





Pollution in the Open Oceans 2009-2013

A report by a GESAMP Task Team





















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GESAMP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

IMO FAO UNESCO-IOC WMO UNIDO IAEA UN UNEP UNDP

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A report by a GESAMP Task Team

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Notes

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Executive Summary

- This review of pollution in the open oceans updates a report on this topic prepared by GESAMP five years previously (Reports and Studies No. 79, GESAMP, 2009). The latter report, the first from GESAMP focusing specifically on the oceans beyond the 200 m depth contour, was prepared for purposes of the Assessment of Assessments, the preparatory phase of a regular process for assessing the state of the marine environment, led jointly by the United Nations Environment Programme (UNEP) and the Intergovernmental Oceanographic Commission (UNESCO-IOC).
- 2. For purposes of the present report, GESAMP reconvened the Task Team on Pollution of the Open Oceans originally assembled for the 2009 review, with some changes in participation. The report contributes to a thematic assessment of the open oceans, lead by UNESCO-IOC, that forms part of a Transboundary Waters Assessment Programme (TWAP) enabled by the Global Environment Facility (GEF) and implemented by UNEP. The TWAP entails a baseline assessment of five transboundary water systems: aguifers, lakes, rivers and 55 large marine ecosystems (LMEs), that together account for almost 70% of the Earth's surface. It aims to help GEF to prioritise areas for intervention in the management of shared water systems, and to help governments in managing their shared water bodies.
- Assessments of the open oceans must take 3 account of the highly varied hydrography, climatic conditions, habitats and patterns of resource exploitation across the major ocean basins, as well as pollution resulting from human activities both on land and at sea. Accordingly, this review of recent scientific knowledge on ocean pollution addresses just one of the many forms of pressure on ocean ecosystems and should be considered in the light of other pressures and changes affecting the marine environment. A feature of pollution in the open oceans, as opposed to coastal waters, is that the major sources of potentially polluting substances are the atmosphere and commercial shipping. GESAMP emphasizes that for many (but not all) substances introduced to the oceans through human activity there is presently no clear evidence of harmful effects i.e. a criterion of pollution. Nevertheless, the possibility of cumulative effects due to multiple stressors cannot be discounted.
- 4. The Task Team reviewed scientific literature on selected substances and conditions published in the preceding c. 5-year period (i.e. 2009-2013) as well as a few papers from earlier years overlooked in the 2009 report. The report covers most of the

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substances reviewed 5 years previously, apart from waste materials introduced by shipping, and includes a section on radioactivity (subsequent to the Fukushima incident) and expanded coverage of mercury and micro-plastics. The geographical scope of the review is also similar, covering the major ocean basins, but now includes deepwater sections of the Arctic and Mediterranean for which relevant information is available.

- Nitrogen & iron: Nitrogen from anthropogenic 5. sources (industry & agricultural livestock) continues to dominate nitrogen inputs from the atmosphere to the oceans. The concentration of nitrogen in the atmosphere has probably been increased by at least a factor of 3 due to anthropogenic activities over the last ~150 years. This major perturbation in the natural cycle of nitrogen has potentially significant impacts on marine ecosystems, especially in the nutrient-depleted gyres of the major ocean basins. Significant advances have been made in the modelling of nitrogen fluxes to the oceans; fluxes are projected to increase in the years up to 2100. Studies in the marginal seas downwind of the intense N emission regions of East Asia, have reported observable impacts of N deposition on the biogeochemistry of the ocean. Due to the essential role of iron in photosynthesis (and thus its links to nitrogen), the effect of anthropogenic emissions in increasing the flux of soluble Fe (from combustion sources, or through enhancing solubility of Fe from mineral dust) to the ocean has also received considerable attention. The importance of this soluble Fe input to the ocean is difficult to quantify because it occurs against the background of a very large Fe input associated with the natural mineral dust cycle.
- Mercury: Unlike other metals, mercury in the 6. atmosphere exists to a significant degree in gaseous form and undergoes reactions leading to a variety of both gaseous and particulate mercury species. Atmospheric input of mercury to the global ocean is much more important than riverine input. The current atmospheric loading of Hg is three to five times pre-industrial levels and the surface ocean loading roughly twice pre-industrial values. Mercury measurements have improved significantly in quantity and quality in the last five years and a global mercury monitoring network has been established. Studies of the atmospheric oxidation of Hg and its cycling and methylation in the oceans have provided a link between deposition, methylation, entry into the food web and bioaccumulation. It is likely that the loading of mercury to the sub-surface ocean, where mercury is methylated and enters the food web, will continue

even if anthropogenic emissions remain constant due to cycling of legacy mercury. If anthropogenic emissions do not decrease quite radically it is probable that methyl mercury concentrations in pelagic piscivorous fish will continue to increase. GESAMP considers it imperative that atmospheric monitoring continues and that campaigns to measure Hg compounds in open ocean water column are continued in the future, particularly in major fisheries.

- Noise: By the 1960s, the average ambient noise 7. level in the deep ocean had increased 10-100 fold in frequencies important for whales, fish and invertebrates. At some sites it is continuing to double in intensity every decade. Shipping is the largest anthropogenic source of low-frequency sound: most of the noise comes from propellers. There are additional, more localized impacts from offshore and coastal developments, including intense sounds from oil and gas exploration and naval sonar. Baleen whales, most acoustically sensitive invertebrates and fish are sensitive to low sound frequencies, which can travel long distances in seawater, and are most likely to be affected by long-term increases in low frequency ambient noise. Turtles have demonstrated avoidance behaviour have subject to low-frequency noise associated with seismic surveys. Noise may disrupt animals that use sound on ocean reefs. There are significant gaps in the scientific literature concerning the impacts of anthropogenic noise on marine ecosystems. The resulting uncertainty makes it difficult to balance the need for precaution in protecting marine ecosystems against the potentially large costs to socially important activities such as commercial shipping, offshore energy, and military readiness. In the view of GESAMP, a monitoring programmes for noise should be incorporated into planned global ocean observation programmes. There is also an urgent need for expanded research on the impact of anthropogenic noise on marine life. Particular attention must be paid not only to cumulative longterm effects, but also to synergy between noise and other anthropogenic pressures on marine ecosystems. For example, ocean acidification is increasing sound propagation; the extent of this effect on ocean noise is just beginning to be addressed. Numerous measures have been recommended for mitigation of noise, but there are no systematic programme to assess or monitor actual noise levels in the oceans at scales useful for predicting impacts on marine life.
- 8. <u>CO₂/acidification</u>: Ocean uptake of CO₂ emissions by human activity is the dominant cause of observed changes in surface ocean pH and carbonate chemistry. Acidification of the global surface oceans is a pervasive threat to all marine life. It will promote large changes in marine ecosystems globally and may already be doing so. Ocean acidification will have wide-ranging consequences by changing biogeochemical cycles, metal

speciation and the production of climatically active gases. The strength and impact of acidification are a direct function of CO₂ emissions by human activity and resulting ocean CO, uptake. Global average surface ocean pH is expected to decrease from a pre-industrial value of 8.2 to pH of 7.8 to 7.9 by 2100, if CO₂ emissions continue to be high or to a pH of 7.9 to 8.0 by 2100, if CO, emissions are mitigated. The response of organisms and ecosystems to acidification is uncertain but there will be both winners and losers. Some noncalcifying taxa may experience a positive effect, such as an increase in growth and photosynthesis. Calcifying species are particularly vulnerable. Corals, echinoderms and molluscs show medium sensitivity and crustaceans low sensitivity. Initial results indicate that fish may have a strongly negative response to ocean acidification, possibly as a result of a high sensitivity of their larvae. The global, pervasive threat of ocean acidification creates an urgent need for long-term, global monitoring of the impact of ocean acidification on marine organisms and ecosystems. Volcanic CO, vent systems provide valuable natural analogues of possible ecosystem responses and adaptation to ocean acidification.

Persistent Organic Pollutants (POPs): Since 2009, 9. there has been progress in monitoring POPs, PBTs and CFCs, in the marine environment, mainly in the Northern hemisphere. Predatory species frequenting different oceanic regions can provide unique insights into the fate of chemicals of concern; such an approach may provide vital information for marine environmental assessment in the future. Distinct differences exist in body burdens of POPs between geographic locations, notably high levels in Monk seals, swordfish and killer whales close to industrial and population centres such as the Eastern Mediterranean and off California. Species in remote locations and with open ocean life-histories, such as the relatively low trophic-status leatherback turtle, generally have low POPs levels, although by no means negligible. Downward trends in many POPs reported in Atlantic cod and British Columbia harbour seals are encouraging, although concentrations in some populations of killer whale remain high. In general, contaminant levels in open ocean biota appear lower in comparison to conspecifics inhabiting the coastline. Confounding factors are the paucity of information on the diet and migratory patterns leading to POPs exposures for many populations examined. In addition to atmospheric deposition and various biological factors, local pollution sources can strongly influence observed body burdens, even in remote areas. The Arctic shows strong indications of decreasing tissue levels of PCBs, DDT and many of the 11 original SC listed POPs. On the other hand, levels of some currently used chemicals such as PFCs, BDE-209, and more recently chemicals such as HBCDD, show significant increases in some Arctic biota. Reports of POPs body burdens being associated with health

effects are, in general, tenuous and non-specific, even for marine mammals. Concentrations of POPs absorbed onto or within microplastics close to pollution sources are very high in comparison with those from remote areas and open seas; they can be of the same order of magnitude as those found in sediments in those areas. Such high concentrations may be toxic to marine animals.

- 10. Marine debris: Debris from both land- and seabased activities can be found floating, drifting and on the seabed throughout the marine environment and, in the view of GESAMP, is a matter of special concern. Shipping remains a significant source along busy shipping lanes and fishing-related debris is common wherever commercial fishing takes place. Floating plastics are transported by ocean circulation and have been found in the most remote parts of the ocean. Plastics fragment principally through exposure to UV, especially when exposed to physical and higher temperatures typical of shorelines. However, the fragments can remain in the marine environment for a substantial period of time. Surveys on remote shores and mid-ocean islands are particularly useful at demonstrating long-distance transport and potential effects. Debris is widespread across the shelf, in deep water canyons and in the mid-ocean (e.g. Fram Strait, North Atlantic). The effects of macro-scale debris, by ingestion or entanglement, have been clearly demonstrated for a wide variety of fauna (e.g. birds, fish, reptiles, marine mammals). Some species may already be affected at population level; examples are the Northern Right Whale, (Eubalaena glacialis) by entanglement, or vulnerable species such as the leatherback (Dermochelys coriacea) and loggerhead (Caretta caretta) sea turtles by ingestion of plastic. Floating durable debris can provide an effective vector for transporting organisms, ranging from viruses to macro-algae and macrofauna such as molluscs; this may be responsible for introductions of non-indigenous and problem species. Plastics may contain a variety of chemicals introduced to achieve particular properties, some with known toxicological properties, and many organic contaminants already in the environment (e.g. PCBs, DDT, flame-retardants) are absorbed into the polymer matrix if present in the surrounding seawater. Plastic fragments can be ingested by various organisms and contaminants could pass the aut barrier, with potential for toxicological effects. Whether or not this represents a significant risk is unclear. The most cost-effective way of reducing anthropogenic debris in the marine environment is to prevent its introduction. This will require a multifaceted approach, involving industrial sectors and public education in addition to regulatory action. This is being pursued on national, regional and global scales, with the GPML¹, led by UNEP, being the most ambitious to date.
- 1 Global Partnership on Marine Litter (http://gpa.unep.org/ index.php/global-partnership-on-marine-litter).

- 11. Radioactivity: The accident at the Fukushima Daiichi nuclear power plant on 11th March 2011, caused by the Tohoku earthquake and tsunami, resulted in an unprecedented release of radioactivity to the ocean from a single point source, both by direct release to the ocean and from atmospheric deposition. The predominant radionuclides released were isotopes of caesium and iodine, together with substantial quantities of ⁹⁰Sr and lesser quantities of plutonium and short-lived radionuclides. There is evidence that contaminated groundwater and run-off via rivers continued to act as a source to the ocean long after the accident. Marine sediments contaminated by Fukushima ¹³⁷Cs appear to be an additional continuing source of caesium to the overlving biota and to benthic and demersal organisms. Rapid atmospheric transport resulted in widespread dispersion of Fukushima radionuclides in the northern hemisphere, including the shortlived ¹³¹I (half-life 8 days). Dispersion in surface waters was dominated by the Kuroshio Current, with transport to the north-western coast of North America estimated to have occurred by early 2014. Despite the relatively high levels of contamination, and uptake by a wide variety of biota, the radiological consequences of the accident in the marine environment, and from human consumption of seafood, has been rather low.
- 12. Deep-water extraction of seabed resources: Although the literature on this topic has not been reviewed by the Task Team, the team believes that the potential for environmental damage by such activities is sufficiently great that the matter should be addressed by the international community. As conventional sources of fossil fuels and minerals become depleted, extraction industries have turned their attention to the considerable reserves that exist on and beneath the seabed at deep-water locations. The technology to open wells at these deep-water sites already exists and continues to be developed. The long-term environmental costs of major oil leakages at deep-sea locations, their implications for ecosystem viability and associated ecosystem services, warrant further scientific analysis supported by modelling of different scenarios. Deep sea mining for valuable metals is a relatively new field which is also on the increase and the environmental impacts are largely unknown. Further research into the nature and scale of impacts is essential to better understand the significance of these operations for ocean ecosystems.
- 13. <u>Matters of special concern</u>: Chapter 3 of the report identifies four separate categories of impact on the open oceans that, in the view of GESAMP, are of special concern because of their potential to damage marine organisms and ecosystems well beyond local level. For this reason, they warrant serious attention and mitigative action by the international community. Two of these, atmospheric inputs of nitrogen and CO₂, were highlighted previously in GESAMP (2009). In light

of the increasing weight of evidence of their potential for widespread effects, GESAMP has now extended the list to include deep-water mining/ exploration and marine debris.

- 14. Improving pollution assessment: Chapter 4 of the report discusses a number of issues relevant to the review and assessment of pollution in ocean environments. Periodic assessments of the state of the marine environment are essential to inform the management of activities that have potential to harm marine life and disrupt marine ecosystem function. There is a need to improve assessment capabilities, as well as their reliability, and also to clarify the criteria used to determine priorities. The topics addressed include the distinction between pollution and contamination, the selection of indicators, the need for long-term datasets and the significance of multiple stressors.
- 15. <u>Syntheses</u>: As a means of comparing current levels of scientific knowledge on each of the contaminant

categories reviewed in the report, the Task Team has constructed a one-page table (Table ES1) which gives a subjective assessment of the degree of human input and whether or not there is clear evidence of effects. The table also provides an indication of trends in environmental levels or loads of the contaminants and GESAMP's perspective regarding their relative, overall environmental significance. The fact that living components of the marine environment are subject to multiple stressors, many at low levels but nevertheless acting in consort, is recognized throughout the report. To illustrate the potential for combined effects on various taxonomic groups including humans, Table ES2 contrasts the ranges of impacts from different contaminants and, in particular, highlights the broad scale of effects that may arise from unmitigated ocean acidification. In general, the net effect of multiple stressors on individual groups of organisms is unknown.

Торіс	Natural occurrence	Human input	Demonstrable effects (from human input)	Trend/Load	High status as a hazard ?	
Oil	Y	Y ++	Y	→	Y	
Debris	N	Y ++	Y	7	Y	
Radioactivity	Y	Y +	N	→	N	
Carbon						
CO ₂ /ocean acidification	Y	Y +++	Y	7	Y	
POPs/PBTs	N	Y +++	Y	7	Y	
DDE	N	Y +++	Y	•	N	
Nutrients/metals						
Ν	Y	Y +++	Y	7	Y	
Р	Y	Y +	Ν	Я	N	
Fe (soluble)	Y	Y ++	N	7	Y	
Pb	Y	Y ++	N	R	N	
Cu	Y	Y ++	Y	7	Y	
Other trace metals	Y	Y ++	N	7		
Mercury	Y	Y +++	Y	7	Y	
Noise	Y	Y+++	Y	7	Y	

Table ES1: Current scientific knowledge of open ocean contaminants: synthesis and assessment

Yes/No + Low++ Moderate +++ High

Confidence levels							
HIGH	MEDIUM	LOW					

.....

Table ES2: Taxonomic groups most impacted by ocean contaminants reviewed in this report

	Humans	Marine mammals	Reptiles	Seabirds	Fish	Invertebrates	Corals	Phytoplankton
Oil		++		+++	++			
Debris	+	++	+++	++	+	+	+	
Radioactivity	+							
Carbon/CO ₂	+	++		++	++	+++	+++	+++
POPs	+	+++		+++	+			
Mercury	+++	+++		+				
Nutrients								+
Metals								+ ^{/Cu}
Noise		+++			++	+		

Slightly impacted + Moderately impacted ++ Heavily impacted +++

1 Introduction

1.1 Background

Monitoring conditions in the vast open oceans beyond the continental shelves is no easy task. The oceans constitute a global and international resource and no one country or region is responsible for the research and monitoring needed to assess their condition. Whereas certain physical features can now be examined from space, spanning large areas at a time, most chemical and biological measurements require in situ sampling entailing considerable ship-time and cost. Classical indicators of marine pollution continue to be largely chemical and biological and it is not surprising that the database on open ocean pollution is extremely small compared to those for shelf seas and coastal areas. Nevertheless, ocean health is of utmost importance to humanity and a proper scientific basis for assessing trends in physical, chemical and biological features of the oceans is essential.

The first review of scientific knowledge regarding pollution of the open oceans was published by GESAMP in 2009 (Reports and Studies No. 79). That report was prepared as a contribution to the Assessment of Assessments, the start-up phase for a UN Regular Process for the Regular Reporting and Assessment of the State of the Marine Environment, including Socio-Economic Aspects (UNEP & UNESCO-IOC, 2009). In keeping with the groundrules established for this project, the GESAMP review as far as possible focused on published assessments/reviews of substances and activities '..liable to cause harm to the marine environment' i.e., the classical definition of marine pollution. However, in a number of cases it was evident that existing assessments did not reflect the true state of scientific knowledge at that time and it was therefore necessary to draw on the wider scientific literature to complete the picture. A notable conclusion from this review was that, despite the paucity of data on many ocean pollutants, the relevance, reliability and geographic coverage of the available information was, for a majority of pollutants, sufficient to assess their environmental impact. In general, the adequacy of the existing data was considered to be either 'moderate' or 'good'. Only in the case of noise was the information regarded as 'poor'. The report included more than 200 selected references.

GESAMP's 2009 review also identified priority issues affecting the open ocean that, in the opinion of the experts involved, warranted special attention by those engaged in the Regular Assessment process. The parameters of most concern were inputs of nitrogen and pCO, and their potential effects on ecosystem function. The need to extend measurements of these parameters in space and time and, in the case of CO₂, for improvements in methodology, were clearly identified.

The present report examines new information and scientific perspectives on the open oceans that have emerged in the 5 year period since GESAMP first addressed this topic. Not all of the topics covered by the 2009 report are addressed in the same degree of detail while coverage of certain other topics has been extended. For example, contamination arising from shipping activities, ballast water and dumping is now considered of lesser priority in the open oceans whereas new information has enabled improved assessments of ocean noise, mercury and micro-plastics.

The report contributes to a thematic assessment of the open ocean, led by the Intergovernmental Oceanographic Commission (UNESCO-IOC), and is one of 5 types of transboundary water system being evaluated under the global Transboundary Waters Assessment Programme (TWAP), enabled by the Global Environment Facility (GEF) and implemented by the United Nations Environment Programme (UNEP). In addition to the open oceans, the TWAP encompasses aquifers, lakes, rivers and 55 large marine ecosystems (LMEs) that together account for almost 70% of the Earth's surface.

Transboundary water systems are often interlinked by environmental, political, economic and security interdependencies. The TWAP aims to provide a baseline assessment to identify and evaluate changes in these water systems caused by human activities and natural processes, and the consequences these may have for dependant human populations. Through indicators and mapping, the Open Ocean component will identify how ocean issues have local impact, where possible giving future projections. Four particular themes are to be investigated:

- Climate change, variability and impacts
- Ecosystems, habitats and biodiversity
- Fisheries, impact and sustainability
- Pollution and contaminants

Although the present report focuses exclusively on the last of these themes, the information contained herein will be evaluated in conjunction with the other 3 themes in assessing the combined impact of ocean conditions at regional and local levels.

1.2 Terms of reference

The reviews undertaken by GESAMP are commissioned by one or more of its sponsoring agencies and address topics that the agencies and their member States deem to be of international significance, either now or in the future. The brief for the present report is as follows:

1. To update, and extend as appropriate, previous overviews of substances and energy introduced to the marine environment that may adversely affect marine ecosystems or resources, present risks to human health or interfere with legitimate uses of the sea.

- 2. Conceived as a thematic, initial assessment, the first session will focus on data from the last 5 years: this first task will feed into the GEF/ IOC/UNEP Transboundary Waters Assessment Programme (TWAP).
- 3. To examine environmental assessments, scientific reviews and the wider scientific literature to derive recent information on the status of these substances and materials in terms of such matters as their sources, input loads, environmental levels and impacts.
- 4. To identify any patterns and trends (spatial and temporal) in the inputs, distributions and impacts of these substances and materials.
- 5. To highlight information gaps and scientific uncertainties that constrain assessments of particular substances and materials, whether at regional or global level, with particular regard to their significance for the marine environment and human health.
- 6. To prepare reports that summarise existing scientific knowledge on substances and energy in the marine environment and to inform policy makers by clearly identifying issues of special importance for science and management.

1.3 Task Team arrangements

As in the case of its previous report on ocean pollution, GESAMP convened a small Task Team comprised of specialists in various fields of marine science and environmental contamination embracing atmospheric chemistry, toxicology, chemical hazards, noise and ocean debris. At least half of the team had contributed to the previous report. The list of Task Team members is shown in Annex I.

The Task Team worked within a narrow timeframe of approximately 8 months, according to the timetable established for the TWAP. A 2-day scoping meeting, involving a core group of task team members, was held at IMO headquarters in London during August 2013 to discuss the thematic scope of the review and to organise membership and meeting arrangements. It was decided initially to hold two drafting sessions but this was reduced to a single workshop due to the limited availability of certain key contributors. The team subsequently met for 4 days in Monaco (25-28 February 2014) for detailed consideration of draft texts. The remaining work was completed through correspondence, coordinated by the Chairman.

1.4 Geographical scope

The geographical scope of GESAMP's previous review of ocean pollution was defined as areas where the water depth exceeds 200m around the boundaries of the major continental land masses' as well as all waters surrounding archipelagos regardless of depth. It was explained that the

inclusion of archipelagos was necessary because measurements at island stations are frequently used to represent conditions in the surrounding seas. particularly air-borne contaminants and marine debris distributed by ocean currents. In keeping with the relative scarcity of data compared to those for coastal areas, as well as outputs from modelling, summaries of atmospheric inputs in the previous review tended to be summarised on the basis of the major ocean basins i.e. Atlantic, Pacific and Indian. The present report adopts a similar approach but its geographical scope has been extended slightly to include deep-water (>200 m) areas of the Mediterranean and Arctic.

The range of literature consulted in preparing this review is broad and includes thematic assessments by international agencies, literature reviews and research papers published in the last 5 years. A small number of particularly relevant papers overlooked in the 2009 review have also been referenced. As in the case of Reports and Studies No.79, the report also contains a substantial bibliography, organized by contaminant category, for the benefit of those researching particular marine pollution issues.

1.5 Purpose of the report

Reviews of the findings from environmental research, such as this, and environmental assessments in particular, have various uses and they are by no means entirely scientific. Such reviews and assessments can be of value to students of marine sciences, and are often of interest to those engaged in particular fields of marine research. Possibly their most important role is, however, to inform environmental management by distilling broad fields of scientific investigation and to express key findings in non-technical language.

GESAMP reviews draw attention to issues that have, or could have, particular relevance for the health of the marine environment and that warrant in-depth consideration by managers and policy-makers with responsibilities for protecting marine resources. GESAMP, and the Task Team that prepared this review, consider that environmental conditions in the open oceans, their biodiversity, productivity and sustainability, warrant the attention of the international community because, along with changing climate, they could play a pivotal role in regulating future life on Earth. Accordingly, the inclusion of the open oceans within the ranks of transboundary waters currently under assessment, is well justified.

Whereas the concept of managing the open oceans is difficult to grasp, there are clear signs that anthropogenically induced changes have occurred beyond the continental shelves and there are upward trends in contaminants such as nitrogen and micro-plastics that warrant management action. Because the open oceans constitute international waters, no individual State or region has sole

responsibility for such action, nor would unilateral actions prove effective. Although it is not the function of GESAMP to find solutions to problems of the marine environment, it is reasonable to surmise that most scientists engaged in ocean research would anticipate and encourage actions by governments and inter-governmental organizations to resolve evident threats to the oceans periodically brought to their attention.

2. Thematic reviews

2.1 Preamble

In this chapter we review information on selected contaminants and conditions in the open oceans that has emerged since GESAMP reported on this topic approximately five years ago. The subjects are in no particular order and not all of the subjects addressed in the previous report are covered here; also, to avoid excessive repetition, the introductory texts outlining the various sources and causes of contamination are more concise. The coverage of each subject is similar in structure, embracing a summary of new information, future data requirements and conclusions. However, the material presented under a particular heading varies considerably in length, according to the extent of new findings, the need for explanatory text and the individual perspectives of the authors.

