Figure 3.2.6: Relative portioning of mercury into the different compartments of the marine environment.

Relevance to the North West Shelf

Mercury entering the NWS external to the natural cycle appears to be predominantly associated with barite (Hinwood et al. 1994) and is therefore going to be strongly associated with cuttings piles, though chronic inputs from PFW will also be important. Given that cuttings piles are known to be anoxic, the concern is for the potential for production of methylated species and the associated risk of bioaccumulation. However, there are also the competing processes of sulphide formation, which could be an ultimate sink for the mercury within the cuttings piles. Insufficient data is available to determine which of these may dominate. Both inorganic and organic mercury salts form strong complexes with organic ligands in sea water and sediments, the strongest complexes being formed with sulfhydroxyl-containing organic compounds, followed by amino acids and hydroxy carboxylic acids. Degradation and remobilisation of the mercury from these complexes is slow in the absence of biological activity (Wood, 1987). The sites most strongly associated with methylation of mercury are anoxic sediments, particularly with the presence of sulphate reducing bacteria, although some methylation can occur abiotically. Bioturbation of anoxic sediments can facilitate mixing of pore waters rich in methylated mercury into the overlying water column (Neff, 2002).

Potential for bioaccumulation and toxicity

Mercury is well known to be highly toxic, and the above diagram indicates the potential for bioaccumulation, but the form of mercury in the marine environment strongly influences this aspect of its chemistry. Mercury complexed with macromolecular organic matter in sediments will have a reduced bioavailability. For example, the accumulation of mercury by benthic invertebrates is reduced by 20 to 80 times when the mercury is complexed by cysteine or proteins (Jenne & Luoma, 1977). However, complexation of methyl mercury with cysteine or thiourea complexes increases with the degree of complexation. In addition, it is known that methyl mercury is more readily accumulated than inorganic mercury, but the degree to which this occurs cannot be explained due to the increased lipophilicity of the methylated species. It appears phytoplankton more readily accumulate this form, which is then more easily accumulated by zooplankton and so on up the food chain. Thus the most important method of mercury accumulation in organisms is by ingestion, and the most important forms are the methylated species (Neff, 2002).

The issues surrounding why some higher trophic organisms accumulate higher levels of mercury than others (mostly fish consumers) have been extensively reviewed by Neff (2002). The major factor in concentration through the food chain appears to be related to the more efficient transfer and retention of methyl mercury than the inorganic form.

3.2.7 Zinc (Zn)

Zinc is another trace metal which exhibits a nutrient like distribution (Bruland, 1983) being depleted in surface waters and enriched at depth. The oceanic concentration with depth shows a strong correlation with silicate. The natural concentration of zinc in sea water lies between 15 and 460 nmol kg^{-1} (mean ca 50 nmol kg^{-1}; Bruland, 1983) while in sediments it can be as high as 1800 mmol kg^{-1} in polluted sediments, but is only around 0.1 mmol kg^{-1} in natural marine sediments (Moore & Ramamoorthy, 1984). This represents a concentration factor of about twofold from oceanic water.

Zinc will complex with chloride ions to form $ZnCl_2$ but at pH of 8 and above Zn tends to be hydrolysed and will form $Zn(OH)_2$ (Moore & Ramamoorthy, 1984), which can promote the overall solubility. In the presence of organic material, Zn will form complexes with organic ligands, though there is competition from Ca^{2+} and Mg^{2+} ions and this complexation is not as strong as for Cu and Pb. This can be important in sediments, where organic matter concentrations tend to be greatest. However, the greatest scavenger of zinc from solution into the sediments appears to be Fe-Mn oxides (Grieve & Fletcher, 1977) and Nriagu and Coker (1980) estimated that <5% of Zn in sediments was bound to the organic matter.

Relevance to the North West Shelf

Zinc is discharged in both Produced Formation Water and drill cuttings (as an impurity in barite), but the major discharge is associated with the Parker Point Power Station. Again, there is a need to understand the dispersion and sediment-water interactions in shallow coastal environments to understand the likely effect, if any, of the discharge of zinc from the power station. The current levels of discharge and dispersion of PFW on the NWS probably mean that the area of most concern with respect to zinc released due to petroleum activity is again cuttings piles. In anoxic sediments zinc can be absorbed to iron-manganese oxides or become associated with the organic/sulphide fraction. There can be a net efflux from sediments into the overlying water column, but this tends to be greatest from oxidised rather than anoxic sediments. Resuspension of anoxic sediments, approximately 1% of the particle bound zinc is redissolved (Petersen et al. 1997).

