# **POLLUTION IN THE OPEN OCEANS: A REVIEW OF ASSESSMENTS AND RELATED STUDIES**





















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# POLLUTION IN THE OPEN OCEAN: A REVIEW OF ASSESSMENTS AND RELATED STUDIES

August 2009

**UNEP and UNESCO-IOC, 2009** 







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### **PREFACE**

The original text of this report was prepared by a GESAMP Task Team convened in response to a request from two Sponsoring Organizations of GESAMP (UNEP and IOC of UNESCO) for a review of available information on pollution of the open oceans. The review contributed to the Assessment of Assessments (AoA) launched by the UN General Assembly (Resolution A/60/30) in November 2005. The AoA was the first step in developing a Regular Process for assessing the state of the marine environment, including socio-economic aspects. UNEP and IOC of UNESCO were appointed to jointly lead the AoA.

The review was substantially completed within four months and submitted to the AoA process in March 2008. Subsequently, at its 35th session in May 2008, GESAMP requested that the review should be restructured as a report for publication in its Reports and Studies series. Comments and suggestions from GESAMP Members, as well as members of the Group of Experts established for the purposes of the AoA, were taken into account in preparing the present document.

In keeping with its review status, the large amount of reference material assembled for the original task has been preserved and should form a valuable resource for future assessments of the open ocean. Apart from documents referred to in text and listed in the composite reference list, a thematic bibliography provides additional material for those wishing to pursue particular topics in greater detail.

### **EXECUTIVE SUMMARY**

- This report was prepared as a contribution to the Assessment of Assessments (AoA) start-up phase for a UN Regular Process for the Global Reporting and Assessment of the State of the Marine Environment, including Socio-Economic Aspects, launched in 2005. It responds to a request from the Group of Experts, established to conduct the AoA, for GESAMP to examine the assessment landscape for pollution of the open oceans by shipping and through the atmosphere. A Task Team was convened for the purpose.
- 2. No co-ordinated, comprehensive assessments of the state of the world's open oceans, either collectively or individually, have been undertaken to date. On the other hand, there have been several important thematic assessments of contaminants in the open ocean. A number of past assessments addressed the global marine environment in its entirety but these focused largely on the shelf and marginal seas where the most serious problems were believed to occur and which were comparatively well studied. The same position exists in the narrower field of pollution of the oceans through shipping and the atmosphere.
- 3. Accordingly, in reviewing the pollution assessment landscape for the open oceans, the reviewers extended their literature searches to thematic assessments and reviews, as well as research papers of particular relevance and importance to an understanding of pollution in the open ocean environment. This approach yielded a significant amount of knowledge on open ocean environments relevant to assessments.
- 4. The scale, variability and relative remoteness of the open oceans makes them inherently difficult to study. Regular, standardised and geographically widespread sampling regimes, as might be considered for assessment purposes, could prove logistically complex. Thus, it is logical to examine the scientific record in relation to the study of contaminants and related processes in the open ocean in order to determine the relevance and value of this work for assessment of ocean health. GESAMP strongly recommends that the regular process include reviews of the wider scientific literature.
- The review is structured around a set of substances selected on the basis of their known properties and significance for ocean environments, including the goods and services they provide and their role in global cycles e.g. ocean/atmosphere exchanges. All

- of the substances (as well as ship-generated noise) are known contaminants in the oceans that have either been shown to cause pollution (i.e. harmful effects) or have potential to do so.
- 6. The literature reviewed deals predominantly with substance emissions, inputs and ambient concentrations. Taking into account the time and expertise available, it was not possible to undertake a detailed review of the effects of substances in the open ocean. The literature regarding contaminant effects in ocean environments is by no means extensive. Nevertheless, concise accounts of the known biological and other effects of the substances are included in the thematic summaries presented in Chapter 3.
- 7. Table A lists the number of publications selected for review by substance and ocean basin. It also distinguishes between the different forms of literature reviewed, showing the small number of assessments available in comparison to reviews and scientific papers. For some substances, only a few publications were analysed by means of the template developed for the Assessment of Assessments of which this study is part. The template structure was not ideally suited to the examination of thematic literature on the open oceans.
- The amount of information available on substances in the open ocean varies widely and, for some substances, the record is extremely patchy in space, time or both. The literature examined by the Task Team focuses predominantly on the quantification of emissions and inputs either by direct measurement or through use of models to obtain estimates. Despite the relative paucity of data in comparison to shelf sea areas, for a number of contaminants the use of models has yielded realistic estimates of inputs and exchanges over large areas of ocean. In such cases, apparent gaps in information do not necessarily preclude a good understanding of the current environmental significance of the substances on broad temporal and spatial scales.
- 9. Atmospheric Heavy Metal Inputs: Available evidence provides no indication that the atmospheric input of heavy metals has produced toxic effects in open ocean regions. The concentrations of heavy metals (from all sources) in open ocean waters are generally lower than concentrations that would be of concern for most human health and ocean impact purposes, with the exception of mercury

concentrations in fish consumed by humans. For lead, and in some areas for mercury and copper, there is evidence that atmospheric deposition has led to elevated concentrations of the specific metal in some open ocean surface waters. This is not the case for the other metals. Most of the data available are from the North Atlantic Ocean. The South Pacific and both the North and South Indian Oceans suffer from an almost complete lack of data on atmospheric concentrations and deposition of heavy metals. However, since the impact of heavy metal deposition to the ocean is expected to remain minimal, while a continuation of scientific studies is important, no extensive monitoring program seems necessary. On the other hand, particular encouragement should be given to additional scientific studies in the Indian and South Pacific oceans. The GEOTRACES project will collect data on worldwide distributions of Fe, N, P, Cu, lead isotopes, Zn, Cd, Mn, from the surface to seafloor, with techniques that should allow determination of sources. These will be useful for later assessments.

- 10. Atmospheric Volatile Organic Compounds (VOCs) Inputs: The data are very sparse on the atmospheric transport, concentration, and deposition of VOCs from the continents to the ocean in all ocean basins. Best estimates are that atmospheric deposition may account for 4 to 6% of the total input of the heavier hydrocarbons (i.e., oil) to the global ocean. The data are particularly sparse for these heavier hydrocarbons over all ocean basins, and increased scientific studies are required to evaluate their importance as sources for oil in the sea. There is no evidence that the atmospheric input of lighter VOCs (e.g., C<sub>2</sub>-C<sub>7</sub> hydrocarbons as well as other light organic species such as aldehydes, ketones, alcohols, etc.) to the ocean is causing any serious impacts, and in fact the ocean is a net source for some of these substances found in the atmosphere. For the lighter VOCs a continuation of scientific studies is important in all open ocean basins, but as in the case of heavy metals no extensive monitoring program is required.
- 11. Atmospheric Carbon Dioxide, Sulphur Dioxide, and Nitrogen Oxide Inputs: Atmospheric inputs of anthropogenic carbon dioxide (CO<sub>2</sub>) and to a lesser extent of sulphur and nitrogen compounds promote ocean acidification. Ocean acidification is a threat to a diverse range of marine organisms, in particular calcifying species, and to marine ecosystems. Ocean acidification is expected to severely impact tropical coral reefs and calcareous zooplankton in high-latitude areas by the middle of this century. The WGBU (German Advisory Council on Global Change) proposes that surface water pH should not drop by more than 0.2 units below the pre-industrial average of 8.18 in any larger ocean

- region. A stabilization of atmospheric CO2 at 450 µmol/mol would be consistent with this safeguard. There is a need for long-term, global, sustained observations of oceanic CO2 uptake, ocean acidification and marine ecosystems. Analytical techniques for pH and other CO2 parameters in seawater need to be improved and made suitable for autonomous observation on voluntary observing ships or buoys. Surveys by the Continuous Plankton Recorder (CPR) should be expanded to the global oceans. More research is needed on the long-term effects of ocean acidification on marine organisms with an emphasis on calcifying species. The contribution to ocean acidification by the addition of anthropogenic sulphur and nitrogen compounds requires further study.
- 12. Atmospheric Nutrient Inputs: Many of the nutrients considered (iron, phosphorus, cobalt) have atmospheric inputs to the ocean dominated by natural processes, mostly transport of mineral dust from desert regions. Inputs of nitrogen and zinc are more strongly influenced by anthropogenic processes, but only in the case of nitrogen is there a major perturbation of the natural cycle and potentially significant impact on marine ecosystems; this is especially the case in the nutrient-depleted, subtropical oligotrophic gyres of the major ocean basins. We do not have a clear understanding of the effects of atmospheric nitrogen deposition on phytoplankton and nitrogen fixing organisms in the oceans. No true assessments exist for any of the nutrients considered and reviews exist only for iron and nitrogen. The other nutrients can be assessed solely on the basis of scientific research papers. Data coverage is patchy, with most available for the North Atlantic and very little for any nutrient in the South Pacific and North and South Indian Oceans. The absence of data for the North Indian Ocean is of particular concern as this region is likely to be heavily impacted by emissions from the surrounding land masses. GESAMP considers that monitoring of atmospheric nitrogen inputs to the ocean, and their effects, will be important for the Regular Process. Mechanisms for such monitoring are currently inadequate or nonexistent in all ocean basins.
- 13. Atmospheric Persistent Organic Pollutants (POPs, PBTs, CFCs) Inputs: POPs in the definition of the Stockholm Convention (SC) (2001) are being measured in the atmosphere in a number of international programs, some of which have a bearing on the marine environment. The original list of 12 POPs (Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, PCDDs, PCDFs and PCBs) has since been expanded by the SC to cover a range of additional substances. There is little monitoring data on the atmospheric input of POPs directly to the open

- oceans and any assessment in the future would be almost entirely dependent on data from the regional seas. Organochlorine residue data reported in various ocean-dwelling species, e.g. tuna and cetaceans, were not considered for this review as the role of atmospheric transport in such bioaccumulation is difficult, if not impossible, to ascertain.
- 14. Oil Inputs: Oil enters the open ocean from a variety of anthropogenic sources, including spills and operational discharges from ships, offshore exploration and production, leakage from sunken vessels, and deposition of hydrocarbon components (volatile organic compounds and polycyclic aromatic hydrocarbons) from cargo transfers and exhaust emissions. In addition, there is a continual input of oil from natural seeps in the sea bed. Inputs of oil to the open ocean have been well studied in a number of international and regional assessments. While the data on oil spill incidents and operational discharges are most accurate and comprehensive for North Atlantic and Northeast Pacific waters, overall global or even regional data on total oil inputs are deemed to be sufficiently accurate to develop broad estimates and assessments. In open ocean waters, oil is readily degraded and dispersed and any impacts such as the occasional oiling of diving birds or hydrocarbon tainting of fish tend to be short-term or localised. The diluted and dispersed oil droplets are usually readily metabolized by oleophilic microorganisms. Despite the many political and social implications of oil spills, open ocean incidents generally create fewer impacts than those in inshore waters. Two significant global assessments of oil inputs to the marine environment were conducted in the last decade that included estimates of inputs from shipping accidents. Better comprehensive data collection systems would enhance the accuracy of input estimates and trends, and while data gaps exist, it is probably not necessary to conduct further studies on the impacts of vessel spills in the open ocean.
- 15. Inputs of Other Ship-based Contaminants: Chemical spills, operational discharges and discharges from oil exploration and production are relatively rare events and likely to have highly localized impacts. Although there are few studies on chemical spills or discharges in the open ocean, current information indicates these to be minor sources of contamination. In the future, collection of data on contaminant releases from ships should, where possible, include data on chemical incidents. Impacts of particulate matter derived from ship exhaust emissions include potential human health impacts, reduced visibility and effects on climatic processes. Three main studies of ship emissions all address particulate matter as part of their estimations, and since these build on databases that are continuously updated, their

- methodology and results may be of relevance for a future Regular Process.
- 16. Most ballast water research has been focused on coastal waters due to concerns such as invasive alien species introductions and toxic algal blooms. There is very little information on the impacts of open ocean ballast water exchange but it is perceived to be a safe practice and has been recommended by the International Maritime Organization (IMO) for reducing introductions in inshore waters. It should be noted that in the near future ocean-going ships will have to treat their ballast water prior to discharge. Similarly, the impacts of sewage discharged from ships in the open ocean can be considered negligible due to the small quantities currently being discharged and the high dilution rates in the open ocean.
- 17. There is concern regarding the impacts of noise generated from shipping as well as offshore oil exploration, dredging, fishing, sonar and naval operations on marine species and ecosystems. However, despite increased research efforts there remain significant information gaps and a more thorough assessment of noise levels, sources and impacts, including a long term monitoring program, is recommended.
- 18. <u>Inputs of Marine Litter/Debris</u>: There have been no regional or international assessments of marine litter/debris in the open oceans. Deposits on island shores, often in remote and uninhabited areas, provide good indicators of ocean-derived debris such as fishing gear and waste from vessels. They also show that plastics, in particular, are transported over considerable distances by ocean currents. From the extensive literature on marine debris, it is known that plastic materials and fishing gear are widespread in the oceans and can become concentrated in certain areas. Pre-production plastic pellets, and fragments of larger plastic items, are probably ubiguitous in seawater. Impacts are evident but the risks of wider environmental damage may be underestimated. Systematic sampling at strategic mid-ocean locations is needed to assess trends. Measures to reduce inputs have been largely ignored.
- 19. Overview of current knowledge and capabilities: Table B gives an overview of the relative strengths and weaknesses of current scientific knowledge and capabilities, for each of the substances (or substance types) reviewed, in the context of investigations of marine environmental conditions. The table should not be used to determine priorities. The ratings reflect a multidisciplinary consensus view based on the experience and judgement of Task Team members. It is clear that for most substances, despite short-

comings in such fields as data coverage, data quality, sampling regimes and methodologies, the current state-of-the-art is generally sufficient, although not necessarily optimal, for purposes of global ocean assessments.

- 20. The assessment of contamination is greatly facilitated in the case of substances for which the environmental effects (or potential effects) are well understood and for which there are sufficient reliable data to show that inputs and/or ambient concentrations are typically well below known effect levels. This was a major consideration in assigning the *overall position* ratings given in Table B.
- 21. Need for an improved definition of assessment: In the view of the Task Team, definitions of (marine environmental) assessment proposed to date are not sufficiently specific either to evaluate past assessments or to design future assessments. A clearer and more complete definition of assessment would have assisted the present review of previous studies and publications. A more satisfactory definition would clearly identify the purpose, scale and time-frame of an assessment in order to guide, and optimize the benefit from, the science on which assessments depend.
- 22. Identifying gaps in information: A clearer definition of an assessment would also help in identifying gaps in information concerning particular substances and topics. Although assessments aim to describe current conditions, and the extent to which they constitute hazards or risks to the environment and human society, it may not be necessary to describe in detail all changes and effects associated with particular practices or substances in all parts of the area to be assessed. The significance of an information deficit, rather than the deficit itself, is the key issue. Table B indicates that the assessment of substances in the open ocean is not always critically hampered by poor temporal or spatial data coverage.
- 23. Identifying best practice: An objective of the Assessment of Assessments (AoA) was to evaluate the practices applied in conducting assessments and to determine what practices might be considered 'best practices' for purposes of the regular process. The Task Team assumed that the 'practices' referred to were those used in drafting an assessment report e.g. synthesis and analysis of scientific and socioeconomic information, as well as procedures used in selecting priority issues and determinands, rather than the methodologies used in acquiring scientific data e.g. sampling, measurement, statistical design and so forth. As very few of the publications reviewed were designed as comprehensive

- assessments of open ocean environments, it was not possible to derive meaningful recommendations on the design and conduct of a regular process for ocean assessment. Nevertheless, it will be apparent that studies of open ocean environments, and the complex processes such as air-sea exchanges that affect them, require specialized expertise and that ocean assessments might best be accomplished by scientific institutions that maintain such expertise.
- 24. Priority issues: Matters of particular relevance to the health of the open oceans are atmospheric inputs of nitrogen and CO<sub>2</sub> and their possible roles in acidification and ecosystem function. The regular process should also take particular account of developments in the field of carbon capture and storage (CCS) in the open ocean as well as the proposed use of iron and nitrogen to fertilize the oceans, with the intention of stimulating algal growth and drawing down CO<sub>2</sub> from the atmosphere.

Table A. Numbers of Reports/Studies reviewed \*

Торіс				C	cean S	ector				Res.	Templates
	NA	SA	NP	SP	NI	SI	Global	Assessments	Reviews	Papers	completed
Ocean acidification	0	0	0	0	0	0	19	12	0	7	4
CO <sub>2</sub> and SO <sub>2</sub> from Ships	0	0	0	0	0	0	29	15	1	13	3
Atm. N	13	7	7	2	2	2	6	0	7	23	10
Atm. Fe, P, Co	22	11	10	3	3	2	8	0	9	41	18
Atm. Zn	10	4	2	2	2	1	0	0	0	16	9
Debris	3	3	7	3	2	3	11	0	4	25	13
Heavy metals	28	13	10	3	1	2	8	0	4	46	50
VOCs	7	2	6	3	7	5	8	2	0	26	28
Ship-based inputs - Operational discharges	2	0	0	0	0	0	2	3	0	0	3
- Oilspills	2	1	1	1	1	1	4	4	0	1	4
- Chemical spills	0	0	0	0	0	0	1	1	0	0	1
- Heavy	1	0	0	0	0	0	2	3	1	1	4
- PAH	2	1	1	1	1	1	4	4	0	1	4
- NO <sub>x</sub>	0	0	1	1	0	0	8	1	0	9	3
- VOCs	1	0	0	0	0	0	3	2	0	1	3
Shipwrecks	1	1	1	3	1	1	1	3	0	1	1
Offshore E & P	3	0	0	0	0	0	5	3	1	1	5
Noise	0	0	0	0	0	0	0	3	7	3	4
Natural seeps	2	0	0	0	0	0	5	3	1	1	5

NA- North Atlantic Ocean; SA- South Atlantic Ocean; NP- North Pacific Ocean; SP- South Pacific Ocean; NI- North Indian Ocean; SI- South Indian Ocean

<sup>\*</sup> Where several substances are addressed in the same report, a template may be recorded more than once in this table.

Table B. Open ocean assessment landscape overview

	Geograph	ic coverage <sup>a</sup>	Data	Data	Sampling	Adequacy of	Knowledge	Overall
Topic	Extent	Adequacy	reliability <sup>b</sup>	relevance c	regularity d	methodology e	of effects f	position <sup>g</sup>
CO <sub>2</sub> (inputs)	XX	XX	XXX	XXX	XX	XX	XX	XX
SO <sub>2</sub>	Х	Х	Х	Х	Х	Х	XX	XX
Heavy metals - Hg	Х	XX	XX	XX	Х	XXX	XXX	XX
- Pb, As, Cd, Ni, Cu	Χ	Х	XX	Χ	Х	XX	XXX	XX
VOCs	Х	Х	XX	Х	Х	XX	XXX	XX
Debris	Х	XXX	XX	XXX	Х	Х	XXX	XXX
Nutrients - N	XX	XX	XXX	XXX	XX	XXX	XX	XX
- Fe, Co, P	XX	XX	XXX	Χ	XX	XX	XX	XX
- Zn	Χ	Χ	XXX	Χ	Х	XX	XXX	XXX
Noise	Х	Х	XXX	Х	Х	XX	XX	Х
Oil - spills from ships	XXX	XXX	XX	XXX	XX	XX	XXX	XXX
- op. discharges	XX	XX	XX	XX	Х	XX	XXX	XX
- exploration and production	XX	XX	XX	XX	XX	XX	XXX	XX
- shipwrecks	XXX	XXX	XXX	XX	Х	XX	XXX	XXX
- natural seeps	XXX	XXX	XXX	XX	Х	XX	XXX	XXX
- PAHs (exhaust)	Х	Χ	Х	Х	Х	Χ	XXX	XX
Chemical, spills	Х	Х	Х	Х	Х	Х	XXX	XX
Chemical, expl. and prod.	XX	XX	XX	XX	XX	XX	XXX	XX
Sewage	Х	XXX	XX	XXX	Х	XXX	XXX	XXX
Ballast water	Х	XXX	XX	XX	Х	XX	XX	XXX
Dumping of waste	XX	XXX	XX	XXX	-	-	XXX	XXX
POPs and PBTs	Х	Х	XX	XX	Х	XXX	XXX	XX
CFCs	XX	XX	XXX	XXX	XXX	XXX	XXX	XXX

Rating scheme: Good: XXX; Moderate: XX; Poor: X

a **Geographic coverage:** Relates a) to the relative distributions of existing information across the 6 ocean basins (Chapter 1) and b) to the adequacy of this coverage for purposes of regular assessments (levels, impacts, significance) of the substances concerned in the open ocean.

b Data reliability: An estimate of the relative accuracy and precision of data published in peer-reviewed scientific literature.

c Data relevance: An evaluation of the utility and value of the data for purposes of assessing ocean health.

d Sampling regularity: A determination of the adequacy of sampling regimes (frequency, timing, sample replicates etc.) used to date for purposes of decadal assessments of status &trends.

e **Adequacy of methodology:** An indication of the suitability of currently available methodologies (sampling, analysis, data processing, evaluation and interpretation etc.), for generating data needed for assessment purposes i.e. the requirement for research and development.

f Knowledge of effects: The general level of scientific understanding with regard to the effects of a substance on marine life, marine ecosystems and human health.

g **Overall position:** An indication of the current state-of-the-art with regard to investigating the substances (and related processes) in the open ocean and thus the potential for use of these capabilities (and data products) for ocean assessment purposes.

