The Specialist Committee on Assessment of Ocean Environmental Issues

Final Report and Recommendations to the 24th ITTC

1. INTRODUCTION

1.1 Membership

The Committee appointed by the 23rd ITTC consisted of the following Members:

- Dr. Chang-Gu Kang (Chairman).
  Korea Research Institute of Ships and Engineering (KRISO) and Korea Ocean Research and Development Institute (KORDI), Korea.
- Dr. Brian Veitch (Secretary).
  Memorial University, Canada.
- Prof. Gwyn Griffiths.
  University of Southampton, UK.
- Prof. Yusaku Kyozuka.
  Kyushu University, Japan.
- Prof. Toru Sato.
  University of Tokyo, Japan.
- Dr. K. Hirata (November 2002).
  IPT, São Paulo University, Brazil.
- Prof. K. Nishimoto (November 2003).
  IPT, São Paulo University, Brazil.

1.2 Meetings

Four formal meetings of the Committee were held as follows:

- Vancouver, Canada, April 2003.
- Kyushu, Japan, January 2004.
- St. John’s, Canada, August 2004.
- Southampton, U.K., January 2005.

1.3 Committee Tasks

The tasks mandated by the 23rd ITTC were reviewed by the Committee and a decision was taken to elaborate upon the assigned tasks. The tasks in their expanded forms are presented following:

Task 1: Review the ocean environment pollution problems caused by: (a) spilled oil, (b) other chemicals (CO_2, nutrients, produced water, and ship discharges of ballast water), (c) marine debris, and (d) seabed litter.

Task 2: Review the state-of-the-art technology for management, control and recovery of (a), (b), (c), and (d) in the ocean.

Task 3: (1) Review the experimental and numerical modelling techniques for prediction of the distribution of (a), (b), (c), and (d); and (2) Review the field/oceanographic experimental equipment and sensors related to the detection and measurement of (a), (b), (c), and (d).

Task 4: Investigate and evaluate testing and certifying procedures for recovery tools and equipment for (a), (b), (c), and (d) with an ultimate goal of proposing standard procedures.

Task 5: Cooperate with organizations in other fields to deal with broader environmental problems.

1.4 Organization

In each section, the review covers the environmental pollution problems posed by the pollutant, state-of-the art technology for management, control and recovery, existing experimental and numerical modelling techniques for prediction of the distribution of the pollutant, and field equipment or sensors related to the detection and measurement of the pollutant in the marine environment. A fuller account of field equipment and sensors is reported by Griffiths (2005).

2. OIL

2.1 Introduction

International marine oil transportation has grown dramatically since World War II. More than 1.7 billion tonnes of oil are transported annually by ship from producing and refining countries to consuming countries. The size of tankers has increased commensurately: at the end of World War II, the largest tankers were approximately 25,000 deadweight tonnes (DWT); today, they are more than 550,000 DWT. The world fleet of tankers grew from 160 million DWT in 1971 to about 267 million DWT in 1994.

Transportation of oil by sea leads seemingly inevitably to oil spills that disturb, stress or destroy the natural ecosystem in the marine environment. The main concern is prevention of oil spill accidents, followed by effective and efficient response when it occurs.

2.2 Pollutant Characteristics / Pollution Problem

According to Lentz and Felleman (2003), estimates of annual input of oil into ocean environments from all anthropogenic sources during the 1990s range from 242,000 to 6.1 million tonnes. The annual average is estimated to be 600,000 tonnes per year, although this is uncertain. A breakdown of the data by three defined source categories indicates vessel source spills far exceed the inputs from production and land-based sources combined, representing over 68% of the total input. The next largest source is land-based sources (23%), with production representing the smallest input by volume (9%). Inputs from vessel sources fall again into two categories: accidental spills (e.g., groundings and collisions) and operational discharges (e.g., oil discharged from tank cleaning, oil contained in discharged ballast water, oil from machinery spaces and discharge in bilge water). It is reported that roughly 34% of vessel input (107,000 tonnes) comes from accidental spills, while 66% (312,000 tonnes) comes from operational discharges. Data compiled by Etkin (2001) indicate that in the 1990s, accidental spills of oil totalled 104,996 tonnes/yr. Of this annual estimated volume, 88,972 tonnes were spilled from tankers, 2,606 tonnes from barges, 5,592 tonnes from non-tanker vessels, 4,646 tonnes from onshore pipelines, 2,747 tonnes from onshore facilities, and 403 tonnes as a result of offshore exploration and production activities. Fortunately, the statistics show that oil spills worldwide have generally decreased, despite the increase in transportation volumes.