Potential for bioaccumulation and toxicity

Zinc is an essential micronutrient for all marine organisms, which means that they can regulate tissue concentrations, and in most cases this regulation extends over a wide range of ambient concentrations. Organisms can accumulate zinc from a variety of sources. For many filter feeders, organically bound zinc is less available than the free ion (Vercauteren & Blust, 1996) while some benthic feeders accumulate zinc from ingested particles. Thus, this variability in mode of accumulation means that different taxa will be affected in different ways by zinc contamination, depending very much on its speciation within the environment. The toxicity of zinc also varies widely, for example phytoplankton and some crustacean larvae are the most sensitive, while fish tend to be the most tolerant (Neff, 2002). This makes assessing what may be toxic concentrations difficult without species specific information.

3.3 Tributyltin (TBT)

The distribution and fate of tributyltin (TBT) in the marine environment has been the subject of an extensive review by Batley (1996), so the following is a summary of that information. For more detailed information the reader is directed to the Batley review.

Concentrations of TBT in waters can range from <1 to 1000 ng l^{-1} and for example, a large commercial ship leaching TBT can contribute more than 200 g to surrounding waters during a three day port visit. Due to the hydrophobic nature of TBT, it tends to accumulate in the surface microlayer, especially if other organic compounds are present, such as petroleum residues. A variety of enrichment factors (2 to >40) between the surface microlayer and surrounding underlying water have been reported, but this variability probably reflects other constituents within the microlayer and suspended solids.

Once in the environment, TBT is subject to both biotic and abiotic degradation involving sequential dealkylation to dibutyltin (DBT), monobutyltin (MBT) to inorganic tin(IV). The primary degradation pathway for TBT is thought to be first order and biotic with a half life of approximately six to nine days, though this is affected by temperature and concentration and may be limited by light and nutrients, which has implications for degradation at depth. The half life of DBT degradation to MBT is significantly longer (12 to 18 days) and it is reasonable to assume that complete dealkylation requires significantly more time. One estimate has the complete process having a half life of 50 to 75 days. However, there is also evidence that the liberated tin species can undergo methylation in sediments, producing a series of methyltin species.

Evaporation has been proposed as a potential pathway for the loss of TBT, though estimates of half lives vary from 1.2 to 3 585 days. By assuming that the majority of TBT is present as TBTCl, Watanabe et al. (1992) settled on an evaporative loss half life of 70 days in their mesocosm experiments. Photolytic degradation is another potentially important abiotic degradation pathway. Unfortunately, there has been no consistency in the approach to assessing the contribution of this mechanism, with a variety of open and closed systems and irradiating wavelengths being used. Calculated half lives to date range from 3.8 to 48 hours, which are quite rapid rates of decay. However, the conditions and concentrations used to determine these rate are quite artificial.

TBT is a hydrophobic compound, and is therefore expected to be more associated with particulates than dissolved fractions. The degree to which this is true appears to depend on the organic carbon content of the particles and any other limiting factors such as water chemistry (e.g. salinity, DOC content), although these processes are poorly understood. However, it without taking into account to what degree partitioning is to occur, it occurs quickly and reaches equilibrium within hours.

Relevance to the North West Shelf

On the NWS, the main areas of concern regarding to TBT contamination, are the major ports at Port Hedland and Dampier, through direct leeching from ships and from the dredging of sediment to keep access clear. Thus, the behaviour of TBT in turbid waters and anoxic sediments are those most likely to be relevant.

Concentrations of TBT in sediments varies, as expected, widely depending on location, with concentrations ranging from <0.2 to 38 000 ng Sn g^{-1}. Once in sediments, TBT degradation follows a similar path to in solution, but rates tend to be much slower, though sediment processes have been scarcely studied. It appears that TBT on particles at the sediment-water interface may be degraded at similar rates to those seen in solution. However once sediments become buried and begin to become anoxic, the half life can begin to increase to the order of several years. This may well be due to the formation of TBT-sulphide, which is quite stable while ever the sediments are anoxic. Dredging of these areas has the potential to remobilise TBT which may have previously been present as TBT sulphides. Again, this is reviewed extensively by Batley (1996) and the reader is referred to this publication for more information.

Potential for bioaccumulation and toxicity

By definition, TBT is accumulated by marine organisms and is toxic. The major concerns with respect to TBT are its sub-lethal effects, primarily imposex in gastropods. There is also concern for the potentially high degree of food chain magnification (Jacobson & Willingham, 2000). There is a plethora of literature relating to toxicity of TBT and its derivatives (e.g. Birchenough et al. 2002) and it’s not the role of this review to summarise that data.