### 1 INTRODUCTION

### 1.1 Background

In November 2005, UNGA (UN General Assembly) Resolution A/60/30 launched the start-up phase, or the Assessment of Assessments (AoA), of the UN Regular Process for the global reporting and assessment of the state of the marine environment, including socioeconomic aspects. Later, in December 2006, the 61st session of the UN General Assembly urged the Ad Hoc Steering Group to complete the AoA within two years. The United Nations Environment Programme (UNEP) and Intergovernmental Oceanographic Commission (IOC) of the United Nations Educational, Scientific and Cultural Organization (UNESCO) were appointed to jointly lead the AoA.

In March 2007, a Group of Experts (GoE) for the AoA was convened for its first meeting, having been selected and approved by the Ad Hoc Steering Group. During this meeting, an overall working approach for the AoA was discussed and developed. The GoE also developed an annotated outline of the AoA, a work plan and timetable, as well as templates to be used in the analysis of individual marine assessments.

The AoA constituted a thorough review of the assessment landscape for oceans and coasts. It evaluated previous assessments at national regional and global levels in an attempt to distil best practices and suggest a framework for the UN Regular Process. For this purpose, the world was divided into 21 regions that were addressed individually by the GoE. In addition, a number of supra-regional issues were identified (fisheries, shipping, etc.).

In September 2007, GESAMP received a request from the lead agencies to contribute to the AoA, by conducting a specific review of existing global and regional marine assessments related to marine pollution, including ship-based pollution and atmospheric inputs to the ocean. GESAMP responded positively to this request and established a Task Team to address this issue. A comprehensive report was submitted to the GoE in April 2008. Subsequently GESAMP agreed that the report should be published as part of its Reports and Studies series. Accordingly, the present report is based substantially on the April 2008 report taking into account amendments proposed by both GESAMP and Task Team members.

### 1.2 Terms of Reference

Following discussions by GESAMP members, the lead agencies and the Group of Experts of the AoA, as well as the GESAMP Task Team, the following terms of reference were developed for this task:

The review should:

- 1 Focus on marine pollution, including ship-based pollution and atmospheric inputs, in the open ocean (refer to Section 2);
- .2 Include an analysis of current assessments, reviews, syntheses and studies, as available. The analysis will address, in particular, coverage and gaps (geographically and thematically) and overall relevance to the regular process.
- Adhere to the extent possible to the methodological guidelines and time-line established by the GoE;
- .4 In completing its analysis of the assessment landscape, the Team should attempt to summarise its findings on an ocean basin basis, taking into account criteria developed by the Group of Experts.

### 1.3 Team Composition

In accordance with its mandate, the GESAMP Task Team comprised experts on ship-based pollution, atmospheric inputs of pollutants and nutrients to the open ocean, marine ecotoxicology and chemical hazards. As part of the capacity building efforts of GESAMP, the Team also included a junior scientist to examine aspects of ship-based pollution.

The Task Team members are listed in Annex 1.

### 1.4 Meetings

The Team was convened for two meetings and one telephone conference (1 February 2008). During the first meeting, held at IMO, London, 15-17 November 2007, the Terms of Reference, scope and methodology were discussed and tasks distributed within the Team.

The second meeting was held in Mescalero, NM, USA, 24-28 February 2008, during which the final draft of the report was substantially completed.

### 1.5 Purpose of the Report

The report aims to provide an overview of the assessment landscape for pollution of the open ocean via shipping and the atmosphere (i.e. contaminant inputs in particular) including a critical review of the geographical and thematic coverage of our current knowledge and the nature and significance of information gaps.

### 2 SCOPE, APPROACH & RELATED CONSIDERATIONS

### 2.1 Geographic and thematic

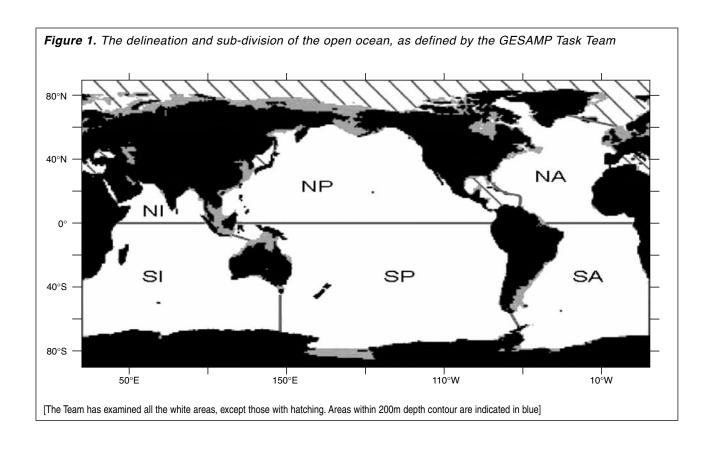
At its first meeting the GESAMP Task Team recognized the importance of having a clear definition of the geographic scope of its work. It was decided that the 'open ocean' should include ocean areas where the water depth exceeds 200 m around the boundaries of the major continental land masses. This definition excludes the marginal enclosed and semi-enclosed seas that were reviewed separately by the GoE but includes all ocean regions bordering archipelagos regardless of water depth. Because atmospheric inputs are largely dependent on the nature of sources in the adjoining land masses, the Team has sub-divided the global ocean into the major ocean basins (Pacific, Atlantic, Indian) and further into the northern and southern hemispheric portions of those basins (Figure 1).

The inclusion of archipelagos within our coverage of the open oceans is necessary because measurements at island stations are frequently used to represent conditions in the surrounding seas. This is particularly the case for atmospheric measurements, but also for marine debris, e.g. plastics from vessels and mainland sources, that are widely distributed by ocean circulation and often deposited on island shores, including those of remote and uninhabited islands.

In considering its mandate, the Task Team agreed that its literature searches should not be limited to 'broad assessments' of oceanic regions, as these have rarely been conducted, but should be extended to all reliable sources of information relevant to pollution of the open oceans, including inputs of contaminants from vessels and the atmosphere. A majority of the evaluations are therefore thematic, focussing on inputs of particular substances or substance types, the chemical species, input fluxes and temporal and spatial variations concerned.

The Task Team has not examined all available literature dealing with biological or ecological effects of inputs to the open oceans and their significance in terms of populations, communities or commercial resources (e.g. fisheries). Nevertheless, concise accounts of the known biological and/or human health significance of individual contaminants are given in the summaries contained in Chapter 3 of the document.

An intentional omission has been radionuclides from anthropogenic sources. Radionuclides enter the sea both through direct discharges and through the atmosphere. However, following the decline in atmospheric radionuclides released from the Chernobyl reactor accident in 1986, the principal pathway is thought to be through land-based discharges from reprocessing plants. In view of the



very low levels of anthropogenic radioactivity currently found even at the most contaminated coastal sites, and the decline in the Chernobyl footprint which, for radiocaesium is just above the detection limit, the impacts of radionuclide contamination at open ocean sites are likely to be extremely small (refer to Section 3.8).

Consistent with its focus on pollutants entering the open oceans from shipping and the atmosphere, the report does not assess literature dealing with the passage of contaminants from shelf-sea areas across the shelf-break. An exception is that of marine debris, where a number of the papers reviewed examine materials found in the open ocean that are almost certainly derived from land-based activities. Otherwise, the magnitude and significance of such processes, either at regional or global scales, or the extent of literature on the topic, has not been determined. Trans-shelf fluxes of anthropogenic substances (e.g. metals, nutrients, plastic debris), particularly in the plumes of some of the world's largest riv-

ers, could be substantial. A review of existing knowledge in this area would be beneficial.

For classification purposes, the open oceans were divided into the following basins (see Figure 1):

- North Atlantic
- South Atlantic
- · North Pacific
- · South Pacific
- · North Indian Ocean
- · South Indian Ocean
- Global

Table 1 lists the substances and substance categories examined by the Task Team chosen on the basis of their known or potential environmental significance and current concerns relating to atmospheric transport, ocean fertilisation and acidification, risks to marine species, communities and ecosystems as well as hazards to human health.

Table 1. Inventory of contaminants in the open ocean

Substance		Vector
CO <sub>2</sub>		Atmosphere, Shipping
SO <sub>2</sub>		Atmosphere, Shipping
VOCs		Atmosphere, Shipping
Nutrients	Fe, N, P, Zn, Co	Atmosphere
POPs, PBTs, CFCs		Atmosphere
PAH		Atmosphere, Shipping
Heavy metals	Pb, Hg, Cd, As, Ni, Cu	Atmosphere
Particles		Shipping
NO <sub>x</sub>		Shipping
Oil	Accidental spills Operational discharges Wrecks Exploration and production Natural seeps	Shipping etc.
Chemicals	Accidental spills Exploration and production	Shipping
Sewage		Shipping
Marine debris		Mainland sources, Shipping
Ballast water		Shipping
Noise		Shipping/Military/Research
Dumped waste		Shipping

### 2.2 Analysis of publications

### 2.2.1 Templates

The Assessment of Assessments process, as designed by the GoE, is based on using templates consisting of a series of questions regarding the origin, purpose, design and conduct of individual assessments previously carried out in different marine areas. The template is not ideally suited to the analysis of scientific publications relating to the open ocean because the available documentation includes few comprehensive assessments. However, the Task Team agreed to utilize the templates in compliance with the GoE's structured approach to the review and to facilitate the transfer of information into an online database designed specifically for this purpose (UNEP-WCMC GRAME Database).

### 2.2.2 Outputs

In addition to completing templates on existing assessments, selected studies and reviews, the Task Team compiled thematic bibliographies of publications containing data and information of special relevance to the assessment of environmental conditions in the open ocean. These bibliographies were provided both as a an input to GoE deliberations and as a resource for use in preparing global marine assessments. The use of bibliographies to a large extent replaced the need for in-text referencing and allowed for a more readable report, especially for a non-scientific readership. The present report, however, reverts to in-text referencing and a composite reference list as normally used for the Reports and Studies series. A number of additional references of relevance to open ocean assessments are retained in a reduced bibliography.

The report summarises the assessment landscape for different substances and contaminant categories. These summaries form the basis of Chapter 3. The chapter commences with a brief look at the open ocean coverage of earlier marine environmental assessments carried out by national and international organizations.

The principal findings of the report, including inventories of the numbers and geographic distributions of documents reviewed, as well as an overall evaluation of the information base currently available for open ocean assessments, are synthesised in the Executive Summary to be found at the beginning of the report.

### 2.3 Related considerations

### 2.3.1 The nature and scope of assessments

A pre-requisite to identifying and reviewing assessment-related literature is a clear definition of assessment for purposes of the AoA. The need for such a definition is stressed in the UNEP-WCMC report (UNEP-WCMC, 2007) which, as an interim measure, takes an assessment to be 'a scientific evaluation of an aspect of the marine ecosystem, environment, group of organisms or

an associated process'. This is not dissimilar to an earlier definition proposed by GESAMP (1994) as follows: Marine environmental assessment is the collection, analysis and interpretation of information with the purpose of assessing the quality of marine areas.

In the report of its first meeting (GRAME/GOE/1/7), the Group of Experts for the Assessment of Assessments agreed that the Regular Process should aim to include the elements of a definition of assessment<sup>1</sup> given in an earlier document from UNEP (2005).

The position is not entirely satisfactory as none of these definitions identify the different components of an 'evaluation' which would normally be expected to cover the causes, severity, trends and significance of conditions in both environmental and socio-economic terms.

Conceptually, an optimum environmental assessment framework should aim to link driving forces, pressures, state, impacts and responses – the so-called DPSIR approach adopted by the European Union and projects such as the Global International Waters Assessment (GIWA) completed in 2006. In practice, the different stages are unlikely to be integrated within a single managed programme and it is probably inevitable that future assessments will need to make use of a multiplicity of information and data sources with little consistency in regard to timeframes and geographical coverage.

Further discussion of this issue amongst Task Team members raised the question of how, in general, information is compiled for purposes of comprehensive regional assessments. It seems likely that comprehensive assessments would need to draw extensively on the open scientific literature in addition to research and monitoring conducted by state and/or international agencies specifically for assessment purposes. Without this, potentially important information could be overlooked. The range of relevant literature could include individual research papers, thematic reviews and reports from institutes and agencies engaged in marine environmental activities. In depth evaluations of some environmentally important, although not extensively studied, issues may exist only in a few isolated publications.

Looking ahead, GESAMP considers that the regular process for the conduct of global marine assessments,

<sup>&</sup>quot;An Integrated Scientific Environmental Assessment is a critical, peer-reviewed evaluation of information, for purposes of guiding decisions on a complex public issue, following a well-defined process. The scope (topic under consideration) is defined by multiple stakeholders, who are typically decision-makers. Findings are policy-relevant but not prescriptive, and reflect, for example, an "if ... then ..." approach. It is conducted by a credible group of experts with a broad range of disciplinary and geographical experience and representation, in a balanced and transparent manner. It reduces complexity but adds value by summarizing, synthesizing and building scenarios, and identifies consensus by sorting out what is known and widely accepted from what is not known or not agreed. It sensitizes scientific communities to policy needs and the policy community to the scientific basis for action (UNEP, 2005)."

no matter how meticulously it may be designed, will most likely be constrained by data shortages of a thematic and/or geographic nature. Such difficulties could be compounded if the process was based exclusively on dedicated monitoring of pre-selected variables.

For these reasons, the Task Team has extended its searches beyond commissioned assessments and thematic reviews to include publications that, in the opinion of the Team, make a significant contribution to the understanding and evaluation of features, conditions and processes relevant to pollution in the major ocean basins. As such, they help in describing and defining the assessment landscape for the oceans.

In addition to the studies reviewed in the substance summaries (Chapter 3), additional literature relevant to assessment of the open oceans is identified in the thematic bibliographies.

# 2.3.2 The assessment landscape for the open oceans

This contribution to the Assessment of Assessments complements the work of other experts working on shelf sea areas by reviewing the pollution assessment landscape for the open oceans. At the outset, the Task Team was aware that comprehensive assessments of open ocean areas, lying entirely outside the 200 m depth contour, had seldom, if ever, been conducted.

A notable exception is an assessment of the Wider Atlantic prepared under the auspices of the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Commission, 2000). This is one of five sub-regional assessments that together cover the entire north-east Atlantic region. The area lies between 62° and 36° N, and between 42° W and the 200m contour to the east (apart from the Bay of Biscay and Iberia where the boundary becomes 10°W). It thus encompasses the north-eastern sector of the North Atlantic Ocean. Under the terms of the Convention contracting parties are required to publish reports at regular intervals on the quality of the marine environment. In addition, an action plan issued at the signing of the Convention contained a commitment to prepare an assessment by the year 2000. Task Teams were established for each sub-regional assessment, each with a lead country to provide technical and secretarial support. Unlike the OSPAR Convention (North-East Atlantic) shelf areas where much of the required data was generated by a Joint Assessment and Monitoring Programme (initiated in 1995), most of the data on contaminants in the Wider Atlantic was obtained from the scientific literature. The report describes the geography, hydrography and climate of the area, the human activities that affect it, its chemical and biological features, the causes and implications of changes, improvements that have been achieved and, finally, necessary managerial and scientific actions to address degradation. The key findings, drawing attention to the importance of atmospheric inputs, are not dissimilar to those of this report (*Chapters 3 and 4*).

At a thematic level, even the more specialised field of ocean pollution by substances and wastes has not been assessed comprehensively, across all ocean basins. This is not unexpected as many of the more sensitive and heavily impacted ecosystems occur on the shelf, a relatively more accessible environment. On the other hand, the open oceans are by no means ignored by marine science and there is a substantial amount of scientific literature on particular ocean features and processes. Only a portion of this, however, is focused on pollution.

It is appropriate to recall that GESAMP's definition of *pollution*<sup>2</sup> distinguishes between the mere introduction of substances and energy into the marine environment (i.e. contamination) and introductions that have a detrimental impact (i.e. pollution). Whereas there is considerable evidence of contamination in both shelf and ocean environments, the incidence of pollution is more difficult to assess.

For these reasons the Team has focused on individual contaminants entering the oceans from ships and the atmosphere. It did not, however, consider the transfer of contaminants across the shelf break by means of ocean currents, because for most contaminants there appears to be little or no information on this topic. The search for information was prioritised, giving preference to thematic reviews, followed by more general reviews that include contaminants of interest and finally scientific papers and reports providing data or other information on inputs, levels, trends or exchanges of substances obtained from measurements made either at ocean sites or on islands indicative of open ocean conditions.

In the opinion of the Team, all of the documents reviewed make important contributions to our understanding of ocean contamination processes and related anthropogenic practices. They include benchmark studies providing data essential for ocean assessments and various thematic reviews that synthesise existing knowledge on serious ocean pollution issues.

Inevitably, many of the documents cited did not lend themselves to analysis using the template developed by the Group of Experts. Because only a few of the studies constitute assessments, it was often not possible to answer questions within the template dealing with the administrative and strategic background to the study

<sup>2 &</sup>quot;Pollution means the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to maritime activities including fishing, impairment of quality for use of sea water and reduction of amenities."

or explain why particular aspects of the design (area, methodology etc.) were favoured over others. In many cases the reasons for selecting particular targets, locations and procedures are simply that the studies are continuations or extensions of previous work by the same authors and institutes. With regard to methodologies, the Team was generally reluctant to describe techniques as 'best practice' but nevertheless we are confident that the approaches used in the studies we selected are, in a majority of cases, amongst the best currently available within the fields concerned.

Some of the publications reviewed are not entirely related to conditions in the open ocean and contain data and information for coastal regions as well as for offshelf areas. They are included either because they are the only or best available publications of their type applicable to the ocean basins concerned, or because they provide data of particular importance for assessment purposes that are otherwise rare or non-existent. A number of publications deal with the effects and significance of contaminants as well as providing data on substance levels and distributions. Another consideration in selecting publications for analysis was to ensure that, for each substance evaluated, the set of papers selected would reflect the relative availability of information across all ocean basins.

### 2.3.3 Identifying gaps in information

Gaps in information (Section 1.2.2) for purposes of environmental assessment fall into one of two categories. The first concerns topics on which there is no information at all and the second is where some information is available but, for a variety of reasons, is considered inadequate. The latter is by far the most problematic. Environmental assessments must invariably rely on packages of information that are extremely small in relation to the geographic areas and time-frames to be assessed. In many cases periodic, localised measurements must be taken to represent conditions over much larger expanses of space and time. Thus, for topics on which some information is available, it can be difficult to decide if, and to what extent, gaps exist. This is certainly the case for the open oceans.

Although assessments are aimed at describing current conditions, and the extent to which they constitute hazards or risks to man and the environment, it is not necessary to describe in detail all changes and effects associated with particular practices or properties throughout the entire assessment area. In many cases it will be clear from available information that a problem exists and that remedial measures are required. On the other hand, if the changes occurring are not yet considered problematic, but could escalate, then some form of trend monitoring will be necessary and the absence of time-series measurements would be an important gap in information. Similarly, where remedial measures have

been introduced, their efficacy cannot be assessed in the absence of standardized and repetitive measurements; this is another form of information gap.

For present purposes, GESAMP has attempted to identify available literature on all of the most likely sources of pollutants to the open oceans. As expected, there are substantial differences in the amount, quality and utility of data available on individual sources. There are sizeable gaps in the records, in both space and time, for every source examined. In the time available it was not possible to identify and describe the precise nature of the gaps and the information required to fill them. As an alternative, for each substance category the experience and opinions of Task Team members were used to indicate the relative adequacy of existing information for purposes of open ocean assessments (Table B).