The environmental impacts of oil spilt into the ocean are highly variable. The initial impact may vary from minimal (e.g., following some open ocean spills) to the death of everything in a particular biological community, depending on factors such as the type of oil spilled, the quantity and duration of the spill, seasonal, oceanographic and meteorological conditions, the nature of exposed biota, habitat and substratum, geographic location, and type of spill cleanup used. Oil spills often impact fisheries resources through the following ways: direct effects on the fish themselves (lethal and sub-lethal), direct effects on fisheries (tainting, or interference with fishing activities), and indirect effects through ecosystem disturbance (e.g., impacts on food chains). Generally, the short-term effect of oil spills on marine species and communities are well known and predictable. However, concerns are often raised about possible longer-term (chronic, sub-lethal) population effects through, for example, low levels of residual oil affecting the ability of certain species to breed successfully. In fact, extensive research and detailed post-spill studies have shown that many components of the marine environment are highly resilient to short-term adverse changes in the environment in which they live and that, as a consequence, a major oil spill will rarely cause permanent effects. The range of biological impacts after an oil spill can encompass physical and chemical alteration of natural habitats, e.g., resulting from oil incorporation into sediments; physical smothering effects on flora and fauna; lethal or sub-lethal toxic effects on flora and fauna; and changes in biological communities resulting from oil effects on key organisms, e.g., increased abundance of intertidal algae following the death of limpets which normally graze the algae.

The seriousness of oil spill impacts is primarily related to the speed of recovery of the damaged habitats and species. However, misunderstanding often arises because of the use of different criteria to determine recovery. Given the difficulties of knowing exactly what pre-spill conditions were, and how to interpret them in the face of natural ecological fluctuations and trends, it is unrealistic to determine recovery as a return to pre-spill conditions. The environmental impact of oil spills has been extensively researched over the past 30 years and a considerable amount has been learnt about the nature and duration of such effects. As a result, our predictive capability is probably better for oil spills than for many other types of marine pollutant (Dicks, 1998).

2.3 Technology for Management, Control and Recovery

There are two approaches for responding to oil spills at sea: containment and recovery of oil using booms and skimmers, and the enhancement of natural dispersion of the oil by using dispersant chemicals. Once oil strands on shore, a shoreline cleanup will be necessary. Alternative techniques are constantly being sought and old techniques reassessed: two techniques currently receiving renewed attention are *in situ* burning and the enhancement of the natural biodegradation of oil through the application of micro-organisms and/or nutrients.

Obe (2000) has analyzed the factors that determine the seriousness of marine oil spills and the fundamental technical difficulties of combating them at sea, in coastal waters and on shorelines. In this section, the limitations identified by Obe of the various response techniques are reviewed, including containment and recovery using booms and skimmers, chemical dispersion, protective booming and shoreline cleanup.

Containment and Recovery. The use of floating booms to contain and concentrate floating oil prior to its recovery by specialized skimmers is often seen as the ideal solution since, if effective, it would remove the pollution from the marine environment. Unfortunately, this approach suffers from a number of fundamental problems, not least of which is the fact that it is in direct opposition to the natural tendency of the oil to spread, fragment and disperse. Thus, even if ship-borne containment and recovery systems are operating within a few hours of an initial release (which is rare) they will tend to encounter floating oil at an extremely low rate. Wind, waves and currents, even quite moderate ones, also limit the effectiveness of recovery systems on the open sea by making deployment difficult and causing oil to splash over the top of booms or be swept underneath. Even when oil has been concentrated within a boom, many skimmers are only effective for a limited range of oil types, with severe limitations on the pumping of viscous oils and 'chocolate mousse'. Thus, it is rare, even in ideal conditions, for more than a relatively small portion (10-15%) of the spilled oil to be recovered from open water situations. In the case of the Exxon Valdez, for example, where enormous resources were dedicated to offshore oil recovery, the percentage was at most 9% (Obe, 2000).

Dispersants. The goal of the controlled use of dispersants is to reduce the overall impact of an oil spill on environmental and economic resources (Obe, 2000). In a number of countries the use of dispersants is severely restricted on environmental grounds, although the rapid dilution of the small dispersed oil droplets to below concentrations likely to cause biological damage has been shown to be rapid in open sea conditions. In these circumstances the decision to use dispersant, or not, is based on a comparison of the probabilities of significant damage being caused by dispersed oil droplets in one case and untreated floating oil slicks in the other.

In Situ Burning. An alternative technique involves concentrating the spilled oil in fire-resistant booms and setting it alight. *In situ* burning is not a new concept, but has recently received renewed attention, particularly in the USA. In practice, it is difficult to collect and maintain oil at sufficient thickness to burn. Further, as the most flammable components of the oil evaporate quickly, ignition can also be difficult. Residues from burning may sink, with potential long-term effects on seabed ecology and fisheries. There may be health and safety concerns related to the atmospheric fall-out from the smoke plume, and concerns that the fire might spread out of control (Obe, 2000).