3.4 Hydrocarbons

The occurrence, fate and effects of oil spills on the NWS have been extensively reviewed by Volkman et al. (1994) and little has changed since that review. The greatest risk of an oil spill on the NWS arises from shipping activity, from chronic release such as bilge water and tank washing, to spills from accidents. This means that the oil most likely to be spilt is bunker, which is a heavy oil. Oils produced on the NWS tend to be light, and will therefore evaporate relatively quickly given the warm climate. Bunker oils are not readily subjected to dispersion, evaporation or biodegradation, which increases their potential to become stranded and therefore to impact on coastal communities. One study (Duke et al. 1998a; Duke et al. 1998b) used an experimental spill to assess the effects of oils on mangrove communities. Although bunker oils were found to be less toxic than lighter oils, they will be more persistent in the environment. However, the toxicity data was highly variable and more work would be required to fully understand the factors affecting the fate, persistence and effects of oils in tropical ecosystems.

An area of interest that is receiving increased attention is the long term fate of hydrocarbons associated with drill cuttings. The majority of drilling fluids used on the NWS are water based, however, there are times when a greater degree of lubrication is required (e.g. directional drilling), and where diesel based fluids may once have been used, synthetic based muds (SM) are becoming more accepted.

Although not always strictly hydrocarbon based, synthetic muds contain a variety of compounds which are at least mainly hydrocarbon in nature. These include esters, linear-alpha olefins (LAO), poly-alpha olefins (PAO), alkanes and ethers. Given the variety of structures involved, their fates within the marine environment and specifically the cuttings pile, will also vary. In the one detailed study of degradation of SM in the laboratory, Munro et al. (1998) found that the type of base oil, the sediment type and concentration, all affected degradation rates. Interestingly, in this study the ester degraded significantly faster than the blend and both the ester and the blend degraded more rapidly in the muddy sediment than the coarse sand. The NWS sediments tend to be dominated by coarse carbonate sands though, of course, the drilling fluids are initially associated with the cuttings pile. The ester degradation rates varied in the order mud > fine sand > coarse sand. This suggests quite strongly that anaerobic processes are involved in the degradation of the esters whereas, if the blend contains alkanes, this will be degraded very slowly under anaerobic conditions.

Thus, it may well be that ester based oils will degrade quite quickly within the anaerobic environment of a cuttings pile, but other synthetic components may not. However, these are laboratory based results and little is known about their behaviour in real cuttings piles, or about the chemistry of the cuttings piles themselves.

3.5 Produced Formation Water (PFW)

Produced Formation Waters (PFW) are the subject of an extensive review by Neff (2002) and there is little point in trying to reproduce that here.

It is worth noting that, despite PFW having been identified as a key contaminant on the NWS, it is in fact a cocktail of contaminants. The major contaminants in terms of concentration, are the organic constituents (generally present at the mg/L range) but many of the metal contaminants discussed above will be present, albeit at much lower concentrations than the organics (generally present at the μg/L range) and a range of naturally occurring radioactive materials (NORM).

Relevance to the North West Shelf

PFW production on the NWS has been reviewed by Black et al. (1994) as part of a review of the likely impacts of production activities. Thus this discussion will only use data which adds to that review.

There has only been one detailed study into the fate of Produced Formation Water (PFW) on the NWS (Burns et al. 1999; Holdway & Heggie, 2000). This study focused primarily on real-time mapping of BTEX (benzene, toluene, ethylbenzene and xylenes) which are the volatile hydrocarbon components of PFW. The authors showed that dilution of the PFW was in the order of 1/2500 to 1/25000 and that dispersion by currents accounted for 89% of the hydrocarbons, with no long term sedimentary accumulation. The plume from the discharge was observed to travel several kilometres, with some accumulation of non-volatile hydrocarbons in the surface microlayer. However, data from Utvik (1999) has shown that BTEX are only a minor component in PFW from North Sea platforms, and that organic acids can be 10 to 100 fold greater in concentration and Black et al. (1994) suggested that Australian PFW may have a similar composition.

Potential for bioaccumulation and toxicity

Obviously the different components of PFW will have differing potentials for bioaccumulation and toxicity. BTEX are known to be toxic at high concentrations, however the high dilution factors and rapid dispersion of these compounds makes accumulation and toxicity unlikely at current discharge levels. The multi ring aromatic hydrocarbons (naphthalenes, phenanthrenes and dibenzothiophenes) occur at much lower concentrations in PFW than the BTEX. However, they tend to more readily become associated with particulates in the water column and are therefore potentially available to filter feeders and/or transported into the sediments. These aromatic compounds are potentially modified by a variety of processes such as photo-oxidation and microbial action, both of which can affect and potentially enhance the toxicity of these compounds. However, although there has been evidence for sedimentary accumulation in areas around platforms in shallow water (Neff, 2002), the NWS study by Burns et al. (1999) found no evidence for sedimentary accumulation.