2.2 Nutrients and Heavy Metals

2.2.1 Introduction

This section considers the impacts of those chemicals known to be nutrients and certain heavy metals on the open ocean. Because direct emissions of these chemicals from land (e.g. through river and groundwater inputs) are very efficiently removed in coastal waters, transport through the atmosphere provides by far the most important pathway for the introduction of these contaminants into the open ocean. The chemicals considered in this section are:

Nitrogen (N); as nitrate (NO ₃ ⁻), ammonium (NH ₄ ⁺) and N-containing organic compounds (ON)							
Phosphorus (P); as phosphate (PO ₄ ³⁻) and P-containing organic compounds (OP)							
Iron (Fe)							
Zinc (Zn)							
Cobalt (Co)							
Nickel (Ni)							
Cadmium (Cd)							
Lead (Pb)							
Copper (Cu)							
Arsenic (As)							

Nitrogen and phosphorus are primary nutrients for marine photosynthetic organisms, being significant components of many cellular metabolites. There are large areas of the global ocean in which concentrations of these elements are sufficiently low to limit the growth of photosynthetic organisms either year-round (e.g. in the sub-tropical ocean gyres) or on a seasonal basis (e.g. in temperate waters).

Iron is a very important micro-nutrient due to its functional role in enzyme systems in photosynthetic organisms. Open ocean concentrations of Fe are extremely low (≤ 1 nmol L⁻¹) and in some areas (e.g. the Southern Ocean, equatorial Pacific and sub-Arctic Pacific, which together comprise 30-40% of the global ocean) are low enough to limit primary production, even though N and P are present in abundance.

A number of other heavy metals (Zn, Co, Ni, Cd, Cu) are also known to have functional roles in the enzyme systems of marine micro-organisms, and some of these metals may play a role in co-limiting primary productivity in a few marine environments (e.g. Dixon, 2008). Other heavy metals (Pb, As, Ni, Cu, Cd) are of concern due to their potential toxicity. It should be noted that Ni, Cd and Cu are listed as both micro-nutrients and potential toxicants because, although essential for life, elevated concentrations are also known to be harmful.

In GESAMP (2009) concluded that the atmospheric burden of reactive nitrogen had been significantly enhanced by anthropogenic activity since the Industrial Revolution and that this was likely to impact some open ocean ecosystems through chronic, low-level inputs. None of the other nutrient species were considered to be strongly perturbed, although such perturbation was considered difficult to discern against the highly variable natural inputs of these elements associated with mineral dust. GESAMP (2009) noted that atmospheric deposition of Pb had been shown to raise surface water Pb concentrations, but that no harmful effects of this elevated concentration had been reported. The report also noted that the International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention, 2001) might have altered the role of shipping in introducing heavy metals into the ocean.

2.2.2 Summary of new information

Observations of atmospheric concentrations and chemical characterisation

There has been a considerable body of work on atmospheric inputs of nutrients and heavy metals to the open ocean since the publication of GESAMP (2009). Here we identify 64 scientific research papers published since 2008 that report measurements of the concentrations of nutrients or heavy metals over the ocean or at marine land sites. The geographic distribution of the measurements contained in these papers is summarised in Table 2.2.1.

Location of measu- rements	N	Ρ	Fe	Zn	Co	Ni	Cd	Pb	Cu	As
Total, All regions	35	15	20	10	9	10	7	12	10	5
North Atlantic	9	4	7	2	1	2	1	3	2	1
Mediter- ranean	4	4	5	2	1	2	2	2	2	
South Atlantic	3	1	1							
North Pacific	12	6	2	3	2	2	1	4	2	1
South Pacific	3		1					1		
North Indian	6*	1	3	1	2	2	2	2	2	1
South Indian	4*		4	3	4	3	2	3	3	3
Arctic	3									

 Table 2.2.1.
 Number of scientific papers that report

 observations of atmospheric nutrients and heavy metals
 in each ocean region

^r Number of reports for the Indian Ocean includes 2 studies, conducted during the period 1995 -1998, which were overlooked in GESAMP (2009).

Much of the new data has been collected under the auspices of the international Surface Ocean – Lower Atmosphere Study (SOLAS) and GEOTRACES programmes, both of which have directed research work to improving understanding of atmospheric inputs to the oceans. In common with the status of studies at the time of R&S 79, the vast majority of work has been conducted in the North Atlantic and North Pacific Oceans. Of the data reports for the North Pacific, most are confined to the marginal semi-enclosed seas of the northwest of the basin. Very few published studies exist for the South Pacific, South Atlantic and South Indian Oceans in the period 2008 to present.

Those studies which considered N chiefly reported nitrate and ammonium concentrations, with only 13 considering ON. Similarly, only 4 of the studies on P considered OP. The identity and sources of ON and OP remain unclear. However, progress has been made through the application of techniques such as ultra-high resolution electrospray ionization mass spectrometry, which has shown that the composition of ON compounds in rainwater at Bermuda varies with seasonal changes in anthropogenic and marine sources (Altieri, et al., 2012). Stable isotopic composition has also been exploited as a tool to examine sources of atmospheric nitrogen in total N (Agnihotri, et al., 2011; Knapp, et al., 2010), NO3- (Gobel, et al., 2013; Morin, et al., 2009) and reduced N (Knapp, et al., 2010). The stable isotopic composition of oxygen can provide additional information on the formation and removal pathways of atmospheric nitrate (Gobel, et al., 2013; Morin, et al., 2009).

Almost all of the studies reporting concentrations of Fe and other heavy metals determined the soluble fractions of these metals. This reflects

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the understanding that soluble metal fractions are much more readily available to marine biota and this bioavailability determines the extent of any impact (nutrient or toxicity) of the heavy metal input to the ocean. A number of studies were also conducted on the solubility of atmospheric Fe in environmental samples (Buck, et al., 2013; Buck, et al., 2010; Hsu, et al., 2010; Kumar and Sarin, 2010; Kumar, et al., 2010; Ooki, et al., 2009; Sholkovitz, et al., 2009; Takahashi, et al., 2011; Trapp, et al., 2010; Wozniak, et al., 2013; Zhang, et al., 2013) and in controlled laboratory experiments (Cwiertny, et al., 2008; Deguillaume, et al., 2010; Journet, et al., 2008; Paris and Desboeufs, 2013; Rubasinghege, et al., 2010; Shi, et al., 2011; Shi, et al., 2011; Shi, et al., 2009) in continuing efforts to understand the processes that control Fe (and other heavy metal) solubility. Recent developments in single aerosol particle analysis have provided novel means to study atmospheric Fe solubility (Moffet, et al., 2012) and stable isotope analysis have provided insights into atmospheric sources of Fe (Mead, et al., 2013). There are a number of processes that might influence Fe solubility (Baker and Croot, 2010). A global compilation of atmospheric Fe solubility observations (Sholkovitz, et al., 2012) may be a useful tool to assess the relative importance of these processes. At present there is no consensus as to which processes are the major controls on Fe solubility, possibly because the influence of these processes varies regionally (e.g. Buck, et al., 2013).

Of the 64 publications identified, 11 studied Fe in combination with one or more other heavy metals and 9 studied N in combination with P. Three or four publications studied Fe in combination with N, P or both N and P.

Observation- and modelling-based estimates of flux to the ocean

Several studies examined the atmospheric input of N to the ocean on regional (Zhang, et al., 2010) or global (Krishnamurthy, et al., 2009; Krishnamurthy, et al., 2010; Lamarque, et al., 2013; Okin, et al., 2011; Reay, et al., 2008) scales using atmospheric chemical transport modelling. N deposition to the open ocean is greater downwind of major industrial/ domestic combustion and agricultural emissions (Figure 2.2.1). Fluxes are projected to increase in the years up to 2100 (Lamarque, et al., 2013). Figure 2.2.1 shows predicted oxidised (NOy) and reduced (NHx) nitrogen deposition fields for the years 2000, 2030 and 2100 from Lamarque et al. (2013), based on the Representative Concentration Pathway (RCP) 8.5 scenario. Other RCP scenarios (2.6 and 4.5) predict slightly lower increases in NOy deposition at 2030 and slightly greater decreases in NOy deposition by 2100, but all three scenarios suggest strong increases in NHx deposition. Increases in N deposition are predicted to be significant around South Asia, with RCPs 2.6 and 8.5 indicating a doubling of N deposition to the region by 2100. Projected increases in NHx deposition are linked to increasing use of inorganic



Figure 2.2.1: Global deposition fields of NOy and NHx for the years 2000, 2030 and 2100 (projected for RCP8.5 scenario) from Lamarque et *al.*, 2013.

fertilizers in order to meet global food demand, and the absences of measures to limit atmospheric N emissions associated with that fertilizer use (Lamarque, *et al.*, 2013).

Validation of such models is generally done through comparisons to land-based observations (e.g. Lamarque, et al., 2013), because of the lack of suitable datasets over the open ocean. Baker et al. (2010) used a large dataset of ship-based observations of atmospheric N (and P) concentrations to show relatively good agreement between observation-based and modelled atmospheric input estimates over the North and South Atlantic (within uncertainties in the observations and the modelling). Atmospheric chemical transport modelling has also been used to study the inputs of inorganic (Mahowald, et al., 2008) and organic (Kanakidou, et al., 2012) P to the global ocean. The latter work also explicitly modelled the atmospheric supply of ON to the ocean.

Several publications reported the results of modelling studies that aimed to quantify the atmospheric flux of soluble Fe to the ocean (Han, *et al.*, 2012; Ito, 2013; Johnson, *et al.*, 2010; Krishnamurthy, *et al.*, 2009; Krishnamurthy, *et al.*, 2010; Luo, *et al.*, 2008; Mahowald, *et al.*, 2009; Okin, *et al.*, 2011). In each case, it was necessary to model the flux of total Fe to the ocean (which is dominated by mineral dust inputs) and derive the soluble Fe flux from the total flux and other sources of soluble Fe. A number of studies also used atmospheric chemical modelling to study the processes potentially responsible for altering the solubility of Fe in the atmosphere (Han, et al., 2012; Ito and Feng, 2010; Ito, et al., 2012; Shi, et al., 2011). The various assumptions made about the influences on aerosol Fe solubility in these models result in very large differences in the geographic distribution of soluble Fe to the ocean. Projected changes in the relative anthropogenic emission rates of acidic (NOx and SO₂) and basic (NH₂) gases (Lamarque, et al., 2013; Wang, et al., 2013) are likely to affect the acidity of aerosols downwind of major emission regions, and this may then influence the generation of soluble Fe during atmospheric transport.

Large spatial-scale sampling of total and soluble Fe in the North and South Atlantic has been used to estimate the atmospheric flux of both parameters to these ocean basins independently of atmospheric chemical transport modelling (Baker, *et al.*, 2013). Comparisons of the results of that study to the models of Mahowald *et al.* (2009) and Johnson *et al.* (2010) showed good agreement between either total or soluble Fe fluxes in some ocean regions, but neither model reproduced both observation-based fluxes very well. One study attempted to simulate the atmospheric flux of soluble Cu to the global ocean (Paytan, *et al.*, 2009). **Figure 2.2.2:** Reconstructed and observed surface seawater Pb concentrations around Bermuda and the isotopic composition of that Pb (from Kelly *et al.*, 2009)



Fig. 3. Surface coral from North Rock and seawater from Station S, BATS and BTM. Inferred Pb concentrations (in pmol kg⁻¹) from surface coral proxy records and D_P values listed in Table 1.

Of the global atmospheric nutrient flux modelling studies, one considered both inorganic N and Fe (Krishnamurthy, *et al.*, 2009) and two considered N, P and Fe (Krishnamurthy, *et al.*, 2010; Okin, *et al.*, 2011). Okin *et al.* (2011) estimated atmospheric inputs of ON, as well as inorganic N). Both of the latter two studies concluded that the relative proportions of the atmospheric supply of N and Fe with respect to atmospheric P supply far exceed the relative consumption of N : P and Fe : P by phytoplankton growth, conclusions that are consistent with observational data.

Impacts of atmospheric deposition on marine biogeochemistry

Direct attribution of the impacts (e.g. the development of phytoplankton blooms) on the ocean from individual atmospheric deposition events is extremely difficult, because of the difficulties in observing deposition events and unambiguously discriminating between substances supplied by those events and other sources of those substances, and between the influence of the deposition events and other stimuli on production (Boyd, et al., 2010). A few studies have reported perturbation of the biogeochemistry of the surface ocean, based on direct observation of individual deposition events. The effects observed include: vigorous growth of the picoplankton Synechococcus (attributed to N, P and Fe inputs from Asian dust) in the Kuroshio Current, northwest Pacific (Chung, et al., 2011), stimulation of a phytoplankton bloom (attributed to N and Fe inputs from Asian dust) in the Yellow Sea (Shi, et al., 2012) and increased concentrations of Fe-binding organic ligands with consequent increases in the availability of nutrient Fe (attributed to the deposition of Saharan dust) in the tropical North Atlantic (Rijkenberg, et al., 2008). Incubation experiments, in which leachate of East Asian aerosol (containing NO3⁻, NH4⁺, PO3⁻, Fe, Cd, Pb, Co, Ni, Cu,



Fig. 6. 206 Pb/ 207 Pb ratios of Bermudan corals from North Rock and seawater from Station S, BATS and BTM.

Zn and other substances) was added to samples of water taken from the South China Sea induced responses in several different bacterial phylogenetic groups (Guo, et al., 2013). Some other incubation studies, in which aerosol samples were added to surface water from the Red Sea, produced elevated N and P concentrations, but did not result in stimulation of phytoplankton growth (Paytan, et al., 2009). This was attributed to a potential toxic effect from aerosol Cu. Kim et al. (2011) used a timeseries of observations of N and P concentrations in the waters of the marginal seas of the northwest Pacific to show that N availability has increased in this region since 1980. They then used high temporal correlations to argue that this increase in N availability was due to increases in atmospheric N flux originating from intense emission regions in East Asia.

Remote sensing and modelling approaches have also been used to study the impacts of atmospheric deposition on the ocean. Ohde and Siegel (2010) used remotely-sensed proxies for plankton biomass, upwelling and dust transport to study the influences on phytoplankton blooms off northwest Africa over the period 2000-2008. They identified 6 dust storm events (out of a total of 57) which appeared to be associated with subsequent increases in chlorophyll concentration. They attributed this effect to the input of Fe with the dust, but also noted that upwelling was a more important influence on chlorophyll concentrations. The occurrence of a large and unusual phytoplankton bloom in the oligotrophic western North Pacific has been attributed (through the use of atmospheric chemical transport modelling and remote sensing) in part to the stimulation of nitrogen fixing organisms by dust-borne nutrients (Fe and P) (Calil, et al., 2011). Plankton modelling suggests that the oceanic response to atmospheric N inputs, in terms of carbon export to deep waters, is dependent on plankton C:N ratios, which vary regionally as a function of surface water nutrient status (Mourino-Carballido, et al., 2012).

Two modelling studies examined aspects of the influence of anthropogenic activity on the input of soluble Fe to the ocean. Mahowald et al. (2009) estimated that 95% of atmospheric Fe is derived from dust, with only 5% attributed directly to anthropogenic sources. However, they also suggested that human activity has significantly enhanced dust production (by up to 50%) and that soluble Fe may also be significantly enhanced by human activity. Ito (2013) modelled the influence of atmospheric emissions from shipping on soluble Fe and suggested that projected increases in international shipping might significantly enhance the input of soluble Fe to the high latitude North Atlantic and North Pacific.

Modelling and remote sensing approaches have both been used to assess the potential impact of aerosol Cu toxicity on oceanic phytoplankton productivity (Jordi, et al., 2012; Paytan, et al., 2009).

The effect of atmospheric Pb deposition on surface water Pb concentrations since the Industrial Revolution has been reconstructed using the signature of Pb concentrations recorded in corals growing around Bermuda (Kelly, et al., 2009 - see Figure 2.2.2). The isotopic composition of this Pb evolved according to the dominant anthropogenic Pb sources to the region over the period, i.e. being indicative of North American gasoline emissions for the period ~1900 - 1970, increasing importance of European gasoline emissions from ~1970 - 1980 and other anthropogenic sources (e.g. coal burning) thereafter. Despite the very significant enrichment in seawater Pb concentrations over the 20th century, no negative impacts of this potentially toxic heavy metal have been reported.

2.2.3 Future data requirements and rationale

The N : P ratio of marine microbes varies widely between species (Arrigo, 2005). The very high N : P ratio of atmospheric deposition is therefore likely to be more favourable to species with high N : P requirements. Atmospheric deposition may therefore have the potential to influence species distributions within marine microbial communities. Further work on the ecological impact of this perturbation will be required.

The deposition of soluble Fe to the open ocean plays a major role in regulating marine productivity. It is very likely that anthropogenic activity has perturbed the natural Fe cycle, and especially the quantity and distribution of soluble Fe input to the ocean, due to changes in dust generation, alteration of the acidity of the atmosphere and direct emission of soluble Fe from anthropogenic sources. Assessment of the present and future impact of this perturbation requires a comprehensive understanding of:

- both natural and anthropogenic sources of Fe to the atmosphere:
- the processes that control Fe dissolution from atmospheric aerosols, both in the atmosphere and after deposition to the ocean; and
- the present and future emissions of substances (e.g. nitrogen and sulphur oxides and ammonia) that alter Fe solubility during atmospheric transport.

All aspects of the cycle of soluble Fe input to the ocean are currently subject to significant uncertainties and further work is required to resolve these

The net impact of dust/aerosol deposition on marine productivity is not well understood at present. Mineral dust is certainly a vector for the input of nutrient elements, such as Fe, P and other micro-nutrient heavy metals, to the open ocean. Addition of potential toxicants (e.g. Cu) to dust from anthropogenic sources, or enhancement of the soluble (bioavailable) fraction of those substances in dust through interaction of dust with other contaminants, has the potential to change the balance between nutrient/toxicity effects of dust deposition. Effective assessment of this issue will require better understanding of the factors that control the dissolution of heavy metals from mineral dust in seawater and the complex interactions between deposited dust and marine microbial communities.

The international GEOTRACES programme has a major role to play in advancing understanding of the atmospheric inputs of heavy metals and nutrients to the oceans. Atmospheric inputs are considered core measurements for the observational work carried out on GEOTRACES-approved cruises. The extensive studies of both seawater concentrations and stable isotope ratios for a number of elements (e.g. Cu and Zn, Dong, et al., 2013) have the potential to increase greatly our ability to assess the sources and impacts of pollution in the open ocean.

2.2.4 Conclusions

Although a large body of work has been carried out on atmospheric inputs of nutrients and heavy metals to the open ocean since R&S 79, the main conclusions of this report are similar to those of R&S 79. The contaminant of most concern is N, whose atmospheric input is dominated by anthropogenic activity. A few studies, mostly of work in the marginal seas downwind of the intense N emission regions in East Asia, have reported observable impacts of N deposition on the biogeochemistry of the ocean. The role of anthropogenic emissions in increasing the flux of soluble Fe (either by direct emission from combustion sources, or through the secondary enhancement of the solubility of Fe associated with mineral dust) to the ocean has also received considerable attention. The importance of this anthropogenic contribution to soluble Fe input to the ocean is very difficult to quantify however,

because it occurs against the very large Fe input associated with the natural mineral dust cycle. Since R&S 79, some studies have suggested that atmospheric inputs of Cu may be large enough to induce toxic effects in marine phytoplankton. This warrants further investigation.

2.3 Mercury

2.3.1 Introduction

The main pathway of mercury (Hg) to the open oceans is via atmospheric transport and deposition. The species which is emitted to the atmosphere from terrestrial sources is predominantly elemental mercury, Hg(0) but the main species deposited by both dry (gas phase and associated with particulates) and wet processes to the ocean surface, is inorganic oxidised mercury, Ha(II), However, the species which has an effect on ecosystem and potentially human well-being through the consumption of fish is monomethyl mercury (MeHg). Hence, the oxidation capacity of the marine boundary layer (MBL), the methylation potential of the ocean, and ocean productivity all contribute to the eventual impact of Hg on ocean ecosystems. Hg is also a rather unusual as contaminant in that some seas and ocean regions are net sources of Hg to the atmosphere (Andersson et al., 2011, Zagar et al., 2013).

Mercury and its compounds, particularly methyl mercury (MeHg), have neurotoxicological properties and are particularly significant for foetal development, as was first observed in the aftermath of the Minamata disaster where women who developed relatively slight symptoms gave birth to infants with significant neurological problems. MeHg bioaccumulates efficiently (mostly in muscle tissue) and is therefore found in the greatest concentrations in piscivorous fish towards the top of the food chain. Thus, fish such as tuna, swordfish, king mackerel and shark tend to have a relatively high Hg content, as do some species of whale. MeHg is not only crosses the blood brain barrier, but can also cross the placenta. A number of cohort studies have investigated the link between maternal diet, children's later diet, and cognitive development. While there is a consensus that MeHg does have a negative neurological impact, and can also affect physical growth, the levels of MeHg at which the negative influence outweighs the benefits that come from fish consumption is not entirely clear. The consumption of long chain polyunsaturated fatty acids has clear beneficial effects on physical and cognitive development and therefore avoiding oily fish is not to be recommended.

To quote from the United Nations Environment Programme (Chemicals and Waste - Mercury) website:

"In February 2009, the Governing Council of UNEP adopted Decision 25/5 on the development of a global legally binding

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instrument on mercury. At the Conference of Plenipotentiaries held from 9 to 11 October 2013 in Minamata and Kumamoto, Japan, the "Minamata Convention on Mercury" was formally adopted and opened for signature by States and regional economic integration organizations" (UNEP 2013a)

Therefore, since R&S 79, mercury has risen upwards on the political agenda as the deadline for the Convention approached. A number of assessments and reports on Hg have been published by international bodies, improved compartmental modelling studies of the global biogeochemical cycle of Hg have been performed and numerous studies relating to the tropospheric and also specifically MBL oxidation of Hg have been published. Much of the work on Hg emissions, fate and transport has been performed under the auspices of UNEP to inform the preparation of the Minamata Convention (UNEP 2014).

2.3.2 Summary of new information

The most recent anthropogenic mercury emission inventory is for the year 2010 (AMAP/UNEP 2013b). The 2010 inventory estimates a similar total anthropogenic emissions to the previous inventory (AMAP/UNEP 2008). However, the 2010 inventory reveals a quite different breakdown of mercury sources compared to previous inventories. In the 2008 inventory (reference year 2005), the single most important emission source was electricity generation in coal fired power stations. In the latest inventory (reference year 2010), the most important source is artisanal and small-scale gold mining. The difference is significant for two reasons. First, it shifts the global distribution of the emissions southwards, as most artisanal mining takes place in the tropics whereas energy production is concentrated in northern mid-latitudes. Second. the form of emissions is different: while coal fired power plants emit elemental, oxidised and particle bound Hg, artisanal mining emits effectively 100% elemental Hg. Oxidised and particle bound Hg are deposited locally whereas elemental Hg is subject to long range transport. The difference in these two inventories result from updated methodology and improved scientific knowledge and do not necessarily reflect a change in emission over time.

The UN-ECE (United Nations Economic Commission for Europe) Convention on Long-range Transboundary Air Pollution (LRTAP) established a Task Force on Hemispheric Transport of Air Pollution (TF HTAP) in 2004, the first comprehensive assessment by the Task Force was published in 2010 and includes a significant section on Hg (Pirrone and Keating, 2010).

In 2011, the Arctic Monitoring and Assessment Programme (AMAP) published an assessment of Hg in the Arctic (AMAP 2011), and in late 2012 a special issue of Environmental Research entitled 'Marine mercury fate: From sources to seafood consumers' (Chen et al., Eds., 2012), which provides a wide-ranging overview of research on marine Hg. A comprehensive review entitled 'Mercury as a Global Pollutant: Sources. Pathways and Effects', which summarises the plenary talks from the 10th international conference on Hg as a global pollutant, was published in the past year (Driscoll et al., 2013). A series of review/ policy papers on the next generation of air quality monitoring includes a paper dedicated to future needs and requirements to ensure that monitoring of atmospheric mercury becomes both consistent and widespread (Pirrone et al., 2013). Reviews of measurements in polar regions (Dommergue et al., 2009), of land-based atmospheric measurements (Ebinghaus et al., 2009) and over-water atmospheric measurements (including exchange and water column measurements) (Sprovieri et al., 2010), have all been published since R&S 79. A comprehensive list of Hg measurement review articles can be found in the bibliography.

In the five years since GESAMP (2009), UNEP has published two Global Atmospheric Mercury Assessments, one in late 2008 and the most recent in 2013 (UNEP, 2008, 2013). Each assessment was accompanied by a Technical Background Report which reviews Hg sources, emissions, transport and fate (AMAP/UNEP, 2008, 2013). In addition to the Assessments and Technical reports, the UNEP Mercury Fate and Transport Partnership published a report entitled Mercury Fate and Transport in the Global Atmosphere Emissions, Measurements and Models which was later published in book form (Pirrone and Mason, 2009).

Kinetics of elemental Hg oxidation

One aspect of modelling the atmospheric deposition of Hg that is not yet entirely clear, is the precise mechanism/reaction by which elemental Ho (relatively volatile and insoluble) is oxidised to Hg(II) which is far less volatile, more soluble and therefore more readily deposited. The role of bromine initiated oxidation of Hg is well established in the Arctic boundary layer, when Hg depletion events occur contemporaneously with ozone depletion events (see AMAP, 2011 and references therein). Many models have used and still use gas phase Hg oxidation mechanisms based on reactions with ozone and the OH radical; however, it seems likely that Br has an important role, especially in the MBL (Hedgecock and Pirrone, 2004, Holmes et al., 2009, 2010, Wang et al., 2013). Unfortunately, uncertainty in the oxidation mechanism (Hynes et al., 2009) as well as in Br compound emission source strengths, also lead to uncertainty in Hg deposition flux estimates to the open ocean. The role of bromine and its compounds in the oxidation of Hg(0) has significant implications for the global deposition pattern of oxidised Hg species. When modelling studies which use the O₂/OH oxidation pathway are compared to those using the Br mechanism, it is clear that the models using Br predict higher deposition of Hg(II) over the world's oceans, shifting

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the deposition away from subtropical to higher latitudes (Figure 2.3.1). This difference in model outputs reflects the difference in the distributions of O_3 /OH and Br containing compounds.