Problems Related to High-Density Oil. High-density oil has high viscosity, a tendency to sink, and presents particular challenges for clean-up operations. According to the International Tanker Owners Pollution Federation (ITOPF) statistics, over the past 25 years about 40% of the 450 ship-source oil spills attended on-site by ITOPF's staff have involved medium or heavy grades of fuel oil, either carried by tankers as cargo or used by larger vessels as bunker fuel. All of the most significant incidents over the last 10 years have involved spills of heavy fuel oils, which include *Nakhodka* in Japan, *Baltic Carrier* in Denmark, *Erika* in France, and *Prestige* in the North Sea.

2.4 Numerical and Experimental Modelling Techniques

Oil spill drift prediction models have been coupled with geographic information systems, such as environmental sensitivity index (ESI) maps, and/or real time databases of wind and other oceanographic parameters. A model coupled with an ESI map can help response planners to predict simultaneously how spilled oil might move and spread within a particular body of water, and how it might affect sensitive sites and valued ecological resources. Incorporating real time meteorological data can reduce the uncertainty of oil spill trajectory predictions.

For example, an oil spill trajectory prediction model with a real-time database was used in Japan after the *Nakhodka* oil spill in 1997. Site data were transmitted from vessels to the database, and processed for the trajectory analysis.

2.5 Equipment for Detection and Measurement of Pollutants

In Situ Measurements. Oil, either as a surface film, emulsion or in the dissolved phase, can be detected and measured using fluorescence with excitation in the UV (typically around 360 nm) and emission from 410 nm to 600 nm (e.g. Henry and Roberts, 2001). Such measurements may be made on captured samples using a laboratory fluorometer, e.g. a Turner Designs Model 10-AU field fluorometer[1], or they can now be made *in situ*, e.g. using an Applied Microsystems Ltd. Spill-Sentry system (Andrews, 1997). The Spill-Sentry uses a 3-channel UV fluorometer that can be configured to observe the sea surface or the water column from a mooring. Using the spectral information, the class of hydrocarbon can be determined. The detection limit for dissolved hydrocarbons is below 5 ppm and a surface layer of less than 200 nm can be detected.

Underway measurements of dissolved hydrocarbons can be made using similar principles. The UV Aquatracka from Chelsea Technologies Ltd., for example, can be towed within an undulating vehicle such as SeaSoar, and the data returned to the ship via the tow cable. Thus real-time 2-D maps of dissolved hydrocarbon distributions can be obtained. Depth rating is to 600 m in the standard instrument, but a 6000 m version is available.

Sensors based on optical fibres have been used to study hydrocarbons in the sea. Kawahara et al. (1983) showed that hydrocarbons altered the refractive index of an unclad fibre that had been coated with a compound that absorbed hydrocarbons. In this case, light loss was proportional to hydrocarbon concentration.

Methane detection can be implemented with a metal oxide semiconductor sensor such as the Capsum METS, where the hydrocarbon diffuses from the seawater through a silicone membrane (10μm to 100μm depending on depth rating) onto the active semiconductor. Sensors are available with a depth rating of 2000 m to 3500 m with a detection range of 50 $nmol\cdot l^{-1}$ to 10 $\mu mol\cdot l^{-1}$. The sensor is not particularly fast, as the gas must diffuse through the membrane, an indication can be present in 3 s, but it takes some 5 minutes to reach 90% of the final value.

Remote Sensing Technologies. In order to conduct an effective oil-spill response, it is necessary to detect the oil pollutant as soon as possible and to predict the future position of the oil slick. For small spills, detection can be done by visual observation, but for any spill that covers more than a few kilometres, some form of aerial observation is needed. In some cases, visual observations from an aircraft are adequate, but as the area of the spill becomes larger, satellite imaginary is needed to provide a synoptic view of the spill.

Regarding the remote sensor type, several different bands of the electromagnetic spectrum are used to track oil slick by remote sensing as follows: radar - SLAR/SAR (3-30cm); microwave - radiometer (3-8mm); thermal infrared - video camera or line scanners (8-14μm); visual - film, video camera and spectrophotometer (350-750nm); ultraviolet -- film, video cameras and line scanners (250-380nm). For rain, fog or cloud, the only useful wavelengths are greater than 3mm. For clear days, the two infrared, visual and ultraviolet bands are acceptable. With the exception of the ultraviolet band and the laser fluorosensor, all the methods of detecting oil on water are indirect and subject to the diction of false targets.