To date, there appears to be little data on how organic acids behave in the environment, though they are primarily in the C1 to C6 range, which means they will be quite volatile. Being acids they do have the potential to be more water soluble, especially at the pH of sea water where they will be fully dissociated, with the longer chain lengths potentially accumulating at the surface microlayer. With respect to the NWS, the primary concern would appear to be how these PFW components behave after discharge, specifically their short term fate and any potential interactions with organisms such as coral, especially those with larval stages which may be associated with the surface microlayer.

3.6 Summary

The major gaps in understanding of contaminant behaviour, and therefore potential bioavailability, on the NWS relate to a lack of detailed understanding of the chemistry and behaviour of some of the major contaminants. This makes it difficult to predict with the fate of many of these contaminants. Some aspects can be predicted, and observed such as depletion in oxygen through nitrate to sulphate reduction in cuttings piles. There is also the possibility that microbially mediated reactions may lead to dissolution of some contaminants from sediments. The composition of cuttings piles is complex, and no two are alike. In some cases there is significant variability in their epifauna and infauna. There is still uncertainty over what happens to dissolved and particulate pollutants (metals, organic substances etc.) during its accumulation, if it is then left alone, or if it is subsequently disturbed – for example, after a cyclone event. This is only now starting to be addressed in the North Sea, where there is substantially more activity than the NWS, through a program entitled Managing Impacts in the Marine Environment (MIME) funded by the Natural Environment Research Council (NERC) and from another study funded by UKOOA (United Kingdom Offshore Operators Association).

There is also a discrepancy in the time frames for some of the inputs. For example, many of the contaminants are present in the power station discharge, PFW and drill cuttings, but often at much higher concentrations in the latter. Inputs from the Power Station and PFW are likely to continue for many years more than those from drill cuttings which presents a classic chronic versus acute assessment problem. However, the fact remains that much more is known, or can be inferred, about the dispersion and dilution of discharges than about the longer term fate of drill cuttings, either within the pile or once dispersed.

Based on the current state of knowledge, it would seem desirable that management of these discharges is not performed on an annual loading basis, but that it should be performed within a structured and more holistic framework which takes into account as many factors as possible, such as contaminant speciation and water column and sediment chemistry following discharge.

4. TOXICOLOGY

4.1 Overview

There are large amounts of toxicological data available for species and chemicals involved in the oil and gas industry in the North Sea, Gulf of Mexico and elsewhere, but far fewer data for Australia in general and the NWS in particular. Sub-lethal toxicity is difficult to assess, quantify and monitor because it is far less obvious than lethal effects and is displayed in a range of forms such as altered metabolic rates, reproductive failure and physical deformities. Such effects are usually detected only after a long period of low level exposure. A significant difficulty in assessing the toxicity of contaminants is that different marine organisms vary greatly in their sensitivity to contaminants. In most instances, toxicity data is based on research and tests conducted overseas and based on test species not found in NWS waters. As such the data may not be generally applicable to the marine environment of the NWS.

Although the mode of action of a toxicant (e.g. uptake, excretion and cell metabolism characteristics) generally doesn't change between biota, species sensitivities do differ, and temperature has a marked effect on the uptake kinetics of toxicants. It is therefore usually inappropriate to extrapolate toxicity results for one species to another (Depledge et al. 1994), especially from temperate to tropical species.

Data from bioassays performed in Australia that are relevant to the NWS are collated in DA Lord and Associates (2002). All of the data presented, with the exception of the Bass Strait data, were obtained from bioassays using Australian tropical species or validated surrogate species, and were conducted using temperatures and salinities similar to those found on the NWS. Toxicity data from platforms in Bass Strait have been included to highlight the lack of data available on PFW toxicity from platforms on the NWS. The data from Bass Strait platforms are comprehensive as they show toxicity of the PFW to several species from different trophic levels. Much of the data is from acute toxicity tests, mostly LC50 results (concentrations that are lethal to 50% of the test population) or NOECs (no observable effect concentrations). Sub-lethal and chronic tests for Australian species are less well established than acute toxicity tests, but are important for determining the full environmental implications of contaminant discharge.

4.2 Toxicological data

4.2.1 Metals (Barium, Cadmium, Copper, Lead, Mercury and Zinc)

Barium is a major component of drilling fluid but is considered of low toxicity. No studies could be located on the effect of barium on NWS species (or any Australian species), and ANZECC & ARMCANZ (2000) have no guidelines for barium. It is noted that overseas studies have shown a barium concentrations of 200 µg/L to cause abnormal development effects and morphology on mussel larvae (*Mytilis californianus*) (Spangenberg & Cherr, 1996), and concentrations of barium in drilling fluid can be orders of magnitude higher than this.