The planning of an assessment should take into account the scope, scale and time-frame of assessment-related studies already underway, including their statistical design. Likewise, studies commissioned specifically for assessment purposes should take account of the planned assessment schedule and objectives. This approach should, over time, reduce the number and significance of major information gaps.

### 2.3.4 Best practice

Part 1 of the Assessment of Assessments is designed to provide 'a current state of knowledge of existing assessment processes and related activities'. One objective of the AoA was to evaluate the practices applied in conducting assessments and to determine what practices might be considered 'best practices' for purposes of the regular process. In addition, the AoA aimed to determine:

- · which practices might be improved;
- the uncertainties associated with specific practices; and
- the preconditions that should be met if specific practices are to be applied for purposes of the regular process.

In considering this part of its mandate, the Task Team presumed that the 'practices' referred to were those used in preparing an assessment report e.g. coordination of contributors, synthesis and analysis of scientific and socio-economic information and procedures used in selecting priority issues and determinands. The term might also be applied to the methodologies used in acquiring scientific data e.g. sampling, measurement, statistical design and so forth, but this is far too broad a subject to be addressed in detail at this early stage in developing the regular process.

In the absence of criteria as to what constitutes a satisfactory *assessment* process, it is difficult to comment on the suitability of procedures adopted by individual studies. Most studies of environmental conditions in the

open ocean are not designed as assessments and may have very different objectives. Consequently, experimental design, data processing and interpretation are seldom optimal for assessment purposes. Few, if any, environmental standards or criteria apply to conditions in the open ocean and, outside fisheries science, it is generally difficult for scientists to evaluate the severity or acceptability of particular conditions or to comment on management-related issues.

In many respects, open ocean environments differ markedly from coastal and shelf-sea areas and their investigation requires highly specialised techniques and personnel. Consequently, one of the *best practices* in conducting open ocean assessments would be to utilize the expertise of research institutes and data centres specialising in ocean sciences such as ocean/atmosphere exchanges, climatology and remote sensing, one of which would take the lead role in preparing the assessment report. A small network of establishments, strategically located to cover the major ocean basins, could be developed for this purpose.

In relation to methodologies, GESAMP acknowledges the importance of identifying those suitable for broad application, including where long-term trend measurements are required. In evaluating the status of knowledge on contamination in ocean environments, GESAMP has endeavoured to identify publications describing methodologies that could, with confidence, be used routinely in the fields concerned. This was also a consideration in selecting papers for analysis using the AoA templates and for inclusion in the summaries (Section 3) and bibliographies. However, most methodologies are subject to continuous change and improvement. Reducing uncertainties, for example, by improving the accuracy, precision, stability of measurement systems, should be seen as an integral part of the methods development process.

### 3 SUMMARY OF EVALUATIONS

### 3.1 Past Global Marine Assessments

A number of global marine assessments, both comprehensive and thematic, have been carried out over the past 25 years. The extent to which these assessments dealt with anthropogenic inputs to the open oceans is summarized below.

GESAMP undertook a series of reviews on the implications of contaminants for the marine environment (GESAMP, 1982, 1990, 2001a, 2001b). The reports found that the open ocean was less affected by pollutants than coastal areas.

The GESAMP (1982) report indicated increased concentrations of carbon dioxide (CO<sub>2</sub>), lead, and some radionuclides in the open ocean, as well as increases of tar-balls, oil slicks and heavy metal levels along shipping lanes. No significant effects of these contaminants were detected within open ocean ecosystems.

The GESAMP (1990) report found that low levels of lead, synthetic organic compounds and artificial radionuclides were widely detectable in the open ocean, while oil slicks and litter were common on shipping lanes. These contaminants were biologically insignificant or had a low impact on marine organisms in the open ocean. Nutrient fluxes were detectable beyond the continental shelves. The report recommended baseline measurements at a small number of monitoring sites.

In its report *A Sea of Troubles*, GESAMP (2001a) concluded that the open ocean was contaminated with substances that are widely dispersed by atmospheric transport, such as nitrogen, lead, mercury and volatile organic substances (VOCs). The action points recommended in the report were: 1) to reduce activities resulting in atmospheric transport of pollutants to the ocean, 2) to monitor the exploitation of deep-sea non-living resources, and the oceanic responses to climate change and nitrogen inputs and to take appropriate action, 3) to assess the consequences of human interventions such as iron fertilisation and deep ocean carbon sequestration and 4) to recognize that global approaches are required to address problems in the open ocean.

Protecting the Oceans from Land-based Activities (GESAMP, 2001b) and the UNEP (2006) document Towards an UNEP Environmental Watch System mainly discussed impacts in the coastal zone. The Millenium Ecosystem Assessment (MEA, 2005) provided a comprehensive overview of anthropogenic inputs to the global oceans, including CO<sub>2</sub>, SO<sub>2</sub> and nitrogen. It may provide a useful reference for global assessment purposes.

The 2005 UK Royal Society report 'Ocean acidification due to increasing atmospheric carbon dioxide' (Raven et al., 2005) raised major concerns on the impacts of ocean acidification for marine plankton, in particular for calcifying organisms and marine ecosystems. Oceanic CO<sub>2</sub> uptake has already reduced surface water pH by 0.1 units since pre-industrial times. The socio-economic effect of ocean acidification could be substantial. The report indicated that unless significant reductions are made in global CO<sub>2</sub> emissions, the Southern Ocean will become undersaturated by 2100 for aragonite, which is used by some organisms to make calcareous shells and skeletons. The report concluded that ocean acidification is a powerful reason, in addition to climate change, for reducing anthropogenic CO2 emissions into the atmosphere.

The report by the German Advisory Council on Global Change (WGBU; Schubert et al., 2006) discussed ocean acidification by oceanic uptake of anthropogenic  $\mathrm{CO}_2$ . The report proposed a safeguard for ocean acidification, limiting the pH decrease of oceanic near-surface waters to 0.2 pH units below the pre-industrial average in any larger ocean region. The safeguard demarcates the limits of desirable and sustainable development trajectories in regard to  $\mathrm{CO}_2$  emissions.

The growing importance of environmental assessment to policy review and formulation is shown by several recent global initiatives that address aspects of the open oceans. The Millenium Ecosystem Assessment (MEA, 2005) assessed the consequences of ecosystem change for human well-being and established the scientific basis for actions needed to enhance the conservation and sustainable use of ecosystems and their contributions to human well-being. Whereas the MEA assessed changes to both coastal and marine (ocean) areas, overfishing was considered to be the major issue currently affecting the open oceans. In addition, the significance of nutrient inputs and CO<sub>2</sub> sequestration for productivity, especially of fisheries, were said to warrant more detailed investigation. The Group on Earth Observations (GEO, 2007), established in 2005 and involving over 100 governments and leading international organizations, is coordinating the construction of a Global Earth Observation System of Systems (GEOSS), to be in place by the year 2015. The GEO recognizes the need to link and expand Earth observations systems, thereby ensuring that data and information remain universally accessible and allowing users to gain a complete picture of the planet. The GEO does not undertake assessements per se but will generate data products in fields such as ocean-atmosphere exchanges, ocean circulation, sea levels and marine biogeochemistry that will be essential for future assessments of the open oceans.

The Global International Waters Assessment (GIWA; UNEP, 2006) comprised a systematic assessment of environmental conditions and problems in transboundary waters including marine, coastal and freshwater areas as well ground waters. It focused on freshwater shortage, pollution, overfishing and other threats to aquatic living resources, habitat and community modification, and global change, using causal chain analysis to link problems with their socio-economic causes and effects. The GIWA recognized the inextricable links between freshwater and coastal marine environments and thus, with the exception of certain island chains in the Carribean, Indian and Pacific Oceans, it did not extend beyond the continental shelf.

### 3.2 Atmospheric Inputs

### 3.2.1 General Introduction

Gaseous and particulate substances present in the atmosphere can deposit and/or exchange directly on the ocean surface, and they can also be incorporated in precipitation. Direct measurement of the fluxes of most gases and of particles from the atmosphere to the sea surface have been attempted, but they have generally been unsuccessful or the meaning of the results open to significant doubt. However, provided great care is taken in rain sample collection and analysis, meaningful information can be obtained for precipitation fluxes. In most cases the deposition of particles and gases, whether directly or through rain, is obtained by an indirect modelling approach.

The atmospheric residence time of a contaminant is perhaps the most critical factor in determining whether there will be significant transport of the contaminants to open ocean regions. In general, if the atmospheric residence time of a substance is short, i.e., days, the substance will only be transported on the local to regional scale. Substances with residence times of weeks can be transported on the hemispheric scale, while those with residence times of more than 1-2 years can be transported globally (Seinfeld and Pandis, 1998).

Substances present on particles, such as most heavy metals, will generally have relatively short residence times (days to a week or so), and their removal, either by rain or dry deposition to the ocean surface, will generally be on a local to regional scale, in particular close to coastlines for terrestrial sources or near major shipping lanes for ship-based sources. This is also the case for gases with short residence times. Long-lived gases such as CO<sub>2</sub> and some of the persistent organic pollutants (POPs), which have atmospheric lifetimes of decades, are distributed more uniformly globally and their input to the ocean is largely independent of the distribution of their sources.

The rapid industrial and economic growth in the developing world will result in increasing transport and deposition of a variety of chemicals into the ocean downwind of those areas. For example, Duce et al. (2008) have calculated that from 2000 to 2030 the deposition to the ocean of anthropogenic nitrogen species will increase by a factor of 2 in marine areas around Southeast Asia, the Bay of Bengal and the Arabian Sea, with increases of up to 50% off west Africa and up to 30% across essentially all of the North Pacific. Elliott et al. (1997) have shown that increasing development in China will result in significant changes in the atmospheric chemistry and subsequent deposition to the North Pacific Ocean of nitrogen and iron species, with possible impacts on plankton ecodynamics.

### 3.2.2 Heavy Metals

Introduction

A number of heavy metals are transported in the atmosphere from the continents to open ocean regions. While atmospheric metal deposition is greater in coastal regions and the data are more numerous in these regions, this analysis focuses on the open ocean and considers the heavy metals mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), nickel (Ni) and copper (Cu). While there are natural sources for all of these metals, anthropogenic sources dominate for those observed in the remote marine atmosphere, particularly in the Northern Hemisphere. However, the sources differ widely depending on the metal.

Evaluating heavy metal inputs from the perspective of ambient concentrations has frequently been considered, since actual data on metal deposition to the open ocean are very sparse. The highest concentrations of heavy metals in both the atmosphere and marine waters are generally found near-shore close to industrialized and highly populated areas, but the atmospheric particles carrying these metals can be quickly transported to open ocean regions. Data are very sparse for all of these metals entering the open ocean from the atmosphere and in most cases there is little information on the speciation (i.e., chemical form) of the metals when they are deposited on the ocean surface. Perhaps the most extensive review of the atmospheric input of heavy metals to the open ocean was GESAMP (1989) and the iournal publication which was derived from it (Duce et al., 1991). However, these publications are now almost 20 years old. GESAMP has recently undertaken two new working groups in this overall area: GESAMP Working Group 37 - Expanded scientific review of mercury and its compounds and threats to the marine environment; and GESAMP Working Group 38 - Atmospheric Input of Chemicals to the Ocean.

In addition to sources on the continents, heavy metals are emitted to the atmosphere through the combustion of fuels by ships. Assuming that much of the heavy metal content of ship exhaust eventually ends up in open ocean waters, these should be considered in an assessment of heavy metals entering the marine environment. The OSPAR Commission (2000) looked specifically at heavy metals leached from ships at sea in the Northeast Atlantic (Greater North Sea) region and concluded that the greatest heavy metal impact from ships was from the leaching of anti-fouling paints and coatings and from anodes. While atmospheric inputs were considered in this assessment, there was no estimation of the extent to which atmospheric concentrations could be attributed specifically to shipping. Many experts hypothesize that the heavy metal inputs from shipping may be more from spilled and discharged oil, and from anti-fouling and anticorrosive paints and coatings used on ships, than from atmospheric emissions.

There have been no true assessments of the impact of atmospheric heavy metals on the open ocean, but there have been a number of scientific papers in the peerreviewed literature that have addressed aspects of this topic in different regions. For the open ocean regions covered by the Task Team report, Table A (see Executive Summary) shows the geographical distribution of the reports that have provided the information summarized here. Clearly there has been much more work done in general on metals in the Atlantic Ocean than the other oceans, and also much more in the Northern than the Southern Hemisphere. For example, 56% of the reports evaluated for metals considered input to the North Atlantic. Table 2 presents information on the number and percentages of the total heavy metal papers that were found for each metal in the various regions. These results will be discussed below under each individual metal. Many of the referenced papers evaluated the input of additional metals to the ocean. These other metals, if evaluated, are indicated on the individual templates for each study, and they include such metals and metalloids as selenium, antimony, manganese, cobalt, and chromium.

### Description and Origin

### Mercury

The atmospheric chemistry of mercury and its deposition to the ocean are very different from the other heavy metals addressed here. This is primarily because mercury exists to a significant degree in gaseous form in the atmosphere and undergoes a number of reactions leading to a variety of both gaseous and particulate mercury species. This is in contrast to the other metals, which primarily exist in particulate form in the atmosphere and are, to a large extent, non-reactive. The dominant form of mercury in the atmosphere is gaseous elemental mercury, although gas phase ionic mercury is also found. The primary form of mercury that is deposited to the ocean is divalent ionic mercury (Hg <sup>2+</sup>) in rain, but the dry deposition of gas phase ionic mercury may also be important (Fitzgerald et al., 2007).

There is clear evidence that human activities have severely altered the atmospheric cycling of mercury. It has been estimated that in the past 200 years the global atmospheric burden of mercury has increased about three-fold as a result of human activities. This has lead to perhaps a doubling of the input of mercury from the atmosphere to the ocean over that time period (Slemr and Langer, 1992). Human activities clearly dominate terrestrial natural sources for mercury in the atmosphere. However, the mercury input to the ocean may actually be decreasing in some regions in recent times. For example, there is evidence that in the upper reaches of the water column of the ocean near Bermuda, mercury may have decreased by a factor of about two from 1979 to 2000 (Mason and Gill, 2005). Even though there is some evidence that mercury emissions from North America have decreased recently, unlike lead in the same general region, there

Table 2. Number of papers (and % of total) that included measurements of the indicated metal in each region

Locations of Measurements	Lead	Mercury	Cadmium	Arsenic	Nickel	Copper
Total, All Regions	39 (76%)	13 (25%)	25 (49%)	19 (37%)	27 (53%)	29 (57%)
North Atlantic	15 (54%)	6 (21%)	9 (32%)	4 (14%)	9 (32%)	11 (39%)
South Atlantic	10 (77%)	3 (23%)	6 (46%)	1 (8%)	8 (62%	8 (62%)
North Pacific	7 (64%)	0 (0%)	6 (55%)	6 (55%)	4 (36%)	5 (45%)
South Pacific	3 (75%)	0 (0%)	1 (33%)	2 (67%)	2 (67%)	2 (67%)
North Indian	1 (100%)	0 (0%)	0 (0%)	1 (100%)	1 (100%)	0 (0%)
South Indian	1 (50%)	0 (0%)	1 (50%)	1 (50%)	1 (50%)	1 (50%)
Global Ocean*	2 (22%)	4 (44%)	2 (22%)	4 (44%)	2 (22%)	2 (22%)

<sup>\*</sup> Most of these papers made estimates for the global ocean but did not give details for specific geographical regions.

was no evidence that the atmospheric mercury concentration near Bermuda had changed during the same period. Atmospheric input of mercury to the global ocean is much more important than riverine input.

### **Other Heavy Metals**

Human activity has resulted in large quantities of lead being emitted to the atmosphere, and since this lead is on very small particles it can be transported long distances before returning to the Earth's surface. While such sources as smelters and industrial activity are important, until recently the primary source for atmospheric lead was the combustion of leaded fuels. However, as a result of the gradual phasing out of leaded fuels for motor vehicles there has been a dramatic decrease in the input of atmospheric lead to the ocean over the past 20-25 years (Huang et al., 1996; Wu and Boyle, 1997). Figure 2 presents measurements of atmospheric and surface oceanic lead at or near Bermuda from the early 1970s to 2000. The atmospheric concentration decrease is reflected in a decrease in lead in the surface ocean water. Similar results have been found around Hawaii. Fortunately lead has a relatively short residence time in the ocean (~10-20 years), so the change of the atmospheric input flux can be seen fairly quickly in the oceanic concentrations.

Like lead, evidence suggests that human activities have resulted in significantly more cadmium being emitted to the atmosphere than that from natural sources (Duce et al., 1991). Detailed sources for most of the atmospheric cadmium are uncertain but are likely to be a variety of industrial processes. The input of cadmium to the atmosphere from such natural sources as crustal weathering and the ocean itself are considered to be minor. Atmospheric input may dominate riverine input of dissolved cadmium to the global ocean.

Figure 2. Change in atmospheric and oceanic lead concentrations from the 1970s to the late 1990s near Bermuda 180 Marine dissolved Ph 160 Atmospheric Pb ı seawater, pmol/kg aı he atmosphere, 10<sup>-10</sup>ç 140 100 .⊑ 80 concentration 60 40 윤 20 1975 1985 1995 2000 Year Figure reprinted from Duce, 2001.

Estimates are that the anthropogenic and natural emissions of arsenic, nickel and copper to the global atmosphere are of the same order of magnitude (Duce et al., 1991). Particularly important sources are metal production and smelters as well as arsenic use in agriculture, but there are a number of other anthropogenic sources as well. The most important natural source for arsenic may be volcanoes. Atmospheric and riverine inputs of dissolved arsenic and nickel to the global ocean appear to be similar, while atmospheric input of dissolved copper may be somewhat larger than riverine input.

### Impact and Significance

### Mercury

Mercury is a highly toxic metal and there are numerous examples of its toxicity in coastal and enclosed sea areas, starting with the notorious Minamata Bay incident. However, there is no evidence that there have been any toxicity effects as a result of mercury in the surface waters of the open ocean. There is considerable evidence that some fish in open ocean regions concentrate mercury to levels that are harmful to humans if too much of that fish is consumed. Mercury has a number of chemical species in the ocean, including dissolved elemental mercury, monomethylmercury, dimethylmercury, and a variety of organic and inorganic complexes of Hg(II). Both mono- and di-methyl mercury accumulate in marine organisms and their consumers, including humans, but by far the greatest concern relates to monomethylmercury, the more abundant and toxic of these compounds. It is generated from inorganic forms of mercury by microorganisms (Fitzgerald et al., 2007).

There are a number of vertical profiles of total dissolved mercury that show higher concentrations near the open ocean surface, strongly suggesting that atmospheric deposition is important for those surface samples (Fitzgerald et al., 2007). Studies suggest that the concentrations of dissolved gaseous mercury are often supersaturated in surface waters, resulting in a significant flux of elemental mercury to the atmosphere in those regions (Fitzgerald et al., 2007). Indeed, there is evidence that the fluxes of mercury from the ocean to the atmosphere globally are similar to the level of anthropogenic emissions.

### Other Heavy Metals

While lead is toxic to marine organisms if the concentrations are sufficiently high, toxic responses typically occur at concentrations considerably higher than measured ambient levels in open ocean waters. Atmospheric deposition of lead has resulted in a measurable increase in surface water lead concentrations above those expected in the absence of such deposition (Wu and Boyle, 1997; Boyle et al., 2005). While this is most noticeable in the North Atlantic, it could even be seen 20-30 years ago in the South Pacific . Lead is one of the few metals for

which atmospheric deposition has clearly perturbed its surface water concentrations. However, it must be pointed out that until recently there have been relatively few credibly accurate measurements of many of these heavy metals in open ocean regions.

Cadmium may also exhibit high toxicity but to date there is no evidence that its input to the open ocean has had any such effects. Levels of cadmium commonly measured in offshore waters (0.01 to 0.1  $\mu$ g L<sup>-1</sup>) are likely to be sufficiently low so as not to significantly impact marine biota. Levels of cadmium in fish, with the exception of shellfish in some nearshore areas, are unlikely to be of concern for human health. In addition, unlike lead there is no evidence that the input of cadmium from the atmosphere to surface ocean waters has disturbed its natural distribution in those waters. Indeed, in studies of surface waters in the North Pacific it has been shown that atmospheric cadmium is not an important source (Patterson and Duce, 1991).