Ha+Br model





Biogeochemical Hg cycle

Significant progress in modelling the biogeochemical cycle of mercury has been made since the last report. Models have progressed from being static, using estimated fluxes between environmental compartments (Figure 2.3.2), to dynamic (at least in part) where coupled ocean-atmosphere models are employed (Amos et al., 2013, Corbitt et al., 2011, Driscoll et al., 2012, Holmes et al., 2009, Mason et al., 2012, Selin et al., 2008, Selin, 2009, Sunderland et al., 2009). This has improved constraints on the global Hg budget and begins to give more detailed insights into the residence times of Hg species in environmental compartments. Combining these models with experimental data has also led to studies tackling the problem of determining the processes, location in the water column and ancillary water parameters that influence mercury methylation and bioavailability (see particularly Sunderland et al., 2009, Driscoll et al., 2012 and Mason et al., 2012, Blum et al., 2013, Cossa, 2013, Parks et al., 2013). The atmospheric burden of Hg has increased between 3 and 5 times compared to pre-industrial levels, the surface ocean concentration has approximately doubled, while ocean intermediate and deep waters are enriched by 25 and 11% respectively.

Advances in global dynamic compartmental modelling studies now give clearer insight into how much of the Hg currently cycling between environmental compartments is 'legacy' Hg. So-called legacy Hg refers to Hg emitted as a result of anthropogenic activities that has already been deposited to a terrestrial or marine surface and which is still cycling between environmental compartments, not having yet been removed by deposition with sediment to the deep ocean floor. This may include mercury released in pre-industrial times; taking this Hg into account increases estimates of anthropogenic enrichment over natural levels (see Amos *et al.*, 2013 and references therein).

A declining trend in Hg concentrations in the North Atlantic

Trends in atmospheric Hg concentrations have been studied only recently, since measurement time series of sufficient length (and reliability) became available. Of most interest to open ocean studies is a study of the North and South Atlantic Oceans, where atmospheric and water column measurements have been made since the 1980s. Long term monitoring at Mace Head on the west coast of Ireland suggests a decrease in the Hg(0) concentration measured there over the years (Slemr *et al.*, 2011, Soerensen *et al.*, 2012), notwithstanding the fact that global anthropogenic emissions inventories have remained relatively constant or show slight increases (Streets *et al.*, 2011, AMAP/UNEP, 2008, 2013); this decrease also appears in North Atlantic cruise data. These observations could be linked to decreases in the Hg(0) concentration in subsurface waters which in turn has led to a decrease in the Hg re-emitted from the ocean. Possible causes are decreases in Hg(II) emissions from North America, and/or reductions in direct coastal inputs. The implication, should the observed decrease result from a decrease in oceanic input, is that the surface and upper waters of the oceans can respond on a decadal time scale to changes in Hg input fluxes.

Methylation of Mercury in the Open Ocean

A number of recent studies indicate that methylation of Hg occurs in the upper layers of the ocean (<1000 m) (Sunderland et al., 2009, Mason et al., 2012 and references therein) (Figure 2.3.3). Methylation of Hg appears to be correlated to the rate of organic carbon mineralisation (Sunderland et al., 2009); this is the first time that the open ocean MeHg concentration has been linked to an oceanic physico-chemical parameter. Sunderland et al. (2009) suggest that settling particulate organic carbon is a source of Hg(II) to microbially active subsurface waters which have higher microbial activity than surface waters, and also that the particulate organic carbon acts as a substrate for microbial activity which results in Hg methylation in the water column. This is a significant advance in understanding because the methylation of inorganic mercury is the critical step which renders Hg both



Figure 2.3.2: Current estimates of the fluxes and pools of mercury at the Earth's surface derived on this work, and building on previous studies, (99,140,148,181,183,193 see original references in Driscoll *et al.*, 2013) Hg(II) includes both gaseous and particulate forms, plus a negligible contribution (1 Mg) from inert particulate mercury. The percentages in brackets are estimated increases in pools and fluxes due to anthropogenic activities over the past 150 years. Fluxes are in Mg yr–1 and reservoirs are given in Gg. Reproduced from Driscoll *et al.* (2013).



Figure 2.3.3: Overall budget for the sources and losses of total and methylated (in bold) mercury to the mixed layer and the subsurface ocean (defined as waters above the permanent thermocline) using data and information discussed throughout the paper. Fluxes are in Mg yr–1 and reservoirs are given in Mg. Reproduced from Driscoll *et al.* (2013).

more toxic and more readily bioaccumulated. A very recent study which examined Hg stable isotope ratios in pelagic and surface fish in the North Pacific, suggests that methylation occurring below the ocean surface mixed layer is responsible for up to 80% of the MeHg found in pelagic fish (Blum *et al.*, 2013). An interesting result from this study, which reinforces previous findings from Choy *et al.* (2009), is that the depth at which fish forage plays a role in determining their Hg accumulation. The use of stable isotope ratios is a very recent addition to the analytical techniques used in Hg studies (see Blum 2012, Sonke and Blum, 2013).

A possible exception to the finding that atmospheric deposition is the most important source of Hg to the oceans, may be the Arctic which appears to be influenced by riverine inputs, in part because it is semi-enclosed and partly as a result of ice cover (Fisher *et al.*, 2013).

A new and increasingly comprehensive database on environmental Hg

There is a need for geo-referenced databases in which: a) metadata are comprehensive and conform to accepted standards; b) data has been subjected to documented QA/QC procedures; and c) data are available to the scientific community and also to the general public in appropriate formats. The inclusion of Hg monitoring as GEO task HE-02-C1 and the beginning of the European GMOS project (see below) led to the establishment of the of the GMOS Spatial Data Infrastructure (SDI) which, following international protocols for interoperability, provides data and services to partners and also the public. The main task of the SDI is to collect data in almost real time from monitoring sites and to provide site managers with QA/QC tools to ensure that their instruments are running according to standard operating procedures. In addition to this, the SDI is a repository for historical and more recent oceanographic campaign data, and is being extended to include Hg measurements made in fish, lichens and mosses. This has become possible through a Memorandum of Understanding signed with numerous data providers worldwide.

http://sdi.iia.cnr.it/geoint/publicpage/GMOS/sdi/

2.3.3 Future data requirements & rationale

"Limited oceanic mercury (Hg) data, particularly MeHg, has confounded our understanding of linkages between sources, methylation sites, and concentrations in marine food webs" (Sunderland et al., 2009).

The implementation of the Minamata convention, whilst being a challenge (Selin, 2013), will improve the current situation in terms of atmospheric Hg monitoring. As described above, the main challenges for open ocean Hg research are firstly the understanding of the water column methylation process and, secondly, quantifying the magnitude and time scale of the ocean's response to changes in Hg deposition fluxes which could result from anthropogenic emission controls. The ultimate goal is to predict changes in fish MeHg concentrations and thus human exposure.

While nations may have a vested interest in monitoring their own coastal fisheries, open ocean monitoring requires a concerted, and coordinated, international effort. The techniques currently in use for atmospheric and marine measurements of Hg and its compounds are expensive, and in most instances require the presence of skilled technicians/ scientists. Thus, ocean monitoring is costly in terms of equipment and personnel. The development of new monitoring techniques is a high priority both for atmospheric and aquatic measurements (Pirrone *et al.*, 2013).

The current situation in terms of atmospheric monitoring has improved since R&S 79 as international initiatives have placed Hg high on the agenda (GEO task HE-02-C1, the UNEP MFTP, TF-HTAP, Minamata Convention), and global and regional monitoring efforts have been expanded (e.g. www.gmos.eu, Gay et al., 2013). The GMOS project is of particular relevance as a number of the monitoring sites included or established within the GMOS network are remote island locations which provide atmospheric concentration and precipitation flux data that are directly pertinent to the open ocean. A number of research cruises have been undertaken since the last report and, as described above, the combination of Hg measurements with other sea water parameters has advanced understanding of the processes occurring in the water column which lead to bioaccumulation of Hg. There remains, however, an almost total lack of monitoring in the southern hemisphere, and little in the tropics.

The increasing complexity of biogeochemical Hg cycle models permits predictions of future trends in Hg loading in environmental compartments, and although it seems that anthropogenic emissions have remained relatively constant for the last ten or fifteen years, models suggest that the Hg burden in the intermediate ocean will continue to increase for some time to come (with the exception of the N. Atlantic) (Amos et al., 2013). Amos et al. (2013) state "The accumulated burden of legacy anthropogenic Hg means that future deposition will increase even if primary anthropogenic emissions are held constant." In order to have any possibility of confirming or not the model predictions, and to increase confidence in the models themselves, it is imperative that the atmospheric monitoring network is not only maintained but expanded (Selin, 2014). There is also a need for future cruise campaigns to ensure that trends in atmospheric and water column Hg will be identifiable; this could include the retracing of previous cruise routes on a regular basis to provide consistent spatial, and longer temporal, datasets.

2.3.4 Conclusions

The global biogeochemical cycle of mercury has been significantly perturbed by human activity over the last 500 years but particularly since the industrial revolution. The current atmospheric loading of Hg is three to five times pre-industrial levels and the surface ocean loading roughly twice pre-industrial loads.

Global policy, by means of the Minamata Convention, is beginning to address Hg usage and emissions from anthropogenic sources, whether intentional or not.

Measurement data have improved significantly in quantity and quality in the last five years and a global mercury monitoring network has been established. It is however imperative that atmospheric monitoring continue and that repeated oceanographic campaigns to measure Hg compounds in the open ocean water column are performed in the future, particularly in major fisheries.

Studies of the atmospheric oxidation of Hg and its cycling and methylation in the oceans have provided a link between Hg deposition, Hg methylation, entry into the food web and bioaccumulation.

Legacy mercury (Hg emitted as a result of human activities over the last few centuries) will be a major part of the oceanic Hg budget for some significant time to come.

The average age of oceanic water masses enables an estimate of the time they take to respond to changes in anthropogenic inputs; there is quite strong evidence to suggest that the subsurface North Atlantic has responded to decreased Hg inputs over the last twenty to thirty years. Such decreased loading is reflected in surface water Hg concentrations and in the atmospheric Hg concentrations over the ocean. This would appear to be due to the reduction in Hg loading and the relatively young average age of the surface and subsurface water masses specific to the North Atlantic.

With the exception of the North Atlantic, surface ocean Hg loading seems likely to continue to increase even if anthropogenic Hg emissions remain constant due to the cycling of legacy Hg. This region of the ocean is where Hg methylation occurs and where Hg enters the food web. If anthropogenic emissions do not decrease quite radically, it is probable that MeHg concentrations in pelagic piscivorous fish will continue to increase.

2.4 Carbon/CO,

2.4.1 Introduction

In May 2013, the weekly atmospheric dry mole fraction of carbon dioxide (CO₂) exceeded 400 µmol mol-1 at Mauna Loa, Hawaii (Tans and Keeling, 2014), a level not seen in the past 740,000 vears (EPICA Community Members, 2004), Carbon dioxide emissions resulting from human activity are responsible for the rapid increase in the atmospheric dry mole fraction of the greenhouse gas from a preindustrial value of 278 µmol mol-1 (Figure 2.4.1) (Ciais et al., 2013). In 2100 the atmospheric CO dry mole fraction is expected to reach 670 to 936 μ mol mol⁻¹, if anthropogenic CO₂ emissions remain high, or 421 to 538 μ mol mol⁻¹, if CO₂ emissions are drastically reduced (Meinshausen et al., 2011). The oceans have absorbed about 30% of the CO, emitted by human activity since pre-industrial times (Sabine et al., 2004; Khatiwala et al., 2013), thus reducing global warming.

Ocean uptake of anthropogenic CO_2 is the dominant cause of observed changes in surface ocean pCO_2 (partial pressure of CO_2), pH and carbonate chemistry (Figure 2.4.1) (Doney *et al.*, 2009; Rhein *et al.*, 2013). Ocean acidification has been defined as 'a reduction in ocean pH over

an extended period, typically decades or longer' (IPCC, 2011; Rhein et al., 2013). Ocean acidification can result from natural inputs, such as volcanic activity and methane hydrate releases, as well as from human activity: the term anthropogenic ocean acidification refers to manmade contributions to ocean acidification (IPCC, 2011). Atmospheric inputs of nitrogen and sulphur compounds (0.8 Tmol yr¹ of reactive sulphur and 2.7 Tmol yr¹ of nitrogen) produced by fossil fuel burning and agriculture also promote ocean acidification (Doney et al., 2007). On a global scale the contribution of these sulphur and nitrogen inputs to ocean acidification is small in comparison to those from ocean carbon uptake, but it may be large close to source regions (Doney et al., 2007).

Ocean acidification has reduced global surface ocean pH from 8.2 in pre-industrial times to 8.1 at present (Figure 2.4.1) (Orr *et al.*, 2005; Raven *et al.*, 2005). Ocean acidification reduces the carbonate ion concentration and saturation state of the carbonate minerals aragonite and calcite. Ocean acidification is an all-present phenomenon for marine organisms and a particular threat for marine calcifiers and the ecosystems they are part of (Raven *et al.*, 2005; Schubert *et al.*, 2006; Kroeker *et al.*, 2013; Whittmann and Pörtner, 2013).



Figure 2.4.1: 'A smoothed time series of atmospheric CO₂ mole fraction (in ppm' or μ mol mol-1') at the atmospheric Mauna Loa Observatory (top red line), surface ocean partial pressure of CO₂ (pCO₂; middle blue line) and surface ocean pH (bottom green line) at Station ALOHA in the subtropical North Pacific north of Hawaii for the period from1990–2011 (after Doney *et al.*, 2009; data from Dore *et al.*, 2009). The results indicate that the surface ocean pCO₂ trend is generally consistent with the atmospheric increase but is more variable due to large-scale interannual variability of oceanic processes.' (Figure and caption reproduced from Rhein *et al.*, 2013).

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Figure 2.4.2: Surface water observations of the fugacity of CO_2 (fCO₂, closely related to pCO₂) in a) January, February, March and b) July, August and September 2000 to 2009 in version 2 of the Surface Ocean CO_2 Atlas (SOCAT). The figure highlights the collection of surface water fCO₂ measurements on Antarctic supply ships and on ships of opportunity, for example between Asia, Australia and North America and between the Americas and Europe. (Reproduced from Bakker *et al.*, 2014b)

2.4.2 Summary of new information

Carbon

Both anthropogenic influences and variation in natural processes affect ocean carbon uptake and ocean acidification (Le Quéré *et al.*, 2007; Lenton *et al.*, 2009; Watson *et al.*, 2009; Rhein *et al.*, 2013). Observation-based studies and models indicate an anthropogenic ocean carbon sink of 2.0 Pg C yr¹ with a range of 1.9 to 2.5 Pg C yr¹ (1 Pg is equivalent to 10¹⁵ g) for the year 2000 and an increase in this sink

of 0.15 to 0.5 Pg C yr¹ decade⁻¹ from 1990 to 2009 (Wanninkhof *et al.*, 2013a). Ocean carbon uptake exhibits multi-year and regional variation (Corbière *et al.*, 2007; Schuster and Watson, 2007; Ishii *et al.*, 2009; Schuster *et al.*, 2009; Takahashi *et al.*, 2009; Watson *et al.*, 2009 ; Fay and McKinley, 2013). For example, surface water pCO₂ increased by 1.6 to 2.2 µatm yr¹ for 1995 to 2009 at the time series stations ALOHA, BATS, ESTOC and Island Sea, while atmospheric pCO₂ increased by 1.9 µatm yr¹ (Rhein *et al.*, 2013). Synthesis products, such as GLODAP, CARINA, PACIFICA and SOCAT (Key *et al.*, 2004; Tanhua *et al.*, 2010; Pfeil *et al.*, 2013; Suzuki *et al.*, 2013; Bakker *et al.*, 2014b), have greatly improved access to quality controlled carbonate chemistry data for the global oceans and coastal seas (Figure 2.4.2). Mapping techniques are being developed for the creation of basin-wide maps of surface water pCO₂ and air-sea CO₂ fluxes from observations (Boutin *et al.*, 1999; Olsen *et al.*, 2008; Takahashi *et al.*, 2009; Telszewski *et al.*, 2009; Landschützer *et al.*, 2013; Nakaoka *et al.*, 2013; Rödenbeck *et al.*, 2013). An intercomparison of flux estimates by such methods is in progress (Rödenbeck, personal communication).

The parameterisation of air-sea gas transfer and the wind field product contribute uncertainty to observation-based estimates of ocean carbon uptake (Wanninkhof *et al.*, 2009, 2013a; Garbe *et al.*, 2014). In addition, bottom-driven turbulence, current speed and water depth affect gas transfer in shallow waters (Upstill-Goddard, 2006; Bakker *et al.*, 2014a).

Calculation of the anthropogenic ocean carbon sink from surface ocean pCO_2 observations requires correction for outgassing of riverine carbon inputs (Sarmiento and Sundquist, 1992; Wanninkhof *et al.*, 2013a). Anthropogenic changes of riverine carbon inputs need to be considered in global carbon budgets (Regnier *et al.*, 2013).

Heterogeneity in coastal systems is a major complication in the quantification of air-sea CO_2 fluxes in these waters. Recent estimates converge on a CO_2 source of 0.25 ± 0.25 Pg C yr¹ in estuaries with a sink of similar magnitude (0.2 to 0.3 Pg C yr¹) on continental shelves (Chen and Borges, 2009; Laruelle *et al.*, 2010; Regnier *et al.*, 2013; Wanninkhof *et al.*, 2013a).

The role of sea ice in air-ice-sea CO_2 transfer is poorly known (Loose and Schlosser, 2011; Loose *et al.*, 2011; Garbe *et al.*, 2014). Uncertainty exists on the magnitude of air-ice CO_2 fluxes, the role of snow cover, sea ice biogeochemistry and sea ice heterogeneity. Relatively few direct measurements of air-ice CO_2 fluxes have been made using different methods and without intercomparison (Garbe *et al.*, 2014).

Ocean Acidification

Global surface ocean pH is expected to decrease from a pre-industrial value of 8.2 to a pH of 7.8 to 7.9 by 2100, if CO_2 emissions remain high, or to a pH of 7.9 to 8.0, if CO_2 emissions are mitigated (Figures 2.4.3, 2.4.4) (Feely *et al.*, 2009; Steinacher *et al.*, 2009; Joos *et al.*, 2011; Ciais *et al.*, 2013).

High-latitude oceans and upwelling regions are particularly vulnerable to ocean acidification (Orr *et al.*, 2005; Feely *et al.*, 2008, 2009; Steinacher *et al.*, 2009; AMAP, 2013). Aragonite saturation of most polar waters is lower in winter than in summer



Figure 2.4.3: Modelled global surface ocean pH from 1870 to 2100. Blue line indicates pH values in case of very low anthropogenic CO_2 emissions to the atmosphere; red line corresponds to pH resulting from high CO_2 emissions (Reproduced from IGBP, IOC, SCOR (2013), after Bopp *et al.* (2013))

(McNeil and Matear, 2008). If anthropogenic CO_2 emissions remain high, ocean acidification will promote local undersaturation for aragonite in the Arctic Ocean by 2020 with undersaturation becoming widespread by 2050 (Steinacher *et al.*, 2009). By 2030-2050 local, wintertime undersaturation will occur in the Southern Ocean (Orr *et al.*, 2005; McNeil and Matear, 2008). By 2100 the entire Southern Ocean (Orr *et al.*, 2005) and parts of the North Pacific Ocean will be corrosive to aragonite (Fig. 4) (Feely *et al.*, 2009).

In upwelling systems, CO_2 -rich upwelled waters mix with surface water containing anthropogenic CO_2 . In addition, upwelled water in some upwelling systems has left the surface ocean relatively recently (e.g. 50 years ago) and carries an increasing anthropogenic CO_2 load (Feely *et al.*, 2008, 2010b; Gruber *et al.*, 2012).

Ocean acidification also affects the deep ocean. The aragonite and calcite saturation horizons, the depths below which seawater is undersaturated for the calcium carbonate minerals, are moving upwards in all basins. For example, by 2100 the aragonite saturation will reach the surface in the Subarctic Pacific Ocean and Southern Ocean and will move upward from 2820 m to 110 m depth in the northern North Atlantic Ocean under a high CO_2 emission scenario (Orr, 2011).

Organism and ecosystem impacts of ocean acidification

Ocean acidification will have winners and losers (Doney *et al.*, 2009; Whittman and Pörtner, 2013). The extent to which marine organisms will be able to adapt to ocean acidification is poorly known (Hofmann *et al.*, 2010). Ocean acidification will affect individual species, as well as the ecosystems they are part of (Doney *et al.*, 2009). Ocean acidification will promote large changes in species composition and marine ecosystems (Whittman and Pörtner, 2013), notably in the high-latitude oceans (Orr *et al.*, 2005; Steinacher *et al.*, 2009; Bednaršek *et al.*, 2012a; AMAP, 2013).

Marine organisms have been incubated under a range of pH and pCO₂ conditions. A caveat is that most manipulation experiments are short in duration (0 to 100 days) (Hofmann et al., 2010; Kroeker et al., 2013). Meta-analyses of manipulation experiments identify a variety of responses in marine phytoplankton and animals for high CO, emission scenarios (Kroeker et al., 2010, 2013; Whittman and Pörtner, 2013). Responses include decreases in survival, calcification, growth and development (Kroeker et al., 2013; Whittman and Pörtner, 2013). The responses vary between life stages and taxonomic groups. Calcifying species are particularly vulnerable. Corals, echinoderms and molluscs have a medium sensitivity to ocean acidification and crustaceans a low sensitivity (Kroeker et al., 2013; Whittman and Pörtner, 2013). Ocean acidification may have a negative impact on fish larvae (Whittman and Pörtner, 2013). However, the confidence in this finding is low and further research on the vulnerability of fish is required (Whittman and Pörtner, 2013). Some non-calcifying taxa show an increase in growth and photosynthesis (Kroeker *et al.*, 2013). Multiple stressors, such as species interactions, lack of food and concurrent warming, increase the sensitivity of organisms to ocean acidification (Kroeker *et al.*, 2013; Whittman and Pörtner, 2013).

Volcanic CO, vents, low-pH groundwater springs and upwelling systems provide natural analogues for studying the impacts on, and adaptation of, marine species and ecosystems to ocean acidification (Hall-Spencer et al., 2008; Wootton et al., 2008; Andersson et al., 2011; Crook et al., 2012). However, rapid fluctuations in carbonate chemistry often complicate interpretation of the results (e.g. Hall-Spencer et al., 2008; Inoue et al., 2013), which mainly apply to sessile, benthic organisms. Species composition across pH gradients was studied at a shallow CO, vent site in the Mediterranean Sea. At very low pH (pH 7.4-7.5) scleractinian corals (stony corals) were absent, while the abundance of other calcifying species (coralline algae and sea urchins) was strongly reduced (Hall-Spencer et al., 2008). Seagrass production was highest at pH 7.6, well above levels in ambient seawater with a pH of 8.1-8.2 (Hall-Spencer et al., 2008). Gradual changes in species composition were observed near volcanic vents off Japan from reef-building, stony corals in ambient water (pH 8.1-8.3) to non-reef-building, soft-tissue corals at low pH (pH 7.5-8.3) and an absence of corals at a very low pH of 7.3-7.5 (Inoue et al., 2013). Coral species diversity at vent sites in Papua New Guinea decreased along a pH gradient of 8.1 to 7.7 (Fabricius et al., 2011). Calcification rates of a Caribbean reef-building coral (Porites astreoides) decreased along a natural gradient in pH and aragonite saturation, while skeletal erosion and predation on the corals increased (Crook et al., 2013).

Anthropogenic ocean acidification is an additional stressor for tropical corals already experiencing rising sea water temperatures (Guinotte *et al.*, 2003; Cao and Caldeira, 2008; Guinotte and Fabry, 2008; Feely *et al.*, 2009; Burke *et al.*, 2011). Unless CO₂ emissions are rapidly reduced, the majority of tropical coral reefs will experience aragonite levels below 4.0 by 2030 (Burke *et al.*, 2011). Such levels are considered less than optimal for coral growth (Guinotte *et al.*, 2003; Burke *et al.*, 2011). Wide-spread, diverse cold-water corals growing below 100 m depth in the northern North Atlantic Ocean (Roberts *et al.*, 2006) will be exposed to water undersaturated in aragonite by 2100, if CO₂ emissions remain high (Orr, 2011).

Extensive dissolution of live pteropods (*Limacina helicina Antarctica*) has been observed in Southern Ocean waters, impacted by upwelling and anthropogenic CO_2 uptake (Bednaršek *et al.*, 2012a). Animals outside the upwelling area did not exhibit such shell dissolution. The abundance and

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Figure 2.4.4: Global distribution of modelled, decadal mean a, b) surface water pH and c, d) aragonite saturation state for the global oceans in pre-industrial times (1850-1860) and for 2090-2100. Future conditions assume a high CO_2 emission scenario. The pH scale is from 7.1 to 8.3. The aragonite saturation scale ranges from 1.0 to 3.0. (Reproduced from IGBP, IOC, SCOR (2013) with model values from Tatiana Ilyina, Max Planck Institute for Meteorology)

size of two mussel species (*Mytilis californianus*, *Mytilus trossulus*) declined upon a reduction in pH at Tatoosh Island (Wooton *et al.*, 2008), situated in the upwelling system along the North American West coast.

There is ample evidence that anthropogenic ocean acidification will impact some marine

organisms and will change the composition of communities (Turley and Boot, 2011). Changes in abundance of specific organisms will affect their food source, competitors and predators (Turley and Boot, 2011). For example, pteropods are an important zooplankton species in the high-latitude oceans (Hunt *et al.*, 2008) and a major food source

for juvenile pink salmon (Armstrong et al., 2005), other fish species, sea birds (Hunt et al., 2008) and possibly for whales (Wesławski et al., 2000). A decline in the abundance of pteropods will affect their predators (Turley and Boot, 2011).