There are few data on sub-lethal responses of NWS biota to cadmium, lead, mercury and zinc, but some data for copper. The acute toxicity data available for cadmium, lead, mercury and zinc after allowing for a tenfold reduction in concentrations for conversion from acute to chronic effects indicate ANZECC & ARMCANZ (2000) guidelines are appropriate for use in NWS waters.

Low concentrations of copper can impair or inhibit settlement of the coral larvae *Acropora tenuis* (Reichelt-Bruchett & Harrison, 2000). At levels of copper as low as 42 µg/L settlement of coral larvae was reduced with an EC50 (concentration of a compound where 50% of its effect is observed) value of 35 µg/L and at 200 µg/L all larvae died. Negri and Heyward (2000b) also showed that exposure to copper had an adverse effect on the fertilisation of the coral *A. millepora* with an IC50 (a measure of a compound's inhibition (50% inhibition)) of 17.4 µg/L. Fertilisation success of the coral *Goniastrea aspera* was reduced to 41% by exposure to copper at 20 µg/L (Reichelt-Bruchett & Harrison, 1999). Reichelt-Bruchett and Harrison (1999) have shown copper to be more toxic to coral fertilisation than zinc or cadmium. The ANZECC & ARMCANZ (2000) guideline for copper of 1.4 µg/L is a high reliability value (i.e. based on sub-lethal tests or chronic NOECs) that encompasses the sub-lethal responses for NWS corals (which are among the most sensitive of organisms to copper). The ANZECC & ARMCANZ (2000) guideline is therefore considered appropriate for use in NWS waters.

Metals such as barium, copper, lead and zinc, are commonly found in elevated concentrations in cuttings piles around drilling platforms (Francis, 1995; Oliver & Fisher, 1999). Oliver and Fisher (1999) have estimated that elevated metals in sediments around drilling operations that used non-water-based drilling fluids could be observed for 1.6 to 3 km for a multiple well operation and 0.4 to 1.2 km for a single well drilling operation. However, concentrations although elevated above background, are still well below ANZECC & ARMCANZ (2000) guidelines, indicating little likelihood of adverse effects due to metals.

4.2.2 TBT

Species shown to be affected by TBT in Australia include molluscs, oysters and neogastropods. Australian studies show that exposure to TBT can result in imposex in neogastropods (Reitsema and Spickett, 1999). Imposex and other effects, such as reduced growth and reproduction, can occur at concentrations as low as 2 ng/L (Jacobson & Willingham, 2000). Negri and Heyward (2000b) also report effects on the metamorphosis of the coral *Acropora millepora* larvae with an IC50 of 2.0 ng/L. The ANZECC & ARMCANZ (2000) 95% species protection guideline of 6 ng/L may not be sufficiently protective in NWS waters where corals occur: the 99% species protection guideline of 0.4 ng/L may be more appropriate in such areas.

In the Northern Hemisphere, sub-lethal effects and mortalities have been observed in echinoderms, molluscs, bryozoa, annelids, coelenterates and algae at similarly low TBT concentrations as for NWS species (1 to 150 ng/L; Waldock, 1994; Mouhri et al. 1995; Mercier et al. 1997; Jak et al. 1998; Kusk & Petersen, 1997). Uptake of TBT via the food chain has been found to be important as bioconcentration factors can be as high as 10,000 (Jacobson & Willingham, 2000). Northern Hemisphere data also indicate that TBT may bioaccumulate up the food chain. Guruge et al. (1996) and Kim et al. (1996)

have shown that high order predators such as cormorants, seals and dolphins off the coast of Japan have elevated levels of TBT. While TBT can be excreted in small amounts from the body by the moulting of hair and feathers, there is concern that female body burdens of TBT decrease as a result of the TBT being transferred to developing embryos.

4.2.3 Hydrocarbons

Crude oils contain components that are volatile and evaporate rapidly, as well as hydrocarbons that are slightly soluble and others which will weather to form tarry residues. Different oils vary in these properties, but it is the dissolved components of oil which have the potential to cause toxicity to marine organisms, and the components that contribute most of the toxicity are the aromatic hydrocarbons (Neff, 1997). The light crude oil and natural gas condensate more typical of the NWS may contain up to 50% aromatic hydrocarbons (Neff, 1997). The most common aromatic hydrocarbons in crude oil are benzene, toluene, ethylbenzene and xylene (BTEX). Crude oils can also contain up to 10% PAHs (polycyclic aromatic hydrocarbons, composed of two or more benzene rings), with common PAHs being fluorene and phenanthrene. Due to the widely varying composition of petroleum hydrocarbons, ANZECC & ARMCANZ (2000) guidelines are of limited use