There is no commercial satellite dedicated to marine oil spill response, so it is necessary to make attempts using existing satellite based sensors to track oil. Table 2.1 provides a summary of the relevant satellites and their sensors. The sensors onboard a satellite can be passive, such as SPOT's High-Resolution Visible (HRV) sensor, or active, for example RADARSAT equipped with SAR sensors. Passive optical sensors require daylight and clear skies for useful images. With respect to oil spill response, active sensors are likely to be the most useful as they are not unduly limited by cloud cover or daylight. SAR sensors are currently found onboard the Radarsat and ERS

[1] http://www.oilinwatermonitors.com

satellites. These have a swath width on the order of hundreds of kilometres. This scan width is an order of magnitude larger than the typical airborne SLAR. This means that satellite systems can effectively cover a much larger segment of the ocean than aircraft, but there is the limitation of overpass frequency, which is a couple of days for these satellites.

Table 2.1- Summary of relevant satellite sensor (Lehr et al., 2002).

	Passive Optical Sensor			Active Radar Sensor	
Satellite	SPOT	Landsat	IKONOS	ERS-2	Radarsat-1
Sensor	HRV	ETM+	IKONOS	SAR	SAR
Sensor Type	Multispectral	Multispactral	Multispectral/ Panchromatic	Radar-SAR	Radar-SAR
Resolution(m)	20	30	4 / 1	30	10 - 100
Revisit time (days)	26	16	~ 3	35	~3 to 5

Lehr et al. (2002) has examined the current status, opportunities, and limitations of satellite remote sensing. According to his review, the detection technique of spilt oil using satellites seems to face several challenges such as cost, platform availability, detection capacity, discrimination of oil slicks from other surface phenomena and over-washing and subsequent subsurface behaviour. He concluded that none of the limitations, with perhaps the exception of subsurface behaviour, are necessarily insurmountable as the technology improves – costs are decreasing, new satellites are being launched, sensor resolution is improving and new methods are being developed to reduce false positives. He also noted that satellites may play an important role in spill response beyond identifying slick location by providing ancillary environmental information or relaying surface drifter data.

Also, there is currently much interest in the development of new sensors for the remote detection of submerged oils and related petroleum products in the water column (Brown et al., 1995). Much of this interest has been spawned by recent spill events including *Erika* off the coast of France and the transportation of products such as Orimulsion, which can also submerge in the water column if it enters the marine environment. A number of sensors including laser fluorosensors and sonar are showing promise for the rapid detection of submerged oils. It is anticipated that this field of research and development will expand in the coming years.

Laser Induced Fluorescence: Is an active technique that has a high specificity by examining the spectral distribution of the induced fluorescence. The technique is claimed to be able to detect oil in complex environments such as beaches, kelp beds and within areas of sea ice. The LEAF instrument (Laser Environmental Airborne Fluorosensor) [2] was a joint development between the Minerals Management Service of the US Department of the Interior, Environment Canada, the Canadian Petroleum Association and others. An updated system (SLEAF) was built in 2000 to incorporate a scanning laser to broaden the field of view. While there are numerous reports available on the instrument's testing, there is little information on its recent use.

Frequency Scanning Radiometer: Was a project at MIT commissioned by the US Coast Guard to design and build a remote sensing

[2] www.mms.gov/tarprojects/161.htm

instrument that could estimate the thickness of oil spills as well as their extent. While laboratory trials were successful, at a range of up to 90 m, under field conditions the ability of the instrument to detect and quantify spilled oil decreased markedly with increasing sea state. As of 2003 the US Coast Guard considered that "the FSR remains in the prototype sensor category, its overall potential and prospects for future development have to be more fully defined" (US Coast Guard, 2003).

Shipboard Navigational Radar: Operating at X band, was demonstrated to be capable of detecting slicks formed from five barrels of crude oil during trials from the Canadian Coast Guard cutter *Mary Hitchens* in 1987. Detection was possible in winds of over 30 knots (Tennyson, 1988) and at ranges of up to 17 km. However, Brown et al. (1995) caution that the technique had only been used where the presence and location of the slick was known.

Laser Ultrasonic: Techniques have been evaluated for their potential to estimate oil spill thickness (Choquet et al., 1993). This innovative technique used three lasers. The initial flight tests were unsuccessful and the current status of this technology is unknown.

Compact Airborne Spectral Imager (CASI): Despite difficulties over interpretation and specificity, oil on the sea surface can be detected and, to some extent classified into broad categories such as light refined, light crude, heavy crude and heavy refined oil. Interpretation needs to consider the viewing angle, the properties of the underlying water, the incident light conditions, the depth and the characteristics of the seabed. Airborne remote sensing using the CASI instrument during the 1996 *Sea Empress* oil spill off Milford Haven gave data on the position, extent and motion of the surface oil while changes in thickness could be estimated (Byfield, 1999). Measurements of actual thickness, discrimination of cargo oil from fuel oil and quantitative estimates of the dispersed oil were not possible at the time.