Ocean acidification will impact on marine ecosystem services, such as fisheries, aquaculture harvests, coastal protection and tourism (Table 2.2.1) (Cooley et al., 2009; Le Quesne and Pinnegar, 2012; AMAP, 2013; Branch et al., 2013). Many commercially exploited shell fish and fish species will be impacted by ocean acidification (Cooley et al., 2009; Le Quesne and Pinnegar, 2012; Branch et al., 2013). Such impacts may affect coastal regions and developing nations disproportionally (Cooley et al., 2009). For example, larval growth of the Pacific oyster (Crassostrea gigas) declines, as the aragonite saturation decreases from 3.2 to 0.8, corresponding to a pH reduction from 8.2 to 7.6 (Barton et al., 2012). Oyster hatcheries on the US West coast, a US\$ 278 million industry in 2009 (PCSGA, 2009; Feely et al., 2012), are at risk of upwelled waters with an increasing anthropogenic CO₂ concentration (Barton et al., 2012; Feely et al., 2012). In response, several oyster hatcheries are now monitoring seawater carbonate chemistry and are selectively introducing seawater intake into the hatcheries (Feely et al., 2012).

Other impacts of ocean acidification

Ocean acidification will change biogeochemical cycles (Doney et al., 2009), the speciation of metals in seawater and the interactions between metals and marine organisms (Millero et al., 2009). Ocean acidification is likely to affect the marine production of climatically active trace gases, such as dimethylsulphide (DMS), iodocarbons, and bromocarbons (Hopkins et al., 2011; Six et al., 2013).

Several studies have suggested that ocean acidification may reduce sound absorption in the oceans (Hester et al., 2008; Brewer and Hester, 2009; Ilyina et al., 2010). However, changes in oceanic noise levels by ocean acidification were negligible between 1965 and 2000 (Ainslie, 2012) and future changes are predicted to be minimal (Joseph and Chiu, 2010; Reeder and Chiu, 2010; Udovydchenkov et al., 2010). Ocean acidification may affect the optical properties of seawater by changing the abundance of calcium carbonate coccoliths (Balch and Utgoff, 2009).

Geoengineering

Geoengineering efforts for mitigating climate change can be put into two categories: activities that remove atmospheric CO₂ (carbon dioxide removal techniques) and those that reduce the absorption of solar radiation by the Earth (solar radiation management techniques) (Shepherd et al., 2009). This second category of geoengineering approaches would not reduce ocean acidification (Doney et al.,

2009; Shepherd et al., 2009; Williamson and Turley, 2012).

2.4.3 Future data requirements & rationale

There is a need for long-term, sustained observations of ocean carbon uptake and ocean acidification in the global oceans and coastal seas (IOCCP, 2007; Borges et al., 2010; Feely et al., 2010a; Gruber et al., 2010; Monteiro et al., 2010), improved analytical techniques for pH and carbonate chemistry measurements (Byrne et al., 2010; Gruber et al., 2010; Monteiro et al., 2010), as well a need for long-term, global monitoring of the impact of ocean acidification on marine organisms and ecosystems (Royal Society, 2005; Schubert et al., 2006; Feely et al., 2010a; Iglesias-Rodriguez et al., 2010; ICES, 2013; Newton et al., 2014).

Sustained observations and data synthesis of carbonate parameters are essential for quantifying long-term variation in ocean carbon uptake and ocean acidification (IOCCP, 2007; Borges et al., 2010; Feely et al., 2010a; Gruber et al., 2010; Monteiro et al., 2010; Bakker et al., 2014a; Newton et al., 2014). Data records of surface water CO. and ocean carbonate chemistry span less than two decades in most regions and have large data gaps in near-shore waters, shelf seas, the Indian Ocean, the Arctic Ocean and much of the southern hemisphere oceans (Bakker et al., 2014b). Data collection by biogeochemical sensors on moorings, drifters and self-propelled instruments is becoming increasingly important for analysis of variability of carbonate chemistry on hourly to monthly time scales, on 0 to 100 km horizontal scales and for the full water column.

Time-series observations and long-term research provide an invaluable record of carbonate chemistry and marine ecology (e.g. Ducklow et al., 2009). Long-term monitoring of seawater carbonate chemistry, marine species and ecosystems are central to any assessment of the impacts of ocean acidification on marine life. Monitoring strategies are being discussed, for example a Global Ocean Acidification Observing Network and an OSPAR monitoring strategy (Feely et al., 2010a; Iglesias-Rodriguez et al., 2010; Lindstrom et al., 2012; ICES, 2013; Newton et al., 2014). Indicator organisms and key indicators need to be identified for quantifying the effects of ocean acidification on marine organisms (e.g. Bednaršek et al., 2012b; ICES, 2013).

Guidelines have been published for carbonate chemistry and ocean acidification measurements and reporting (Dickson and Goyet, 1994; Dickson et al., 2007; Riebesell et al., 2010). The accuracy of carbonate chemistry measurements required strongly depends on the application (Newton et al., 2014). Analysis of long-term change in, for example pCO₂ or pH, and most carbonate chemistry calculations require high accuracy, while a lower accuracy is sufficient for manipulation experiments and some process studies. A distinction is being made between accuracy required for assessing the 'climate' and the 'weather', for example in the design of a Global Ocean Acidification Observing Network (Newton et al., 2014).

Technological development of accurate, and ideally user-friendly and low-maintenance, instrumentation and sensors for carbonate chemistry measurements (Moore et al., 2009; Byrne et al., 2010; Gruber et al., 2010; Monteiro et al., 2010) is necessary. Biogeochemical measurements from new sensors and alternative platforms, such as moorings and drifters, are gradually becoming available and it is important that such data are incorporated in data products. For example, the Surface Ocean CO Atlas (SOCAT) has revised its quality control criteria. to enable the inclusion of data from alternative CO sensors and platforms (Wanninkhof et al., 2013b).

2.4.4 Conclusions

Carbon

Anthropogenic CO₂ emissions are rapidly increasing the atmospheric CO_2 content (Figure 2.4.1). Atmospheric CO, levels at Mauna Loa (Hawaii) exceeded 400 µmol mol-1 in May 2013. The CO emissions by human activity and the resulting ocean CO, uptake are the dominant cause of ocean acidification (Figure 2.4.1) (Doney et al., 2009; Rhein et al., 2013). Ocean carbon uptake exhibits regional and multi-year variation. Natural and anthropogenic processes affect ocean carbon uptake. Major uncertainties in guantification of the ocean carbon sink originate from the air-sea gas transfer parameterisation, riverine carbon inputs, and carbon cycling in coastal seas and ice-covered oceans.

Ocean acidification

Surface ocean pH has decreased by 0.1 unit since the industrial revolution and is expected to decrease by a further 0.2-0.3 units by 2100. unless anthropogenic CO2 emissions are strongly reduced (Figures 2.4.3, 2.4.4). Ocean acidification will promote large changes in marine ecosystems globally with both winners and losers (Doney et al., 2009; Hofmann et al., 2010; Whittman and Pörtner, 2013) and may already be doing so (Wootton et al., 2008; Barton et al., 2012; Bednaršek et al., 2012a). Calcifying organisms are particularly at risk. Ocean acidification will impact on biogeochemical cycles and the production of climatically active gases (Doney et al., 2009; Hopkins et al., 2011).

Marine ecosystems in the high-latitude oceans are especially vulnerable to ocean acidification. Local aragonite undersaturation in the Arctic Ocean is becoming more widespread (Steinacher et al., 2009; Yamamoto-Kawai et al., 2009). Aragonite undersaturation will extend throughout the Arctic Ocean by 2050 and throughout the Southern Ocean and parts of the North Pacific Ocean by 2100, unless CO₂ emissions are drastically reduced (Figure 2.4.4) (Orr et al., 2005; Feelv et al., 2009; Steinacher et al., 2009). Cold-water corals in the northern North Atlantic Ocean will be exposed to water undersaturated for aragonite by 2100 (Orr, 2011). By 2030 less than half of tropical coral reefs will be in areas with aragonite levels optimal for coral growth (Burke et al., 2011). Upwelling systems are at risk, as an increasing anthropogenic CO, load is added to CO₂-rich upwelled waters (Feely et al., 2008; Barton et al., 2012; Bednaršek et al., 2012a; Gruber et al., 2012).

The effect of anthropogenic ocean acidification on coastal regions, which host aquaculture, fisheries and tourism, is a major concern (Cooley et al., 2009; Ciais et al., 2013). Anthropogenic ocean acidification may already contribute to problems in oyster hatcheries on the North American Pacific coast (Barton et al., 2012; Feely et al., 2012). Similar conditions may exist elsewhere. Unless anthropogenic CO₂ emissions are brought under control soon, anthropogenic ocean acidification will impact on marine ecosystems and ecosystem services worldwide (Cooley et al., 2009; Le Quesne and Pinnegar, 2012; AMAP, 2013; Branch et al., 2013).

Observational requirements

Early detection of long-term variation in ocean carbon uptake and ocean acidification requires sustained, high-quality monitoring of seawater carbonate chemistry at time-series stations and on ships of opportunity (Figure 2.4.2). The pervasive impacts of anthropogenic ocean acidification create an urgent need for long-term, global monitoring of seawater carbonate chemistry, marine organisms and ecosystems (Royal Society, 2005; Feely et al., 2010a; ICES, 2013; Newton et al., 2014). Volcanic CO, vents and upwelling systems provide natural analogues for studying the response of marine ecosystems to ocean acidification (e.g. Hall-Spencer et al., 2008; Wootton et al., 2008). Data collection by biogeochemical sensors on moorings, drifters and self-propelled instruments is becoming increasingly important.

2.5 Persistent Organic Pollutants (POPs), Persistent, Bioaccumulating and Toxic substances (PBTs) and Chlorofluorocarbons (CFCs)

2.5.1 Introduction

In our previous review of pollution in the open oceans (GESAMP 2009), we reviewed the regulatory status of POPs and PBTs under international conventions and regional legislation in order to assess which were regularly monitored as part of pollution reduction policies. The open oceans are clearly vulnerable to contamination as a result of atmospheric transport and other mechanisms; in the absence of any dedicated assessments, it was felt that the second GESAMP review of pollution in the open oceans should go one step further by reviewing information on the accumulation of POPs in biota and detecting any apparent gradients and trends. A concise overview of POPs associated with microplastics, is also included. The regulatory status of POPs and PBTs has been updated and some trends have been noted.

A glossary of chemical terms is given at Annex II.

Regulatory matters

POPs and the Stockholm Convention: The Stockholm Convention (SC, 2001), which entered into force in 2004, is intended to protect human health and the environment from the effects of persistent organic pollutants and defines how POPs are to be identified. The signatories agree to eliminate (Annex A), restrict the use of (Annex B), as well as limit the unintentional production of POPs (Annex C). The substances regulated under the SC are shown in Table 2.5.1 on the following page. In addition to the chemicals originally listed, many new chemicals were added in 2011 and more are being investigated. POPs are persistent (semi-) volatile chemicals that are often transported through the atmosphere and typically have long atmospheric residence times.

PBTs: PBT classification is a hazard-based system examining degradation of the substance in air, water, soil and sediment as a measure of persistence, bioaccumulation in biota including fish, as well as toxicity to aquatic organisms. The classification vPvB refers to very persistent, very bioaccumulating substances. PBT programmes are operational in the European Union, the USA. Canada and some other regions/nations, using similar but not identical threshold values. The classification of a substance as PBT (or vPvB²) in the EU under the REACH Regulation is part of the process to prioritize chemicals, leading to further evaluation but more importantly to the eventual application of risk management measures, e.g. restriction (a ban) or authorisation (licensing of specific uses in order to allow time for substitution). The following substances have been identified in the EU (December 2013) as having PBT and/or vPvB properties, or are considered to have properties of 'equivalent concern' for the environment:

- anthracene³ and anthracene oil⁴ (3 ring PAH),
- bis(tributyltin)oxide (TBTO; anti-fouling biocide),
- chlorinated paraffins short-chain (C10-C13; plasticisers, additives in metalworking

fluids, flame retardants and paints),

- coal tar pitch (high temperature; primarily used in electrodes, e.g. for aluminium smelting),
- decabromodiphenyl ether (decaBDE, flame retardant)
- hexabromocyclododecane (HBCD; flame retardant),
- musk xylene (synthetic fragrance),
- octyl and nonyl phenol and their ethoxylates (surfactants)
- pentadecafluorodecanoic acid and its ammonium salts (textile waterproofing, nonstick coatings),
- perfluorinated deca- undeca-, dodeca-, trideca- and tetradecanoic acids (cement manufacture, fire-fighting foams, wetting agents and water treatment),

Chlorofluorocarbons (CFCs): CFCs are low molecular weight, halogenated alkanes or alkenes (C1 to C3) and are used in refrigeration, as solvents and as propellants. They can be powerful greenhouse gases which affect the ozone layer. Older types generally have very long half-lives in the atmosphere of up to 100 years or more. Intermediate types are not saturated with halogen but usually contain fluorine and chorine or bromine, while newer types contain only fluorine and hydrogen, or a double bond on the carbon backbone to ensure far more rapid degradation. According to the most recent WMO (2010, Chapter 5, p1) assessment of ozone depletion, updating assessments in 2002 and 2006, "The accelerated HCFC phase-out agreed to by the Parties to the Montreal Protocol in 2007 is projected to reduce cumulative HCFC emissions by 0.6-0.8 million ODP-tonnes [0.4-0.6 GtCO₂-eq per year] between 2011 and 2050 and bring forward the year equivalent effective stratospheric chlorine (EESC) returns to 1980 levels by 4-5 years". As concluded in the 2009 Open Ocean report, no direct impact of CFCs on the open ocean is to be expected.

<u>Monitoring Programmes:</u> In support of the efforts of the contracting parties of the SC to routinely monitor POPs in the environment, Tang (2013) provided a review of analytical methods covering developments between 2008 and 2012, including sample preparation, clean-up and detection of 22 of the SC-listed POPs. The SC Global Monitoring Plan, in support of the implementation of the Convention, collects data on the SC-listed substances in human blood and milk, water and air; some of the regional supporting monitoring programmes report POPs concentrations in fish.

The UN Regular Process for Global Reporting and Assessment of the State of the Marine Environment, including Socio-economic Aspects held several Regional workshops in 2012 and 2013. Two of these, in Brussels (UNESCO-IOC, 2012) and in Brisbane (SPREP, 2013), provided updates on regionally available assessments, mainly

² very Persistent very Bioaccumulating

³ Anthracene is used to produce anthraquinone, a precursor used for bleaching and dyestuffs

⁴ Anthracene oil (paste) is used as an intermediate for the production of pure anthracene and carbazole. It is also used as an intermediate for the production of carbon black

³⁰ ● POLLUTION IN THE OPEN OCEANS 2009-2013

Table 2.5.1: Stockholm Convention listings of persistent organic pollutants (POPs)

	Annex A (Elimination)	Annex B (Restriction)	Annex C (Unintentional release)
0	riginal listing of POPs on the SC Annexes		
• • • •	Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, hexachlorobenzene, Mirex, Toxaphene, Polychlorinated Biphenyls (PCBs)		 Hexachlorobenzene Polychlorinated biphenyls (PCB) Polychlorinated dibenzo-p- dioxins (PCDD) Polychlorinated dibenzofurans (PBDF)
• • • •	 α- and β-hexachloroyclohexane (HCH) Chlordecone, Endosulfan (Technical) and its related isomers hexabromobiphenyl hexa- and heptabromodiphenyl ethers (commercial octabromodiphenyl ether) Lindane, Pentachlorobenzene tetra-, and pentabromodiphenyl ethers 	 Perfluorooctane sulfonic acid and its salts and perfluo- rooctane sulfonyl fluoride 	Pentachlorobenzene
P	OPs added to the SC Annexes in 2014		
•	Hexabromocyclododecane		
С	nemicals under review		
•	Short chained chlorinated paraffins Chlorinated naphthalenes Hexachlorobutadiene Pentachlorophenol and its salts and esters		

sourced from the GRAMED⁶ database. A survey of these sources revealed few new assessments of contamination in the marine environment with a bearing on the open oceans.

The Arctic Marine Assessment Programme (AMAP, 2010) and the Oslo and Paris Commission (OSPAR⁶, 2011 and 2012) both produced new assessments during the period reviewed here.

The UNEP-initiated Regionally Based Assessment of Persistent Toxic Substances (RBAPTS⁷)

project gathered data and assessed the sources, environmental concentrations, transboundary movement and effects of some of the above substances (UNEP, 2003); it has not been repeated in the interim.

2.5.2 Summary of new information

This section reviews the presence of some of the POPs and PBTs identified in the preceding section in open ocean biota. This aim is to determine whether or not the general lack of data on POPs in the open oceans has improved in the last 5 years, thereby facilitating future assessments.

⁵ http://www.unep-wcmc-apps.org/gramed/

⁶ OSPAR Coordinated Environmental Monitoring Programme Data http://dome.ices.dk/osparmime/main.html

⁷ http://www.chem.unep.ch/pts/regreports/regreports_ copy(1).htm

Recent assessments

Oslo and Paris Commissions (OSPAR): OSPAR Quality Status Report 2010^a is aimed at providing updated data for coastal zone management and is not a classical scientific assessment as such, although a large scientific database is central to its activities^a. In general, OSPAR monitoring stations are coastal in location and few if any are located in OSPAR Region V, i.e. the wider Atlantic.

Arctic Monitoring and Assessment Programme (AMAP): As part of the 2009 AMAP assessment, Riget *et al.* (2010) assessed available time series of legacy POPs in biota from the Arctic, covering freshwater fish, Arctic cod, seabirds, ringed seal,

beluga whale, polar bear and reindeer.

"Most of the analysed time-series of legacy POP compounds showed decreasing trends, with only a few time-series showing significantly increasing trends. Compounds such as α -HCH, γ -HCH and Σ DDT had a relatively high proportion of time series showing significantly decreasing trends; ΣChlordanes had the lowest proportion. β-HCH was an exception, where longrange transport through the ocean, and not the atmosphere, may explain several increasing trends that were detected in the Canadian Arctic. Moving east from the Canadian Arctic there was a trend towards a greater proportion of significantly decreasing trends."

They further reported that the trends observed in biota were consistent with those reported for Arctic air, where concentrations of legacy POPs are also decreasing (Hung *et al.*, 2010). They noted that recent decreases in air showed signs of levelling off which they interpreted as a possible indication that atmospheric concentrations are being less driven by primary sources and more by environmental processing and degradation.

As part of the same AMAP assessment, de Wit et al. (2010) provided a review of brominated flame retardants in the Arctic. They showed $\Sigma PBDE$ concentrations (their Fig. 14) in ringed seal blubber (Pusa hispida) to be ca. 60 at Svalbard, between 20 and 40 at E Greenland and Hudson Bay, but generally below 10 (ng/g lipid weight) across most of Arctic Canada and into Alaska. Ikonomou et al.,(2005) reported a temporal trend in PBDEs in ringed seals from Holman Island, W Canadian Arctic rising from ca. 0.5 in 1981 to between ca. 3 and 5.5 ng/g lipid weight) in 2000 to 2003. De Wit el al (2010) interpreted this as a stabilisation or even a recent decrease in SPBDE levels. The ringed seal is reported by Hammill (2009) to be circumpolar and found in the Baltic, Barents Sea, Hudson Bay, Greenland, the Bering Sea and the Sea of Okhotsk, feeding on fish and invertebrates. For

beluga (Delphinapterus laucas), de Wit et al., (2010, their Fig. 15) showed concentrations of ca. 70. measured at Svalbard and 20 to 50 ng/g lipid weight at most stations in Hudson Bay and across Arctic Canada. No temporal trends could be detected in beluga from the SE Beaufort Sea, for either Σ PBDEs (n = 17) or HBCD; the former peaked in 2001 at 23.7 and the latter at 2.2 ng/g lipid weight. However at Baffin Island, ∑PBDEs increased exponentially from 1982 to 2005 with a peak at 30 ng/g lipid weight and a doubling time of 11 years. The beluga or white whale according to O'Corry-Crowe (2009), inhabits the cold waters of the Arctic and sub-Arctic and are largely coastal feeders in spring and summer. They are thought to feed on polar cod but also on deep water benthic prev. These can be regarded as relatively low levels compared to some considered in the case studies further below.

Letcher *et al.* (2010) examined exposure to organo-halogen contaminants and their effects in Arctic wildlife and fish species. They reported that: "tissue concentrations in several arctic marine mammal species and populations exceed a general threshold level of concern of 1 part-per-million (ppm [1000 ng/g]), but a clear evidence of a POP/OHC-related stress in these populations remains to be confirmed. There remains minimal evidence that OHCs are having widespread effects on the health of Arctic organisms, with the possible exception of East Greenland and Svalbard polar bears and Svalbard glaucous gulls."

Butt et al. (2010) reviewed the concentrations of various PFCs in Arctic environmental compartments. They noted that in wildlife PFOS (see glossary) was generally the highest. Bossi et al. (2005) reported PFC levels in long-finned pilot whale (Globicephala melas) liver from the Faroe Islands collected in 2001, showing comparable levels of PFOS (28, 39 and 65) and PFOSA (43, 62 and 47 ng/g ww) for juvenile, adult females and adult males respectively. However, Butt et al. (2010) reported PFOS levels of up to ca. 350 ng/g (wet weight) in other studies with the same species from the Faroe Islands. PFOA was generally infrequently detected and present only at low concentrations in arctic biota. The majority of temporal trend studies are from the Northern American Arctic and Greenland and show generally increasing levels of PFCs from the 1970s, although some studies from the Canadian Arctic show recent declines in PFOS levels. In contrast, they reported that ringed seals and polar bears from Greenland continued to show increasing PFOS concentrations.

Other recent reviews/trend data: Braune et al. (2005) reviewed spatial and temporal tends of POPs and Hg in fish, seabirds and marine mammals from the Canadian Arctic, concluding that: "Concentrations of most legacy OCs (PCBs, DDT, etc.) significantly declined in Canadian Arctic biota from the 1970s to the late 1990s, and today are generally less than half the levels of the 1970s, particularly in seabirds and ringed seals. Chlorobenzenes and endosulfan were among the few OCs to show increases during this period while Σ HCH remained relatively constant in most species. They also noted that: "a suite of new-

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⁸ http://qsr2010.ospar.org/en/index.html

⁹ http://dome.ices.dk/osparmime/main.html

use chemicals previously unreported in Arctic biota (e.g. PBDEs, SCCPs, PCNs, PFOS and PFCAs)", has been recently found...". In reality, many of these had first been reported much earlier.

Houde et al. (2011) reviewed the monitoring of PFCs in a wide range of freshwater and marine biota, focussing in particular on polar bear, seals and dolphin, noting that: "High concentrations of PFCs continue to be detected in invertebrates, fish, reptiles, and marine mammals worldwide. PFOS is still the predominant PFC detected (mean concentrations up to 1900 ng/g ww) in addition to important concentrations of long-chain perfluoroalkyl carboxylates (PFCAs; sum PFCAs up to 400 ng/g ww). Several reports have indicated a decrease in PFOS levels over time in contrast to PFCA concentrations that have tended to increase in tissues of aquatic organisms at many locations. They reported that marginal PFOS and PFCA increases in adult harbour seal livers of the N.W. Atlantic were observed between 2000 and 2007, also indicating continuous sources of PFOS in this environment.

Law et al. (2012) reviewed temporal trends of POPs in blubber and liver samples from cetaceans stranded on UK coasts between 1990 and 2008. They describes the status of cetaceans (primarily harbour porpoises, Phocoena phocoena; n = 489), reporting that concentrations of the flame retardants PBDEs, HBCD, and the organochlorine pesticides HCB, 5HCH and Dieldrin had declined, while concentrations of PCBs had plateaued on Eastern, Western and Scottish coasts, following earlier reductions due to regulation of use. They concluded that blubber PCB concentrations were at toxicologically significant levels in many harbour porpoises and regularly occurred at even higher levels in bottlenose dolphins and killer whales, due to their higher trophic level in marine food chains.

Law et al. (2014) provided a global review of the flame retardants HBCDD and PBDEs in the environment at large. Decreasing time trends for penta-BDE congeners were seen at various locations for soils, sewage sludge, fish, marine mammals and many birds, while increasing time trends continued in polar bears and some birds at high trophic levels. However concentrations of BDE209 continued to increase. They identified a knowledge gap in relation to metabolism and/or de-bromination of BDE209 (to lower congeners) and HBCD in birds. They called for further monitoring of human exposure and environmental contamination in areas of e-waste recycling and concluded that further data on temporal trends of PBDE and HBCDD concentrations are needed before the current status and impact of regulation on these compounds can be fully assessed.

Lebeuf *et al.* (2007) reported on trends in 'legacy' PBT concentrations in the blubber of stranded beluga whales (n=86 adults from 1987 to 2002) in the St. Lawrence Estuary, Canada. Concentrations of most of the POPs (PCB, DDT, HCB, Σ HCH and Chordanes) examined in beluga had decreased by

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at least a factor of two (t1/2 = 15 years) between 1987 and 2002 while no increasing trends were observed for any of the other PBTs examined. They also noted that BDE-209 had surpassed the legacy PCBs and DDT as the top contaminant by concentration in some compartments, reporting that: *"limited biomagnification of BDE-209 in aquatic food webs reflects its high log Kow and preferential partitioning into the particle phase*. They considered that as a result, large environmental reservoirs of BDE-209 were being created in sediments, and that these sould present a long-term threat to biota because BDE-209 breaks down into more persistent, more bioaccumulative, more toxic, and more mobile PBDE congeners in the environment.