For arsenic, nickel and copper there is no evidence that atmospheric input to the open ocean has had any toxicity effects. For arsenic and nickel there is no clear evidence that the atmospheric input has had any significant effect on their vertical distributions in the open ocean. Arsenic is found as arsenite and arsenate in the ocean, as well as monomethyl and dimethyl arsenic species, but with no apparent relationship to atmospheric deposition (Cutter and Cutter, 1998; Cutter et al., 2001). There is concern about copper used as an anti-fouling agent on ships, and it is clear that some copper will enter the ocean from that source. There is some evidence that there are occasionally higher copper concentrations in the surface waters than sub-surface waters in some regions, suggesting the influence of atmospheric deposition. There is also evidence that much of the copper in marine rainfall is organically complexed, and that is the case for copper in the open ocean as well (Witt and Jickells, 2005).

### Documentation

### <u>Mercury</u>

As Table 2 indicates, there was a lower percentage of papers evaluating mercury inputs to the ocean than any of the other heavy metals assessed, only 25%. To some extent this is because mercury in the atmosphere is not as easily sampled and analyzed as most of the rest of the heavy metals. Studies of the Atlantic Ocean completely dominated the literature for mercury, and there were no studies at all that focused on the Pacific or Indian Oceans. However, a number of studies evaluated mercury input to the global ocean. UNEP has an extensive program evaluating the global impact of mercury, and they will issue a report in late 2008 on its atmospheric emissions, inventory, sources, and transport. This will consider mercury in the ocean and atmosphere.

### Other Heavy Metals

There have been a number of papers in the peer-reviewed scientific literature addressing the input of lead to the open ocean, and it can be seen from Table 2 that about three fourths of all the papers evaluated for metals for this exercise addressed lead inputs. These have been primarily in the North and South Atlantic regions, with a modest number of studies in the Pacific Ocean, and virtually none in the Indian Ocean. The emphasis on the North Atlantic in particular is logical, since its smaller size and location downwind of North America, a very large source of anthropogenic lead when lead was added to motor vehicle fuel, would indicate that the maximum impact would be expected in this oceanic basin (Veron et al., 1992).

Approximately half the papers (Table 2) that evaluate atmospheric heavy metals consider cadmium, so the database is reasonable overall. However, by far the majority of the papers cover the North and South Atlantic and North Pacific, with essentially no coverage in other areas. This may not be too serious, however, since the primary anthropogenic sources are in the northern hemisphere and even there the impact of atmospheric cadmium appears to be negligible.

Somewhat over one third of the papers evaluated for heavy metals considered arsenic. It is interesting that for arsenic there appears to be about the same number of studies in the Atlantic as in the Pacific Ocean, much different from most metals. Again, for the Indian Ocean and all ocean basins in the Southern Hemisphere, there are very few data. Like cadmium, this may not be too serious since the primary anthropogenic source areas are in the Northern Hemisphere, and even there the impact of atmospheric arsenic on the open ocean appears to be negligible.

About half of the papers evaluated considered nickel and copper in the atmosphere, with over half of those considering the North and South Atlantic, and somewhat fewer considering the North and South Pacific. There were virtually no studies of these metals in the Indian Ocean.

Adequacy of Literature and Significance of Information Gaps

### All Metals

Although 50 papers were reviewed on the topic of heavy metal input to the ocean, only a small fraction really addressed the primary issue of deposition and impacts of this material on oceanic processes. Many simply presented concentrations of the metals in the atmosphere, while a few went a step further and calculated or measured actual deposition to the ocean surface. An even smaller fraction provided the chemical speciation necessary to evaluate the impact of this deposition. While the number of papers might indicate that the North Atlantic

has been well studied, in fact even for this area there is relatively little information on temporal and geographical trends, seasonal differences, etc. But the situation is much worse for all the other basins, in particular the South Pacific and the North and South Indian Oceans. For these areas we have essentially no knowledge of the importance of atmospheric deposition of heavy metals. However, we are fortunate because the South Pacific and South Indian Oceans are generally far from large anthropogenic sources and the impact of atmospheric deposition would in general be expected to be small (with the possible exception of mercury, because the atmospheric residence time of elemental gas phase mercury is on the order of years). That is not the case, however, for the North Indian Ocean, where large anthropogenic source regions on the Indian sub-continent might be expected to cause potentially very significant fluxes of these metals from the atmosphere to the ocean.

Actual estimates of inputs of heavy metals from shipping sources were not calculated in any of the studies, but there are adequate data for use in making such assessments if the per-unit concentrations of heavy metals in fuels are applied to known combustion rates of these fuels by vessels in different ocean sectors.

Whereas all heavy metals can be toxic to marine life if the concentrations are sufficiently high, there has been no evidence of any such effects in the open ocean due to the input of heavy metals from the atmosphere. The examples for lead in the global ocean, and for mercury and copper in some regions, represent the only cases where it has been documented that inputs from the atmosphere have perturbed the surface water concentrations.

### Conclusions

While there have been no comprehensive true assessments of the impacts of these heavy metals on the global open ocean, there have been sufficient individual scientific studies to give us a reasonable sense of the importance of atmospheric input for these six metals. In no case is there evidence that the atmospheric input of these metals to open-ocean basins has resulted in toxicity to marine organisms or their consumers. In fact, the concentrations of heavy metals as measured in samples of open ocean waters are generally lower than concentrations that would be of concern, with the exception of mercury concentrations in some fish consumed by humans. For lead, and in some areas for mercury and copper, there is evidence that atmospheric deposition has led to elevated concentrations of the specific metal in surface waters. This is not the case for the other metals. Most of the data available on this topic are for the North Atlantic Ocean, with the South Atlantic and North Pacific having the next most data. The South Pacific and both the North and South Indian Ocean suffer from an almost complete lack of data on atmospheric concentrations and deposition of heavy metals.

Shipping is likely to be a minor source of inputs of heavy metals to ocean waters through atmospheric emissions. The inputs from leaching of anti-fouling paints and coatings are likely to be significantly larger than the inputs from deposition from shipping exhausts. In the light of the IMO International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention), which came into force in September 2008, this topic may warrant further investigation.

### 3.2.3 VOCs (Volatile Organic Compounds)

### Description and Origin

VOCs (volatile organic compounds) are organic chemical compounds that have a sufficiently high vapour pressure under normal atmospheric conditions to vaporize and exist in the atmosphere in the gas phase. A wide range of organic molecules, such as aldehydes, ketones, and hydrocarbons, are VOCs. The primary interest in VOCs in the context of this report would be the heavier hydrocarbons (generally greater than ~C<sub>10</sub>-C<sub>15</sub>), which are common in oil and other petroleum products. However, there have been very few measurements of these heavy hydrocarbons in the remote atmosphere over the ocean and their flux into the sea. In most cases these heavier species exist primarily in the aerosol phase in the atmosphere, although there is a low vapour phase concentration for most of them (National Research Council, 2003: GESAMP. 2007). Most of the VOCs that have been measured in the gas phase in the remote marine atmosphere are much lighter compounds, primarily C<sub>2</sub>-C<sub>7</sub> hydrocarbons, including acetylene, ethane, ethene, propane, propane, n-butane, i-butane, n-pentane, i-pentane, n-hexane, and benzene as well as other light organic species such as acetonitrile and oxidized species such as acetone, methanol, acetaldehyde, propanal, and other light ketones, aldehydes, and organic acids. Halogenated hydrocarbons are considered in Section 3.2.6.

While most of the VOCs are emitted on the continents, sea-going ships emit VOCs into the atmospheric marine boundary layer as they combust 160 million tonnes of fuel annually. These emissions have increased in the last 50 years as shipping activities have increased by 35 percent. VOCs are also released during loading and unloading operations in ports, ship operations, and bunkering, and some fraction of these emissions returns to the sea surface.

### Impact and Significance

With regard to the lighter VOCs, there does not appear to be a significant impact on ocean processes from their deposition to the ocean. In fact, for many of these compounds in the atmosphere their source is actually biological processes in the ocean (Galbally et al., 2007; Rudolph and Johnen, 1990; Sartin et al., 2002). It appears that in truly remote regions over the ocean VOCs with atmospheric residence times of roughly a

week or less, such as ethene, propene, the pentanes and pentenes, the hexanes and hexenes, and such oxygenated compounds as propanal and acetaldehyde are generally derived from the ocean.

VOCs with an atmospheric residence time of more than about a week, such as acetonitrile, ethane, propane, the butanes, and possibly methanol, are transported primarily from anthropogenic sources on the continents. For example, acetonitrile over the ocean appears to be largely derived from biomass burning on the continents (Bange and Williams, 2000). For acetylene there was no agreement in the literature as to whether it was primarily natural or anthropogenic in origin. It is known that for acetone, large sources from both the marine and terrestrial biospheres are important; acetone is also formed in the atmosphere through the oxidation of hydrocarbons. In virtually all cases it is likely that there are both continental and marine sources and that their relative importance depends upon the atmospheric lifetime of the compound and the distance it has travelled from continental regions (Jacob et al., 2002) . However, even for those VOCs that are transported from anthropogenic sources on the continents and deposited in the ocean, there is no evidence that there have been any deleterious effects in the ocean. Some of these compounds are important in the context of chemical reactions that relate to the oxidizing capacity of the atmosphere and to the formation and reactions of ozone. In that sense their continuing measurement in the atmosphere is quite important. Most studies have concluded that the effect of VOCs from shipping emissions on ozone to be very small, with the increase in ozone concentration estimated to be less than 1  $\mu$ g L<sup>-1</sup> in the areas of maximum impact, e.g., on the Arabian peninsula (Endresen et al., 2003).

### Documentation

A number of studies and assessments of shipping emissions have included estimates of VOC emissions. However, only two recent studies have evaluated comprehensively the input of heavier VOCs from the atmosphere to the ocean as part of the assessment of oil in the marine environment. "Oil in the Sea III" (NRC, 2003) addressed the atmospheric deposition of what they called petroleum hydrocarbons from the atmosphere to the ocean. Petroleum hydrocarbons were defined as n-alkanes between  $C_{10}$  and  $C_{33}$  chain length and also polycyclic aromatic hydrocarbons, although it was recognized that there are many other compounds in oil. However, these compounds make up the largest fraction of petroleum. The total emissions to the atmosphere from ships was estimated to be 1.65 Mt yr<sup>-1</sup> of non-methane VOCs. Of that amount a fraction returns to the sea surface - estimated to be 3,300 t yr<sup>-1</sup> worldwide.

The National Research Council (NRC) included a calculation of the total input of heavier hydrocarbons from the atmosphere to the global ocean. Their analysis was

based on data and methods developed in a paper published over 25 years ago ((Duce and Gagosian, 1982) and used in a previous NRC (1985) report on this topic. Unfortunately there are no other data on the heavier hydrocarbons in the atmosphere over the ocean. The NRC concluded that the best estimate of the total input of these heavier hydrocarbons from the atmosphere to the ocean was ~54 kt yr<sup>-1</sup>, with a range of between 24 and 204 kt yr<sup>-1</sup>. The best estimate figure would account for ~4% of the total input of oil to the ocean.

GESAMP (2007) addressed only the input of oil to the ocean from sea-based activities (i.e., it did not consider atmospheric transport from the continents, only the input of VOCs that had been emitted directly from ship operations). Total emissions to the atmosphere from these sources were estimated to be 3 million t yr-1. The fraction of that amount returned to the sea surface was estimated to range from 250 t yr-1 to 68 kt yr-1, with a best estimate of 68 kt yr<sup>-1</sup> worldwide. Using that figure, it was calculated that about 6% of the total oil entering the ocean came from these ship-released VOCs. The order of magnitude difference (3.3 kt vs 68 kt) of this estimate compared to the NRC estimate stems from the inclusion of methane and a differing assumption by GESAMP regarding the fraction that is actually deposited into marine waters.

Another recent review (Endresen et al., 2003) provided estimates of VOC emissions from ships that ranged from 2.0 to 3.9 Mt yr<sup>-1</sup>. No attempt was made to estimate the degree to which these atmospheric emissions entered surface waters of the ocean.

Of the studies reviewed, 28 evaluated the atmospheric distribution of lighter VOCs over the ocean. As shown in Table A (*see Executive Summary*), there were actually more studies over the Indian Ocean than any other ocean for the VOCs, unlike the heavy metals. This is largely due to the extensive study of VOCS during the large INDOEX research program in the late 1990s. In general, studies were distributed more equally around the globe than those for the heavy metals. It should also be noted that almost one third of the documents addressed the issue on a global scale.

# Adequacy of Literature and Significance of Information Gaps

There are very few studies of VOCs over the oceans, especially studies of the heavier hydrocarbons in the marine atmosphere - those compounds that could contribute most to negative impacts when entering the marine environment. For estimates of the atmospheric input of these heavier hydrocarbons we are still largely relying on data and methods from one paper that was published 25 years ago (Duce and Gagosian, 1982). The two comprehensive reports on oil in the sea (NRC, 2003; GESAMP, 2007) certainly provide an excellent and

comprehensive overview of the issue of oil in the sea and also do provide the best information that we have on atmospheric inputs and their impact. However, to understand the possible importance of the input of VOCs (and particularly the heavier ones) to the ocean, much more research needs to be done on the atmospheric concentrations and deposition of these substances over the remote Northern and Southern hemisphere oceans.

Estimates of VOC emissions from ships and the degree to which those emissions enter ocean waters are based on known usage of fuels and various assumptions concerning the entry of emissions to marine waters. The NRC (2003) estimates were based on a rigorous analysis of the scientific literature with regard to deposition rates, which are key to calculating inputs to marine waters. This estimate probably represents the best estimate of VOC inputs to marine waters to date. None of the estimates attempts to separate inputs to coastal zones from those to open ocean waters; determination of potential impacts to open ocean waters would require this kind of analysis.

### Conclusions

Data on the atmospheric transport and deposition of VOCs from the continents to the ocean are very sparse. Best estimates are that atmospheric deposition may account for ~5% of the total input of the heavier hydrocarbons (i.e., oil) to the global ocean (NRC, 2003; GESAMP, 2007). There is no evidence that the atmospheric input of lighter VOCs to the ocean is causing any serious impacts. In fact, the ocean is a net source for some of these compounds in the atmosphere.

VOC emissions from shipping likely have minimal impact on open ocean waters per se. Further monitoring or estimations of inputs of VOCs from shipping emissions will not add significantly to any efforts to reduce impacts to the open ocean. Overall reductions in emissions from shipping will result from the more stringent emission limits adopted by IMO in the revision of MARPOL Annex VI. These include reductions in emissions of  $\rm NO_x$  and  $\rm SO_x$  for all ships, as well as the introduction of a mandatory VOC management plan for tankers carrying crude oil and will concurrently reduce VOC emissions both as part of exhaust emissions and cargo vapours.

# 3.2.4 Carbon Dioxide, Sulfur Dioxide and Nitrogen Oxides

### Description and origin

Human activities are releasing 7.2 Pg C yr<sup>-1</sup> (Pg =  $10^{15}$  g) of carbon dioxide (CO<sub>2</sub>) into the atmosphere and promote atmospheric deposition of 26 Tg S yr<sup>-1</sup> (Tg =  $10^{12}$  g) of reactive sulfur and 38 Tg N yr<sup>-1</sup>of reactive nitrogen to the coastal and open ocean (Denman et al., 2007; Doney et al., 2007). Carbon dioxide is a long-lived gas, such that CO<sub>2</sub> emissions of 0.3 Pg C yr<sup>-1</sup> from shipping (Orr et al., 2005) affect the oceans in proportion to their

contribution to global anthropogenic  $CO_2$  emissions. By contrast, sulfur dioxide ( $SO_2$ ) and nitrogen oxides (NOx) have short atmospheric lifetimes, so that shipping-related emissions of ~4 Tg S yr<sup>-1</sup> of  $SO_2$  and ~3 Tg N yr<sup>-1</sup> of NOx (Corbett and Koehler, 2003) may have significant local impacts along shipping routes.

The oceans are absorbing about 30% ( $2.2 \pm 0.5$  Pg C yr<sup>-1</sup>) of anthropogenic CO<sub>2</sub> emissions, thus slowing down the increase in atmospheric CO<sub>2</sub> concentration and associated climate change (I5). Recent research, however, suggests that oceanic CO<sub>2</sub> uptake in certain ocean regions is more variable than previously thought (Corbière et al., 2007; Lefèvre et al., 2004; Schuster and Watson, 2007).

Oceanic uptake of anthropogenic  $CO_2$  lowers the pH and the carbonate ( $CO_3^2$ -) concentration, and increases the  $CO_2$  concentration, of marine surface waters. The resulting decrease of surface water pH has been estimated as 0.11 pH units since pre-industrial times (Raven et al., 2005). Atmospheric deposition of sulfur dioxide and nitrogen oxides equally promotes ocean acidification, which on a global scale is only a few percent of that by anthropogenic  $CO_2$  uptake, but impacts can be much larger (10-50%) near source regions in coastal seas and shipping lanes (Doney et al., 2007; Corbett and Koehler, 2003).

Deep-ocean  $CO_2$  storage and seepage of sub-seabed  $CO_2$  storage would result in very strong local acidification and acute  $CO_2$  toxicity (Caldeira et al., 2005; Haugan et al., 2006).

### Impacts and significance

Higher CO<sub>2</sub> concentrations and ocean acidification may well have a variety of physiological effects on marine phytoplankton (e.g. on photosynthesis, growth rates, species composition), but most of these effects are poorly understood (Schubert et al., 2006) and have at best been assessed in small scale controlled experiments. Some marine organisms make a calcium carbonate (CaCO<sub>3</sub>) skeleton or shell (Table 3). Aragonite and calcite are two important forms of CaCO<sub>3</sub>, with aragonite as the most soluble form. Ocean acidification lowers the saturation state for carbonate precipitates and hampers calcification (Feely et al., 2004, Raven et al., 2005; Riebesell et al., 2000). Tropical surface waters would become marginal for coral reefs if the atmospheric CO2 content reaches 517  $\mu$ mol/mol, which could happen by the middle of this century (Sabine et al., 2004). Pteropods, a type of planktonic mollusc, may loose part of their habitat as polar and sub-polar surface waters become undersaturated for aragonite, possibly as early as 2050 (Orr et al., 2005). Ocean acidification may have a considerable impact on calcifying organisms and the food-webs of which they are part (Orr et al., 2005; Raven et al., 2005; Schubert et al., 2006). A loss of warm-water coral reefs would have negative effects on a range of associated services includ-

Table 3. Marine calcifying organisms (after Raven et al., 2005)

Organism	Photosynthetic	Carbonate form	Habitat
Coccolithophores	Yes	Calcite	Planktonic
Macro-algae*	Yes	Aragonite or calcite	Benthic
Foramenifera	Some	Calcite	Benthic
	No	Calcite	Planktonic
Corals: warm water	Yes (in symbiosis)	Aragonite	Benthic
Cold water	No	Aragonite	Benthic
Pteropods	No	Aragonite	Planktonic
Non-pteropod molluscs*	No	Aragonite or calcite	Benthic or planktonic
Echinoderms	No	Mg-calcite	Benthic
Crustaceans*	No	Calcite	Benthic or planktonic

<sup>\*</sup> Not all members of this group are calcified.

ing fisheries, tourism and recreation, shoreline protection, nutrient cycles, and biodiversity (Buddemeier et al., 2004; Raven et al., 2005). The impact of ocean acidification on fisheries via a reduction of other calcifying organisms is difficult to predict (Raven et al., 2005).

### Documentation

The increase of oceanic CO2 concentrations is well documented from 1985 onwards as part of BATS (Bermuda Atlantic Time Series) and HOT (Hawaii Ocean Time Series). A North Atlantic Observing Network on VOS (Voluntary Observing Ships) is currently providing, for the first time, basin-wide, seasonal and annual estimates of North Atlantic CO2 air-sea fluxes from 2005 to 2008. Data coverage is reasonably good for the North Pacific, but large temporal and spatial gaps exist in surface water CO<sub>2</sub> data in the South Atlantic, the South Pacific, and the Indian Ocean, especially at high southern latitudes (IOCCP, 2007). The distribution of anthropogenic CO<sub>2</sub> in the open oceans has been estimated from measurements of inorganic carbon parameters and other physiochemical data along deep vertical sections (Sabine et al., 2004). Methods for calculating anthropogenic CO2 are an active field of scientific research.