More recent research has led to improved algorithms for classifying oil based on CASI data, using water-leaving radiance from surface and dispersed oil, which may provide a basis for determining the absolute thickness of surface oil, and for estimating the concentration and quantity of dispersed oil (Byfield, 1999).

Oil in Sediments. Spilled oil that finds its way into sediments on the seabed may persist for decades. In deep, cold waters degradation processes are likely to be slow. Monitoring procedures following major spills vary. In the example of the grounding of the *Braer* off Shetland on January 5, 1993, (the 11^{th} largest oil spill as of 2003) samples of seabed sediments are still collected annually from selected areas for laboratory analysis to assess the continuing implications for fish and shellfish. Simple grabs and corers are used for sample collection. The standard analytical techniques conform to the ISO17025 standard with quality assurance by the UK Accreditation Service (UKAS). No description of any long-term *in situ* measurements of spilled oil within sediments has been found.

Land-Based Inputs of Oil to the Sea. Land based inputs of oil to the sea were seen as the most uncertain by the recent NRC review on the inputs and fate of oil in the sea (NRC, 2003:78). The uncertainty in the global input covered three orders of magnitude: from a minimum of 6,800 tonnes to a best estimate of 140,000 tonnes and a maximum of 5,000,000 tonnes. It is therefore *possible* that this source of oil to the sea dominates all others. The measurement challenge is incredibly difficult because the sources are so numerous, including: wastewater discharges; industrial discharges into watercourses; refinery operations; urban runoff and ocean dumping. To reduce this uncertainty, the NRC report recommended that 'all major rivers that have significant urban development in their watersheds be monitored for petroleum hydrocarbons and PAH (polyaromatic hydrocarbons)' (NRC, 2003:79).

The recommended sampling frequency was monthly from the bottom, mid-water and surface. Such samples could be analyzed by any of the instruments and methods described above for bulk oil concentration. Analysis for the concentrations of individual compounds would need to be done using a mass spectrometer, chromatograph or other similar instrument.

2.6 Testing and Certifying Procedures

The overall objective of the certification concept is to stimulate improvements of oil spill response capability through the introduction of a set of quality standards for oil spill response equipment.

The American Society for Testing and Materials (ASTM[3]) has developed procedures, guidelines and standards for the testing and certification for tools and equipment for oil and hazardous spills, which includes skimmers, pumps, and absorbents (for examples - see ASTM, 2001, 2002a,b,c, 2003). In addition, they developed standards on how to carry out oil spill response operations (ASTM, 1999).

In most countries, the testing and certification of oil spill equipment and tools is carried out by government or government-supported entities. For example, the United States has operated the Oil and Hazardous Materials Simulated Environmental Test Tank (OHMSETT[4]). OHMSETT has a large test tank (203 m long, 20 m wide, 3.4 m deep) allowing testing of full-scale equipment. The tank's wave generator creates realistic sea environments, while data collection and video systems record test results. At OHMSETT, the following test parameters are controlled or measured: sea state (wave height, length, and period), tow speed, meteorological data, water temperature and salinity, volume of oil encountered and recovered by test equipment, oil-water ratios, physical characteristics of experimental oil, and behaviour of treated oils. OHMSETT has tested various oil spill equipment including booms, skimmers, sorbents, temporary storage devices, pumping systems, remote sensing devices and fire-resistant booms. Many public and private sector entities have contracted the use of OHMSETT as a research centre to test oil spill containment and clean-up equipment and techniques, to test response equipment, and to conduct training with actual oil spill response technologies.

2.7 Cooperation with Other Organizations

Organizations which cover relevant issues are listed as follows:

- International Maritime Organization (IMO)
- Office of Response and Restoration, US National Oceanic and Atmospheric Administration (NOAA)

3. MARINE DEBRIS AND LITTER

3.1 Introduction

Marine debris and litter is recognized as a major marine pollution that destroys the ecological, economic, cultural, recreational and aesthetic values of the marine ecosystem and its components (Laist, 1997). Many academic studies have dealt with the problems of debris in various marine environments, such as the European coasts (Galgani et al., 2000), Mediterranean seas (Golik, 1997), Caribbean region (Coe et al., 1997), and the United States (Ribic et al., 1997). The studies have covered wide topics relating to marine litter, such as the amounts, types and distribution and biological impacts of marine debris in their respective environments, and the sources of and solutions to the marine debris problem.