Discharges of PFW, other operational activities and natural seeps release hydrocarbons into the NWS region, but the major environmental concern for the NWS from oil is the effects of an oil spill. Globally, there has been a great deal of research on the impacts of oil spills on mangroves, which are particularly sensitive to hydrocarbons. Much of the NWS coastline and islands has a fringe of mangroves, and crude oil and diesel have been shown to have severe impacts on Australian mangroves (Duke et al. 1998). Mangroves are susceptible to the oil depositing on breathing roots, stems and sediments (Duke et al. 1998). Mangroves are also vulnerable to oil spills as they depend on the burrowing activities of infauna to aerate the roots. Mangroves can die within several weeks of an oil spill due to mortalities of these invertebrates and deposition of oil (Duke et al. 1998). Further, residual oil in sediments appears to retard the growth of seedlings.

For NWS corals, Negri and Heyward (2000a) found that crude oil inhibited larval metamorphosis of *Arcopora millepora* at concentration of 82.4 μg/L total hydrocarbon concentration, but at the lower concentration of 32.5 μg/L when combined with the oil dispersant Corexit 9527. Gulec et al. (1997) and Gulec and Holdway (2000) also found the combination of dispersants Corexit 9500 and Corexit 9527 with crude oil resulted in increased toxicity of oil to Australian species of fish and invertebrates. The surfactant properties that allow the oil dispersants to work are non-specific and can affect the lipid-bilayer membranes of living cells (Singer et al. 1995), and oil dispersants can have acute toxicity effects at lower concentrations than the oils they are used to disperse (Singer et al. 1993; Singer et al. 1994). Surfactants can also disrupt the endocrine system in many aquatic organisms (Bechmann, 1999). The above results indicate dispersants should be used with caution on oil spills in Australian waters, particularly near coral reefs.

Most petroleum hydrocarbons are lipophilic and can be bioconcentrated by aquatic biota (Black et al. 1994). They can also be transferred to the gonads and then to the offspring. Long term exposure to sub-lethal concentrations are known to include behavioural alterations, reduced growth and reduced reproduction in exposed populations (Black et al. 1994). There is a small amount of data on PAH levels in Australian biota (Pendolley, 1992; Black et al. 1994; Burns & Codi, 1998), but no published information on any related biological effects. Biomarkers such as EROD, DNA adducts, antioxidant enzymes and inhibition of AchE activity, are very useful for determining if an organism has been exposed to PAHs (Burgeot et al. 1996; Gagnon, 1999), but do not predict long-term impacts of PAHs on reproduction, animal health or population health. Other biomarkers such as histopathology, steroid analysis and haematology are needed to determine the health of organisms. Future studies on chronic, low-level effects due to hydrocarbon concentrations in NWS waters and sediments will need to place results into context against chronic, low-level effects due to natural hydrocarbon seeps. Effects due to natural seeps can range from biostimulation (due to a heightened supply of organic carbon) to toxicity, depending on the type and concentrations of hydrocarbons released. The balance between enrichment and toxicity effects due to natural seeps (and attendant effects on biodiversity and abundance) depends on the tolerance of different biota to hydrocarbons, and the scale over which effects are considered: species abundance and diversity may be depressed close to natural seeps, but with increasing distance from the seep there may be increased abundance of tolerant species, and at large spatial scales there may be slightly increased biodiversity overall (e.g. Steichen et al. 1996).

The relevance of overseas studies to the NWS is questionable due to the widely varying composition of oils worldwide, but some work on the photoreactivity of hydrocarbons is worth mentioning. Research has shown that sediment-dwelling bivalves have the ability to transfer PAHs to their offspring, and maternal transfer of PAHs to their planktonic larvae has environmental implications as many PAHs have the ability to become photoreactive, and potentially become more toxic (Pelletier et al. 2000; Batley, pers. comm.). The phototoxicity of petroleum products depends on the composition and concentration of phototoxic PAHs present, and appears more common in heavier crude oils (Pelletier et al. 1997).

4.2.4 Drilling fluids and drill cuttings

Currently the majority of drilling fluids used on the NWS are water-based, with some use of synthetic oil-based drilling fluids (either highly-refined mineral oils or vegetable oils, polyglycols and esters; Craddock, 1999). The use of ester-based drilling also appears to be increasing.