Ocean acidification has been determined, either directly or indirectly at BATS, HOT and ESTOC (European Station for Time-series in the Ocean, Canary Islands) (Bindoff et al., 2007). Past and future ocean acidification has been estimated from atmospheric CO<sub>2</sub> scenarios and global circulation models with a representation of the marine carbon cycle (Orr et al., 2005). The continuous plankton recorder (CPR) provides a unique record of past distributions of marine plankton, including of calcareous organisms and larval stages of many benthic organisms. CPR results provide evidence of changes in marine plankton (Beaugrand, 2000), including cal-

careous species in the North Atlantic, but it is unknown whether these changes are a response to ocean acidification or to natural or anthropogenic climate variability.

# Adequacy of literature and significance of information gaps

Several comprehensive, recent reports provide thorough reviews of the current knowledge of ocean acidification (Buddemeier et al., 2004; Haugan et al., 2006; Kleypas et al., 2006; Raven et al., 2005; SOLAS, 2004). Notably the impact of ocean acidification on marine biological production and marine food webs cannot currently be assessed and presents a need for increased research efforts (Haugan et al., 2006; IMBER, 2005; Kleypas et al., 2006; Raven et al., 2005; Schubert et al., 2006; SOLAS, 2004; Orr et al., 2005). These efforts should include both long-term monitoring of marine ecosystems and experiments investigating the long-term effects of reduced pH on marine organisms. The Continuous Plankton Recorder should be deployed on a global scale. Monitoring of oceanic CO2 uptake and ocean acidification requires sustained, long-term, global observations of marine CO2 parameters (IOCCP, 2007). Analytical techniques for marine CO<sub>2</sub> observations need to be improved and simplified for autonomous use and incubation experiments. In particular, a method for accurate pH observations (± 0.001 pH units) should become readily available.

### Conclusions

Atmospheric inputs of anthropogenic CO<sub>2</sub> and to a lesser extent of sulfur and nitrogen compounds promote ocean acidification. There is a need for long-term, global, sustained observation of oceanic CO<sub>2</sub> uptake and ocean acidification by measurement of surface water CO<sub>2</sub> parameters (IOCCP, 2007). Analytical techniques for

pH and other CO<sub>2</sub> parameters in seawater need to be improved. For example, assessment of ocean acidification may require that a second parameter, such as dissolved inorganic carbon, be determined concurrently with pCO<sub>2</sub>. The contribution to ocean acidification by the addition of anthropogenic sulfur and nitrogen compounds requires further study.

Ocean acidification has recently been recognized as a threat to a diverse range of marine organisms, notably marine calcifers, and to the food webs they are part of. A special report (Schubert et al., 2006) by the WGBU (German Advisory Council on Global Change) proposes that the pH of oceanic surface waters should not drop more than 0.2 units below the pre-industrial average of 8.18 in any large ocean region to prevent undesirable or high-risk changes to marine food webs as a result of aragonite undersaturation. A stabilization of atmospheric CO<sub>2</sub> at 450 ppm would be consistent with this safeguard. Ocean acidification also contributes to increases in the Revelle Factor of the oceans, decreasing their potential to remove CO2 from the atmosphere. Scientific assessments of ocean acidification recognize the need for more research on the long-term effects of acidification on marine organisms and on calcifying organisms in particular (Haugan et al., 2006; IMBER, 2005; Kleypas et al., 2006; Raven et al., 2005; Schubert et al., 2006; SOLAS, 2004). Furthermore, there is a need for longterm, global monitoring of marine ecosystems. Surveys by the continuous plankton recorder (CPR) should be expanded to the global oceans.

### 3.2.5 Nutrients

### General Introduction

A number of chemical species known to act as nutrients for marine phytoplankton are transported to the open ocean via the atmosphere. This report focuses on the major nutrients nitrogen and phosphorus and the micronutrients iron, cobalt and zinc. These elements are influenced to varying degrees by anthropogenic activities, and iron, phosphorus, and cobalt have atmospheric sources that are dominated by, or have a significant component from, mineral dust blown off desert regions (Duce et al., 1991; Baker et al., 2006b; Baker et al., 2007). A common theme to these elements, particularly those associated with mineral dust, is that only a fraction of the input to the ocean appears to be soluble in seawater and/or available to the phytoplankton community for uptake (Graham and Duce, 1982; Chen and Siefert, 2003; Jickells et al., 2005; Mahowald et al., 2005b; Duarte et al., 2006). Indeed in most cases the exact identity of the chemical forms that are available to phytoplankton are still in doubt, which makes assessment of the "available nutrient fraction" of each element's input somewhat challenging. In all cases the significance of the atmospheric nutrient input will be dependent on the corresponding concentrations in the receiving surface waters. Thus even large atmospheric inputs may have

negligible impact if the nutrient in question is already present in abundance in the water. Nitrogen and phosphorus are permanently depleted in the oligotrophic subtropical gyres and seasonally depleted in several other regions, so that their atmospheric inputs to these regions are likely to be more important. Duce et al. (2008) specifically addressed the relationship between atmospheric inputs and seawater concentration depletion for nitrogen. The Southern Ocean and equatorial and subarctic Pacific are known to suffer from iron limitation, with several other areas also possibly subject to iron limitation or co-limitation (Boyd et al., 2007). Nitrogen-fixing organisms may suffer from limitation of iron or iron and phosphorus in tropical waters (Mills et al., 2004). There is very little information available on the limitation status of cobalt and zinc in the oceans at present.

The assessment landscape for atmospheric nutrient inputs to the open ocean is very similar to that for atmospheric inputs of heavy metals. There are no true assessments available, but several scientific papers in the peer-reviewed literature covering specific topics in different geographical areas are available. In many cases these scientific studies examine total nutrient element inputs or atmospheric concentrations, but not their "available nutrient fractions". A very few localised studies examine more than one nutrient and a similar number make some attempt to assess the impact of atmospheric inputs on primary production and ocean biogeochemistry. In the cases of nitrogen and iron there are a handful of studies that have attempted to address the atmospheric inputs on a global or regional scale, through the use of modelling.

### Description and origin

### **Nitrogen**

Nitrogen compounds enter the atmosphere from sources that are overwhelmingly anthropogenic: oxidised forms of nitrogen principally from combustion processes (with a now minor natural source from lightning) and reduced forms of nitrogen derived from intensive agricultural practices (particularly intensive livestock farming) (Galloway et al., 2004; Duce et al., 2008). Shipping contributes to oxidised nitrogen emissions, being responsible for ~6-12% of these emissions globally (Corbett and Köhler, 2003). Because of the relatively short lifetime of these species in the atmosphere, shipping might contribute significantly to atmospheric nitrogen inputs near major shipping lanes, although there is very little specific information available on this. Source gases are transformed in the atmosphere to nitric acid/nitrate (oxidised nitrogen) and ammonium (reduced nitrogen). A third, broad category of atmospheric nitrogen species is now recognised: organic nitrogen compounds (Duce et al., 2008). The source of these organic nitrogen compounds is not yet clear, but it seems likely that they are formed in the atmosphere from largely anthropogenic nitrogen (Zhang et al., 2008). These three pools of nitrogen occur in the atmosphere in roughly equal proportions and nitrate, ammonium and probably a significant portion of organic nitrogen are readily utilised by phytoplankton. The concentration of nitrogen in atmosphere has probably been increased by at least a factor of 3 due to anthropogenic activities over the last ~150 years (Duce et al., 2008).

### Iron, Phosphorus and Cobalt

Iron is an essential micronutrient for the growth of marine photosynthetic organisms (Jickells et al., 2005). It occurs at very low concentrations in oceanic waters (<<1 nmol L-1) due to its very low solubility in oxygenated seawater (Liu and Millero, 2002). Atmospheric inputs to the open ocean are disproportionately important for this element because the large continental iron inputs from rivers are removed very close to the coast. Phosphorus is a component of many enzymes and proteins. Cobalt has been known to substitute for zinc in certain enzymes and is also a component of the vitamin B-12 complex.

The sources of iron, phosphorus and cobalt to the open ocean are dominated by the transport of mineral dust from desert regions (Graham and Duce, 1982; Duce and Tindale, 1991; Jickells et al., 2005; Mahowald et al., 2005b). In addition there are also sources of phosphorus from biomass burning and the direct emission of higher plant fragments (e.g. pollen) (Artaxo et al., 1998; Mahowald et al., 2005a; Baker et al., 2006b). Anthropogenic sources of cobalt may be important in some areas.

### Zinc

Zinc is found at the active site of the carbonic anhydrase enzyme, so plays a key part in phytoplankton carbon metabolism (Morel and Price, 2003). The distribution of zinc suggests that anthropogenic sources (high-temperature industrial processes and biomass burning) are dominant (Baker et al., 2007).

### Impacts and significance

### <u>Nitrogen</u>

The impact of nitrogen deposition to the ocean will be dependent on the nutrient concentrations present in the receiving waters. Impacts are likely to be highest in the nutrient-depleted subtropical oligotrophic gyres of the major ocean basins, and minimal in high-nutrient waters such as those found in the Southern Ocean and equatorial Pacific (Duce et al., 2008). Even in the oligotrophic gyres atmospheric nitrogen deposition is highly unlikely to be intense enough to cause dramatic responses in phytoplankton populations (e.g. algal blooms) (Baker et al., 2007; Duce et al., 2008). Impacts are thus more likely to be those associated with chronic elevation of nitrogen inputs above their natural background levels e.g., possible changes in ecosystem structure caused by elevated nutrient availability. One such possible

influence might be to diminish the contribution of nitrogen-fixing organisms to total primary productivity in the oligotrophic gyres. Anthropogenic nitrogen input to the ocean, in stimulating phytoplankton growth, may have been responsible for the removal of a little anthropogenic carbon from the atmosphere, but this effect will have been offset to some extent by increased production of nitrous oxide in the ocean, a more potent greenhouse gas (Duce et al., 2008).

### Iron, Phosphorus and Cobalt

The natural dust cycle (and the nutrient element cycles it drives) is extremely heterogeneous, both spatially (resulting from the location of deserts and atmospheric transport pathways) and over time (influenced by a variety of climatic factors) (Mahowald et al., 2005b). The extent to which this natural cycle has been perturbed by human influence (e.g. changes in aridity or erosion patterns caused by agricultural practices) is uncertain. The impact of other sources, including direct anthropogenic emissions, of these elements is therefore also difficult to assess.

Evaluation of the influence of atmospheric inputs of these mineral dust-associated elements on oceanic productivity is further complicated because only a fraction of their inputs is soluble in seawater. On a global scale, probably only ~1-2% of atmospheric iron input is utilised by phytoplankton (Jickells and Spokes, 2001), but how this percentage varies regionally and temporally and what factors control the "available nutrient fraction" is still unclear (Jickells et al., 2005). For phosphorus this fraction is probably ~10-25% (Graham and Duce, 1982). The other major aerosol phosphorus components also have low solubility (Baker et al., 2006a; Baker et al., 2006c), so that the overall soluble fraction of atmospheric phosphorus is probably of the order of 10%. Some phytoplankton appear to be able to metabolise organo-phosphorus compounds, and so may be able to access a greater part of the atmospheric input.

The ocean regions where primary productivity has been shown to be iron limited are those farthest removed from major deserts (e.g. the Southern Ocean) (Jickells et al., 2005). As for nitrogen, atmospheric phosphorus inputs are likely to be of most significance in the oligotrophic gyres, where macronutrient stocks are perennially depleted. In the tropical North Atlantic, atmospheric phosphorus inputs (from mineral dust) may help to sustain biological nitrogen fixation (Baker et al., 2007). There is currently no information on whether atmospheric inputs of cobalt are of significance for open ocean productivity.

### Zinc

Little is known about the potential impacts of atmospheric inputs of zinc to the ocean, but like the dust-associated elements, it is only fractionally soluble in seawater. There is some evidence from bottle incubation experi-

ments that additions of zinc, either singly or in combination with cobalt, can stimulate phytoplankton growth in some cases (Dixon, 2008). Whether atmospheric inputs of zinc occur in sufficient quantities, or in appropriate locations, for there to be an impact on marine productivity is not currently known.

### Documentation

### **Nitrogen**

A total of 23 published reports on nitrogen species concentrations or deposition to the open ocean have been identified for the purposes of this report. Most of these focus on either nitrate or ammonium or both, with only a handful dealing explicitly with organic nitrogen. Most of these studies report data from the North Atlantic (13), North Pacific (7) and South Atlantic (7), with almost no data for the South Pacific or Indian Oceans. Some, but by no means all, of these studies made some attempt to assess the potential impact of atmospheric nitrogen deposition on marine productivity or biogeochemistry. Seven further studies used global or regional modelling to attempt to estimate nitrogen inputs to the ocean over broader scales. Only one of these included organic nitrogen in its analysis.

### Iron, Phosphorus and Cobalt

A total of 38 data reports on atmospheric iron have been documented in the peer-reviewed literature for the purpose of this assessment. This relatively large number is a reflection of the keen interest shown in iron as a fundamental control on marine productivity, and the significance of atmospheric transport in its biogeochemical cycle, over the past 15-20 years. Most reports are for the North Atlantic (20), South Atlantic (11) and North Pacific (10), to a large degree because the North Atlantic and North Pacific are most directly affected by iron inputs from deserts. Approximately one third of these reports attempted to assess soluble iron inputs from the atmosphere. A smaller proportion addressed the potential impact of these inputs on primary productivity. In addition, 9 global or regional modelling studies of atmospheric iron inputs to the ocean were identified, all of which focused to some extent on iron's influence on marine productivity or its biogeochemical cycle.

A majority of data reports (6 out of 7) for atmospheric phosphorus come from the Atlantic Ocean and three quarters of these are from the North Atlantic. The North and South Pacific have one report each and there are no data for the Indian Ocean. Almost all the reports attempt to assess the soluble fraction of atmospheric phosphorus and a few address its potential impact on primary productivity. There is one regional modeling study of atmospheric phosphorus input to the North Atlantic.

A total of 6 studies on atmospheric cobalt have been identified, 3 of which report data for the North Atlantic. Only

one of the studies identified addressed soluble cobalt concentrations and deposition rates to the ocean.

### Zinc

Of the available reports of atmospheric zinc concentrations over the open ocean, a majority are studies in the Atlantic Ocean (10 of 16). Only one of the studies identified addressed soluble zinc concentrations and deposition rates to the ocean.

# Adequacy of literature and significance of information gaps

In common with the situation for heavy metal inputs to the open ocean, although a seemingly large number of studies (70) have been identified there are some considerable gaps in our knowledge of atmospheric nutrient inputs to the open ocean. Several of the nutrient elements (iron, phosphorus, cobalt, zinc) are only partially soluble in seawater and we do not have a clear understanding of what fraction of the total input of these is available for use in primary production for any of these elements. Most of the studies reported only total atmospheric concentrations, fewer considered deposition rates to the ocean and fewer still attempted to assess the potential impact of deposition on primary production in the ocean. In the case of nitrogen most studies did not consider the organic component of atmospheric nitrogen and very few studies reported data for all the major nitrogen species (nitrate, ammonium and organic nitrogen) simultaneously. Only a small minority (4) of the studies reported data for more than one soluble nutrient (e.g. iron, phosphorus and nitrogen) simultaneously.

In terms of geographic distribution, the situation is very similar to that for heavy metals. The majority of studies report data for the Atlantic Ocean (35) and the North Atlantic in particular (32). There is a serious data gap in the North Indian Ocean (3 studies), which is likely to be heavily impacted by atmospheric inputs from the Indian sub-continent, particularly for nitrogen. In the cases of nitrogen and iron some global modelling studies are available. While these appear to give much better spatial resolution than is available from other studies, they do have some short-comings. For both elements there are problems associated with the limited availability of measurement data with which to develop and calibrate models. For nitrogen, all but one of the models did not include organic nitrogen. The models of soluble iron input to the ocean suffer from further complications arising from our very poor understanding of the factors that control the fraction of atmospheric iron that is soluble in seawater and available to phytoplankton.

### Conclusions

Publications regarding atmospheric inputs of the nutrients nitrogen, phosphorus, iron, cobalt and zinc to the open ocean have been reviewed. No comprehensive assessments exist for any of these elements. The nitrogen system has been strongly perturbed by anthropogenic activity since the Industrial Revolution, with likely impacts on marine ecosystem function from chronic, low-level inputs in some ocean areas. The anthropogenic impacts on the cycles of other nutrients are more difficult to assess, partly because their cycles include a significant component from the highly variable and not well understood natural dust cycle, and in several cases due to the very limited amount of data available. Almost no data are available for the South Pacific and North and South Indian Oceans for any of the nutrients.

In terms of the regular process, the atmospheric inputs of nitrogen are the only nutrient inputs which we consider to require active monitoring because they are dominated by anthropogenic activity, likely to have significant impacts on ocean ecosystem function and are also likely to change over time as a result of changes in the intensity and geographical location of urban/industrial emissions and agricultural practices.

### 3.2.6 POPs, PBTs, CFCs

There has been much recent progress in the identification, hazard evaluation, risk assessment and monitoring of persistent organic pollutants (POP) as well as persistent, bioaccumulating and toxic substances (PBT).

McDonald et al. (2005) assessed a wide variety of data on the cycling of chlorinated persistent contaminants including POPs in the Arctic and concluded that "because there are only sporadic, opportunistic time series for organochlorine compounds in oceans, rivers and lakes, the connection between the atmosphere, which responds rapidly to emissions, and the aquatic biota, which respond to the water, is missing". It should be noted that by comparison

to the open oceans, the data reviewed for the Arctic by these authors appears extensive. The only way to assess the behaviour and effects of the many POPs and PBTs in the open ocean at present is by 'borrowing' data from regional seas and other assessments and preparing a sub-set of that data relevant to the open oceans. This in itself would constitute a major assessment and goes far beyond the current brief.

# Persistent Organic Pollutants (POPs) and the Stockholm Convention (SC)

The Stockholm Convention (2001) is intended to protect human health and the environment from the effects of persistent organic pollutants. The signatories prohibit and eliminate or restrict production and use. The following substances are listed:

Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, PCDDs, PCDFs and PCBs

These 12 persistent, (semi-)volatile compounds are transported through the atmosphere and typically have long atmospheric residence times. Measurements have shown that they are widespread in biota in regions such as the Arctic.

The SC secretariat has developed a preliminary inventory of current and past national, regional and international monitoring programmes based largely on these 12 substances (UNEP-SC, 2007). It provides an overview of monitoring exercises related to the SC's initial list of POPs. The majority of programs listed are for purposes other than monitoring the marine environment. Those international programs with potential relevance to the marine environment are listed in Table 4.

Table 4. International marine monitoring programmes for persistent organic compounds (POPs)

International Assessment	Participation	POPs
Arctic Marine Assessment Program	Arctic – circumpolar (Arctic Ocean, Arctic marginal seas, Arctic territories of the eight Arctic countries) (north of 60° N but also including relevant marine areas south of this latitude, e.g. Hudson Bay	aldrin, chlordane, dieldrin, endrin, DDT, heptachlor, mirex, toxaphene, HCB, PCB and PCDD/PCDF
Background Air Monitoring of POPs in East Asian Countries	Cambodia, Indonesia, Korea (Republic of), Japan, Mongolia, Philippines, Thailand, Vietnam	aldrin, chlordane, dieldrin, endrin, DDT, heptachlor, mirex, toxaphene, HCB, and PCBs
European Air Pollution Monitoring Programme (EMEP)	Belgium, Czech Republic, Germany, Finland, Great Britain, Iceland, Netherlands, Norway, Sweden. European air monitoring program on POPs is support of the 1979 Geneva Convention on Long-Range Transboundary Air Pollution. Some monitoring sites are located in coastal areas.	chlordane, dieldrin, endrin, DDT, heptachlor, HCB, PCB
Global Atmospheric Passive Sampling Study	Several sites in Africa (5), South East Asia, Australia (6), Antarctica (1), Central and South America (11), Europe (9), and North America (1)	aldrin, chlordane, dieldrin, endrin, DDT, heptachlor, mirex, toxaphene, HCB, PCB and PCDD/PCDF

There have been no assessments of atmospheric inputs of POPs exclusively to the open oceans. The UNEP-initiated Regionally Based Assessment of Persistent Toxic Substances (RBAPTS) project was designed to gather data and assess the sources, environmental concentrations, trans-boundary movement and effects of some of the above substances (UNEP, 2003). The report of this project for the Pacific region indicates that data on these substances in the atmosphere are very scarce. However, other regional reports such as that for the Antarctic indicate that useful data are available on deposition of POPs.