[3] www.astm.org
[4] www.ohmsett.com

In responding to growing concern over marine debris, governments have taken actions nationally as well as internationally. Many countries have carried out management policies and practices to control the input from land and ocean activities, to assess their potential impact on marine environments and fishery resources, and to clean up the accumulated debris on the seabed. National policies often include R&D projects to develop an integrated management strategy and practice guidelines on marine litter problems at the national level.

An example can be found in the case of R&D carried out in the Republic of Korea, which includes a survey of the status of marine litter in ports and other coastal regions, including important fishing areas, and the clean-up of marine litter, prevention of the input of litter to coastal environments especially from land-based sources, development of equipment and facilities for survey and clean-up of marine litter, prevention of input, treatment for re-use and disposal of collected materials, and relevant legal and institutional arrangements.

This section summarizes the environmental pollution problems of the oceans caused by the marine debris and litter in the world, and the state-of-the-art technology for management, control and recovery of marine litter in the ocean. The latter is reviewed with special reference to the case of the Republic of Korea.

3.2 Pollutant Characteristics / Pollution Problem

Marine litter is any persistent manufactured or processed solid material which is discarded, disposed of, or abandoned in the marine and coastal environment, sometimes called marine debris. Depending upon its composition, marine litter may sink to the seafloor, drift in the water column, or float on the surface of the sea.

There are multiple sources of marine debris but they can be categorized into two major groups: land-based sources and ocean-based sources. The main land sources of marine debris are combined sewer overflows, storm drains that empty directly into streams, rivers and bays, beachgoers, other non-point sources, solid waste and landfills and industrial activities. Commercial fishing, recreational fishing and boating, and the operational wastes of cargo vessels and offshore mineral and oil and gas exploration, illegal dumping or littering are just some of the ocean-based sources of marine debris.

The various plastic wastes generated from these sources are among the most pervasive and threatening forms of debris found in the oceans. Floating litter poses unique hazards to wildlife, recreation, tourism, fisheries, and humans. Floating debris can also travel long distances over the ocean and can be deposited far from its sources. The widespread nature of marine litter, its inability to recognize borders, and difficulties in identifying marine litter sources have made effective laws difficult to draft and even harder to enforce.

Litter threatens marine life through entanglement, suffocation and indigestion and is widely recognized to degrade the visual amenities of marine and coastal areas with negative effects on tourism and general aesthetics. Thousands of marine animals die every year from entanglement in fishing line, strapping bands, discarded ropes and nets, and plastic six-pack rings. Accidental ingestion is another problem posed by marine debris and many marine animals confuse plastic items for food, which causes internal injury, intestinal blockage, or starvation. Many of the species most vulnerable to the problems of floating debris are endangered or threatened, including marine mammals, sea birds and sea turtles. Floating debris can also endanger human health and safety through disease transmission, sharp objects can cause injury, and floating debris including ropes can disable vessels when propellers become entangled.

Marine litter is a visible threat to wildlife, but also an invisible one. It is found in large quantities on the seabed, where it kills and injures out of sight. 'Ghost fishing' by discarded or lost fishing nets is just one of many examples. Marine litter also threatens marine and coastal biological diversity by destroying coastal 'nurseries', where new life would otherwise emerge. Litter can also transport invasive species between sea areas. According to a survey of the U.S. Academy of Sciences in 1997, the total input of marine litter into the oceans, worldwide, was estimated to be approximately 6.4 million tonnes per year from both land and sea sources[5].

3.3 Technology for Management, Control and Recovery

Many countries have carried out research surveys to reveal the status of marine pollution, including the amount, distribution, and environmental impacts. Korea is also carrying out such baseline studies, but their approach is distinctive in that they have developed technical equipment and facilities to respond practically to the marine litter problem. This section describes the state of the art of relevant techniques for responding to marine litter problems by reviewing the research project 'Integrated Management System for Marine Debris', started in 1999 in the Republic of Korea (Kang, 1999-2003).

In addition to the development of technical equipment, the project includes a field survey on the distribution and amount of marine litter in the Korean seas, and the administrative arrangements on how to manage the marine litter problem at the national level, as well as educational programmes to increase public awareness on the marine litter problem.

The aims of the project are largely to develop 1) equipment for the prevention of inputs from rivers, 2) *in situ* survey devices, 3) clean-up equipment, and 4) treatment and reuse of marine litter.

<u>Prevention.</u> In order to prevent floating land-based debris from entering the coastal region through rivers or channels, devices called 'trash booms' have been developed by modifying oil contaminant booms. These have been applied in estuarine environments in Korea. In developing the trash boom from a viewpoint of hydrodynamics, tension with expected current velocities was determined by a field experimental approach in order to ensure the utility of the trash boom in severe environmental conditions (Kang, 1999-2003). Early field experiments showed several shortcomings. Finally, an improved floating debris containment boom with solid floatation was developed.