Kannan et al. (2000) derived a threshold for PCB-related health effects in marine mammals (17,000 ng/g lipid in blubber) based on captivefeeding studies of harbour seals (Phoca vitulina) and using immunological and endocrine endpoints. Recently, this threshold has been incorporated into risk assessments for cetaceans. For example, Jepson et al. (2005) found that, for harbor porpoises (Phocoena phocoena) having total PCB concentrations in blubber above 17,000 ng/g lipid, total PCBs were significantly higher in porpoises that died of infectious disease compared to those that died from acute physical trauma, while this was not significant with porpoises having PCB concentrations below that threshold. Hickie et al. (2007) demonstrated that nursing killer whales can go from being the least to the most contaminated members of the population in about 1 year because of the rapid transfer of POPs from the mother during lactation (Cockcroft et al., 1989). Growth may dilute the maternally acquired body burden thereafter.

Case studies on POPs in biota

In an attempt to investigate whether information on POPs in biota more relevant to the open oceans could be gathered, GESAMP has prepared a series of case studies focussed on organisms with an oceanic ecology, or coastal species from isolated areas far from local sources of contamination. In interpreting any contaminant body burden data, questions arise as to where the individuals had been in the years and months prior to sampling, on what they had been feeding and ultimately what the observed contaminant burdens represent in terms of exposure.

The case studies look briefly at selected species, swordfish, Atlantic cod, leatherback turtle, monk and harbour seals and killer whale, including their IUCN status, distribution, feeding habits, an estimate of trophic level, and their contaminant burdens. The studies are shown in detail at Annex III and key points derived from the studies are reflected in the conclusions below.

2.5.3 Future data requirements & rationale

POPs and PBTs in biota

The selection of specific POPs and PBTs for routine monitoring needs to be coordinated globally to better focus on the detection of geographical and temporal trends of legacy and, more importantly, emerging chemicals. The motivation is to detect and demonstrate the trends in emerging POPs earlier, in a way that is meaningful and convincing to policy makers. Investment in extended time-series will play an important role in detecting the effects of previous policy measures.

Where the selection of biota for monitoring is concerned, focusing on a limited number of species representative of upper trophic levels may provide better and more comprehensive trend data for global monitoring. Reports of POPs and PBT residues in biota are often fragmented, incompatible and difficult to interpret. A focus on species with well-studied lifestyles, including diet and migratory pattern, may provide a better understanding of contaminant exposures.

Where measurement of contaminant residues is concerned, the techniques used in tissue sampling should be specified, and preferably standardised (e.g. non-destructive (biopsy), hand necropsy); a focus on specific tissues would bring consistency and better inter-comparability between data sets, e.g. blubber and liver in marine mammals, blood and egg yolk in live turtles, liver or muscle in fish. Data should be expressed on a common basis – normalisation to lipid weight would provide a suitable basis for comparison.

The greatest unknown is still the effect of high contaminant burdens on the health of biota, in particular marine mammals. Often the decline in populations has driven the desire to investigate POPs as a potential causative factor. Further studies of health effects as a result of accumulated contaminant body burdens are needed to better understand the risks involved.

POPs in Microplastics

Seawater contains small concentrations of POPs such as PCBs, PBDEs, and PFOA have a very large water-polymer distribution coefficient ($K_{p/w}$), and thus plastics are very efficient at concentrating these pollutants, and large concentrations have indeed been reported, in some cases as large as those found in sediments at the same locations. This review covers the peer-reviewed literature on POPs in microplastics in the open oceans (beyond the continental shelf) published since 2007, the date of the latest study in the last review published by GESAMP (2009). Only 12 published and one paper in press, and one book chapter were found on POPs in microplastics, from 2010 to 2014.

A review of microplastics in the marine environment highlighted the fact that 75-80 million tonnes of plastic packaging are used each year and that there are no reliable estimates of how much enters the oceans (Andrady, 2011). There is no widely accepted definition of what microplastics are, since there are several different definitions in the literature, generally based on size fractions. There should be guidance on a general definition. Since plastics are inert to biota, the main concern is the potential for delivery of POPs to organisms through ingestion. There are various possible types of toxic substance that may be present and released:

- residual monomers from the manufacture process;
- toxicity of intermediates from the partial degradation of plastics;
- POPs absorbed within the microplastics.

The presence of plastics is worldwide (Baztan et al., 2014). A recent review stressed the importance of microplastics as sinks and transfer mechanisms of POPs into biota, particularly for remote areas (Engler, 2012). In one such area, as adjacent to islands in the Canary current, microplastics were found at concentrations exceeding 100 g of plastic L⁻¹ of sediment. A study in the Pacific Ocean. and one location in the Caribbean Sea, reported concentrations of PAHs, PCBs, PBDEs, DDTs, alkylphenols and bisphenol A in the concentration range of 1 to 10,000 ng/g. There was no spatial pattern for any of the pollutants analyzed (Hirai et al., 2011). Polysterene plastic has also been identified as a source of PAHs in the marine environment (Rochman Chelsea M., Manzano Carlos, Hentschel Brian T., Massey Stacy L., and Hoh, 2013).

Background concentrations of POPs in plastic pellets from remote islands were established for the International Pellet Watch (Heskett et al., 2012). Concentration ranges for PCBs (sum of 13 congeners) were 0.1 to 9.9 ng/g, about three orders of magnitude lower than the concentrations around industrialized coasts. DDTs were in the range 0.8 to 4.1 ng/g, and HCHs were from 0.6 to 1.7 ng/g, except for one place (St. Helena) where there is use of the insecticide lindane. These concentrations can be compared with those found by the same project from 30 beaches in 17 countries (Ogata et al., 2009); as expected, concentrations in pellets from beaches close to harbours, urban areas and tourism developments are orders of magnitude higher than those from remote beaches and islands.

The trophic transfer of POPs from microplastics to biota has been demonstrated. Pyrene contained in polysterene microspheres (0.5 μ m in diameter) was transferred from mussels (*mytilus edulis*) to crabs (*Carcinus maenas*) (Farrell and Nelson, 2013). The microspheres were translocated to the haemolimph, pancreas, ovaries and gills of the crabs. This study shows for the first time that trophic transfer of plastics is possible, and also the transfer of POPs in the plastics. The latter was also demonstrated

for seabirds ingesting plastics (Tanaka et al., 2013). PBDEs were analyzed in abdominal adipose tissue of short-tailed shearwaters (Puffinus tenuirostris). Higher-brominated congeners (BDE-209 and BDE-183) were detected in the birds and plastics but not in the natural prey, showing that plastics were the source of these compounds. Bioaccumulation of PCBs in polystyrene microplastics by the lugworm (Arenicola marina) was also reported (Besseling, Wegner, Foekema, Heuvel-greve, and Koelmans, 2013); reduction of feeding activity and weight loss were the main effects observed. Bioaccumulation of POPs associated with plastic debris by myctophid fish was examined at remote sites in the South Atlantic (Rochman et al., 2014). Fish sampled at localities with greater plastic densities had significantly higher concentrations of high brominated PBDEs (i.e. BDE 183 to 209), suggesting that the higher brominated congeners of PBDEs, added to plastics as flame retardants, are indicative of plastic pollution in the oceans.

A model of plastics as carriers of POPs has been developed. The model takes into consideration the dilution of exposure by sorption of POPs into plastics ("dilution"), bioaccumulation of POPs in plastics ("carrier"), and decreased bioaccumulation by the ingestion of clean plastics ("cleaning") (Koelmans *et al.*, 2013). Results show that plastics with low affinity for POPs (polystyrene) will have a marginal effect, dominated by the "dilution" factor, whereas for stronger sorbents the other effects are stronger. In open marine systems the model predicts a decreased effect due to a cleaning mechanism that counteracts biomagnification. From a risk assessment perspective, the differences are considered to be small.

2.5.4 Conclusions

- 1. Suitable analytical methods are available for all major groups of POPs. In view of the occurrence of currently used chemicals in remote locations, there is a need to extend the groups of chemicals measured in ocean compartments.
- 2. Sustained monitoring of biota in space and time remains essential; this has been stressed by almost all assessments on the contaminant status and health of marine biota in recent decades. Priority in monitoring should be given to spatial and temporal continuity, both to detect contaminant decreases in response to management measures and to detect any new contaminants as early as possible.
- 3. It is clear from a survey of open ocean species (or coastal species which find themselves to a greater or lesser extent in the open oceans), that focusing on the contaminant status of a species over part or all of its range can provide unique insights into the fate of chemicals of concern; such an approach could provide vital information for future marine environmental assessments.
- 4. Since 2009, there has been progress in the identification, hazard evaluation and risk

assessment of POPs, PBTs and CFCs, in addition to modest but significant developments in monitoring such substances in the marine environment, mainly in the Northern hemisphere.

- 5. From the case studies described, distinct differences can be seen in POPs' burdens between geographic locations, in particular high levels in Monk seals, swordfish and killer whales close to industrial and population centres such as the Eastern Mediterranean and California. However, these are migratory species and the exposures leading to such body burdens are not always obvious. Data from species with truly open ocean life-histories in remote locations, such as the swordfish and the relatively low trophic status leatherback turtle. generally show low POPs levels, although these are still not negligible. The apparently downward trends in many POPs found in Atlantic cod and British Columbia harbour seals are encouraging, although concentrations in some populations of killer whale remain very high.
- 16. As might be expected, contaminant levels in open ocean biota seem generally to be lower compared to conspecifics in coastal areas. Confounding factors are the paucity of information on the diet and migratory patterns leading to exposure in many populations. In addition to atmospheric deposition and other biological factors pointed out by GESAMP (2011, Annex VIII), local pollution sources, even in remote areas, can strongly influence tissue concentrations.
- 17. The Arctic has been well studied and shows strong indications of decreasing trends in biota of PCBs, DDT and many of the 11 original SC listed POPs. However, some currently used chemicals such as PFC's, BDE-209, and more recent POPs such as HBCDD, seem to be increasing to significant levels in some biota. The highest levels observed are generally close to centres of industry and population.
- 6. Reports of health effects due to POP body burdens in biota are generally not specific or convincing, even in marine mammals.
- There is a need for a general definition of 7. microplastics to improve the comparability of scientific findings on this topic, 'Microplastics' have been detected in the open oceans and on remote beaches and islands and would appear to be a worldwide problem. The transfer of microplastics through marine food chains, along with the POPs absorbed on to them, has been demonstrated. POPs absorbed onto or within microplastics can be toxic to marine animals. Concentrations of POPs in microplastics close to pollution sources are very high in comparison with those from remote areas and open seas and can be of the same order of magnitude as those found in sediments in those areas; such high concentrations may pose a significant risk to marine biota.

2.6 Noise

2.6.1 Introduction

Human activities have accidentally and intentionally increased the level of sound in the oceans (Hildebrand, 2009). Shipping and offshore oil exploration and production activities create low-frequency sound waves that can travel great distances underwater. Furthermore, the use of higher frequency sound sources such as sonar by ships, military operations, fishing and research activities (e.g. for bottom scanning) adds considerably to local noise. In general, as we expand industrial activities in the ocean, this increases "acoustic pollution" of the oceans.

Shipping is the largest anthropogenic 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. When sound from shipping enters a deep ocean sound channel, it can affect the ambient noise hundreds and even thousands of km away from the source. The cumulative effect of these distant sources has been to increase the average deep-water ambient noise level 10-100 fold in frequencies of ~20-200 Hz, a band that is important for whales, fish and invertebrates. This is a striking change in global deep ocean noise, which pervades every ocean. Given the importance of shipping for international commerce, the amount of ocean noise at shipping frequencies tends to correlate with economic activity (Frisk, 2012), with a clear trend of continued increase - a doubling of intensity over each of the last few decades in some sites (Andrew et al., 2002; McDonald et al., 2005).

2.6.2 Summary of new information

The introduction of noise into the marine environment has been shown to have impacts on a broad array of marine species, particularly those species which use sound for communication, navigation, avoidance of predators and searching for food; the importance of sound for these species and their sensitivity to sound mean that anthropogenic noise can have harmful effects. Exposure to anthropogenic sound in the ocean can cause physical injuries, disrupt behaviour, mask communication or other biologically important signals, affect species' abilities to hear at certain critical frequencies, increase their sensitivities to disturbance or cause stress leading to negative physiological effects. These effects are reviewed in Richardson et al. (1995), the National Research Council (2003), Southall et al. (2007), and Nowacek et al. (2007). Increasing concern about long term effects of sound on populations and ecosystems led the National Research Council (2005) to urge development of methodologies to determine whether the effects are biologically significant to individuals or populations. There has also been growing interest in studying whether noise may cause ecosystem

effects, by testing whether high noise levels in a habitat are associated with reduced biodiversity (Parks *et al.*, 2013).

The impacts on cetaceans (whales and dolphins), which have a much broader range of hearing (both ultrasonic and infrasonic) than humans, have been of greatest concern to marine biologists (Figure 2.6.1). But noise can also affect other marine mammal species, marine fishes, reptiles, cephalopods, decapod crustaceans, and perhaps other marine animals and, by influencing the behaviour of individual species, might even disrupt entire ecosystems. Baleen whales, most acoustically sensitive invertebrates and fish are sensitive to low sound frequencies, which can travel long distances in seawater. These species are most likely to be affected by long-term increases in low frequency ambient noise, while many other species are at risk of adverse effects from exposure to intense or frequent higher frequency sound sources. Some of these effects may have economic impacts. For example, Engas et al. (1996) found a 70% reduction in catch of cod and haddock within about 30 km of a seismic survey, with no increase for 5 days after the survey stopped. More scientific research papers examine the impacts of sound on marine mammals than other taxa, and marine mammals have greater protection than other marine species in many jurisdictions, but other species are sensitive and may prove especially tractable for studying masking, hearing and physiological effects (e.g., Regnault and Lagardere 1983; Smith et al., 2004; Vasconcelos et al., 2007) and their consequences for populations. Some fish and invertebrate larvae use sound to select habitats for settlement (Tolimieri et al., 2000; Montgomery et al., 2006); noise may affect ecosystems if it alters settlement patterns.

Several reviews of the scientific literature on ocean noise and its effects on marine life have been published: Richardson et al. (1995), the National Research Council (2003), Riegler (2006), Southall et al. (2007), and Nowacek et al. (2007). Southall et al. (2007) provide a detailed review of sound exposure levels that pose a risk of injury to marine mammals, and they tabulate most behavioural effects of sound on marine mammals reported to that date. Recent work has been able to quantify acoustic dosage: behaviour response functions for some sounds and marine mammal species (Miller et al., 2014). Popper and Hastings (2009) review the effects of anthropogenic sound on fishes. Fewer reviews are available on effects on other vertebrate taxa, on invertebrates or ecosystems, primarily because evidence is scanty for these topics. Turtles have been observed to exhibited avoidance behaviour when subject to low frequency sound from seismic surveys (Dow Piniak et al., 2012). Noise has been shown to distract hermit crabs, making them more liable to predation and result in lower food intake in lobster (Meyer-Rochow et al., 1982).

Various governmental commissions and nongovernmental groups have reviewed the scientific



Figure 2.6.1: Beaked whales stranded in the Canary Islands within 24 hours of nearby naval manoeuvres involving sonar, March 2000. [Credit: Vidal Martin]

literature on impacts of ocean noise on marine ecosystems and, in particular, marine mammals, from a policy perspective. A selection of these is listed at the end of the References for the noise section.

2.6.3 Future data requirements and rationale

Most of the commissioned assessments on ocean noise call for further research on the impacts of noise and call for action to reduce noise to minimize these impacts. There remain large gaps in the scientific knowledge about the actual impacts of noise. A critical information gap relates acoustic exposure to probability of specific impacts. There have been few attempts to systematically measure or monitor noise levels over large time and spatial scales. 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. Given the extent of current ignorance, such a precautionary approach may restrict societally important activities such as international trade, energy exploration, and anti-submarine warfare. On the other hand, our

ignorance of what sounds cause what impacts also poses a risk of unintended harm to marine ecosystems and endangered species.

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 noisecreating 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 programme 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. There is an urgent need for those planning global ocean observing systems to incorporate acoustic monitoring sufficient to estimate ocean noise on scales useful for predicting impacts on marine life. These data should be openly available to managers and decision makers in industry, the military and regulatory agencies.

2.6.4 Conclusions

As the CBD reports: "Anthropogenic noise has gained recognition as an important stressor for marine life and is now acknowledged as a global issue that needs addressing." [UNEP/ CBD/SBSTTA/16/INF/12 page 2] By the 1960s, the average deep-water ambient noise level has increased 10-100 fold in frequencies important for whales, fish and invertebrates, and is continuing to double in intensity every decade in some sites. This global change in the deep ocean is accompanied by more localized impacts of offshore and coastal developments, including intense sounds from oil and gas exploration and naval sonar. 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. The resulting scientific uncertainty makes it difficult to balance the need for precaution in protecting marine ecosystems against the potentially large costs to socially important activities such as commercial shipping, offshore energy, and military readiness. Numerous measures have been recommended for mitigation of noise, but there are no systematic programmes to assess or monitor actual noise levels in the oceans at

scales useful for predicting impacts on marine life. We urge that such a monitoring programmes for noise should be incorporated into planned global ocean observation programmes. There is also an urgent need for expanded research on the impact of anthropogenic noise on marine life. Particular attention must be paid not only to cumulative long term effects, but also to synergy between different ways humans are changing marine ecosystems. For example, noise may both disrupt animals that use sound on ocean reefs and may also mask these sounds from larvae that use reef sound to home in on areas for settlement. The combined effects may have a larger impact on reef ecosystems than either alone. Humans can also affect ocean acoustics in unanticipated ways. Ocean acidification is increasing sound propagation, but the extent of this effect on ocean noise is just beginning to be addressed (Brewer and Hester 2009; Udovydchenkov et al., 2010).

2.7 Marine Debris

2.7.1 Introduction

In the present context, marine debris is defined as: 'any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment' (UNEP, 2009). This may include wood, metal, ceramic/brick, fabric and plastic. The sources of marine debris are many and varied but may be described as having either a land-based (e.g. tourism, industry, tsunamis) or seabased (e.g. shipping, fisheries, historical dumping origin).



Figure 2.7.1: Number of publications and reports discovered by on-line searches using the terms 'plastic pellets' and 'microplastics', 1972-2013. (Compiled by Sarah Gall, Univ. Plymouth for GESAMP WG40).

It is sometimes claimed that 80% of marine litter has a land-based source. Unfortunately, there is very little foundation to this assertion, and it is only true to the extent that most manufacturing takes place on land. Beach surveys carried out close to urban centres or tourist resorts may appear to provide supporting evidence of a land origin, but these can be misleading. For example, in one study of the source of litter on a beach in northern Australia it was concluded that 85% was contributed by commercial fishing, merchant shipping and recreational boating (Whiting, 1998). Clearly, *much* of the debris originates from land but the absolute and relative quantities from particular sources depend on many different factors.

The movement of marine debris has a strong transboundary element. This includes debris in rivers transported across national boundaries, river inputs to coastal waters and exchanges between neighbouring EEZs, LMEs and the open ocean, reaching the most remote maritime regions on the planet (Barnes *et al.*, 2010). This is most obvious for drifting materials with a clear land-based origin, but will apply to any materials capable of being transported, either at the time of entry or following a period of weathering and disintegration.

The topic of marine debris in the open ocean was covered in Reports & Studies No. 79 (GESAMP, 2009). The conclusion was drawn that floating plastics and fishing gear, including plastic resin pellets used during plastic manufacture, were widespread and posed the greatest ecological risk. At the time there was perceived to be a lack of information on the detailed distribution of debris, with reliance placed on observations from remote mid-ocean islands. It was noted that there was reliable evidence that marine litter could affect some species, such as cetaceans and sea turtles, by physical entanglement. However, it was concluded that the impact at a population level and wider ecological effects were unknown.

2.7.2 Summary of new information

There has been a significant increase in knowledge in the past 5 years regarding sources, distribution, fate and effects of marine debris, accompanied by an increase in publications; for example, papers describing the distribution of plastic resin pellets and micro-plastics (Figure 2.7.1). GESAMP established a Working Group in 2014 (WG40) to consider 'Sources, fate and effects of microplastics in the marine environment a global assessment'; it is due to report in November 2014. In addition, two sub-groups were established under the GEF Transboundary Waters Assessment Programme (http://www.geftwap.org) to investigate: i) the distribution of floating macroand micro-plastics in the open ocean and LMEs; ii) POPs in plastic resin pellets. These are reported separately both in the main TWAP report, and via an on-line web-portal developed by UNESCO-IOC (www.onesharedocean.org).



Figure 2.7.2: World plastics production 1950-2012. Includes thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coating and sealants and PP-fibres. Not included PET- and polyacril-fibres. Source: PlasticsEurope (PEMRG)/Consultic downloaded from: www.plasticseurope.org

Trends in underlying factors influencing the generation of marine litter

Many factors influence the quantities of debris entering the marine environment including inadequate infrastructure for waste management, expanding coastal populations, increasing urbanization, growth in coastal tourism & the cruise industry and increased aquaculture production. World plastics production has increased exponentially since the 1960s (Figure 2.7.2).

Availability of data¹⁰

The most extensive data on marine debris comes from beach surveys and clean-ups. These are often organised at a local level but may form part of a much larger initiative, such as the International Coastal Clean-up organised by the Ocean Conservancy (http://www.oceanconservancy. org/our-work/international-coastal-cleanup/) based in the USA. They provide a useful indication of the relative quantities of debris washed up or directly deposited on the shoreline. However, such

¹⁰ All major sources of available data on the distribution of floating macro-debris from direct observation, and on floating micro-debris from towed nets, has been compiled as a separate activity under the TWAP and can be accessed from the UNESCO-IOC on-line data portal or by downloading the TWAP Open Ocean and LME reports (IOC Technical Series, 119).

data are not wholly representative of the types, quantities and sources of marine debris overall. For example, inaccessible or remote shorelines are under-represented, and the results provide no indication of debris lying on the seabed.

The difficulties of acquiring data at-sea are considerable, especially in the open ocean. Until quite recently, data on marine litter were collected opportunistically, for example on cruises for purposes of fisheries research and plankton ecology, or as part of oceanographic training programmes (e.g. Sea Education Association, www.sea.edu). More recently, a number of not-for-profit organisations, or NGOs, have undertaken cruises designed to collect data and raise awareness of the widespread occurrence of plastic debris in the open ocean, (e.g. 5 Gyres, http://5gyres.org/; Algalita Marine Research Institute, http://www.algalita.org/index.php). Most of these surveys employed towed plankton nets (e.g. Manta trawl, neuston net) with a 330 µm mesh.

Information on floating macro- and microplastic, from published and unpublished sources, is to be collated by the TWAP sub-group on *Indicators of floating plastics* (see above); this will include a comprehensive description of metadata, together with maps of sampling locations. However, difficulties have been encountered in obtaining some datasets from the 1970s and 1980s. In other cases details of sampling methods or locations (lat/ long) appear to have been lost.

Information on the distribution of debris on the seabed is even more limited. There have been a number of focussed expeditions but, in general, observations have been made in connection with other activities, such as routine surveys of demersal fish stocks or ecological studies of the seafloor.

Spatial distribution of debris

Floating macro-plastics: The abundance of floating macro-debris is usually estimated from direct visual observations from ships (Figure 3). Observations from planes tend to be restricted to tracking debris from a particular event (e.g. ship wreck, lost aircraft, storm, tsunami). Ryan (2013) has compiled a table of studies of macro-debris distribution covering all ocean basins with the exception of the Arctic (Table MD1). Observations have often been made by research vessels in passage, or carrying out unrelated oceanographic studies. It is inherently difficult to make quantitative estimates of the number of items of floating debris by direct observation, due to a number of factors, for example: size of object, sea state, direction and intensity of light, height of observer above the sea surface, degree of flotation/waterlogging, and distance from the vessel. Attempts are being made to adopt a more rigorous approach, such as restricting observations to those within a defined distance from the vessel (Ryan, 2013).

Growing evidence suggests that certain regions, such as the Bay of Bengal and Indian Ocean, may experience a higher proportion of macro-debris than others. This may reflect the intense population pressures in the region, lack of infrastructure and influence of circulation patterns, such as the Indian Ocean Gyre. Similar recirculation features occur at smaller scales. For example, the Gulf of Carpentaria off northern Australia experiences a clockwise gyre circulation during the south-east trade winds (May – September). This results in an abundance of abandoned or lost fishing gear, largely gill nets, entering the region from Taiwan, Indonesia, Malaysia and Korea (www.ghostnets.com.au).

Floating micro-plastics: Observations of small plastic particles were first reported in the early 1970s off the western coast of the USA, with the authors noting the relative abundance of expanded polystyrene. Similar observations were made in UK coastal waters shortly afterwards. Most early reports referred to a preponderance of plastic resin pellets. In the past decade, interest has grown rapidly and the topic has attracted increased concern (Andrady, 2011). Micro-plastics are usually collected using a towed plankton net (Figure 2.7.4) with a 330 µm mesh, although earlier studies used slightly coarser meshes (e.g. 500 µm). Methods used for the collection, identification and quantification of microplastics have been critically reviewed (Hidalgo-Ruz, et al., 2012).

The most comprehensive dataset on microplastics is for the western Atlantic and was compiled by the US-based Sea Education Association (SEA) (http://www.sea.edu/). Samples collected on annual research training cruises over a twenty-two year period and involving 7,000 students were been stored and catalogued, allowing the material to be re-examined for the presence of micro-plastics



Figure 2.7.3: Floating debris from ship-based observations, the Straits of Malacca: left, 16 km offshore; right, 48 km offshore (Ryan, 2013, reproduced with permission).

(Figure 2.7.5). The data revealed the influence of the major circulation patterns in the region, with highest concentrations (> $2^{*}10^{5}$ items km⁻²) occurring consistently towards the centre of the North Atlantic subtropical gyre. Most of the items (99%) were composed of polymers with a density lower than ambient seawater (0.0265 g ml⁻¹: Morét-Ferguson *et al.*, 2010).