### **Additional POPs**

The POPs Review Committee of the Stockholm Convention has recently recommended the following additional substances for inclusion in the Convention Annexes:

Chlordecone, Hexabromobiphenyl, Lindane, Pentabromodiphenyl ether and Perfluorooctanesulphonate

It has also recently adopted risk profiles for the following chemicals and decided that "they are likely, as a result of their long-range environmental transport, to lead to significant adverse human health and/or environmental effects such that global action is warranted":

Octabromodiphenyl ether, Pentachlorobenzene, Alpha & Beta-hexachlorocyclohexane

Many of these substances are known, or assumed, to be transported in the atmosphere. Because of their surface-active properties, they are predominantly bound to particles rather than being in a gaseous state.

### Persistent Bioaccumulating and Toxic Substances.

PBT classification is a hazard-based system examining degradation of the substance in air, water, soil and sediment, bioaccumulation in biota, including fish, and toxicity in the aquatic environment as well as human carcinogenicity, mutagenicity and repro-toxicity. The classification vPvB refers to very persistent and very bioaccumulating substances. PBT programs are operational in the EU, Canada and some other regions/nations.

In the EU, classification of a substance as PBT or vPvB under the new REACH Regulation will in future lead to restriction of production for a period of some years to allow a socio-economic impact assessment and possibilities for substitution to be examined, prior to phasing out.

In support of this, in the EU, a review of 2600 high production volume (>1000 t yr<sup>-1</sup>) and CMR (carcinogenic, mutagenic and repro-toxic) substances is underway. 127 substances have been selected for further examination (Table 5).

Table 5. POPs and PBTs selected by the EU for review of their risk classifications

State of evaluation	Total: 127
Classified as PBT	23
Classified as PBT and POP	3, including DDT
Still under investigation	30
Pending	8
Not PBT not POP	63

Of the 23 substances classified as PBT or vPvB, three are classified as POPs. A half-life in air of more than two days and a vapour pressure less than 1,000 Pa are taken by some regulatory agencies as indicative of potential for long-range transport. For approximately 11 out of the 23 PBTs, atmospheric transport may be relevant, as indicated by their respective EU Risk Assessment Reports, EU PBT Summary Fact Sheets and IUCLID data files.

Bearing in mind the migration of chemical production from North America and Western Europe where regulation is generally strict, to China, India, the Middle East and Russia, where chemical safety regulation is still developing, such newly classified POPs and PBTs cannot be ignored.

However, where marine environmental assessment is concerned, there is no automatic need to extend monitoring capacity to these additional POP and PBT chemicals. On the other hand, a continuation of research and monitoring focusing on the original 12 POPs should be encouraged. The priority should be further research to establish the significance of these substances with regard to marine environment effects before proceeding with the newer candidates.

There is a general scarcity of information on atmospheric inputs of POPs to the open ocean. Thus, selected data from the margins may be needed for future open-ocean assessments.

### CFCs

CFCs are low molecular weight, highly volatile compounds used in refrigeration as solvents and as propellants. Older types generally have very long half lives in the atmosphere of up to 100 years or more. Newer types are not saturated with halogen and the remaining hydrogens or a double bond ensure far more rapid degradation. They are powerful greenhouse gases and affect the ozone layer. No direct impact on the open ocean is to be expected.

### 3.3 Ship-based contamination

### 3.3.1 Sewage

### Description and origin

While the global discharge of sewage from ships is relatively low when compared to both treated and untreated sewage from land-based sources, concerns have been raised on localized effects of sewage and wastewater discharge from ships, particularly in coastal waters and ports (Mearns et al., 2005; van Hees, 1977). All wastewaters, including greywater and blackwater, have been categorized as sewage for the purpose of assessments.

Assessments of sewage discharge have either focused on individual compounds or initial and secondary dilution rates. Initial dilution is the physical mixing of a relatively small and moving discharge entering a water body, and secondary dilution is caused by mixing by the ship propellers (Colonell et al., 2000). The dilution and dispersion of wastewater discharge plumes have been predicted by a model developed for Alaska waters which predicts initial dilution of approximately 40,000:1 (Colonell et al., 2000).

MARPOL Annex IV defines sewage as "drainage from medical premises, toilets, urinals, spaces containing live animals and other waste waters when mixed with sewage waste streams." Although adopted in 1973, the Annex did not come into effect until September 2003, with subsequent amendments entered into force on 1 August 2005. Annex IV requires ships to be equipped with either a sewage treatment plant, a sewage comminuting and disinfecting system, or a sewage holding tank. Within three miles of shore, Annex IV requires that sewage discharges be treated by a certified MSD (Marine Sanitation Device) prior to discharge into the ocean. Sewage discharges made between three and 12 miles of shore must be treated by no less than maceration and chlorination, and sewage discharges beyond 12 miles from shore are unrestricted. In addition, this Annex establishes certain sewage reception facility standards and responsibilities for ports of contracting parties. Annex IV also establishes a model International Sewage Pollution Prevention Certificate.

### Impacts and significance

Ships' sewage mainly consists of water-borne human waste, and of wastewaters generated in preparing food, washing dishes, in laundries, showers, lavatories, and by medical facilities. The contents that are commonly termed pollutants mainly are biodegradable organic matter, inorganic nutrients and bacteria (principally coliform). Human sewage contains enteric bacteria, pathogens and viruses, and the eggs of intestinal parasites which may pose considerable public health risks (USEPA, 2007; Clarke, 2001). Sewage has been known to lead to deterioration of water quality, alter faunal and floral assemblages near large ocean outfalls, and has been responsible for disease outbreaks attributed to fecal coliforms (Clarke,

2001). A major concern has been the spread of disease micro-organisms in coliform bacteria which are capable of entering a dormant phase and therefore survive in seawater for long periods. While infection may occur through contact with skin abrasions in humans and through ingestion of seawater, the major health risk is the contamination of seafood, particularly shellfish. In addition, detergents and chemicals found in cleaning solutions and toilet disinfectants can be toxic to marine life and humans (Clarke, 2001). The impact of sewage in open ocean waters with high rates of dilution is considerably reduced when compared to nearshore areas. While accumulations of trace metals such as silver have been noted at several deep sea sludge dumping sites (Clarke, 2001), the highly diffused nature of ship sewage in the open ocean does not pose a significant health risk (Raaymakers, 2003).

### Documentation

Due to the greater effects of sewage in coastal areas, much of the research and assessments have focused on ship discharges in inshore waters, especially in areas with heavy shipping such as ports, cruise ship destinations, and coastal shipping lanes. A fairly comprehensive overview of the problem, management and control mechanisms, and potential health and environmental risks was undertaken by van Hees (1977). The United States Environmental Protection Agency (USEPA) has undertaken a series of surveys on the effects of sewage discharge from cruise ships, particularly with reference to Alaska and the Caribbean (USEPA, 2007; USEPA, 2002; USEPA, 2000). Many of these have been reactionary efforts to public opinion or petitions received requesting the USEPA to assess and control wastewater discharge from cruise ships. A two-year survey conducted between 2000 and 2002 reported pH and concentrations of fecal bacteria, nutrients, trace metals and organic chemicals found in over 200 samples of untreated and treated blackwater, and greywater from several dozen cruise ships (Morehouse, 2003).

Surveys by the USEPA indicate that discharges from cruise ships undergo a dilution that is much greater than the initial dilution predicted by the Alaska model of Colonell et al (2000). A Science Advisory Panel commissioned by the Alaska Cruise Ship Initiative (ACSI) to assess wastewater discharge concluded that the high mixing rate behind a discharging vessel should prevent significant accumulation of contaminants in the sea surface microlayer (Mearns et al., 2005).

# Adequacy of literature and significance of information gaps

Cruise ships have been the subject of most surveys due to the amount of wastewater generated onboard. There has also been a greater interest in assessing cruise ship sewage discharges in North American waters, particularly around Alaska and the southern United States and Caribbean, mainly due to extensive cruise

tourism in those regions. However, there appears to be a dearth of information with regard to other regions and commercial shipping. Due to the greater focus on the industry, cruise ships may be obliged to maintain minimum standards with regard to waste disposal and some companies have signed agreements with regulatory bodies on discharge standards and practices (Mearns et al., 2005). Considering the extent of commercial shipping worldwide, it may be necessary to expedite broader assessments of sewage discharge with relation to shipping, particularly in lesser studied areas with heavy ship traffic. However, in the context of the open ocean, the amount of sewage discharged and its impact can be considered to be negligible, and further studies would not be required at this time.

### Conclusions

It appears that sewage discharge from ships in the open ocean does not have major environmental or human health impacts (Raaymakers, 2003), and current open ocean discharge is in compliance with MARPOL Annex IV. While information gaps exist for certain regions, there is no major requirement for further assessments or regulations with relation to the open ocean.

### 3.3.2 Chemical Spills

### Description and origin

Tank ships and dry bulk ships carry a large variety of hazardous substances other than oil. They are subject to similar collisions, groundings and other accidents as oil tankers. Since there are fewer vessels carrying these hazardous substances than there are vessels carrying oil as cargo and/or fuel, there are many fewer chemical spills reported than oil spills.

### Impacts and significance

Since each substance is unique with regard to its physical and chemical characteristics, as well as potential hazards, it has been necessary to develop a methodology to assess the relative hazard potential of each substance to the extent possible from known toxicological and other studies.

A project to assess the environmental hazards of substances carried by ships was undertaken by GESAMP as preparatory work for the development of the International Convention for the Prevention of Pollution by Ships, 1973 (MARPOL 73/78). A similar study was published a decade later with minor revisions and some additional data. Today, the GESAMP Working Group on the Evaluation of Hazardous Substances (EHS) annually updates its hazard classifications based on a revised methodology (GESAMP Reports & Studies No. 64, 2002) that examines the following parameters:

- · Bioaccumulation:
- Damage to living resources (direct and indirect toxic effects);

- Hazards to human health via oral intake or via skin contact and inhalation:
- · Reduction of amenities; and
- · Interference with other uses of the sea.

### Documentation

While data on chemical spills from ships are collected by various national authorities, private companies, industry groups, and commercial entities, there has been no systematic compilation of these data. Neither have there been any analyses or assessments of the extent of chemical inputs to open ocean waters or potential impacts thereof.

# Adequacy of literature and significance of information gaps

There are no studies on the inputs of chemicals from shipping spills on which to base any assessments of their impacts on the marine environment.

### Conclusions

Chemical spills from ships are relatively rare events and likely to have highly localized impacts dependent on a number of factors, including the particular substance(s) involved, the amounts spilled, prevailing environmental conditions (e.g., air and water temperature), the resources exposed and their sensitivities.

It would certainly be helpful if inventories of oil spills would also include information on chemical incidents. Studies into chemical spillages from ships might attempt to identify the most common chemicals spilled, e.g., styrene, rather than expending resources on every individual chemical. The greatest and most serious impacts of these spills are likely to be realized in near-shore waters with restricted water exchange and high biodiversity.

# 3.3.3 Oil from spills, operational discharges and shipwrecks

### Description and origin

Oils are carried at sea in bulk and are used by vessels as fuels and lubricants. These are the principal sources of oil to the open ocean.

Oil spills from ships in the open ocean are generally attributed to structural or mechanical failure, often in storms that cause the ship to break up and sink, or to leakages from cargo or fuel compartments. Oil spills can also occur due to collisions and allusions (hitting a stationary object); these accidents are less likely to occur in open-ocean waters than near shore, except in heavily travelled shipping lanes with limited visibility. Intentional spills also occur, such as when petroleum cargo is jettisoned for safety reasons in an emergency, or as a result of a terrorist or military act (e.g. the 1991 Gulf War spillage).

Certain vessels may discharge oil contained in ballast water and tank washings as part of their normal operations. These discharges are generally restricted to waters at least 80 kilometers from shore. The alternative – deposition of these wastes at port reception facilities – is limited by the number and distribution of these facilities.

A ship that sinks may contain large volumes of oil in the form of cargo (for oil tankers) and fuels, bunkers and oil in machinery space, unless the vessel has released all its oil during break-up. Sunken vessels can then become potential seeps, discharging oil at varying rates over long periods of time. Occasionally, a sunken vessel may suddenly release a large volume of oil if its integrity is compromised due to rusting or other physical change.

#### Impacts and significance

The impacts of *oil spills* depend on oil type, spill location and environmental conditions (as reviewed in NRC, 2003).

Heavier fuel oils tend to be more persistent but less toxic, whereas lighter oils (e.g., diesel fuels) tend to be less persistent but more toxic. Toxic effects may occur amongst fish and other marine biota, as well as marine mammals and birds that ingest the oil. Heavier persistent oils can coat bird feathers and mammal fur. Persistent oils are more difficult to remove from shores. Oil type also determines the rate and degree to which oil disperses (breaks down chemically and physically into smaller droplets and components) and evaporates. Lighter oils with a large aromatic component tend to disperse into the water column more readily and also to evaporate more quickly and completely.

Whereas large amounts of oil sinking onto deep ocean marine ecosystems can be ecologically damaging, oil spills in the open ocean generally have less environmental impact than near-shore spills. This is dependent on currents and winds keeping the oil offshore long enough for the slick to largely disperse or evaporate. Once the oil has dispersed and to a large extent evaporated it is unlikely to significantly impact shorelines other than with tar balls, which, while unsightly and inconvenient on recreational beaches, tend to have less impact on coastal biota than fresh oil.

Operational discharges from ships form a significant part of the total inputs of oil to the marine environment (NRC, 2003; GESAMP, 2007). The impacts of these discharges are generally similar to that of any crude oil or petroleum products released into the marine environment. In the open ocean impacts are likely to be temporary since the oil tends to evaporate and disperse, and thus become more dilute, over a period of weeks following discharge. Where the discharges are in accordance with IMO regulations (MARPOL 73/78), and thus in a relatively dilute form (in parts per million range), they have less impact than oil from an accidental spill.

The International Maritime Organization, through its MARPOL 73/78 Convention has established 21 Special Areas requiring added protection against ship-based pollution and has also adopted Guidelines for the Identification and Designation of Particularly Sensitive Sea Areas (PSSAs) of which 12 are currently in force. These measures are designed to protect designated sea areas either in territorial waters, EEZs and/or the high seas that, on account of their oceanographic and ecological conditions, as well as their shipping traffic, warrant special protection from the environmental impacts of shipping .

The impacts of discharges from *sunken vessels* in the open ocean are generally less severe than those closer to shore. Nevertheless, a 1977 study (Campbell et al. 1977) showed that oil tankers sunk in World War II, over 30 years earlier, were still periodically leaking oil and therefore acting as "seeps". Many of the tankers were still relatively intact, though their structural integrity was uncertain. Other military vessels sunk off Norway and the US Pacific coast have been implicated in "mystery spills", oil discharges that impacted shorelines and other resources. The greatest potential for spillage is with the older vessels that were often built according to lower standards than modern vessels. Much of the oil involved is of the heavier variety and tends to form tar balls rather than larger slicks, unless released in a large mass.

#### Documentation

Most oil spill studies and assessments of impacts have examined spills in near-shore areas that are outside the remit of this report. There have, however, been a number of assessments of oil inputs that include information on the open ocean.

From the early 1980s through 2000, the publication Oil Spill Intelligence Report (OSIR) maintained an oil spill database (often referred to as the "International Oil Spill Database") and released annual statistical summaries of spills in excess of 10,000 gallons (294 tonnes) on land or water worldwide. These data were collected by annually contacting hundreds of port authorities, coast guard and environmental agencies, industry sources, and other entities internationally that had an interest or obligation to record oil spill incidents for the purposes of monitoring spill emergency response operations and/or to record incidents that might have an impact to the environment or economic resources. In addition, statistical summaries were presented at the biannual International Oil Spill Conference for several years. While the data collected on specific incidents were deemed to be generally reliable, there were large gaps in coverage. Small spills, which make up about 80 percent of the incidents, were excluded. Data were obtained from a large international network of sources at a time when there was very little electronic data storage and many national authorities were either not collecting data on oil spills or were reluctant to share that data with anyone outside of their entity.

Nevertheless, the data gave a good sense of general trends in spill numbers and volumes.

Subsequently, Environmental Research Consulting (www.environmental-research.com) independently developed a series of oil and chemical spill databases and began conducting various regional and international assessments of oil spillage. Data on smaller spills are included where available.

Two significant global assessments of oil inputs to the marine environment were conducted in the last decade that included estimates of inputs from shipping accidents (National Research Council, 2003; GESAMP, 2007). They used the same data sources and came to similar conclusions. The studies do not differentiate between open-ocean and coastal spills, although the original data set gives the location of each spill so such an assessment could be made in future.

GESAMP (2007) estimated ship-based oil inputs to the marine environment on a regional and global basis for the years 1988 – 1997. The estimated worldwide annual inputs from spills from tankers were 158 kt yr<sup>1</sup>, and from non-tank vessels 5,000 t yr<sup>1</sup>. Regional estimates were included. The amount of oil spilled per unit transported was shown to be reduced by nearly 50 percent from the previous decade.

Another study conducted by the National Research Council in 2003 using the same data sources and methodologies as GESAMP but covering the years 1990 – 1999 estimated total annual inputs due to spills from tankers to be 100 kt and from non-tank vessels to be 7.1 kt annually. The differences in these values compared to the GESAMP study points to an important factor in the analysis of spill data. Each year the total volume spilled is usually dominated by one or two very large spills. In any given time period, several very large spills can completely change the average value significantly. Likewise, if there are no large incidents (perhaps because the spillage from a vessel was successfully stemmed before the spill became larger), the values will be lower.

In 2003 the National Research Council (NRC) estimated operational discharges from vessels greater than 100 gross tonnage (GT) in various categories, voyage lengths and frequencies. It was estimated that about 270 kt of oil is discharged annually in this manner. GESAMP (2007) used a similar approach, albeit with some different assumptions and data inputs, and developed an estimate of 214 kt yr<sup>-1</sup>, similar to the NRC study. Few studies have measured inputs by taking or estimating measurements of hydrocarbons in seawater. One study found that non-volatile hydrocarbons in the Atlantic Ocean contained aromatics at lower concentrations than would be expected if the source of the hydrocarbons were crude oil or petroleum refinery products. Even along tanker routes the sources

of the hydrocarbons were considered not to be tankers. In Bermuda, tar balls were correlated with known inputs of oil from vessel oil spills in the North Atlantic and, in Jamaica, with oil inputs from recent tanker spills.

Michel et al. (2005) surveyed *wrecks* in the South Pacific region, which was particularly impacted by World War II military vessel sinkings, as well as wrecks throughout the world. An inventory of potentially polluting shipwrecks, comprising tankers of at least 150 gross registered tonnage (GRT) and other vessels of at least 400 GRT varying oil as fuel/bunkers (and for operations) has been completed, including an analysis of the likely distribution and amounts of oil contained in these vessels and associated environmental, regulatory, political, technical and financial issues. The study incorporates all the SPREP data.

The analysis revealed that there were at least 8,569 recorded vessel sinkings worldwide (Figure 3) of which 1,583 were tankers and 6,986 were non-tank vessels. An estimated 2.5 to 20.4 Mt of oil is thought to be present in these wrecks.

Michel et al. (2005) analyzed data on a regional basis, though the regional designations differ somewhat from the designations developed for the Assessment of Assessments. The results are summarized in Table 6 below.

Table 6. Potential Oil Pollution from Sunken Tankships and Non-Tank Vessels

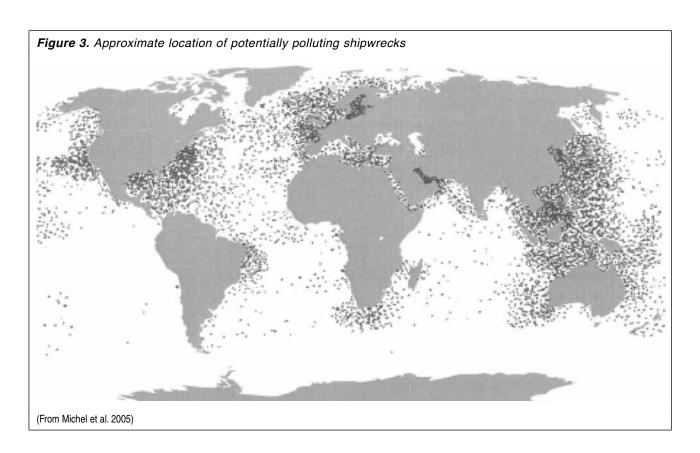
Region <sup>1</sup>	Estimated Oil Content of Shipwrecks			
	Minimum	Maximum		
North Atlantic Ocean	951,000 tonnes	7.5 million tonnes		
South Atlantic Ocean	165,000 tonnes	0.5 million tonnes		
North Pacific Ocean	221,000 tonnes	1.7 million tonnes		
South Pacific Ocean	521,000 tonnes	4.2 million tonnes		
Indian Ocean	264,000 tonnes	2.2 million tonnes		

<sup>1</sup> Regional boundaries, as applied in the Michel et al. (2005) study, were used to estimate the approximate values for the ocean regions established for the Assessment of Assessments.