<u>Recovery.</u> The recovery operation for marine debris is a crucial part in the management strategy of marine litter. The recovery of marine debris embedded in marine sediment requires some specific equipment for ensuring efficient operation. In this respect, Kang (1999-2003) has developed a multipurpose marine waste cleaning ship equipped with recovery devices such as orange grapple, rake, cutter, and pick up net. The basic concept of the "Multi-functional Marine Debris Recovery System" is to build a floating vessel and relevant equipment to work in shallow water to remove marine debris. The vessel has an efficient multi-joint recovery crane whose working depth is about 15 m. The operator of the multi-joint crane on board can switch recovery devices easily and quickly.

In order to maximize the operability in shallow waters, the propulsion system has two azimuth thrusters that can be lifted and tilted by a hydraulic mechanism. Supplementary tools are an auto washer system, fixed gallows and winch system. A detection system for marine

5 http://marine-litter.gpa.unep.org

debris must be able to deal with the high turbidity in shallow water. The development of the whole system including the vessel and auxiliary recovery devices was completed around the end of 2003.

Treatment/Re-use. Consideration should be paid on how to treat the recovered litter. In determining the treatment method, it is necessary to identify the physico-chemical characteristics of objects.

As marine debris contains salt, sludge and other substances, any meaningful treatment must be preceded by an effective pre-treatment technology. It is necessary to develop a chain of processes for pre-treatment: sorting, cutting, lead separation, crushing, salt and sludge cleaning (Kang, 1999-2003). All kinds of marine debris must be pre-treated before the main sub-process, which consists of Refuse Derived Fuel (RDF) production, thermal volume reduction, and incineration. Brief descriptions are given below for each process.

Aside from polystyrene buoys, many items of marine debris (≈50%) can be transformed to RDF. The present RDF production facility was built in 2000 and has capacity of 50kg/hr as a test pilot. Even though the marine debris contains a lot of seawater, it has higher heat release rate than land-based debris.

Polystyrene buoys are one of most cumbersome forms of marine debris because their volume fraction is very high. Kang and colleagues have developed a thermal extrusion system for volume reduction of waste buoys. The Korean government plans to deploy it in another 30 areas of high abundance of waste buoys by 2006.

For some items of marine debris that cannot be transformed to RDF, reusable or recyclable forms, it was necessary to develop a stabilized incinerator for marine debris (Kang, 1999-2003). A test pilot has been built this year, and it has been shown to satisfy the emission standard for discharge gases. There are plans to deploy such equipment on mobile vessels to avoid localizing the treatment of marine litter.

3.4 Numerical and Experimental Modelling Techniques

Most marine litters are input through rivers during the flooding period. In this respect, a few studies were carried out to establish a numerical model to estimate the pathways, accumulation sites, and amounts of land-based debris, taking into account the sinking rates. To test its suitability, a comparison has been made between results from the numerical model and field survey. The results showed that hot spots (high accumulation areas) of marine litter derived from the field survey using trawl techniques are larger and more widely distributed than those from the numerical model. The bias might come from the underestimation of sinking rates being used in the numerical model and implies that more studies need to identify the sinking rates (Kang, 1999-2003).

3.5 Equipment for Detection and Measurement of Pollutants

Marine Debris. Monitoring marine debris *at sea* is difficult, given its diversity and wide distribution. The US Marine Plastics Pollution Research and Control Act (MPPRCA) of 1987 empowered anyone to report a violation, including seafarers, those on beaches and passengers on vessels. Furthermore, the act made provision for a financial reward to those reporting violators.

One approach for estimating the volume of marine debris (NRC, 1995:211) involves recording in a comprehensive database data from vessel garbage logs and from port garbage disposal facilities in an attempt to quantify, on a statistical basis, the ‘missing’ component. However, the task was acknowledged to be enormous.

The issue of marine debris from shipping containers lost overboard is a serious one. Estimates of the number of lost containers, varies from in excess of 10,000 per annum to less than 2,000. If afloat, these pose a danger to navigation, as well as representing a pollution risk. Since 1998 Météo France has used a trajectory prediction model for lost containers[6]. This model has been used several times each year since 1998. The information provided on the trajectory of lost containers is used for navigational warnings and to aid possible recovery.

An indicator of marine debris can be obtained from studies of litter on beaches. Questions will remain over the source of beach litter, whether marine or terrestrial, but surveys on isolated oceanic islands reduce the problem of including locally generated debris in the assessment. In an oft-quoted brief correspondence, Ryan and Moloney (1993) reported on the quantity of marine debris on Inaccessible Island in the Tristan da Cuhna group in the South Atlantic in the years 1984, 87, 88, 89 and 90. Despite the introduction of MARPOL Annex V in 1988 (IMO, 2003) there was no reduction in marine debris observed, rather the authors concluded that there had been an exponential increase. However, the few data points point to caution being needed in data interpretation. For example, if the 1984 data point is omitted from the analysis, a linear trend is a better fit to the remaining data.