This region of the western Atlantic is characterised by the presence of the floating macro-alga *Sargassum*, which is also subject to the ocean circulation. However, the highest concentrations of micro-plastics and drifting *Sargassum* do not coincide, implying additional factors are involved (Amy Siuda, Sea Education Association, pers. comm.) Other organisations and institutes have increased the frequency and spatial coverage of sampling for micro-plastics, confirming their occurrence in all five major ocean gyres; however, sampling has been limited to a relatively small number of transects for logistical and financial reasons (e.g. http://5gyres. org/; http://www.algalita.org/index.php).

An equivalent eleven-year SEA dataset is now available for the northeast Pacific (Law *et al.*, 2014). Over 2,500 plankton tows were analysed in the period 2001 – 2012, with maximum concentrations (>10⁶ tems km⁻²) occurring in the centre of the North Pacific subtropical gyre. Microplastic distributions show a number of scales of spatial variability. The most obvious pattern is related to large-scale ocean circulation, with significantly higher concentrations in the open ocean occurring in the major ocean gyres. Higher concentrations can occur in coastal waters according to the locations of coastal sources.

Table 2.7.1: Mean (and maximum) density of large floating litter items (number km-2) at sea estimated by direct observation; a = Aerial surveys, b = Items < 100 cm sampled with nets. Minimum size is the smallest item size recorded (from Ryan, 2013).

Region	Year	Mean density/ number.km ⁻² (maximum)	Minimum Size (cm)	Source	
Mediterranean	1979	2000	1.5	Morris (1980)	
Mediterranean	1986	0.12	_	McCoy (1988)	
Mediterranean	1997	31.9 (68)	_	Aliani <i>et al.</i> (2003)	
Mediterranean	2000	-23	_	Aliani <i>et al.</i> (2003)	
Nova Scotia	1990	20.1 <i>(31)</i>	-	Dufault and Whitehead (1994)	
North Atlantic	1993	0–20	10	Barnes and Milner (2005)	
South Atlantic	1993	0–10	10	Barnes and Milner (2005)	
North Pacific	1972	4.2	-	Venrick et al. (1973)	
North Pacific	1984–1988	3.6 (15)	2.5	Day et al. (1990)	
North Pacific	1986–1991	0.4 (4.6)	5	Matsumura and Nasu (1997)	
Northwest Pacific	2009	815 <i>(6334)</i>	2	Titmus and Hyrenbach (2011)	
Sea of Japan	1984–1988	10.5 <i>(33)</i>	2.5	Day <i>et al.</i> (1990)	
Sea of Japan	2002	0.4 (3)	5	Shiomoto and Kameda (2005)	
Gulf of Mexico ^a	1992–1994	1.0-2.4	10	Lecke-Mitchell and Mullin (1997)	
W Cape, S Africaª	1985	1.6–19.6	20	Ryan (1988)	
Agulhas Current	1987–1988	0.1 (1)	5	Ryan (1990)	
Chilean coast	2002	11.3 <i>(54)</i>	-	Thiel <i>et al.</i> (2003)	
Chilean fjords	2002–2005	20 (240)	2	Hinojosa and Thiel (2009)	
South China	2009–2010	4.9 (17)	<1 ^b	Zhou <i>et al.</i> (2011)	
Bay of Bengal	2012	8.7 (40)	1–2	Ryan (2013)	
Bay of Bengal	2012	4.9 (22)	5	Ryan (2013)	
Straits of Malacca	2012	578 (4385)	1–2	Ryan (2013)	
Straits of Malacca	2012	219 (2932)	5	Ryan (2013)	



Figure 2.7.4: Manta net (330 µm, typically used for sampling microplastic particles (image courtesy of Richard Thompson, Univ. Plymouth)

In the open ocean, further smaller-scale spatial heterogeneity has been observed, with significant variability being detected at the sub-mesoscale (10s of km) (Goldstein et al., 2013). Some of the variability observed in the data is due to conditions during or immediately prior to sampling. Under calm conditions buoyant plastic fragments will concentrate at the sea surface; during wind events they become mixed over the upper few metres of water, depending on wave energy and duration. This can reduce the observed surface concentration by as much as a factor of ten. Even in calm conditions, microplastic fragments can become concentrated at the sea surface in ribbon-like convergent zones (Kara Lavender Law, pers. comm.), a phenomenon that can be due to either frontal systems or internal

waves. A similar effect can be caused by windrows. Concentrations within these convergent zones will be much higher than the mean concentration in the area.

Reports of sub-surface floating debris are more limited. Plastic fragments have been observed by re-examination of the sampling screens used for the Continuous Plankton Recorder (CPR) (Thompson *et al.*, 2004), a long-standing survey of zooplankton composition and abundance using 'ships of opportunity' such as ferries or trans-ocean cargo vessels (http://www.sahfos.ac.uk).

<u>Seabed debris:</u> Most scientific observations of seabed debris in the open ocean have been made opportunistically, as part of research investigations



Figure 2.7.5: Extract of currently available SEA North Atlantic data on microplastics (Law *et al.*, 2010), by year (1986-2008), from http://www. geomapapp.org/dataholdings/gmadata.php?page=datasets (downloaded ~10th July 2013, B. Combal, UNESCO-IOC)

into seabed biology or biogeochemistry. There have been some dedicated surveys, such as a collation of information on debris distribution on continental shelves NW Europe and in deep waters of the Mediterranean, using a variety of trawls and direct observations using submersible vehicles, revealing the widespread distribution of a variety of debris composition, including fishing gear (Galgani et al., 2000; Sanchez et al., 2013). Debris consisting of fishing gear and miscellaneous plastic items has been found at abyssal depths (Galgani & Lecornu, 2004), on continental slopes and seamounts (Sőffker et al., 2011) and in canyons leading off the continental shelf in the Mediterranean (Galgani et al., 1996;) off the coast of Portugal (Mordecai et al., 2011) and off the coast of California (Schlining et al., 2013), using a variety of sampling and image capture techniques. Debris has been observed in deep water at significant distances from places of habitation. For example, Bergmann and Klages (2012) reported an increase in seafloor debris, over the period 2002 to 2011, at approximately 2500 m in the Fram Strait, between Svalbaard and Greenland. Hoever, it is unclear whether this is representative of the wider region.

Perhaps the greatest potential to routinely gather additional data comes from utilising existing fisheries management surveys, using demersal gears, although this is usually restricted to continental shelves. Trawling may occur and is performed on slopes, down to -800 m, for litter surveys (Galgani et al., 1996 & 2000, Watters et al., 2012, Sanchez et al., 2012). In shallower water, larger items can be identified by acoustic or visual methods, allowing retrieval to be attempted where this can be justified.

Temporal trends

It is inevitable that the total quantity of manmade debris in the ocean has been increasing over recent decades, as a result of society's inability or unwillingness to impose more effective measures to control its release. But, it has proved difficult to quantify the increase from observations at sea. The most extensive data on floating microplastics (spatially and temporally) have been provided by the Sea Education Centre for the northwest Atlantic and northeast Pacific, and an attempt has been made to analyse this dataset to establish underlying temporal trends in spatial extent or mean concentration. Unfortunately this has been problematic due to the variable sampling positions and regions sampled on each research cruise, and it remains an area of active research. A power analysis of a smaller dataset of floating plastic from the northeast Pacific led to the conclusion that it would be difficult to detect changes in abundance without a substantial sampling effort (Goldstein et al., 2013). Thompson et al. (2004) did report a step-change increase in micro-plastic fragments in CPR samples, from the NE Atlantic, between those collected in the 1970s and 1980s and those collected more recently, but this one of the few convincing examples. Sampling

of biota has provided an additional source of information, with changes over time being reported in the type, but not in the total quantity, of plastic ingested in by northern fulmars Fulmaris glacialis in the Greater North Sea (van Franeker et al., 2010) and short-tailed shearwaters in the south-eastern Bering Sea (Vliestra & Parga, 2002). In general, there is evidence of a decrease in 'industrial' sources, such as plastic resin pellets used for transportation by the plastics industry but an increase in consumer plastics.

Impacts of marine debris

Entanglement and ingestion of macro-debris: Incidents of entanglement have been widely reported for a variety of marine mammals, reptiles, birds and fish. In many cases this leads to acute and chronic injury or death. A major review has been conducted recently on the impacts of marine debris on biodiversity, on behalf of the Secretariat of the Convention of Biological Diversity (SCBD-STAP-GEF, 2012). The authors concluded that marine debris was having a substantial impact of individuals, populations and ecosystems. Three examples were given where marine debris may represent an important contributor to species level decline and extinction: Hawaiian Monk Sea Monachus schauinslandi, Loggerhead turtle Caretta caretta and White Chinned Petrol Procellaria aequinoctialis. Evidence of ingestion often comes from the dissection of beached carcasses, which represent an unknown proportion of the total number of individuals affected. Turtles and toothed whales frequently are found to have large quantities of plastic sheeting and plastic bags in their gut compartments (e.g. Campani et al., 2013; de Stephanis et al., 2013: Lazar & Gracan, 2011). The physiology of some species of turtles and toothed whales makes it is extremely difficult for the animal to eliminate the material once ingested. Ingestion of debris has been reported in 46 (56%) of cetacean species with rates as high as 31% in some species (Baulch & Perry, 2014).

Habitat damage: Damage can occur to sensitive habitats when debris smoothers, becomes entangled or is transported by currents or wave. It is most obvious in shallow waters and can lead to significant disruption of warm-water corals and seagrass beds. However, damage has also been observed in deeper waters, principally due to derelict fishing gear (Figure 2.7.6).

Rafting of non-indigenous species: Artificial surfaces in the ocean form a substrate for a wide variety of sessile organisms. The durability of plastic, and other man-made debris, allows it to be transported from the point of origin over long distances, together with any organisms growing on the surface. There are many reported instances of the introduction of non-indigenous species adhered to marine debris, or otherwise using marine debris as a habitat: bivalves, Bryozoa,

cephalopods, Cnidaria, crustaceans, echinoderms, fish, gastropods, macroalgae, pelagic insects, phytoplankton, polychaetes and porifera (e.g. Thiel & Gutow, 2005; Gregory, 2009; SCBD-STAP-GEF, 2012; Goldstein *et al.*, 2012).

Potential physical effects of micro-debris: Micro-debris can be ingested by a wide variety of filter-feeding organisms, ranging in size from zooplankton (Cole *et al.*, 2013) to large baleen whales (Fossi *et al.*, 2012). Some organisms have effective systems for removal of unwanted particles. However, there is some evidence of nano-sized particles causing an inflammatory response (Browne *et al.*, 2008; van Moos *et al.*, 2012). The extent to which translocation across membranes may occur, and whether this is likely to be significant at the concentrations typically found in the environment, reamains uncertain, and this is an area of active research.



Figure 2.7.6: Rope and fishing net enveloping a coldwater reef off the coast of Ireland, 700m water depth (image courtesy of Jason Hall-Spencer, Univ. Plymouth)

Potential chemical effects of micro-debris: Micro-plastics can contain two classes of contaminants: i) chemicals which are deliberately added to the polymer to modify its properties, such as flame retardation, UV resistance and flexibility; and, ii) contaminants in the water column which become absorbed into the polymer structure, such as PCBs, DDT and other persistent, bioaccumulating compounds (http://www.pelletwatch.org/). Both types of chemical may have eco-toxicological effects if they desorb from the polymer once ingested, depending on the kinetics of the reaction and the internal chemical and physical properties of the host organism (Teuten et al., 2009). Update of contaminants from plastics has been demonstrated in laboratory studies. However, organisms are also exposed to contaminants in the water column and in prey species. This adds complexity when attempting to quantify the extent to which contaminants may transfer into organisms via micro-plastic ingestion in the open ocean (Rochman et al., 2014). Recent studies, which have examined the chemical signature of contaminants in both typical prey species and ingested plastics, and compared this with the signature of contaminants in the host organism,

have provided some evidence that such transfer is taking place in some organisms (Tanaka *et al.*, 2013; Rochman *et al.*, 2014). This will be further reported by GESAMP WG40.

2.7.3 Future data requirements and rationale

There is a need for greater quantification of the spatial extent and temporal trends of debris at or near the sea surface, in mid-water and on the seabed. This requires greater emphasis on sampling methodologies and harmonisation, the causes of sampling variability and environmental conditions that may influence the observations (e.g. sea state, lighting conditions). There would be great benefit in developing more automated systems for sample collection and debris identification, including underway water sampling and image capture and automatic image analysis for both floating macro-debris and micro-debris. Greater use can be made of existing monitoring systems, such as the Continuous Plankton Recorder for nearsurface (~ 10 m depth) water sampling and fish stock management cruises of demersal fisheries for recording seabed debris. The use of volunteer recording schemes should be encouraged and facilitated, by providing guidance and report forms (paper and electronic) in the fisheries, commercial shipping and recreational boating sectors.

Ocean circulation models are being used to predict and help interpret the relatively sparse observational data. This approach can be extended to allow higher resolution modelling of meso-scale features, distinguish different types and behaviours of debris and introduce vertical transport. The use of proxy sources of debris provides a helpful approach where data on actual input sources is lacking, which is generally the case. This could be further developed and refined, introducing additional sources (e.g. fisheries), and allowing the potential effects of debris reduction measures to be tested.

The impacts of macro-debris on many species are well documented. Here the emphasis must be on harm reduction, in particular for vulnerable species or sensitive habitats. This will require a complex response, involving many different actors, using a combination of education, voluntary practises (types of gear, location, returning waste to port) and legislation. It is very unlikely that legislation alone will be sufficient, especially where practises take place in remote regions or at sea, where enforcement is difficult. Where harm may be harder to establish, such as for micro-debris, then the research community has a role in adding to and establishing the significance of the emerging evidence on potential effects, particularly taking account of population effects and trophic transfer, including possible transfer to humans. Laboratory results need to be placed in an environmental context, taking heed of latitudinal and other regional differences in sources, pathways and biological endpoints. So far, very little attention has been

paid to debris smaller than 330 μ m, especially at nano-scales. This is an area requiring method development and collaboration with researchers from outside the normal oceanographic community.

Some form of comparative ranking of marine debris is required, in relation to other open ocean stressors (e.g. ocean acidification, temperature increases, non-indigenous species introductions, loss of habitat, sea-level rise, atmospheric deposition of mercury), to ensure that the debate on appropriate responses is well-informed, and that legislation and other measures are cost-effective and proportionate to the estimated risk.

2.7.4 Conclusions

Marine debris enters the marine environment as a result of a wide variety of land- and sea-based activities. There are no reliable, accurate estimates of the quantities of material entering by any of the main sources.

A significant proportion is composed of plastic, which will sink or float depending on the density of the polymer relative to seawater and the nature of the item. Floating plastics are transported by ocean circulation and have been found in the most remote parts of the ocean. Plastic fragments retain the same chemical and physical properties as the original object, and are likely to remain in the marine environment for a substantial, but unknown, time.

Information on the seabed distribution of debris is more limited, but debris is widespread across the shelf, in deep water canyons and in the openocean. Surveys on remote shores and mid-ocean islands, though much less frequent or extensive than on continental coasts, are particularly useful at demonstrating long-distance transport and potential effects.

The effects of macro-scale debris, by ingestion or entanglement, have been clearly demonstrated for a wide variety of fauna (e.g. birds, fish, reptiles, marine mammals). For some vulnerable or endangered species this additional stressor may have an impact at a population level.

Floating durable debris can provide an effective vector for transporting a wide variety of species. There is concern that this may be responsible for introductions of non-indigenous and problem species.

Plastics can contain a wide variety of additives, some of which have known toxicological properties. In addition, many organic contaminants already in the environment (e.g. PCBs, DDT, flame-retardants) and can be absorbed into the polymer matrix. Plastic fragments can be ingested by a wide range of organisms, and there is concern that contaminants could pass the gut barrier, leading to potential ecotoxicological effects.

It is difficult to distinguish the relative contribution of contaminant body burden in an

organism due to food supply or plastic particle ingestion. However, there is limited evidence that plastic-bound compounds do desorb. Whether this represents a significant risk remains unclear.

The disposal of waste from ships and offshore platforms is severely restricted under the revised MARPOL Annex V. Unfortunately, enforcement remains problematic and evidence suggests that shipping remains a significant source along busy shipping lanes.

It is not possible to remove fragmented plastic from the ocean in significant quantities to justify the enormous cost, and potential ecological damage. Focussed programmes can be effective in removing larger items, such as fishing nets, from areas of known accumulation. But, the most effective way of reducing anthropogenic debris in the marine environment is to prevent debris entering. Devising cost-effective solutions to marine debris reduction will require a multi-actor approach, involving industrial sectors and public education, in addition to regulatory agencies. This is being pursued on national, regional and global scales, with the GPML¹¹, led by UNEP, being the most ambitious to date. Meanwhile, the ubiquity of debris in the ocean environment, pervading almost every habitat, is a major concern.

2.8 Radioactivity

2.8.1 Introduction

The oceans are naturally radioactive, principally due to ⁴⁰K and the parent-daughter radionuclides of the uranium- and thorium-decay series. Radionuclides are adsorbed onto sediment particles, taken up by biota or remain in the water column to differing extents, depending on the chemical properties of the radionuclide, the surface properties of the particle and the metabolism and life style of the organism. In addition, the potential radiological hazard imposed is dependent of the type of radiation emitted (gamma ray, beta particle, alpha particle) and the activity or 'concentration' of the radionuclide (activity expressed as number of Bequerels, where one Bq = one radioactive disintegration s^{-1}). The activity of ⁴⁰K in the ocean is approximately 11 kBg m⁻³; Buesseler, 2014). The ⁴⁰K content of an average human is about 4.9 kBq. Although these appear to be large numbers, the type of 'soft' beta activity emitted means that the radiological consequences are negligible. In comparison, the concentrations of the beta-emitting artificial radionuclide 99Tc reached about 500 Bq m⁻³ at the time of the greatest releases in the mid-1990s, in a small area of the eastern Irish Sea (McCubbin et al., 2002). This proved to be socially and politically controversial despite the very low risk to human health. In general, the greatest radiation dose humans are exposed to through a marine pathway is from eating certain types of fresh

¹¹ Global Partnership on Marine Litter (http://gpa.unep.org/ index.php/global-partnership-on-marine-litter)

marine shellfish, due to the relatively high levels of naturally-occurring $^{210}\text{Po},\ \text{part}$ of the ^{238}U decayseries.

'Artificial' radionuclides, created mainly by the development of nuclear weapons and civilian nuclear power production, began to be introduced into the ocean in increasing quantities after World War II. The greatest contribution has been from the atmospheric testing of nuclear weapons, with a areater proportion of tests being conducted in the northern hemisphere. Global fallout of tritium and radiocaesium were readily detected in ocean waters and they were used as tracers of ocean circulation and water mass distribution, being largely present in the dissolved state. Weapons testing on mid-ocean islands in the southern hemisphere led to both farfield and close-in fallout, including contamination by plutonium in the Marshall Islands (USA) and the French Polynesian atolls of Moruroa and Fangataufa. There is evidence that contamination from these test sites is still being released and transported significant distances (e.g. Wu et al., 2014).

Another important source of artificial radionuclides has been the authorised release of lowlevel liquid wastes from nuclear fuel reprocessing facilities at Sellafield (UK) and Cap de la Hague (France) (IAEA, 1991). The radiological consequences of both sources have been minor, both for humans and non-human biota, but the releases have provided excellent point-sources of radiotracers for exploring sediment processes and ocean circulation throughout the North Atlantic and Arctic. Direct releases from both sites are now extremely low compared to their peak. However, the contaminated sediments of the Irish Sea represent a continuing source of ¹³⁷Cs and ²⁴¹Am (growing in from ²⁴¹Pu) to the overlying water.

Disposal of low-level solid wastes took place at several sites in the Atlantic and Pacific, under an international agreement (OECD Nuclear Energy Agency), until 1982 (IAEA, 1999a). The radiological consequences of these activities were assessed and again considered to be minimal. Dumping of medium and high-level wastes was carried out independently, and without international scrutiny, by the USSR and the Russian Federation in the Kara Sea and the Barents Sea, for several decades (IAEA, 1999b. Despite the large amount of radioactivity involved, the release into the environment has been relatively modest, reflecting the efficacy of containers holding the highest-level wastes (e.g. submarine reactors).

There have also been a number of accidental losses of radioactive materials in the open ocean. These range in physical size and quantity of radioactivity from small sealed sources used in well exploration to nuclear-powered submarines, sometimes armed with nuclear weapons. The latter have usually been accompanied by significant loss of life, as escape and rescue of personnel in deep water is extremely difficult. However, the greater proportion of radioactivity appears to be contained within the hull.

Accidents at nuclear power stations, resulting in a significant release of radioactivity, have been few. Those that have occurred are well documented and the consequences have been thoroughly investigated. The most significant accident in the 20th Century was at Chernobyl in 1986. This resulted in a significant release of radioactivity, in particular radiocaesium and radioiodine, which was widely distributed in the atmosphere. Despite the magnitude of the release, contamination of the marine environment, by direct deposition and runoff, was limited to the Black Sea, Baltic Sea, and the eastern North Sea with minimal activity reaching the open ocean.

The methodology of radiological assessment is extremely well developed, probably more so than for any other human-induced hazard. A list of major radiological assessments was included in a brief description of radioactive waste disposal prepared by GESAMP (2009). Following an early focus on human health, the ICRP (International Commission on Radiological Protection) started to consider possible radiological effects on nonhumans, particularly after the Chernobyl accident. A sustained effort in Europe, funded by the European Commission, resulted in a new methodology (ERICA) for assessing effects on a series of 'reference' plants and animals; and this has been further refined and adopted by the international research community (https://wiki.ceh.ac.uk/display/star/Radiation+prote ction+of+the+environment). Consequently, we are better prepared to assess the consequences of a major nuclear accident than before the Chernobyl event. However, the ICRP and ERICA methodologies assume equilibrium conditions. In the event of an accident then dynamic models are more appropriate, based on biological half-life kinetics (United Nations 2014; Vives i Batlle et al., 2014).

The most significant release of articifial radioactivity so far in the 21st Century occurred in 2011. The Great East Japan Earthquake (Tohoku) occurred on 11th March 2011, 70 km off the eastern coast of Japan at a depth of 30 km. It had a magnitude of 9.0 on the Richter scale. The earthquake and accompanying tsunami caused enormous damage and loss of life (estimated at over 15,800 deaths, 6,000 injuries and 2,500 people missing). The tsunami caused catastrophic damage to the Fukushima Dai-ichi nuclear power plants, immobilising the emergency generators and preventing the supply of cooling water to stop the core from over-heating. This resulted in an unprecedented accidental release of radioactivity to the ocean and atmosphere, with about 80% of the released activity ending up in the North Pacific. The radiological consequences to the environment of the disaster have been assessed using both the equilibrium and dynamic methodologies (United Nations, 2014).

Table 2.8.1: Summary of ¹³⁷Cs sources to the environment and ocean in PBq (1015 Bq) prior to the Fukushima releases, adapted from: Buesseler (2014)

Source	Totalª	Total ocean⁵	2011 ocean°	2011 North Pacific ^d
Global fallout	950	600	190	76
Close-in fallout	180	180	56	28°
Total fallout				104
Chernobyl	100	18 ^f	10	n/a
Sellafield	39	39 ^g	30	n/a
La Hague	0.96	0.96 ^h	0.75	n/a

^a Cumulative total at time of reference (Aarkrog, 2003); ^b total deposited on the ocean; ^c total ocean decay-corrected to 2011; ^d fraction of ocean input between 0-90° N in Pacific Ocean; ^e Aarkrog (2003) assumed 50% of close-in fallout from Pacific Proving Grounds deposited north of equator; ^f 10-20% of Chernobyl fallout in 1986 deposited in European Seas; ^g direct release into Irish Sea; ^h direct release into the English Channel; ^{n/a} not applicable.

2.8.2 Summary of new information

Radionuclides released from Fukushima

The accident at Fukushima caused the release of substantial quantities of radioactive isotopes of caesium (134Cs, 137Cs) and iodine (129I, 131I) into the ocean and the atmosphere, as well as smaller quantities of plutonium and a variety of short-lived isotopes. The main input of caesium was directly as contaminated water into the sea within the first month of the accident. The greatest input of iodine was into the atmosphere within the same period. Published estimates of the total quantities of radionuclides discharged vary considerably, depending on the assumptions made. But upper estimates of ¹³⁷Cs releases were of the same order of magnitude as close-in and global fallout from weapons testing in the North Pacific (Tables 2.8.1 and 2.8.2).

Atmospheric releases of radioiodine and radiocaesium were distributed widely through the northern hemisphere. Radioceasium was transported in

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particulate form and radioiodine in both gaseous and particulate forms (Masson et al., 2013). There is evidence of the aerial release and widespread atmospheric dispersion of the short-lived radionuclide ¹³¹I (half-life = 8 days). This radionuclide was detected in rainfall both near Japan (Hou et al., 2013) and following trans-ocean basin transport. For example, it was detected in seaweed and rainwater in British Columbia, Canada (Chester et al., 2013), the Canary Islands in the NE Atlantic (Lopez-Perez et al., 2013) and throughout Europe (Masson et al., 2013), indicating relatively rapid dispersal. Observations of the seabed deposition of ¹³⁷Cs to the northeast of Fukushima, combined with modelling, have indicated a significant contribution from the atmosphere during a period of westerly winds and precipitation from 15th-21st March 2011 (Min et al., 2013).

Observations of ⁸⁹Sr and ⁹⁰Sr in surface seawater off the east coast of Japan in June 2011, led to the conclusion that most of the Sr release which reached the ocean was directly discharged in contaminated water, rather than via the atmosphere (Casacuberta *et al.*, 2013).