(Based on Michel et al. 2005)

## Adequacy of literature and significance of information gaps

While existing oil spill inventories are by no means comprehensive, they do provide a reasonably good indication of the rates of oil spillage from vessels. The IMO operates a reporting system for serious casualties that provides a foundation for a world wide spill analysis. Spillage is known to be more accurately tracked than for other oil losses due to the keen interest in oil shipments and their potential impacts and costs. Incident reporting is understandably higher for territorial seas.



It is probably not necessary to conduct more studies on the impacts of vessel spills to the open ocean. On the other hand, a co-ordinated global programme of data collection using a simple standardized protocol would help in analysing spills, their causes and other factors and thus to inform future regulation and enforcement.

The two comprehensive studies of *operational oil discharges* enable reasonably thorough assessments (National Research Council, 2003; GESAMP 2007) of these sources of oil. While there may be some changes in input quantities with changes in shipping fleets and movements, as well as the establishment of more oily waste reception facilities, it does not seem necessary to conduct additional assessments of these inputs for some time to come. The sources and modes of input are clear and the best ways to reduce them lie in the enforcement of existing national and international regulations and conventions, such as the MARPOL 73/78 Convention under the auspices of IMO.

Michel et al. (2005) provide the most comprehensive review of oil from *shipwrecks* possible using the data available at that time. Further studies of wrecks in the open ocean do not warrant high priority at present.

#### Conclusions

Amounts of oil released to the open ocean from vessels due to spills, accidents and operational discharges, as well as from wrecks, are reasonably well documented (or otherwise estimated) and, in general, the information base is adequate for purposes of environmental assessment. In the overall context of environmental stresses on the open ocean, occasional accidental oil spills are not amongst the highest priorities. Greater availability of oil reception facilities should in the future reduce the extent of operational discharges of oil from vessels. Some of this reduction may be counteracted by increases in shipping. Removing oil from sunken vessels is complex, dangerous and expensive and, in the deep ocean, unlikely to be practical. Occasional releases would best be regarded as natural seeps requiring contingency responses.

## 3.3.4 Exhaust Emissions: Polycyclic Aromatic Hydrocarbons (PAHs)

Description and origin

Polycyclic aromatic hydrocarbons (PAHs) are components of oil consisting of two or more fused rings of benzene (e.g., naphthalenes, phenanthrene, and benzoa-pyrene). They are generally derived from crude oil and petroleum products or the combustion of these products. Crude oil generally contains about 0.2 to 7 percent PAHs, mainly consisting of lower molecular weight compounds. Residual oil used in fuels by most ships (IFO 380 constitutes about 85% of the used fuel - BLG 12/6/1) often contains much higher amounts, in the order of 7-20 percent PAHs. Marine gas oils (distillate) has a considerably lower PAH content of about 0.02 percent.

Other sources of PAHs include combustion of organic materials, including wood. Inputs of PAHs from shipping to the marine environment can occur directly through the

spillage of oil or from atmospheric deposition of petroleum combustion products. This deposition generally occurs in the form of particulate matter.

#### Impacts and significance

PAHs are an important group of marine environmental contaminants. They are of concern because of their high carcinogenic and mutagenic activities. Studies indicate that, even in low concentrations, PAHs may be toxic to marine hiota

#### Documentation

Most studies on emissions from ships that refer to PAHs stress their potential impacts on air quality and human health and do not estimate inputs to marine waters. There are no estimates of PAH inputs to the open oceans *per se*.

The National Research Council (2003) study *Oil in the Sea III* estimates inputs of PAHs from ships into North American waters, all of which are outside the scope of the current review. The study does estimate total worldwide petroleum hydrocarbon inputs from atmospheric emissions into the marine environment as 23 kt yr<sup>-1</sup> to 200 kt yr<sup>-1</sup>, with a best estimate of 52 kt yr<sup>-1</sup>. But this estimate includes inputs of VOCs in addition to PAHs and is not specific to shipping. It includes data on regional seas, coastal zones and other areas, but not specifically the open oceans.

### Adequacy of literature and significance of information gaps

There is only one published estimate of PAH inputs to the open ocean from shipping in the literature. However, it is not specific to open oceans and shipping (NRC, 2003). There are clearly substantial information gaps in regard to this topic.

#### Conclusions

PAHs are potentially hazardous to human health and marine biota. There is only one estimate of worldwide PAH inputs to the marine environment but it is not specific to shipping and not limited to the open oceans. Better inventories of PAHs emitted to the atmosphere in ship exhaust, and improved estimates of inputs of PAHs to the open oceans through this pathway, will be necessary before a proper assessment of trends and impacts of these substances can be conducted.

#### 3.3.5 Natural Oil Seeps

#### Description and origin

Natural discharges of petroleum from submarine seeps have been recorded throughout history. Recent estimates suggest that they constitute almost half of the oil entering the sea from all sources. In recent times, the locations of natural seeps have been used for exploration purposes to determine feasible sites for oil extraction. Most natural seeps are clustered at continental margins. Factors that determine seepage rate in a particular area are related to geological structure and the stage of sedimentary basin evolution.

#### Impacts and significance

Natural seeps of crude oil can cause the same impacts as spills of crude oil, although usually the seepage rate is slow enough that the oil disperses and often forms tar balls before it impacts any shoreline. As with other oil inputs, any seepage that occurs in open ocean waters is likely to have minimal environmental impact. In fact, in many locations in which there are natural seeps, communities of organisms have evolved that thrive on metabolizing the hydrocarbon components of crude oil and natural gas (e.g. methane hydrates), often released in conjunction with the oil.

#### Documentation

While assessments of natural seepage have been conducted in some regions, particularly nearshore California, and in the Indian Ocean and the Gulf of Mexico, locations that are outside the scope of this review, the most comprehensive worldwide assessment of natural seepage is that conducted by Wilson et al. (1974). The two more recent international assessments of oil inputs into the sea relied heavily on the estimates of this study. Estimates of natural oil seepage have involved few actual measurements. The most well-known studies have relied on estimation methodologies based on field data, various observations and basic assumptions.

Wilson et al. (1974) estimated total worldwide natural seepage to be 600,000 tonnes oil annually, based largely on observations of seepage rates off California and western Canada. TNRC (2003) provides a worldwide estimate of natural seepage into the marine environment of 0.02 Mt yr<sup>-1</sup> to 2.0 Mt yr<sup>-1</sup>, with a "best estimate" of 600 kt yr<sup>-1</sup>. This is similar to the value reported by GESAMP (2007).

## Adequacy of literature and significance of information gaps

There are very few studies on natural oil seepage. Even recent estimations of rates of seepage refer to a single study conducted over 30 years ago. With the technology available today a more comprehensive evaluation of natural seepage rates, or at least a verification of previous estimates, is theoretically possible. Due to the considerable resources that might be required to conduct this on a global or even regional scale, the most likely funding would, however, come from industry sources interested in exploitation of areas that contain potentiallyhigh reserves of oil rather than for the purpose of assessing impacts to the world's oceans.

#### Conclusions

Natural seeps are a significant source of oil to the marine environment. The impacts of these inputs on the open ocean environment are likely to be minimal since the oil is largely dispersed and forms tar balls that have less impact than fresh oil. Communities of marine organisms that thrive on petroleum and natural gas hydrocarbon components occur in the vicinity of many natural seeps. No detailed assessments of the environmental implications of oil from seeps have yet been undertaken.

#### 3.4 Noise

#### Description and origin

In the last 50 years, human activities have accidentally and intentionally increased the level of sound in the oceans. Many experts estimate that noise levels are ten times higher than a few decades ago (Dotinga and Elferink, 2000). Shipping, offshore oil exploration and production activities, dredging, and fishing create sound waves that can travel great distances underwater. Furthermore, the use of sonar by ships, research activities (e.g., for bottom scanning) and military operations adds considerably to "acoustical pollution" of the oceans.

Shipping is the largest source of low-frequency sound. Most of the noise comes from propellers. The level of noise tends to increase with greater vessel size, speed, and load.

#### Impacts and significance

The introduction of noise to the marine environment has been shown to have impacts on marine species, particularly cetaceans (aquatic marine mammals, such as whales and dolphins). There may even be indirect ecosystem effects, by affecting specific species and their behaviour, e.g., by affecting prey availability (Simonds et al. 2003). The National Research Council (2005) developed a methodology to determine whether the effects are biologically significant. Many marine species use sound for communication, navigation, avoidance of predators and searching for food, but high levels of sounds or sounds at particular frequencies can have harmful effects. Continuous exposure to acoustical pollution can cause physical injuries, disrupt behaviour, mask communication or other biologically important signals, affect species' abilities to hear at certain critical frequencies or increase their sensitivities to disturbance. These effects are reviewed in Richardson et al., (1995), the National Research Council (2003), and Riegler (2006).

The impacts on cetaceans, which tend to have a much broader range of hearing (both ultrasonic and infrasonic) than humans, has been of greatest concern to marine biologists. But noise can also affect marine fishes, reptiles, cephalopods, and perhaps other marine animals

and, by influencing the behaviour of individual species, might even disrupt entire ecosystems. Effects on organisms other than the baleen whales tend to occur at higher sound frequencies, which travel shorter distances in seawater.

#### Documentation

Various governmental commissions and non-governmental groups have investigated the impacts of ocean noise on marine ecosystems and, in particular, marine mammals. These include the US Marine Mammal Commission (Advisory Committee on Acoustic Impacts on Marine Mammals, 2006); Hildebrand (2007); the Whale and Dolphin Conservation Society (Dolman, et al., 2004); Greenpeace USA and Acoustic Ecology Institute (Cummings and Brandon, 2004); Greenpeace UK (Moscrop and Swift, 1999); the International Council for the Exploration of the Sea (ICES, 2005); National Resources Defence Council (US) (Jasny et al., 2005); Inter-Agency Committee on Marine Science and Technology (UK) (Pomerville and van den Berg, 2001); Scientific Committee on Antarctic Research (SCAR, 2004); ASCOBANS (Agreement on the Conservation of Small Cetaceans of the Baltic and North Seas) (Evans, 2003); ACCOBAMS (Agreement on the Conservation of Cetaceans in the Black Sea, Mediterranean Sea and contiguous Atlantic area) (Roussel, 2002); U.S. National Research Council (2003) and UK Ministry of Defence (QinetiQ Centre for Environmental Studies, 2003). There are also a few scientific research papers that examine the impacts of sound on specific species or ecosystems (e.g., Vasconcelos et al., 2007; Smith et al., 2004, Walmsley, 2007; and VanDyke et al., 2004).

## Adequacy of literature and significance of information gaps

Most of the commissioned assessments on ocean noise include anecdotal evidence of the impacts of noise with some references to specific research studies. There are more thorough reviews of the scientific literature in a number of studies, notably those of Richardson et al., (1995), the National Research Council (2003), and Riegler (2006). There are general calls for further research on the impacts of noise and calls for action to reduce noise to minimize these impacts in the commissioned assessments. There remain large gaps in the scientific knowledge about the actual impacts of noise. There have been few attempts to systematically measure or monitor noise levels or to attribute noise levels to specific sources. Though scientific research is in many cases lacking, most non-governmental groups (e.g., Greenpeace) and many of the governmental commissions favour adopting a "precautionary" approach to ocean noise.

Four mitigation measures have been suggested to reduce the impact of noise on marine ecosystems, and in particular, marine mammals:

- Construction, design and equipment standards for equipment that produces less noise;
- Restrictions or closures of certain ocean areas at specific times (e.g., in areas important for reproduction);
- Routing and positioning measures (e.g., establishment of areas to be avoided by ships); and
- Operational measures (e.g., visual or acoustical monitoring before initiating noise-creating activities to determine if sensitive species are in the vicinity, speed reductions, limitation of the duration of the noise).

Experts in the field of acoustical impacts on the marine environment have pointed to a need for a long-term monitoring program to assess levels of ocean noise and to track future changes. Some entities have recommended the inclusion of acoustic data in global ocean observing systems now being planned by the U.S. and international research foundations. These data should be openly available to managers and decision makers in industry, the military and regulatory agencies.

#### Conclusions

While there is significant interest and concern about the known and potential impacts of ocean noise from shipping and other anthropogenic sources on marine ecosystems, there are still large information gaps in the scientific literature. There are numerous recommended measures for mitigation of noise but no systematic assessment or monitoring of actual noise levels. Many experts believe that a monitoring program for noise should be incorporated into planned global ocean observation programs. It is clear that significantly better information on ocean noise is needed before a proper assessment of the environmental significance of noise can be carried out. New concerns about increased sound propagation with ocean acidification are just beginning to be addressed.

#### 3.5 Marine debris

#### Description and origin

Marine debris consists of solid waste that has entered the sea either from land or from vessels. Releases to the sea occur either intentionally (e.g. discards from vessels including garbage and fishing gear) or inadvertently (e.g. wind-blown or in run-off) through waste outfalls, from offshore platforms, aquaculture installations and littered beaches. The materials involved include metal, glass, rubber and paper products but by far the most abundant and problematic are buoyant and persistent plastics. Plastic pellets used in manufacturing and plastic fragments are widespread in the oceans.

#### Impacts and significance

Marine debris is a serious and widespread problem. Plastic debris has at least six significant types of impact: it can strangle or maim marine birds, mammals and turtles (Henderson 2001) and cause blockages in the

guts of fish and other organisms; it can smother the sea floor; it can damage sensitive ecosystems such as coral reefs (Donohue et al. 2001); it can foul boat propellers and clog water intake ports on engines - endangering the safety of fishermen and boaters; small particles can adsorb persistent organic pollutants (POPs) (Mato et al. 2001, Yukie et al. 2001) and thus introduce POPs to the food chain; it can act as a carrier of living organisms (Barnes 2002, Barnes and Milner 2005), including pathogens, beyond their normal geographic ranges. Apart from this, all kinds of marine debris are damaging to marine-based recreation and tourism.

#### Documentation

In 2005, a UNEP 'analytical overview' (UNEP 2005) identified marine litter as 'a vast and growing threat to the marine and coastal environment'. The pollution of the marine environment by plastic debris has been extensively reviewed by Derraik (2002). Various national and international agencies, as well as GESAMP (2001), have examined the sources and impacts of plastic debris and non-governmental organizations (NGOs) such as Greenpeace (Allsopp et al. 2006) and the California-based Algalita Marine Research Foundation (AMRF; Moore, 2006) have recorded numerous impacts associated with these materials. There is also extensive coverage within the wider scientific literature of the impacts and effects of plastic debris on marine organisms and ecosystems.

Although marine debris can be found in all sea areas, and throughout the open oceans, most of the available literature deals with coastal and shelf areas where quantities are greatest and impacts most apparent. There have been no detailed assessments or reviews of the problem focussing specifically on oceanic areas. No reports of regular, standardised monitoring of debris beyond the shelf have been identified. As a result, qualitative and quantitative data on marine debris in the open oceans are extremely limited. There have been occasional surveys of debris in selected open-ocean areas, especially in the area of the North Pacific central gyre (Moore et al. 2001) where physical hydrographic conditions concentrate floating materials. In 2002, a survey of the area by AMRF found an astounding 6 kg of plastic for each kg of near-surface plankton. There are reports of lost and discarded fishing gear, and waste from vessels, on the shores of many small islands (Barnes, 2005) in the Atlantic (Otley, 2003), Indian (Payet et al., 2004) and Pacific (Gregory, 1999, McDermid, 2004) oceans, some of which are remote and uninhabited. Island chains and archipelagos provide some of the best locations for gauging the extent of debris in the open oceans. The Global International Waters Assessment (GIWA) of the Indian Ocean Islands (Payet et al., 2004) revealed the serious extent of the solid waste/marine debris problems in that area. There are numerous reports of impacts on marine species in offshore areas, mainly due to plastics and fishing gear.

## Adequacy of literature and significance of information gaps

There is almost no information on marine litter and debris in the open ocean comparable to that available for coastal areas such as beaches, which in many countries are subject to regular systematic surveys. It is not possible at present to say how types and quantities of debris are distributed within the oceans or to compare one ocean basin with another. Hydrographic features clearly play an important role in distribution of plastics. One comprehensive review (Derraik, 2002) of scientific literature on plastic debris notes that, although much of the existing information is basically anecdotal, it provides overwhelming evidence that plastic pollution is a threat to marine biodiversity. However, the precise impacts on populations and ecosystems are unknown. Although research and/or coordinated international monitoring may help to clarify distributions trends, impacts and their significance, the cost would be high. It is arguable that there is already sufficient evidence of hazards and risks to enforce measures (e.g. MARPOL 73/78, Annex V) designed to reduce inputs. Additional publications on aspects of marine debris in the oceans are included in the Bibliography (Annex 3).

#### Conclusions

There have been no regional, national or international assessments of marine litter/debris in the open oceans. Deposits on island shores, often in remote and uninhabited areas, provide good indicators of ocean-derived debris such as fishing gear and waste from vessels. They also show that plastics, in particular, are transported over considerable distances by ocean currents. From the extensive literature on marine debris, it is known that plastic materials and fishing gear are widespread in the oceans and can become concentrated in certain areas. Pre-production plastic pellets, and fragments of larger plastic items, are widespread in seawater, even perhaps ubiquitous. Impacts are evident but the potential for wider environmental damage warrants further investigation. Measures designed to reduce inputs have been largely ignored.

#### 3.6 Ballast Water

#### Description and origin

Ballast water management is a complex issue raising the challenge of merging international regulations, ship's specific configurations, and ecological conservation. This complexity is due to ballast water volume, discharge frequency, ship safety and operational issues aligned with regional characteristics to address ecological risks for selected routes (Endresen et al., 2004). International regulations by nature take a relatively long time to enter into force, hence regional and national regulations tend to be developed to meet with more local demands. Such developments are of major concern to the shipping industry, which must operate across different jurisdictions (Endresen et al., 2004).

Ballast water capacity varies as a function of cargo carrying capacity and ship type (Endresen et al., 2003), and the annual ballast water amounts transported has been estimated as a function of the total cargo transported annually (Endresen et al., 2004). The global ballast water required for all cargo transport by sea is estimated to be approximately 3500 Mt yr-1, and the volume of ballast water discharged into the open sea through ballast water exchange operations is estimated at approximately 2800 Mt yr<sup>-1</sup>. (reviewed by Endresen et al., 2004). Internationally, oil tankers account for some 37% of the ballast water annually transported, while dry bulk cargo carriers account for 39% (coal, iron ore, grains and other bulk commodities). The remaining 24% includes general cargo, container vessels, Ro-Ro (Roll on/Roll off vessels), chemical tankers and LNG (Liquid Natural Gas) tankers (Endresen et al., 2004).

Open ocean exchange of ballast water involves replacing coastal water with open ocean water during a voyage, either by emptying and refilling ballast tanks or by flow-through dilution (Endresen et al.,2004). However, open ocean exchange is not always biologically effective (Endresen et al., 2002) and is not always possible to perform due to ship safety and operational issues involved (Endresen et al., 2002), and therefore it is likely that a portion of the ballast water transported annually will have to be treated by other methods, or discharged as untreated ballast water.

#### Impacts and significance

A major concern associated with ballast water has been the spread of invasive alien species and toxic dinoflagellates, and the rate of introductions has been increasing exponentially since the 1800s (Carlton, 2001). Invasive marine species are now considered one of the greatest threats to the world's oceans and the economical impacts of these invasions can be considerable. For example, the zebra mussel alone accounts for over \$500 million a year (Ruiz et al., 2001). Paralytic shellfish poisoning (PSP) has been attributed to the consumption of shellfish contaminated with alkaloid toxins from 11 species of plankton dinoflagellates (Hallegraeff, 1998). Initially, major outbreaks of toxic dinoflagellates and other invasions of marine pests related to ballast water were mostly from temperate waters of Europe, North America and Japan. Since the 1990's incidents have been reported from the Southern Hemisphere, including South Africa, Australia, New Zealand, and Papua New Guinea, as well as the Northern Hemisphere including India, Thailand, Brunei, Malaysia, and the Philippines (Hallegraeff, 1998).