The largest mineral component of most drilling fluids is barite ($BaSO_4$, a mineral with low water solubility and regarded as having low toxicity), which is added as a weighting material. Other ingredients usually include bentonite clay, potassium chloride, various polymers and a suite of specialised, task-specific materials (viscosifiers, fluid loss control agents, emulsifiers, brines, shale control additives, lubricants, detergents, biocides and corrosion inhibitors; Roddie et al. 1999). Arsenic, cadmium, copper, mercury, nickel and lead may sometimes be present as trace contaminants of the bentonite clay and drill cuttings (Hindwood et al. 1994).

The precise composition of drilling fluids is usually commercially confidential, and so chemical descriptions are not readily available. In addition, the drill operator will vary the composition of the fluid to maximise performance throughout the drilling process.

As a result, no two drilling fluids can be considered identical, and environmental effects are best determined by drilling fluid-specific toxicity tests.

Tsvetnenko (1999) has tested the toxicity of the water soluble fraction (WSF) of 11 drilling fluids used on the NWS, using the 96-h IC50 *Isochrysis* sp. assay, the 48-h copepod EC50 with *Gladiofererns imparipes* and the 96-h *Penaeus monodon* LC50 assay. Based on the classification in table 4.2.4 with the algal bioassay, 10 of the 11 drilling fluids were non-toxic and one non-toxic to almost non-toxic. With the copepod bioassay seven drilling fluids were non-toxic and four almost non-toxic. With the prawn bioassay, three drilling fluids were non-toxic, three almost non-toxic and two slightly toxic.

Minimal dilution of most of the tested drilling mud discharges is therefore required to avoid acute toxicity effects in the water column, particularly if the temporal basis for acute toxicity effects is taken into account (i.e. the toxicity tests were based on 48 to 96 hours of continuous exposure). Tests using the water soluble fraction (WSF) of various drilling fluids used on the NWS also suggest that leaching rates for base fluids in cuttings piles are unlikely to present an *acute* toxicity hazard in the overlying water due to the fact that drilling fluids are free of aromatics and are generally poorly soluble (Evans et al. 2000). There are, however, no data on water column concentrations that cause chronic toxicity effects.

Table 4.2.4: Classification of drilling fluid toxicity (after Hinwood et al. 1994).

Toxicity rating	LC50 value (mg/L)
Very Toxic	<1
Toxic	1–100
Moderately Toxic	100–1 000
Slightly Toxic	1 000–10 000
Almost Non-toxic	10 000–100 000
Non-toxic	>100 000

It is commonly reported that water-based drilling fluids are less toxic than their synthetic or oil-based counterparts, but there are few toxicity data on water-based drilling fluids to confirm this. McIlroy (1999) reports that potassium chloride-based drilling fluids show toxicities to mysids and prawns ranging from 9 121 to 76 000 mg/L, depending on the concentration of biocides in the fluid. This approximates the ‘almost non-toxic’ range reported above for synthetic-based drilling fluids tested by Tsvetnenko (1999).

Benthic community data indicating the effects of contaminants in drill cuttings piles are few, and are for the North Rankin A platform and Wanaea 3 platform where synthetic-based drilling fluids were used (Oliver & Fisher, 1999). At the North Rankin A drilling platform, no organisms were present in the cuttings pile itself, where hydrocarbon concentrations were 75 000 mg/kg dry weight. Within 100 m of the cuttings pile, hydrocarbon concentrations in sediments were 2 200 to 7 700 mg/kg dry weight, and the only species present was the polychaete worm *Neanthus cricognatha*. At 400 m from the cuttings pile, the species richness increased rapidly and hydrocarbon concentration decreased rapidly. At the Wanaea 3 platform, benthic community effects could still be observed three years after drilling ceased, with a hydrocarbon concentration of 860 mg/kg at the well head at that time. These data, and the results of Curtin University using *Grandidierella* sp. described above, argue the need for care in assessing the potential toxicity of synthetic-based drilling fluids.

4.2.5 Produced formation water

As for petroleum hydrocarbons and drilling fluids, the composition of PFW varies widely, and environmental effects are best determined by PFW-specific toxicity tests. Acute toxicity data for NWS PFW are few, but indicate low toxicity, similar to Bass Strait PFW. PFW discharged into the sea is rapidly diluted and dispersed, while volatilisation and biodegradation further reduce the amount of hydrocarbons present in the PFW plume (Stephens et al. 2000), and so the likelihood of acute toxicity effects is very low.

Sub-lethal data for NWS PFW are also few. PFW at a concentration of 20% v/v has been shown to inhibit fertilisation of the coral *Acropora millepora* by 25%, and larval metamorphosis by 98% (Negri & Heyward, 2000a). Jones and Heyward (unpublished data) showed that PFW at concentrations greater than 12.5% impaired photosynthetic efficiency of symbiotic zooxanthellae of the hard coral *Plesiastrea versipora*, with no adverse effects at <10% PFW. The potential for sub-lethal effects on NWS corals thus appears low.