Table 2.8.2: Summary of ¹³¹I and ¹³⁷Cs releases to the environment as a result of the accident at the Fukushima Dai-ichi power station (from 2013 UNSCEAR Report, United Nations 2014)

Radionuclide	Inventory in Units 1 to 3 at reactor	Release to the atmosphere	Release to the ocean	
	shutdown ^a (PBq)	(Pbq)	Direct	Indirect ^b
131	6 000	100 – 500°	About 10 – 20°	60 -100 ^g
¹³⁷ Cs	700	6 -20 ^d	3 -6 ^f	5 – 8 ^g

^a Values quoted to two significant figures; ^b indirect releases comprise radionuclides initially released to the atmosphere and subsequently deposited onto the ocean surface; ^c encompasses the full range of estimates reviewed by the Committee; ^d encompasses the full range of estimates reviewed by the Committee apart from two (these two extended up to about 40 PBq but were based on limited information and were less reliable; ^e based on very limited information indicating that the direct release of ¹³¹I was about 3 times greater than that of ¹³⁷Cs; ^f range of estimates derived from more reliable three-dimensional modelling; other estimates were larger, extending up to about 30 PBq, but were less reliable; ^g encompasses the range of (few) estimates reviewed by the Committee.

There is evidence of a significant input of contaminated river water and river-born sediment after heavy rains (Nagao *et al.*, 2011) into the coastal zone, in the months following the accident. Groundwater flowing through the site became contaminated and acted as a continuing source of radioactivity to coastal waters (Maderich *et al.*, 2014). Attempts have been made to retrieve and de-contaminate groundwater, adding significantly



Figure 2.8.1: Surface ocean concentrations from March 21 to July 31, 2011 of ¹³⁷Cs (Bq m_3) for two sites near the Fukushima Dai-ichi nuclear power plant (red circles, north (filled) and south (open) discharge channels^a), Dai-ni NPPs (10 km to the south of Dai-ichi, blue filled trianglesa), lwasawa Beach near Dai-ni (16 km south of Dai-ichi, blue open triangles^a), and 30 km off-shore (green squares, stations 1-8 in original MEXT datab). These are compared on the lower **X**-axis (1960-2010) to the historical record of ¹³⁷Cs off the east coast of Japan (brown circles) and to Chernobyl influenced waters in 1986 in the Baltic and Black Seas (Aoama and Hirose, 2004; Buesseler and Livingston, 1996).

^a Tepco News Release, 2011; http://www.tepco.co.jp/en/ index-e.html; ^b Japanese Ministry of Education, Sports, Science and Technology. More recent results are available from the Nuclear Regulatory Authority, formed in September 2012: http://www.tepco.co.jp/en/index-e.html

Taken from Buesseler, 2011; made available through the American Chemical Society Authors Choice Open Access Policy.

to the burden of site remediation. Most recently (21st May 2014) a system to intercept groundwater before it can become contaminated has been introduced¹². The clean groundwater is released into the ocean after precautionary monitoring.

Intensive monitoring of radiocaesium in coastal waters following the accident has revealed the sudden increase in concentrations compared with pre-accident conditions. Surface concentrations of ¹³⁷Cs were substantially higher than those measured previously in the marine environment (Figure 2.8.1).

Oceanic dispersion

Dispersion and dilution of Fukushima-derived radionuclides in surface water was influenced by the prevailing circulation and wind-driven currents near to the coast (Oikawa et al., 2013; Casakuberta et al., 2013). Once radionuclides came under the influence of the Kuroshio Current there was rapid westwards transport. This has been confirmed from both observations, combined with Argo float releases (Aoyama et al., 2013), and model simulations of the surface transport (Buessler et al., 2012; Lai et al., 2013; Maderich et al., 2014). Rossi et al., (2013) used a model based on a 3D velocity field, representing the ¹³⁷Cs releases by a series of passive Lagrangian particles. The authors predicted that the plume of contaminated water would reach the coast of northwestern America in early 2014 (Figure 2.8.2b). Model simulations provided an estimate that by 2016, 42% of the remaining ¹³⁷Cs would have been advected to a depth of 200-600 m, with 5% at 600-1500 m. By 2031 these proportions will have increased to 48% and 22% respectively. However, a lack of deep-water formation in this region means that penetration to greater depths via water advection alone will be relatively low.

Honda *et al.* (2013) deployed sediment traps in in the western North Pacific subarctic gyre and subtropical gyre, collecting samples in late March and early April 2011. Fukushima-derived ¹³⁴Cs and ¹³⁷Cs were observed at both sites and vertical transport rates were estimated as 22 – 77 m d⁻¹ between the surface and 500 m, and >180 m d⁻¹ between 500 m and 4 810 m. This implies a residence time in surface waters of 130 – 390 y. The form of the particles was not clear.

Uptake by sediments

Analysis of surface sediments off the east coast of the Fukushima Prefecture has revealed marked variations in radionuclide concentrations. The incorporation of caesium into seabed sediments appears to have happened quite rapidly after the accident, with the relatively high inventories and spatial variability observed in sediment samples, a matter of a few weeks post-accident, being a reflection of the transport of seawater characterised by initial high seawater concentrations and the

¹² http://www.tepco.co.jp/en/press/corp-com/ release/2014/1236566_5892.html



Figure 2.8.2: Surface (0–200 m) ¹³⁷Cs concentrations (Bq m-3): (a) In April 2012, (b) April 2014, (c) April 2016, (d) April 2021, and (e) along 37.51° N at the latitude of Fukushima plant (black dashed line in panels a–d). Error bars in (e) represent the standard deviation over the ensemble of 27 simulations. The black square around the Hawaii archipelago and the black line along the North American west coast represent areas of interest. White flow vectors represent an illustrative sense of the large-scale surface circulation at various locations. Taken from Rossi *et al.*, 2013 (Reproduced with permission)

presence of fine clay particles or organic matter (Kusakabe *et al.*, 2013). Although the exact mechanisms remain unknown, it has been speculated that it may be related to the substantial quantities of sediment remobilised by the devastating tsunami (Kusakabe *et al.*, 2013).

Rather few measurements of plutonium radionuclides have been made in connection with the Fukushima accident. Analysis of sediment cores for plutonium isotopes, collected a few 10s of km from the coast in water depths of 140 - 5 400 m, revealed the presence of plutonium from both close-in and global fallout, but there was no detectable signal from Fukushima.

Uptake by biota

Fukushima-derived radionuclides were taken up by a wide variety of organisms, including zooplankton, seaweed, euphausids, crustacea and fish (Buesseler *et al.*, 2012, Madigan *et al.*, 2012; Kanisch and Aust, 2013). Half-lives in tissues have been estimated for a variety of bivalves, crustaceans, pelagic and demersal fish (Iwata *et al.*, 2013). The persistence of relatively high concentrations in particular demersal species of fish indicates a continuing seabed source; this raises questions about the precise cause of such differences in concentration factors.

The presence of ¹³⁴Cs in the highly migratory Pacific Bluefin Tuna caught in August 2011 off the Californian coast, when compared with its absence in Yellowfin Tuna caught in the same location at the same time, provides convincing evidence that this species acted as a transport vector for Fukushimaderived radionuclides (Madigan *et al.*, 2012).

Fukushima-derived $^{134}\mbox{Cs}$ has been detected in low concentrations in fish collected from the

West and East Greenland currents and in the Baltic, showing that uptake occurred following longdistance atmospheric transport (Kanisch and Aust, 2013).

Radiological impact

Dose rates to organisms (pelagic fish, benthic fish, molluscs, crustaceans, macroalgae and polychaete worms) in the immediate vicinity of Fukushima were calculated using both modelled and observed concentrations (Keum *et al.*, 2013; Kryschev *et al.*, 2013). UNSCEAR reviewed the evidence of radiation exposure and concluded that exposure to marine biota was, in general, too low to have caused acute effects. However, some sensitive species may have been exposed to levels likely to cause effects for a limited period close to the release point where concentrations were high. But, it is thought unlikely that effects would have been significant at a population level (Batlle *et al.*, 2014).

2.8.3 Future data requirements and rationale

Fukushima

There is a recognised need for continued monitoring of surface and bottom seawater, seabed sediments and sessile and mobile biota in the vicinity of the Fukushima site and in the wider coastal environs of the east coast of Japan. This will provide additional information on the influence of groundwater entry and sediment desorption, as well as an opportunity to examine observed differences in uptake by particular species. Far-field sampling in the North Pacific and adjoining Seas will provide very useful data to help refine and validate predictive models of the long-term consequences of the disaster. The radiological signature provided by this source offers an excellent opportunity to study the dynamics of the region, in particular the rate of vertical transport and mixing by physical and biological processes.

Other sources

Exploration for seabed minerals (e.g. rare earths, metals) and oil and gas is advancing into deeper and more remote waters. Some form of oversight and assessment will be required to ensure that operators are made aware of the potential risks in areas used for past radioactive waste dumping. For example, exploration is taking place in the Kara Sea, an area used covertly by the USSR and Russian Federation for medium- and high-level waste disposal.

2.8.4 Conclusions

The accident at the Fukushima Dai-ichi nuclear power plant on 11th March 2011, caused by the Tōhoku earthquake and tsunami, resulted in an unprecedented release of radioactivity to the ocean from a single point source, both by direct release to the ocean and from atmospheric deposition. The predominant radionuclides released were isotopes of caesium and iodine, together with substantial quantities of ⁹⁰Sr and lesser quantities of plutonium and short-lived radionuclides.

There is evidence that contaminated groundwater and run-off via rivers continued to act as a source to the ocean long after the accident. Marine sediments contaminated by Fukushima ¹³⁷Cs appear to be an additional continuing source of caesium to the overlying biota and to benthic and demersal organisms.

Rapid atmospheric transport resulted in widespread dispersion of Fukushima radionuclides in the northern hemisphere, including the short-lived ¹³¹I (half-life 8 days). Dispersion in surface waters was dominated by the Kuroshio Current, with transport to the north-western coast of North America estimated to have occurred by early 2014.

Despite the relatively high levels of contamination, and uptake by a wide variety of biota, the radiological consequences of the accident in the marine environment, and from human consumption of seafood, has been rather low.

3. Matters of Special Concern

An important aim of this report is to identify issues affecting the open oceans that, in the view of the Task Team, represent significant risks to ocean ecosystems, both now and in future. These could be any changes, directly or indirectly associated with human activities, threatening the integrity, biodiversity, productivity or sustainability of ocean sectors on large spatial scales. By alerting organizations, policy makers and managers concerned with marine environmental affairs to the risks associated with certain practices or conditions, opportunities arise to a) stimulate research, b) introduce policies and programmes to regulate the activities and b) take mitigative actions.

Selection criteria

Numerous human activities impinge on the marine environment, either because they mobilize materials that are readily transported seawards either in water or through the atmosphere, or because they exploit marine resources for food, industry or recreation. The effects of some activities are small-scale and localised, with minimal impact at ecosystem level, while others are far more extensive and pervasive, causing insidious changes that have potential to disrupt ecosystem function. Many (but not all) of the substances reviewed in this report fall into the latter category and, in deciding on issues that warrant 'special concern', the most important criteria are those that have potential to disrupt ecosystem function. Clearly, another criterion is a sense that the issue has yet to receive the attention it deserves at international level.

As noted in GESAMP's first report on pollution of the open oceans (Reports & Studies 79), shipping and the atmosphere are the two primary sources of ocean pollution. Commercial shipping tends to be concentrated around the major shipping lanes, such as the Straits of Hormuz and Malacca. Ships are significant sources of oil, CO2 and oxides of sulphur and nitrogen along such busy shipping lanes. Losses of deck cargo and poor waste management practices aboard vessels also add to the ubiquitous problem of ocean litter and debris. New shipping lanes may extend the areas impacted. For example, based on climate forecasts for 2040-2059, it is possible that during summer months, when the extent of sea ice is at a minimum, some ships may be able to transit directly across the Arctic Ocean. This route is 20% shorter than today's busiest Arctic shipping lane, the Northern Sea Route, which follows the coast of Russia. This will also open up the region to natural resource extraction, including minerals, oil, gas, and methane hydrates, as well as commercial fishing. The sources of atmospheric contaminants are, of course, much broader than just shipping and include emissions from land-based power generation, industry, traffic and agriculture; such emissions can be widely dispersed and transported long distances before deposition in the oceans.

It is clear that practices with the greatest potential to adversely affect the open oceans are those that occur at many different locations around the world and that release large amounts of biologically active substances, either directly to the sea or to the atmosphere. However, due to the substances they utilise or release, their complexity or the physical conditions under which they operate, certain technologies are more hazardous than others. These include nuclear facilities and a range of operations engaged in the extraction, bulk storage and transport of crude oils. Here, we draw attention to three issues which, from a scientific perspective, are currently of special concern:

Inputs of carbon dioxide

Previously (Reports & Studies 79), GESAMP has highlighted the issue of **carbon capture and storage** as a matter of special concern due to the unknown consequences of artificial fertilization of the oceans with nutrients, such as iron and nitrogen, in order to draw down CO_2 from the atmosphere. GESAMP reiterates its view that proposals to apply this technology at the massive scales needed to significantly reduce levels of CO_2 in the atmosphere need very careful consideration with regard to environmental effects and sustainability. Likewise, the risks associated with the use of sub-seabed geological formations for long-term storage of CO_2 , in particular the effects of leakage, require further research and assessment.

- ✓ Inputs of carbon dioxide
- \blacksquare Inputs of nitrogen and iron
- ☑ Deep-water extraction of seabed resources
- ✓ Litter and debris

In the 5 years since GESAMP's last report on ocean pollution, new data on CO₂ in the atmosphere and its effects on the oceans have added considerable weight to arguments for greater control of anthropogenic CO_a emissions to the atmosphere (see Section 2.4). There is strong evidence that uptake of CO₂ from the atmosphere into the upper layers of the oceans is responsible for declining pH levels in seawater which has serious implications for marine life. Calcifying species are particularly vulnerable to ocean acidification (OA), for example corals, echinoderms, molluscs and crustaceans and there are preliminary indications that fish may have a negative response to acidification. Amongst the many different responses to declining pH levels are alterations in growth, survival, behaviour, the ability to detect prey and to avoid predators; such effects could have implications at both population and community levels as well as for commercial fisheries. The global, pervasive impact of ocean acidification creates an urgent need for long-term,

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global monitoring of its impact on marine organisms and ecosystems and for a drastic reduction of anthropogenic CO₂ emissions.

Inputs of nitrogen and iron

GESAMP also deems it necessary to reiterate its previous advice (Reports & Studies No.79) regarding inputs of nitrogen to the open oceans. It is clear from research that there is a major perturbation in the natural cycle of nitrogen which has potentially significant impacts on marine ecosystems, especially in waters with low ambient nutrient concentrations. Modelling predicts that nitrogen fluxes to the oceans will increase in the years up to 2100. There are observable impacts of nitrogen deposition on the biochemistry of the ocean downwind of the intense nitrogen emission regions of East Asia. Because iron plays an essential role in several key enzymes of photosynthetic organisms, including those associated with nitrogen uptake by phytoplankton, the effect of anthropogenic emissions in increasing the flux of soluble Fe (from combustion sources, or through enhancing solubility of Fe from mineral dust) to the ocean also warrants attention. The collection of time-series datasets on atmospheric fluxes of nitrogen and iron at island stations in each of the north and south basins of the Atlantic. Pacific and Indian Oceans is a minimum requirement for the identification and assessment of trends.

Deep-water extraction of seabed resources

As conventional sources of fossil fuels and minerals become depleted, extraction industries have turned their attention to the considerable reserves that exist on and beneath the seabed at deep-water locations. Very large reserves of oil are known to exist beneath salt layers buried 2-3 km beneath the seabed in deep water (ca. 2,000 m and more) off Brazil, Angola and in the Gulf of Mexico; exploration is likely to reveal other such deposits. The technology to open wells at these deep-water sites already exists and continues to be developed. But despite stringent efforts by the industry to improve safety standards and contingency measures, operating under such extreme conditions presents significant risks for the marine environment. High pressures and temperatures at sub-sea wellheads present risks of explosions and, as shown by the recent Deepwater Horizon incident in the Gulf of Mexico, response times may not be sufficiently rapid to prevent substantial losses of oil. The longterm environmental costs of major oil leakages at deep-sea locations, their implications for ecosystem viability and associated ecosystem services, warrant further scientific analysis supported by modelling of different scenarios.

Deep sea mining for valuable metals is also on the increase. Ocean mining sites are usually around large areas of polymetallic nodules or active and extinct hydrothermal vents at about 1,400 - 3,700 m below the ocean's surface. The vents create sulfide deposits, which contain precious metals such as silver, gold, copper, manganese, cobalt, and zinc, As with all mining operations, deep sea mining raises questions about environmental damages to the surrounding areas. Because deep sea mining is a relatively new field, the environmental impacts are largely unknown. There are concerns that removal of parts of the sea floor might result in disturbances to the benthic layer, toxic levels of contaminants in the water column and sediment plumes from tailings. Further research into the environmental implications of seabed mining technologies, the nature and scale of impacts, is essential to better understand the significance of these operations for ocean ecosystems. In the interim, a code of best practice for deep-sea mining operations¹³, preferably developed by the industry in conjunction with the International Seabed Authority which regulates the exploitation of seabed resources, would be beneficial.

Litter and debris

GESAMP's previous report also drew attention to the ubiquitous occurrence of litter and debris in the oceans derived from shipping, mariculture, discarding, land run-off, shoreline littering and flooding (e.g. tsunamis) and the hazards these present to marine life, navigation and recreation. More recent reports fail to show any degree of improvement in the range and abundance of marine debris; the problem persists and the open ocean is not exempt. There is further evidence of persistent organic pollutants absorbed onto microplastics, providing vectors for the distribution of these contaminants and their transfer to marine organisms. Debris is widespread in deep water canyons and in the mid-ocean (e.g. Fram Strait, North Atlantic). The effects of macro-scale debris, through ingestion or entanglement, have been clearly demonstrated for a wide variety of fauna (e.g. birds, fish, reptiles, marine mammals). For some vulnerable or endangered species this additional stressor may have an impact at population level. The production of plastics worldwide has risen exponentially since the 1950s. The marine environment has become a repository for a significant fraction of plastic waste and better controls over the sources of this waste are urgently needed, such as a global code of practice for plastics disposal. Despite increased opportunities for recycling, the percentage of plastics recycled remains low; 80% of the 30 billion plastic water bottles sold in the US, for example, go to landfill. GESAMP would firmly support initiatives to raise the profile of plastic wastes as potential hazards to the marine environment and coordinated international action to reduce losses of plastic materials to the oceans.

4. Key factors in the review and assessment of marine pollution

This chapter identifies various themes that emerge from the reviews of individual contaminants in the previous chapter and considers a number of associated issues of relevance to the assessment of ocean pollution. There is an obvious need to improve ocean assessment capabilities, including the degree of international cooperation in addressing priorities for research and monitoring, the harmonisation of methods and levels of funding. To achieve such improvements, it would seem essential to raise the profile of the oceans as a global resource requiring far better management than heretofore. In the view of GESAMP, this will necessitate more effective communication of the environmental impacts that are occurring beyond the 200 m contour and the potentially serious implications of certain changes for the sustainability of ocean ecosystems and the services they provide to human society.

Albeit indirectly, the scientific knowledge summarized in this report addresses aspects of the oceans that are significant for human welfare. They will also impact on marine diversity. In this context, the UN General Assembly (Resolution 68/70) scheduled 3 meetings of an Informal Working Group during 2014/15 to discuss the scope, parameters and feasibility of a possible new instrument on biodiversity beyond areas of national jurisdiction (BBNJ) under the UN Convention on the Law of the Sea (UNCLOS). Considering the findings of the present review, this would seem to be a very positive development.

Pollution or Contamination?

In any review of environmental pollution it is important to clarify how the term pollution is used i.e. its meaning in the context of the document. Pollution studies focus on particular substances or properties whose presence is due, at least in part, to human activities and that have the potential, directly or indirectly, to harm either the environment or human health. This link between environmental properties and harm is explicit in GESAMP's definition of marine pollution¹⁴. In practice, pollution indicators tend to be almost any environmental variable influenced by anthropogenic practices for which the levels in air, water, sediment or biological tissues fall within the range that is potentially damaging (see below).

¹⁴ 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 marine activities including fishing, impairment of quality for use of sea water and reduction of amenities.

One of the more intractable problems in conducting reviews and assessments of marine contaminants is that, in some instances, there is little or no direct evidence of harmful effects. Thus, contaminants of toxicological significance that are below their known Threshold Effect Levels (TELs) should, from a technical viewpoint, be termed hazards, not pollutants.

GESAMP's definition of pollution is not universally accepted. Indeed, the term is frequently interpreted as environmental contamination i.e. the mere presence of a substance introduced by human activities. The rationales for and against distinguishing these terms have a lot to do with the degree of 'precaution' considered necessary to safequard the environment. Policies and philosophies on environmental protection can differ widely. It is sometimes argued that any form of contamination due to human activities should be considered harmful unless it can be shown otherwise. However, in the context of marine environmental assessment. such distinctions are to some extent academic. The primary objective is to describe changes that have occurred and, using the best available scientific knowledge, to assess the relevance of these changes to the diversity, productivity and sustainability of marine ecosystems, human health and the economy.

In this report, GESAMP has reviewed the status of 8 different categories of contaminant (including disturbances) that are widespread in the open oceans and that, under certain environmental conditions, can be harmful to living organisms. The levels of all these contaminants are augmented by human activities. However, taking into account current levels in the open oceans, not all can be unequivocally termed pollutants.

Scale - in ocean pollution assessment

It is entirely appropriate that this review of pollution in the open oceans has been prepared in conjunction with the Transboundary Waters Assessment. There are no more transboundary waterbodies than the oceans, shared by all surrounding States; in the case of the Atlantic, more than 40 States. But the oceans are linked and neither ocean dynamics nor marine organisms respect artificial boundaries.

In this account, the periphery of the oceans has been taken as the 200 m depth contour. This, again, is artificial and a matter of convenience as the shelf seas are reviewed separately under the TWAP. Whereas the shelf seas have different characteristics to the oceans, and in many cases are under even greater pressure from human activities, many of the agents of change in the oceans are transferred from the land via the shelves to deeper waters.

An important finding of GESAMP's previous review of ocean pollution is that, despite the paucity of data in the context of the vastness of the oceans, scientific knowledge of a majority of

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contaminants is sufficient to assess their relative impact and significance. With the exception of noise, assessment capabilities for other contaminants were rated as either *moderate* or *good*. It is, perhaps, a mark of progress in marine environmental science that, as stated in this review, it can now be said that current levels of anthropogenic noise *do* impose stress on open-ocean species; however, the extent and significance of these stresses are still to be resolved.

Assessment capabilities for atmospheric inputs of contaminants are greatly facilitated by data from monitoring stations strategically located on islands. Although land-based, being surrounded by the deep oceans islands serve as surrogates for ocean sites. Clearly, they can provide more frequent measurements than obtainable from ships, although the latter are equally important for filling geographical gaps. Such monitoring networks, combined with ever-improving modelling capabilities, provide the basis for scientific analysis of environmental conditions on large geographical scales.

Ship-based sampling for a number of other pollution determinants, such as marine debris, noise and POPs, will continue to be essential. As noted in Chapter 2 of this report, there are valid reasons to support a significant increase in the measurement of these variables in the open oceans, in terms of both frequency and geographical extent.

Indicators of marine environmental health

It is evident that the kinds of indicator suitable for assessment purposes will depend on the contaminants concerned as well as scientific understanding of their effects on the marine environment and human health. There is certainly a need to distinguish between naturally-occurring substances for which environmental levels may be augmented by human activities (e.g. metals, nutrients, CO,, noise) and those that occur in the marine environment mainly (e.g. oil, debris) or entirely (e.g. plastics, POPs) as a result of anthropogenic practices. Only in a few cases (e.g. certain POPs, radionuclides) are relationships between environmental levels and effects sufficiently well understood to set numerical indicators corresponding to threshold effect values. To date, such values have been applied mainly at regional level.

As noted previously, the mere presence of a contaminant does not constitute a satisfactory indicator of pollution. Perhaps the most useful indicators for purposes of assessing marine 'pollution' are *trends* in either inputs or ambient levels of contaminants. Trends in effects are also very relevant to assessments but with few exceptions (e.g. acidification and reefs) are difficult to demonstrate. For purposes of environmental management and policy development, clear and reliable information on the speed and direction of change in contamination status is particularly valuable. Unfortunately, time-series datasets for most ocean contaminants are seldom of sufficient duration for trends to be determined with a high degree of confidence; this is particularly the case for short-term datasets with high levels of temporal and/or spatial variability.

Importance of time-series measurements

At present, assessments of a majority of contaminants in the open oceans are hampered by limited geographic coverage, differing methods of sampling and analysis and the short duration of timeseries datasets. For reasons of cost and logistics, available data tend to be limited to a small number of widely-spaced sites. Thus, much of the available data merely reflect local conditions although, for certain contaminants (e.g. nutrients), contemporary models can provide reasonable estimates of input loads representative of regional conditions.

In the absence of clear evidence of adverse effects, the ability to show with confidence that contamination levels are either stable, increasing or decreasing, is of utmost importance. Allowing for seasonal and inter-annual variation, this generally requires consistent measurements over prolonged periods, preferably a decade or more. It is seldom possible where the available datasets are of short duration or consist of sporadic measurements at scattered locations using different methods of sampling and analysis. Thus, continuity of measurements using standardised methods over extended time periods, preferably a decade or more, is important for trend assessment and funding mechanisms are needed that will facilitate such key monitoring projects.

GESAMP recognizes that there can be a reluctance on behalf of funding sources to support long-term environmental monitoring. This is often the case for national agencies responsible for broad fields of scientific research. Nevertheless, there is now sufficient evidence of a decline in marine environmental quality to warrant investment that will improve trend monitoring capabilities. Because the open oceans are a shared multinational resource, there would be merit in exploring opportunities for improved international cooperation in the prioritization, design and implementation, as well as funding, of long-term ocean monitoring programmes.