However, major impacts have been recorded only from coastal waters, and currently available information indicates that ballast water has minimal environmental impacts in the open ocean. In fact, according to the International Maritime Organization (IMO), open ocean exchange of

ballast water is the recommended method for controlling introductions of marine pests (IMO, 2003).

#### Documentation

Toxic dinoflagellates are probably the best studied model organism to assess the bio-economic risks of ballast water introduction of non-indigenous marine pests. An important review of Australian research efforts on transport of toxic dinoflagellate cysts via ships' ballast water over a period of 10 years was completed in the late 1990's (Hallegraeff, 1998). This information was supplemented with the results of similar studies in Europe, Israel, North America, Canada, Japan, China and New Zealand. Endresen et al. (2004) reviewed estimated global ballast water exchange including open ocean exchange in order to identify major obstacles to open ocean exchange. The review concluded that ship safety aspects due to variable sea conditions and operational aspects such as the length of time required prevented some ships from acquiring ballast water from the open ocean.

## Adequacy of literature and significance of information gaps

Currently, there is very little information on the potential risks of open ocean ballast water exchange; but this practice is considered to be relatively safe. Most assessments have also tended to focus on areas that reported major outbreaks of toxic dinoflagellates such as temperate waters off North America, Europe, and Australia. Although some major cases such as the zebra mussel have been well studied, there is far less information on marine species introductions that have not been associated with disease outbreaks or major economic impacts. However, in an open ocean context, the significance of such information gaps is low due to the potentially low impacts of ballast water in the open ocean.

#### Conclusions

There is increasing recognition on the need to reduce the risk of invasive species introductions, but until international agreement and acceptance of a fully effective, practicable, safe, economically viable and environmentally friendly ballast water treatment is achieved, an international warning network for algal blooms in ports appears to be one of the few options available to minimize risks (Hallegraef, 1998). Currently, mid-ocean ballast water exchange and heat treatment appear to be the best options available for managing ballast water, and no significant impacts of ballast water are known to occur in the open oceans.

#### 3.7 Off-shore Exploration and Production

#### Description and origin

Worldwide there are over 7,000 offshore oil and gas platforms. Nearly 57% of these platforms are in the Gulf

of Mexico. Annually, an estimated 6.4 trillion tonnes of oil and gas are produced globally. In addition to occasional oil spills from offshore facilities, there are also outputs of various substances that are part of routine operations. One study estimates that the oil and gas industry discharges over 800 substances, petroleum and related products being the dominant category.

#### Impacts and significance

Oil and gas exploration and production activities occur mainly in waters less than 200 meters deep, beyond the remit of the present review. Facilities also occur in deeper waters, notably in the Gulf of Mexico which, for purposes of the current exercise, is taken to be a marginal sea and not part of the open ocean.

Nevertheless, potential impacts of exploration/extraction on the *open ocean* may include:

- Spills from platforms and rigs, from offshore supply vessels that service the facilities, or from pipelines that transport oil offshore to land or to offshore storage facilities that spread to open ocean waters; and
- Discharges of oil from diesel-based and other types of drilling muds used at offshore facilities that spread to open ocean waters.

GESAMP (1977) estimated oil inputs to the sea from such sources. The study did not include any attempt to quantify any inputs. The study concluded that in addition to potential inputs of petroleum and natural gas *per se*, there were other effects that should be considered, such as:

- Restriction of activities of other users of the sea-bed, primarily bottom fishermen;
- Redistribution of fish populations that are attracted to the offshore structures;
- Uncontrolled dumping of wastes and debris, which might affect fishing activities;
- Local alterations in sediment structure of the sea-bed due to disposal of formation cuttings and losses of drilling muds;
- Toxic effects on local fish populations and other marine biota from components of drilling muds (e.g., lead and chromium);
- Effects on local fish and shellfish resources from disposal of brine waters;
- Potential impacts from cooling and compression systems used to liquefy natural gas at production sites; and
- Potential accidental release of PCBs from "heater treaters" used to break up oil/water emulsions.

#### Documentation

A comprehensive literature review was conducted by Patin (1999). The author quotes one study indicating that offshore oil production contributes only one percent of contaminants into the marine environment, though this

was limited to nearshore facilities. Total discharges to the sea were estimated at 7 Mt yr<sup>-1</sup> (Windom, 1992).

The National Research Council (2003) produced an estimate for worldwide inputs. Total annual inputs of oil from offshore oil exploration and production facilities, including accidental spills, atmospheric deposition and produced waters, were estimated to be 38 kt. The proportion of this released to the open ocean was not specified.

It should be noted that a large accidental release of oil could occur at any time, releasing considerably more oil than the estimated 38 kt released through produced waters. For example, in 1979, the Ixtoc I well blowout in the Gulf of Mexico released an estimated 476 kt tonnes of oil over the course of 10 months.

GESAMP (2007), using the same accidental spill dataset as the NRC (adjusted slightly to include the years 1988 - 1997), concluded that there was an average of 16,400 tonnes per year of inputs of oil to the marine environment from offshore oil and gas exploration and production operations. Accidental oil spills from offshore platforms added an additional 600 tonnes per year in inputs. The GESAMP study concluded that there were virtually no inputs from atmospheric emissions since, according to information from the International Association of Oil and Gas Producers (OGP), the extraction and processing of oil occurs in a "closed system". Accidental and operational releases from pipelines associated with offshore activities added an additional 2,800 tonnes of oil inputs annually, making the total inputs from offshore oil exploration and production about 20 kt yr-1. This amount corresponds to the NRC's minimum estimate (NRC, 2003).

The OSPAR Commission has released annual reports on discharges, spills and emissions from offshore oil and gas installations in the Northeast Atlantic, mostly in the North Sea and not in the open ocean.

The OGP has produced annual reports on the environmental performance of the oil exploration and production industry. These reports review *inter alia* the gaseous emissions, aqueous discharges, discharges of non-aqueous drilling fluids (NADF) on cuttings, accidental spills of oils and chemicals on a worldwide and regional basis. Once again, the analyses largely involve facilities in locations onshore, nearshore and in offshore areas not within the scope of the current review. Other inputs estimated annually include: CO<sub>2</sub>, CH<sub>4</sub>, non-methance VOCs, SO<sub>2</sub>, NO<sub>x</sub>, operational oil discharged in produced water, oil spills, and chemical spills.

## Adequacy of literature and significance of information gaps

There are a sufficient number of rigorous assessments of impacts of oil and gas exploration and production

conducted on a regular basis that estimate inputs of a variety of relevant substances. The degree to which these inputs impact on the open ocean must be extrapolated from this. This might be done by an analysis of the location of these facilities in relation to the defined open ocean basins.

#### Conclusions

Since offshore oil and gas production largely occurs in nearshore waters or in deeper waters that are outside the scope of this study the direct impacts of discharges on the *open ocean* are likely to be minimal. There is, however, always the possibility that a large catastrophic well blowout at an offshore facility could temporarily impact open ocean waters. With the more recent move for offshore oil exploration and production activities into increasingly deeper water, there is the possibility that there may be more direct impacts on the open ocean, as defined in this study. Such deeper water facilities have been established in the Gulf of Mexico, for example, but these waters were not included in the scope of this study.

#### 3.8 Dumping from Vessels

Apart from the historical dumping (and certain accidental losses) of radioactive wastes, the dumping of waste at sea, whether or not regulated under the global or regional dumping agreements in place, is mainly carried out in coastal waters and therefore not addressed in this report.

Some dumping activities are carried out in the open oceans involving the dumping of spoilt cargoes from ships, mostly materials of natural origin, which would - in terms of quantities – not be regarded as normal discharges under MARPOL 73/78, Annex V. Only very few of these operations are covered under a formal permit issued in accordance with the London Convention or Protocol, but it can be assumed that many more of these operations are carried out unregulated when it suits the master or the owner of a ship. When a permit is issued, the operator of the vessel is normally required to conduct the dumping in deep waters en route to the next port of call.

From 1946 to 1982, low-level radioactive wastes were dumped at selected sites in the Gulf of Mexico, Atlantic and Pacific oceans. The amount of radioactive material dumped at sea is much less than that added to the oceans as a result of atmospheric nuclear weapons testing between 1954 and 1962 (GESAMP, 1990). The practice of dumping low-level wastes was discontinued in 1982 in accordance with a Resolution of the London Convention (1972).

Dumping of low-level radioactive waste in the Atlantic, Pacific and Arctic oceans (Arctic includes high-level waste) is addressed by the following reports:

- IAEA, 1991. Inventory of radioactive material entering the marine environment: sea disposal of radioactive waste. IAEA Tecdoc 588.
- IAEA, 1999. Application of radiological exclusion and exemption principles to sea disposal, IAEA Tecdoc 1068
- IAEA, 1999. Radioactivity in the Arctic Seas, IAEA Tecdoc 1075.
- IAEA, 1999. Inventory of radioactive waste disposals at sea, IAEA Tecdoc 1105.
- OECD-NEA, 1985. Review of the continued suitability of the dumping site for radioactive waste in the North-East Atlantic. Nuclear Energy Agency, OECD, Paris.
- OECD-NEA, 1989. Interim oceanographic description of the North-East Atlantic site for the disposal of lowlevel radioactive waste.

#### Accidental losses:

• IAEA, 2001. Inventory of accidents and losses involving radioactive material, IAEA Tecdoc 1242.

The first category includes open and covert practises by individual nation states, as well as practices carried out under international auspices. The second category includes losses of sealed sources (used in offshore exploration), nuclear-powered submarines, and submarines and aircraft containing nuclear warheads. As many of the radionuclides involved have very long half-lives, are present in relatively large quantities and are of radiological concern, these should be considered as potential sources of harm to the ecosystem, following current ICRP (International Commission on Radiological Protection) approaches to estimating effects on non-humans.

# 4 MATTERS OF SPECIAL CONCERN FOR THE REGULAR PROCESS

## 4.1 Recommendations for Monitoring Inputs to the Open Ocean

We have identified two areas where atmospheric inputs to the open ocean are of significant concern: changes in ecosystem function caused by nitrogen inputs and ocean acidification arising mostly from  $\mathrm{CO}_2$  inputs. We consider that these inputs would need to be addressed directly by long-term sustained observation programmes under the regular process in order to assess their impact on the global open ocean.

Nitrogen inputs to the open ocean occur primarily via dry deposition of aerosols and via rainfall. We consider that collection of aerosol and rainfall samples on a routine basis can only be done satisfactorily at land-based (island) stations, and even then development work will be necessary to ensure adequate data quality for rainfall sampling. Operation of at least one island sampling site in each of the north and south basins of the Atlantic, Pacific and Indian Oceans will be necessary. These island sites will provide baseline information on temporal variability in nitrogen inputs, which is essential if trends in inputs are to be identified. This information will need to be augmented by more occasional, targeted use of ship-based sampling, possibly from volunteer observing ships, in order to assess the geographic variation in nitrogen inputs.

There are on-going programmes acquiring data on the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in surface ocean waters through the use of volunteer observing ships. These are already making an important contribution to our understanding of how CO<sub>2</sub> enters the oceans. GESAMP considers that the Regular Process should serve as a catalyst to maintain these programmes and if possible encourage them to expand into ocean regions not currently covered, such as the the South Pacific Ocean, the Indian Ocean and the South Atlantic. Assessment of ocean acidification will require that a second parameter of the dissolved carbonate system (total dissolved inorganic carbon, total alkalinity or pH) be determined concurrently with pCO<sub>2</sub>. Currently available instrumentation for this second parameter is not suitable for autonomous deployment on volunteer observing ships, so development work on this instrumentation is required. The Regular Process should also encourage the continuation of programmes, such as the Continuous Plankton Recorder (CPR) survey and the long-term microbiological sampling at time series sites, e.g. the Bermuda Atlantic Time-Series (BATS) and Hawaii Ocean Time-Series (HOT), which have the potential to identify shifts in marine ecosystem function. Similarly, the long-term seawater CO2 and/or pH records established at BATS, HOT and the European Station of Time Series in the Ocean, Canary Islands (ESTOC) should be promoted and similar sites established in other ocean basins.

## 4.2 Carbon Capture and Storage (CCS) in the Open oceans

IPCC (2005) provided a comprehensive report on CO<sub>2</sub> capture and storage (CCS); ocean storage was mainly focused on deepwater open storage of liquid CO2. One of the CCS aspects not covered was the artificial fertilization of the oceans. In recent years, several experimental attempts have been made to fertilize the oceans with nutrients such as iron and nitrogen in order to stimulate algal growth and draw down CO2 from the atmosphere. This is being seriously considered by some as a commercial way of gaining carbon credits in Emissions Trading Schemes. GESAMP & the Scientific Committee on Ocean Research (SCOR) recently noted in a joint statement that "Proposals to realize the potential of ocean fertilization on such scales suffer a major weakness: one does not know how the oceanic ecosystem will respond". The efficacy of such approaches is unknown and given the scale of the CO<sub>2</sub> problem, where IEA estimates that ca. 26 Gt/y of CO<sub>2</sub> (7.1 Pg C /yr) is being produced globally and predicts that this may rise to ~39 Gt/y CO<sub>2</sub> (10.6 Pg C/yr) by 2030, such efforts would have to be truly massive to put a dent in world CO<sub>2</sub> emissions. The consequences for the oceans, from whichever storage method may be utilized, need careful consideration with regard to environmental effects and sustainability. Research on technologies for sub-seabed storage is proceeding in a number of countries and, although certain geological formations appear to have potential for safe, long-term storage of CO2, concerns remain over the risks of leakages from such facilities.

#### 5 CONCLUSIONS

#### 5.1 Assessment landscape for the oceans

No comprehensive assessments focusing specifically on the open oceans, or individual ocean basins, have been undertaken to date. There are several possible reasons for this. It reflects a belief that the oceans are not as severely affected by human activities as the marginal seas as well as the relative paucity of data on the oceans in comparison to near-shore areas. It could also be a recognition of the environmental diversity and variability of the oceans, the difficulties of access or the absence of an international monitoring framework for assessment purposes. The same situation applies in the case of pollution – no assessments of the various forms of pollution by substances and wastes, covering large areas of the open ocean, have been carried out so far. The present report, therefore, embraces thematic assessments and reviews as well as relevant research papers.

#### 5.2 Relevance of the report

This review of the scientific literature concerning pollution of the open oceans through shipping and the atmosphere has provided an insight into the scope, scale and relevance of past work in this field. Particular attention has been given to publications containing data and information that would make an important contribution to assessments of the ocean environment i.e. state of the oceans reports. The publications deal inter alia with contaminant sources, input fluxes, air/sea exchanges, spatial distributions, ambient concentrations and, in many instances, their environmental relevance. The report includes thematic bibliographies with over 200 selected references. It provides a useful basis for identifying information gaps that may inhibit ocean assessments and should help in determining priorities for future research and monitoring.

#### 5.3 Status of knowledge

Despite limited geographic coverage, for most of the major contaminant classes (excluding noise) associated with shipping and the atmosphere there is sufficient knowledge to yield reasonable estimates of quantities entering the oceans and/or individual ocean basins. In contrast, information on the extent of contamination by persistent organic compounds (POPs) is almost entirely lacking. Clearly the accuracy of estimates may vary depending on whether they stem from direct measurements, modelling or data that are, in themselves, estimates. The latter are often the only figures available for contaminants such as oil from spillages, operational discharges and seeps, and exhaust emissions from ships. In almost all cases information on ambient concentrations in the open oceans, in different environ-

mental compartments (water, tissues and sediments), are scarce. Overall, the information base is greatest for the Atlantic Ocean and least for the Indian Ocean. The effects of contaminants in the open ocean have seldom been studied and have not been a focus of this review.

#### 5.4 Adequacy of knowledge

In comparison to shelf areas, the amount of information regarding contamination and/or pollution of the open oceans is small. Nevertheless, an analysis of the geographical coverage, reliability and relevance of contaminant data obtained from the open oceans to date, combined with an examination of sampling methods, sampling regularity and the general level of knowledge on the effects of the contaminants, suggests that for most substances the information is adequate for assessment purposes. Apart from noise, the adequacy of information is considered either 'moderate' or 'good'. This apparent contradiction stems from the generally low level of contaminant inputs to the oceans in comparison to the shelves, the vastness of the oceans and knowledge of the effects of contaminants based on their intrinsic properties, eco-toxicological profiles (including dose/ effect relationships) and knowledge of their impacts in other aquatic environments. Clearly, more information is required on persistent organic compounds that have a propensity for accumulation in food chains. Insufficient information is available on the effects of noise in the ocean environment on cetaceans and other marine organisms. Although the impacts of existing levels of many contaminants are considered minimal, it may be a requirement of assessments to follow trends over time. For this reason, more regular measurements (or estimates) will be needed for the majority of contaminants.

## 5.5 Use of templates for evaluating assessment literature

The structure of the template developed for the Assessment of Assessments proved unsuitable for evaluating studies not specifically designed as environmental assessments. Many of the questions relating to institutional arrangements could not be answered satisfactorily without consulting the authors or institutes responsible; this was not possible in the time available. In the case of research papers, the reasons for selecting particular topics, locations and designs — aspects explored by the template — were generally not specified. Many studies are continuations or extensions of previous research in keeping with the interests and expertise of the authors (and/or institutes) involved. Because the template was not concerned with the outcome of studies, it was not possible to accurately reflect the relevance or

importance of a publication in the context of environmental assessment. These issues will need to be addressed in the design of any future AoA initiatives that employ questionnaires in template format.

#### 5.6 Gaps in information

Identifying gaps in information for purposes of ocean assessment is problematic. For the majority of known contaminants, the temporal and spatial coverage of open ocean data is uneven and sparse. This can be expected in view of the large spatial scales involved. Nevertheless, for many contaminants the existing data coverage is sufficient to show the likely extent of contamination and this, combined with an understanding of the intrinsic properties of the substances, may provide a good indication of the environmental and human health significance of current inputs and concentrations. This is certainly the case for metals and nutrients but less so for most organic chemicals of anthropogenic origin. Certain ocean basins e.g. the North Atlantic have been more extensively studied for a range of contaminants than others. There would undoubtedly be advantages, from both scientific and managerial standpoints, to improved spatial coverage in some ocean basins. Similarly, where there are good reasons to follow trends in contamination, more regular sampling may be required. GESAMP's advice concerning priority data gaps is given under the individual contaminant headings in Chapter 3.

#### 5.7 Best practice

An objective of the Assessment of Assessments was to identify examples of best practice in the context of marine environmental assessment. The Task Team felt that further guidance with regard to the meaning of best practice was necessary before this matter could be systematically addressed. For example, the term could be applied to the conduct of assessments (design, co-ordination, evaluation etc.), to the selection of particular methodologies (sampling, analysis, quality assurance etc.) or both. Clearly, there is no experience with regard to the former in the realm of the open oceans. With regard to methodologies, however, most of the publications selected for review, analysed by means of templates and listed in the bibliographies, describe methodologies that are considered through peer review to be suitable for the purposes intended. Nevertheless, methodologies tend to be subject to continuous improvement and evolve through time.

#### 5.8 Definition of assessment

The Task Team also recommends further consideration of the definition of *assessment* in order to clarify the aims and key components of marine assessments. A concise definition of the term, with annotations thereto, would be preferable. This would help to guide the design of

scientific research and monitoring intended to provide information for assessment purposes. A more precise definition of assessment for use in developing the regular process would greatly facilitate the identification of relevant literature as well as the most appropriate methodologies for use in data collection and evaluation. In this way, it should also help to improve the precision and validity of data addressing identified priorities and information gaps.

#### 5.9 Matters of special concern

Matters that warrant high priority within the regular process are atmospheric inputs of nitrogen and CO2 and their possible roles in ecosystem function and acidification respectively. Current programmes for monitoring these inputs, as well as programmes that may detect associated ecosystem changes and responses (see Section 4.5.1), should be continued and, where necessary, expanded. The regular process should also take into account developments in the field of carbon capture and storage (CCS), in particular the proposed use of iron and nitrogen to fertilize the oceans, thereby stimulating algal growth and drawing down CO2 from the atmosphere. The efficacy of such approaches is unknown. Nevertheless, any large or meso-scale programmes of this kind, even on an experimental basis, will require close scrutiny with regard to environmental effects and sustainability.

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#### **ANNEX 3: BIBLIOGRAPHIES**

A categorized selection of publications, relevant to assessing pollution of the open oceans, supplementing citations in the text

#### ATMOSPHERIC INPUTS

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