The work of Burns et al. (1999) has demonstrated sub-lethal effects on marine plankton and bacteria up to 1.8 km from the Harriet A production platform, corresponding to hydrocarbons in the surface microlayer as low as 9.4 to 110 µg/L. This contamination of the sea surface microlayer may have implications for the development of any embryonic or larval life-stages of species in the zooplankton, but the percentage of NWS waters thus affected would be minimal.

4.2.6 Other substances

Naturally Occurring Radioactive Materials (NORM)

Naturally occurring radioactive materials (NORM) in PFW have long been a concern in the oil and gas industry (Hart et al. 1999). Production processes concentrate radium (Ra) isotopes in mineral scale inside production equipment, and this scale can build up over time (Marler, 1994). Significantly elevated concentrations of Ra226/Ra228 eventuates in low specific activity (LSA) scale (Lysebo et al. 1999). Exposure to these radium isotopes can result in the ingestion of alpha particles which have very low penetration but can cause significant cell damage over a short range (Marler, 1994; Australian Drinking Water Guidelines, 1996). Alpha particles also have an affinity for high-density tissue such as bone and will remain in the bone for a considerable time (Marler, 1994). Other isotopes of the uranium and thorium decay series that may be present in PFW are uranium 238, thorium 232, uranium 235 and the shorter lived daughter nuclides radon 222, polonium 210 and lead 210 (Szymczak, 1999).

There are few data on the toxicity of LSA scale (Roddie et al. 1999), although there are data on the effects of low level radioactivity in general. On the NWS, the work of Colman and West (2000) for the Cossack-Pioneer offshore facility found PFW discharge was not causing any build-up of radionuclides in sediments around the facility. No other work on NORM for the NWS was found. It would be useful to carry out a preliminary risk assessment to see whether further research is needed on the sensitivity of NWS species to radionuclides.

4.3 Discussion

There are several toxicological data gaps limiting the interpretation of environmental impacts of contaminant inputs to the NWS. In summary, these are:

- Lack of toxicity and characterisation data for PFW. The Department of Minerals and Petroleum Resources require that all facilities on the NWS characterise their PFWs by October 2001. These assessments are not yet to hand (G. Cobby, pers. comm.).
- Lack of toxicity and characterisation data for drilling fluids and cuttings.
- Lack of data on the long-term impacts of cuttings piles, particularly those generated from synthetic-based drilling fluids.
- Lack of chronic bioassays using NWS species, particularly for oil/gas industry hydrocarbons.
- Lack of information on biological effects due to low-level hydrocarbons concentrations in the tissues of NWS species. Effects will need to be placed into context against those due to natural seeps. There is some research on hydrocarbon biomarkers for fish, but this needs to be expanded to include invertebrate species, and biomarkers that will detect impacts on the reproductive success and health of the animal and population.
- Lack of information on contamination of the sea surface microlayer, and sub-lethal effects on embryonic and larval organisms. This would theoretically be of less importance in open ocean waters than in sheltered locations, as the sea surface microlayer (and any associated enrichment of hydrophobic materials) would be broken up. It is also recognised that sampling the sea surface microlayer is not a trivial exercise, and obtaining sufficient sample to measure is a considerable challenge.
- Lack of sub-lethal responses of resident populations in nearshore environments (especially corals) and around platforms (especially impacts on reproduction and ability to recruit). As with point six above, it is recognised that this would be a difficult exercise: selecting control sites and de-convoluting impacts is likely to be a considerable challenge.

Acute toxicity data for the NWS are fragmentary and incomplete, but indicate that acute toxicity effects due to contaminant inputs to the NWS are likely to be rare, particularly when the temporal basis of the toxicity tests used (i.e. 48 to 96 hours of continuous exposure) is borne in mind. Where there are effects, these are likely to be transient and/or highly localised (e.g. the effects of drill cuttings on benthic communities).

Chronic effects due to metals are also unlikely, based on application of the ANZECC & ARMCANZ (2000) guidelines to contaminant input data. Therefore, the development of chronic and sub-lethal tests for discharges associated with the oil/gas industry should be given high priority. If toxicity is found, toxicity identification and evaluation protocols could be employed to identify the key toxicant classes responsible, to help target necessary management actions. Development of chronic and sub-lethal tests would also enable use of the ANZECC & ARMCANZ approach of developing guidelines (from multi-species tests, or from chronic and sub-lethal tests for a minimum of five species from four trophic groups), which is recommended for the development of NWS environmental guidelines.

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