Multiple stressors

When interpreting data on environmental conditions, and on contaminants in particular, it is important to bear in mind that biological effects may occur gradually over time and that, in conjunction with natural variation, the effects of chronic exposures may go unnoticed. Whereas the assessment of effects from individual contaminants in the open oceans can be problematic, assessing the combined effects of many different forms of contaminant is even more complex. Populations and communities of marine organisms occupying a variety of ocean ecosystems and habitats, are subject to a multiplicity of changes¹⁵ ranging from physical (e.g. temperature, noise, pH) to chemical (e.g. POPs in tissues) to biological (e.g. food supply). Although a minor change in any one variable may be harmless, at some level all changes will impose a stress that can interfere with growth, reproduction or behaviour and thereby jeopardize populations and the communities of which they are part.

At present, methodologies for estimating the combined effects of different forms of stressor do not exist. Yet, drawing on principles from toxicology, it is conceivable that the effects of certain stressors acting in combination could be either additive or even synergistic. There is already speculation that cumulative stresses, for example tissue contaminants, noise and changes in food supply, may already be responsible for changes in reproduction, behaviour, and perhaps even the viability, of some top predators such as marine mammals. Such negative changes undoubtedly constitute pollution and, in the opinion of GESAMP, new and improved measures to reduce known stresses on living components of ocean ecosystems warrant detailed consideration at international level. The proposed new instrument to protect ocean biodiversity (see above) is one such initiative and should help to dispel any impression that the oceans are somehow less vulnerable that the shelf seas.

Changing perspectives

Almost 25 years ago, in a report on the state of the marine environment (GESAMP, 1990¹⁶), the following statement appeared in the opening summary:

"The open sea is still relatively clean. Low levels of lead, synthetic organic compounds and artificial radionuclides, though widely detectable, are biologically insignificant. Oil slicks and litter are common along sea lanes but are, at present, of minor consequence to communities of organisms living in open-ocean waters"

This was in stark contrast to GESAMP's assessment of near-shore waters where, it was said, trends in coastal development, and habitat loss in particular, would, if unchecked, "*lead to global deterioration in the quality and productivity of the marine environment*".

Clearly, perspectives on environmental issues have changed radically over the last 20+ years and today, scientists and the general public alike, might find it hard to be as positive about the condition of the open oceans as the 1990 report! Greater awareness of the importance of our natural

¹⁵ See also Executive Summary, Table ES2.

¹⁶ GESAMP (1990). The state of the marine environment. Reports & Studies No. 39, 111p.

resources, a more cautionary approach to their use, more and better scientific knowledge and 20 years additional experience, would suggest that there is no longer room for complacency in our approach to protection and management of the open oceans.

5. Conclusion

The deep oceans, occupying about 65% of the Earth's surface, are significantly contaminated with the by-products of human activities; all major ocean basins are affected. Substantial quantities of contaminants are introduced from land, through shipping, and via the atmosphere. Scientific knowledge of pollution in the open oceans is steadily improving and some important advances have been made in the past 5 years. No early decline in the bio-availability of mercury is predicted and without mitigation atmospheric inputs of CO₂ will increase acidification of surface waters. In the Arctic, environmental levels of some recentlymanufactured POPs are on the increase. Various taxonomic groups are adversely affected by noise generated by shipping, sonar devices and seismic surveys. Atmospheric inputs of CO₂ and nitrogen, as well as the extent of solid debris (e.g. plastics, netting) in the water column and on the seabed, are matters of special concern. Another, rapidly

emerging, threat is the exploration and extraction of minerals and hydrocarbons on or within the deepocean seabed, due to the potential of such activities for large-scale uncontrollable impacts.

Information on the temporal and spatial extents of contaminants in the deep ocean is sparse but in most cases, through deduction and modelling, is sufficient to determine general patterns. There is a pressing need for time-series datasets from strategically selected sites to more accurately discern trends; this requires greater commitment to long-term funding for such measurements. Whereas effects on species and communities can be seen locally, the real biological impact of particular contaminants is unknown. Indeed, taking into account the complex relationships within ocean ecosystems, it is likely that such understanding will remain beyond the capabilities of science for the foreseeable future. Nevertheless, it is reasonable to assert that the cumulative effects of multiple stressors on some ocean communities, including fishing pressure and the upward trend in water temperatures, eventually will force changes in the structure and function of those communities that may be neither beneficial nor reversible; at some locations they may already be doing so. Accordingly, there is a strong case for more effective measures to reduce inputs of contaminants to the oceans.

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Annex I

Task Team membership

Name	Affiliation	Contribution
Rick Boelens	Independent, Ireland	Chairman & editor
Peter Kershaw	Independent, UK	Radioactivity, marine debris & co-editor
Dorothee Bakker	Univ. East Anglia, UK	Ocean acidification
Alex Baker	Univ. East Anglia, UK	Atmospheric inputs of nutrients and heavy metals
lan Hedgecock	Inst. Atmospheric Res., CNR, Italy	Atmospheric inputs of mercury
Tim Bowmer	European Chemicals Agency, Finland	Organic pollutants
Peter Tyack	Univ. St. Andrews, UK	Underwater noise
Michail Angelides	IAEA, Monaco	Metals & organic pollutants

Annex II

Abbreviations of chemical terms Persistent Organic Pollutants (POPs)

POPs Glossary				
BTBPE	1,2-bis(2,4,6-tribromophenoxy) ethane	PBEB	pentabromoethylbenzene	
CFC	clhorofluorocarbons	PBT	Persistent, Bioaccumulating and Toxic	
decaBDE	decabromodiphenylether (BDE congener 209)	PBrT	pentabromotoluene	
EESC	equivalent effective stratospheric chlorine	PCN	polychlorinated naphthalenes	
HBCD	hexabromocyclododecane	PFC	perfluorocarboxylates	
НСВ	hexachlorobenzene	PFOA	perflourooctanoate (C8)	
HCFC	hydrochlorofluorocarbon	PFOS	perfluorooctane sulphonate	
НСН	hexachlorocyclohexane	PFOSA	perfluorooctane sulfonamide	
HxBBz	hexabromobenzene	PFNA	perfluorononoate (C9)	
ос	organochlorine	PFUnA	perfluoroundecanoate (C11)	
ODP	ozone depleting potential	SCCP	short-chain chlorinated paraffin	
PBB	polybrominated biphenyl	ТВВРА	tetrabromobisphenol A	
РСВ	polychlorinated biphenyl	TBEC	tetrabromoethylcyclohexane	
PBDE	polybrominated diphenylether	vPvB	very Persistent, very Bioaccumulating	

Case studies on POPs in open ocean biota and coastal surrogates

In interpreting data on contaminant body burdens, guestions arise as to where the individuals had been in the years and months prior to sampling, on what they had been feeding and ultimately what the observed contaminant burdens represent in terms of exposure. The following case studies look briefly at selected species: swordfish, Atlantic cod, leatherback turtle, monk and harbour seals and killer whales, including their IUCN status, distribution, feeding habits, trophic level and contaminant burdens. The case studies do not consider effects related to the observed contaminant body burdens, as information on effects in these species is lacking or not well analysed.

In preparing the five case studies, contaminant residues were normalised to ng/g on a lipid weight basis. It was necessary to consider several sampled tissues (mostly liver, blubber, coelomic fat, and blood but also other tissues and eggs in the case of turtles). Where killer whales are concerned, it was not always possible to focus on a single sex to further standardise comparison (as used by Krahn et al., 2008); in general, for the other species, mean contaminant values for the sampled populations are used, regardless of sex or age/size. Variation in the level of any given contaminant between individuals in small populations is often large; therefore, ranges or standard deviations are given where available.

The case studies focus mainly on ΣPCB , **ΣDDT** (or p.p-DDE) and **ΣPBDE** but contain some data also on HCB, Σ HCH and Σ Chlordane. While other substances such as TBTs and HBCDD were occasionally reported, there is insufficient data for these to be analysed. In each case the lowest residue levels identified geographically are used as a benchmark against which to look for potential geographical tends. Reference is made to any available data on temporal trends.

Case study 1 FISH: Sword fish, Xiphas gladias from the Mediterranean and the Atlantic

The swordfish is pandemic, in tropical, temperate and sometimes cold waters. It is a truly oceanic, fast-swimming predatory species feeding on fish, crustaceans and squid from the surface to well over 500m depth. Stefanelli, et al. (2004) compared levels of PCBs and DDT in swordfish from the Mediterranean (Straights of Messina, Italy) and the Azores Islands (Atlantic, 38°N); the locations are 3,500 km apart. More recently, Corsolini et al., 2008 sampled swordfish from Calabria, close to the aforementioned Italian site, measuring DDT, PBDEs, PFOA and PFOS, while De Alvedo e Silva, et al. (2007) measured PCBs and DDT in swordfish from the Brazilian EEZ (Atlantic ca. 20°S). PCB concentrations in swordfish muscle from the Straits of Messina, Italy were 2000 (200 - 8352), compared to 127 (185 – 715) ng/g lipid from the Brazilian EEZ. The PCB concentrations in the liver of the Straits of Messina fish were 2236 (373 - 6782), compared to the liver values of 473 (45 - 2675) ng/g lipid in the Azores.

DDT concentrations in swordfish muscle from the Straits of Messina, Italy were 1300 (75 to 4025), compared to 45 (4 - 205) ng/g lipid from the Brazilian EEZ. PCB concentrations in the liver of the Straits of Messina fish were 2136 (236 - 9864), compared to the liver values of 309 (<0.01 - 1973) ng/g lipid in the Azores. The data reported by Stefanelli (2004) are largely confirmed by Corsolini et al. (2008) for the eastern Mediterranean, with very similar PCB and DDT concentrations.

With regard to levels of Σ PBDE, including those in killer whales off California (see below), Corsolini et al. (2008) reported very high ∑PBDE concentrations of 6,689 (<22 - 20,876) and 13,862 (7,394 – 69,900) ng/g in muscle and liver of swordfish respectively for the eastern Mediterranean. PFOA and PFOS were not detected (<0.3 and <1.5 ng/g respectively) in the same samples.

The swordfish can be considered a truly oceanic species. PCBs and DDT were found in all populations reported but were clearly at lower concentrations in open ocean areas away from pollution sources.

Case study 2 FISH: Atlantic Cod, Gadus morhua temporal trends

The Atlantic cod, a demersal predatory fish, has an intermediate trophic status. One quite remote OSPAR monitoring station is located at Bjørnerøya, Vagan, Norway. A two decade time series dataset of contaminants in the livers of Atlantic cod exists for this station, showing a downward trend in p,p'-DDE concentrations from means of ca. 200 ng/g lipid in 1991 to ca. 50 ng/g lipid weight in 2011, as well as declining concentrations of several PCB congeners, HCB and HCHs. On the other hand, BDE 47, a marker for PBDEs, appears stable at ca. 6 ng/g lipid between 1995 and 2011. This can be compared with Sturludottir et al. (2014) who provided temporal trend data in cod between 1990 to 2011 from NW and NE Iceland. The map locations of the catch

stations were up to 100km offshore in waters of ca. 50 to 500m depth. They reported that all the PCBs, DDT. HCB. chlordanes and toxaphenes showed decreases of 2 to 3 % per year while HCH showed a 9% decrease. Julshamn et al. (2013) reported Σ PCB and Σ PBDE concentrations of 92 +/- 67 and 4.5 +/3.5 ng/g wet weight respectively in the liver of Atlantic cod (n = 784, lipid content 51 to 54%) caught in 2009/10 from 32 offshore locations in the Barents Sea. The locations of the reported catch stations were within a 600 km radius of the north coast of Norway (i.e. some close to Svalbard) in shelf waters not deeper than 300 m. The PBDE values can be considered as low and of the same order as killer whale liver from the Ross Sea, Antarctica (see below).

For the NE and NW Atlantic, the data on PCBs, DDT and other POPs such as HCB, chlordanes and toxaphenes in cod seem consistent with a slow downward trend. The Icelandic and Barents Sea locations especially are representative of the open ocean.

<u>Case study 3</u> Oceanic turtles: the leatherback, *Dermochelys coriacea*

The leatherback turtle is listed as vulnerable by IUCN (2013) but the 7 sub-populations vary in terms of conservation status; the NW Atlantic population considered here is of 'least concern' (IUCN, 2013). It is considered to be an oceanic, deep-diving species, unusual in being an obligate 'medusivore', i.e. feeding on jellyfish, salps and siphonophores, whose swarms it follows, leading to a pelagic existence and a relatively low trophic status. Contaminant levels have been reported from necropsies of stranded (Davenport, et al., 1990, UK; Oros et al., 2008, Canary Islands; Stewart et al., 2011, N & S Carolina), or entangled adults (Mackenzie et al., 1997, UK), as well as biopsied blood from nesting females and samples of fresh and post-hatch eggs (Giurlet et al., 2010, French Guyana; Stewart et al., 2011, Florida). Giurlet et al., (2010) provided the lowest adult blood ΣPCB s and ΣDDT levels of 224 and 55 ng/g respectively for a nesting population in French Guyana, while Stewart et al. (2011) reported only slightly higher blood levels of 445 and 76 ng/g lipid from east Florida. With regard to turtle eggs, those from nesting leatherbacks in French Guyana again showed the lowest concentrations of 55 and 11 ng/g lipid, while the east Florida population showed ca. x3 higher Σ PCB and Σ DDT levels of 169 and 37 ng/g lipid.

From stranded animals, there are data on four sets of blubber (insulating fat under the carapace), adipose or coelomic fat (surrounding the muscles and internal organs). The lowest levels measured are from Scotland and N & S Carolina, where $\sum PCB$ s, $\sum DDT$ and $\sum chlordanes$ were respectively 182, 58, 27 and 187, 50, 47 ng/g lipid. Coelomic fat and blubber values for the Irish Sea specimen reported by Davenport *et al.* (1990) and the Canary Island specimens reported by Oros *et al.* (2009) were much

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higher for SPCBs at 1200 and ~1200 ng/g lipid weight respectively. Finally, the liver SPCB, concentration of the Scottish specimens was 27 ng/g lipid, while the Canary Island individual contained ~7800 ng/g lipid. The high levels of PCBs in the Canary Islands stranded leatherback turtle is also mirrored by proportionately high levels of liver PCBs in a much greater sample of stranded loggerhead turtle (Caretta caretta), with a mean of ~25,440 ng/g lipid and a high standard deviation from the four Canary Islands between 2002 and 2005. While the dataset generally shows low POPs levels in the E. and W. North Atlantic samples and in the Caribbean, the mid-Atlantic Azores for PCBs, an order of magnitude higher, are unusual. Given the long migrations made by this species, the geographical sampling location is not necessarily determinant as exposure may have occurred elsewhere.

Case study 4 MAMMALS: Pinnipeds

a) Monachus monachus and M. schauinslandi, two severely endangered species of monk seals from Greece, Western Sahara and Hawaii

The Mediterranean and Hawaiian monk seals are both listed by IUCN (2013 and 2008) as **critically endangered**, with a only a few hundred and ca. 1500 individuals remaining respectively. Mediterranean monk seals are primarily benthic feeders with some pelagic prey in their diet and can dive to shelf depths. Both species may occupy a high (but not top) trophic position and despite their coastal habits, living in some extremely isolated locations such as Western Sahara and the NW Hawaiian atolls (over 1000 km NW of Hawaii), can be regarded as reflecting open ocean conditions.

Borrell et al. (2007) reported PCB and DDT concentrations in the blubber of Mediterranean monk seals from Greece of 24,700 and 36,200 ng/g lipid respectively, while during the mid- to late-1990s in a population from Western Sahara concentrations of only 1070 and 450 ng/g lipid respectively had been recorded. Some individuals of the Greek population carried much higher body burdens of PCB and DDT, at 90,000 and 180,000 ng/g lipid respectively, i.e. three orders of magnitude higher than their Western Saharan conspecific. Western Sahara is one of the most sparsely populated areas in the world, while the eastern Mediterranean is heavily industrialised to the north, with intense agriculture all around the basin. Willcox et al. (2004) and Ylitalo et al. (2008) reported SPCBs and SDDT in Hawaiian monk seal from 5 different atolls in the NW Hawaiian Island chain of 730 to 2200 and 483 to 1200 ng/g lipid. Midway atoll is reported to have been contaminated by a variety of pollutants including PCBs (Ge et al., 2013), perhaps explaining the higher PCB concentrations reported in seal blubber there of 4367 ng/g lipid. Lopez et al. (2012) measured the blubber concentrations of SPCBs and ΣDDT in a monk seal population from the

main Hawaiian Islands of 1123 and 423 ng/g lipid respectively, i.e. similar to the ca. 1000km distant atolls. The concentrations of ΣPCB and ΣDDT in the *M. monachus* population from Greece are an order of magnitude higher than those from the Atlantic or the Pacific locations. Strikingly, the ∑PCB and DDT/ p,p'DDE concentrations from the N.W. Hawaiian Islands (Midway excepted) and the Western Sahara are very similar. Those for Σ HCB in *M. monachus* from Greece are two orders of magnitude higher than in M. schauinslandi in the main Hawaiian Islands, the Western Saharan population of *M. monachus* being intermediate. While the mean PCB and DDT levels even in the Greek *M. monachus* population are high, they are still much lower than in killer whales (see following section).

b) Phoca vitulina. harbour seal from the N.E. Pacific - temporal trends

Ross et al. (2013) regarded the harbour seal (Phoca vitulina), another high trophic level, non-migratory, marine mammal, as providing an integrated measure of coastal food-web contamination. They evaluated temporal trends of PCBs, PBDEs, PCDEs and PCNs in blubber biopsies from free-ranging harbour seals in the Salish Sea (British Columbia) from 1984 to 2009. They noted that PCBs dominated in seals at all sites. Over the course of the 25 years between 1984 and 2009 as a result of regulation, PCB concentrations had declined by 81% (from ca. 20,000 to an apparently stable ca. 5000 ng/g lipid); PCDEs and PCNs showed similar declines, consequently reducing the associated health risks to marine wildlife. PBDE concentrations on the other hand had doubled every 3.1 years from 1984 (just detectable) to 2003 (ca. 1000 ng/g lipid), but appeared to be in decline by 2009 (ca. 600 ng/g lipid). Over the period assessed, the seal population rose from 21,000 individuals in 1984 and remained stable at ca. 53,000 harbour seals between 1993 and 2009. While not representative of open ocean conditions, these data support the observations on monk seals from more remote locations, indicating that even after decades of decline in PCB concentrations, the British Columbia harbour seals still have generally higher levels than the Western Saharan or Hawaiian monk seal species.

Case study 5 MAMMALS: Odontoceti -Killer Whales from the N and S Atlantic. Indian and Pacific Oceans

IUCN (2013) lists the killer whale Orcinus orca as "data deficient", its wide distribution making it difficult to census. It is currently seen as a single cosmopolitan species, found in all oceans and most sea areas. O. Orca is most commonly found in coastal, temperate waters particularly those with high productivity (Ford, 2009) but occasionally venturing into colder waters e.g. during seasonal ice retreat in the Arctic. It is regarded as a formidable predator; significantly, the diets of some populations can

contain a substantial proportion of other mammals, placing them at the very top of the trophic chain.

Krahn et al. (2008) measured possibly the lowest reported Σ PCB and Σ DDT blubber concentrations in a fish-eating killer whale population from McMurdo Sound (Ross Sea, Antarctica) at 1600 (540 - 3600) and 4300 (1700 - 10,000) ng/g lipid. Noel et al. (2009) measured PCB concentrations in the blubber of a predominately female population from the remote Crozet Archipelago in the S. Indian ocean, recording a mean value of 13,670 ng/g lipid. Krahn et al. (2007, 2008 and 2009), reported mean SPCB and Σ DDT values of 8 and 5 times higher than the Ross Sea population in three 'resident' (fisheating) populations from the Gulf of Alaska and the Aleutian Islands at 13,000 and 21,000 ng/g lipid (intra and inter-population variability was relatively low), i.e. very similar to levels in killer whales of the Crozet Archipelago. However, a further 'offshore' population from Alaska showed mean ∑PCB and ∑DDT levels of 110,000 (81,000 - 130,000) and 420.000 (290,000 - 510,000) respectively, while a 'transient' (mammal eating) Alaskan population showed levels of 120,000 (59,000 - 250,000) and 200.000 (75,000 - 470,000) ng/g lipid respectively, i.e. all ca. 50 to 90 times higher than the Ross Sea population used here as a benchmark for comparison. They reported the highest mean SPCB and **DDT** levels on record at 630,000 (350,000 -720,000) and 3,700,000 (2,500,000 - 4,600,000) ng/g lipid from a 'transient' (mammal eating) California population, i.e. 394 and 860 times higher than the Ross Sea benchmark. This can be contrasted with a Californian 'resident' population from the Gulf of California, where Fossi et al. (2014) measured SPCB and 5DDT levels of 81,200 ± 71,800 and 557,100 ± 372,200 ng/g lipid.

In other Oceans, ∑PCB and ∑DDT levels were respectively reported in killer whale blubber by Laiston Brito (2012) at 257,200 and 125,600 from Rio de Janeiro State, Brazil, by Kajiwara et al., (2006) at 39,900 ± 14,900 and 107,800 ± 66,500 from N. Hokkaido, by Wolkers et al. (2002) at 26,900 (16,600-44,000) and 11,652 (6,996-19,490; as ppDDE) from Tysfjorden Norway and finally by Krahn et al. (2008) at 20,000 ± 8,300 and 1,200,000 ± 500,000 from 250km off Nicaragua in the E Tropical Pacific (all ng/g lipid). These values, with the exception of the Nicaraguan DDT value, can all be described as moderate or intermediate in relation to the low levels found in the Ross Sea, Antarctica population and the very high California population. The ranges and standard deviations of each sample are generally high; marine mammals in general can show wide differences due to feeding status, also differences between the sexes and between adults and juveniles are well documented.

While the above authors report relatively complete data on chlordanes, HCH, HCB and PBDEs in killer whales around the globe, only PBDE is considered here as it has been described as a 'still emerging' POP. Krahn et al. (2008) reported SPBDE levels in killer whale blubber from the Ross sea,

Antartica of 12 (<LOQ – 74) and from California of 12,600 ng/g lipid (one individual). PBDEs generally followed a geographical trend, being proportionately higher in populations where PCBs were also high. The overall levels seem relatively low at 2 to 3 orders of magnitude below PCB's. No temporal trend data for PBDE in killer whale were located in this case study.

The various populations or ecotypes of killer whale have different relationships with coastal areas and the oceans, as determined by their often quite specific feeding habits. Having a global distribution and as the ultimate top predator, the exceptionally high POP concentrations reported in some populations are of concern and provide a general indication of contamination in coastal and open ocean ecosystems.

Conclusions

Distinct differences can be seen in POPs burdens between geographic locations, in particular, high levels in monk seals, swordfish and killer whales close to industrial and population centres such as the eastern Mediterranean and California. However, these are all migratory species and the exposures responsible for the body burdens are not always obvious. Remote locations and truly open ocean habitats, such as that of the swordfish and the relatively low trophic status leatherback turtle, generally lead to low POPs levels, although these should not be regarded as negligible. The apparently downward trends in many POPs reported in Atlantic cod and British Columbia harbour seals are encouraging, although concentrations in some populations of killer whale remain very high.

Annex IV

GESAMP Reports and Studies

The following reports and studies have been published so far. They are available from the GESAMP website: http://gesamp.org.

- Report of the seventh session, London, 24-30 April 1975. (1975). Rep. Stud. GESAMP, (1):pag.var. Available also in French, Spanish and Russian
- 2. Review of harmful substances. (1976). Rep. Stud. GESAMP, (2):80 p.
- Scientific criteria for the selection of sites for dumping of wastes into the sea. (1975). Rep. Stud. GESAMP, (3):21 p. Available also in French, Spanish and Russian
- Report of the eighth session, Rome, 21-27 April 1976. (1976). Rep. Stud. GESAMP, (4):pag.var. Available also in French and Russian
- 5. Principles for developing coastal water quality criteria. (1976). Rep. Stud. GESAMP, (5):23 p.
- 6. Impact of oil on the marine environment. (1977). Rep. Stud. GESAMP, (6):250 p.
- Scientific aspects of pollution arising from the exploration and exploitation of the sea-bed. (1977). Rep. Stud. GESAMP, (7):37 p.
- Report of the ninth session, New York, 7-11 March 1977. (1977). Rep. Stud. GESAMP, (8):33 p. Available also in French and Russian
- Report of the tenth session, Paris, 29 May
 2 June 1978. (1978). Rep. Stud. GESAMP, (9):pag.var. Available also in French, Spanish and Russian
- Report of the eleventh session, Dubrovnik, 25-29 February 1980. (1980). Rep. Stud. GESAMP, (10):pag.var. Available also in French and Spanish
- Marine Pollution implications of coastal area development. (1980). Rep. Stud. GESAMP, (11):114 p.
- Monitoring biological variables related to marine pollution. (1980). Rep. Stud. GESAMP, (12):22 p. Available also in Russian
- Interchange of pollutants between the atmosphere and the oceans. (1980). Rep. Stud. GESAMP, (13):55 p.
- Report of the twelfth session, Geneva, 22-29 October 1981. (1981). Rep. Stud. GESAMP, (14):pag.var. Available also in French, Spanish and Russian

- 15. The review of the health of the oceans. (1982). Rep. Stud. GESAMP, (15):108 p.
- Scientific criteria for the selection of aste disposal sites at sea. (1982). Rep. Stud. GESAMP, (16):60 p.
- 17. The evaluation of the hazards of harmful substances carried by ships. (1982). Rep. Stud. GESAMP, (17):pag.var.
- Report of the thirteenth session, Geneva, 28 February - 4 March 1983. (1983). Rep. Stud. GESAMP, (18):50 p. Available also in French, Spanish and Russian
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