Communication with Dr Ryan has confirmed that constraints of logistics prevented a continuation of their survey of beach litter on Inaccessible Island. This is unfortunate, as the topic does require meaningful long-term data sets. Ryan and colleagues began a 5-yearly survey of 50 South African beaches in 1984, with the 5th iteration due in 2004 (Ryan, personal communication). However, Ryan noted “for macro debris these are confounded by increased beach clean-up efforts. We persist with them primarily for the meso-debris (2-10 mm), which is largely ignored by beach clean-ups, and shows some interesting trends - virgin pellets decreased in 1999, whereas fragments of user items continued to increase”.

There are also concerns over the objectivity and accuracy of beach litter surveys by groups of volunteers. In surveys by volunteers, without scientific oversight, Amos (1993) concluded that assessments undercounted by some 50%.

Microscopic plastic fragments in ocean waters and within sediments on the seabed have not been studied extensively. Thompson et al. (2004) reported on the collection of samples of micro-plastics from the seabed in coastal waters near Plymouth and 17 other beaches around the UK. Some one third of particles were identified as synthetic polymers. In an attempt to identify trends in micro-plastics abundance in open waters, Thompson et al. examined preserved samples of plankton collected from Continuous Plankton Recorder surveys since the 1960’s. A “significant increase in abundance over time was found, from 0.01 fibres per m^3 in the 1960’s to over 0.03 fibres per m^3 in the 1980’s and 90’s. As this is the focus of recent research little is known on the biological impact of micro-plastics. Thompson et al. (2004) showed that zooplankton, worms and barnacles ingested micro-plastics, but did not attempt to show that toxic substances passed into the animals. More work is needed.

Seabed Litter. It is probably true that little is known on the true extent of litter on the seabed of the world’s oceans. The task of assessment is difficult. The tools that may be used include trawls, remotely operated vehicles (ROVs), divers, sonar and video. Each has its limitations, not the least of which are practical limits on operating depth and the high cost of systems capable of working in the deep ocean. Moore and Allen (2000) noted that in contrast to numerous studies on beach litter “very few

[6] http://www.meteorologie.eu.org/mothy/plaquette_en.html#Containers%20drift%20model

have examined the types and distribution of marine debris on the seafloor".

Stefatos et al. (1999) reported on the first survey of seabed litter in the Gulf of Patras (in 1997) and Echinadhes Gulf (in 1998), both in the eastern Mediterranean Sea. While these areas have relatively low coastal population (250,000 and 50,000 respectively) these waters form the main trade route between Patras, Greece and Italy. The sample collection was by beam trawl with a 15 m wide net at depths of 247-360 m in the Echinadhes Gulf and 80-120 m in the Gulf of Patras.

An earlier seabed litter survey in the eastern Mediterranean (Galil et al., 1995) also used a beam trawl, but only 2 m wide, compared to the 15 m wide trawl used by Stefatos et al. Their survey covered 17 sites from the coast of Israel to Cyprus and from Egypt to Italy.

In an extensive study of debris on the sea floor of European coasts, gathered from 27 oceanographic expeditions, Galgani et al. (2000) used observations from manned submersibles as well as from beam trawls. Debris collected from the trawls was sorted into 7 or 8 categories.

Observations from the submersibles *Cyana* and *Nautile* were made in the NW Mediterranean, the Bay of Biscay and the Celtic Sea, with 60 dives in all. Data were recorded as items per km of track (tracks varying from 730 to 6500 m) and *not* areal densities (items per km^2). Table 2 shows a summary of Galgani et al.'s results for the submersible dives. For comparison, a column has been added with an *estimated* extrapolation to items per km^2, based on an *estimated* visual field of view of 5 m either side of the track of the submersible. This conversion was not attempted by Galgani et al.

The estimated litter areal density at three of the sampling sites visited by submersible exceeded the highest areal density of litter collected with beam trawls irrespective of depth. This may point to the trawl surveys underestimating litter on the seabed.

Table 2- Seabed litter data obtained from manned submersibles, from Galgani et al. (2000), with an *estimated* computation of the areal density.

Locality	**Depth (m)**	**Items per km**	***Estimated* items per km^2**
NW Mediterranean off Nice and Marseilles	-	104	10,400
NW Mediterranean at 43° 45' N 8° 43.5' E	1,300-1,400	92	9,200
Submarine canyon off Nice	2,700	9.1	910
Off Cape Breton canyon, Bay of Biscay	1,450-1,850	22	2,200
Off Cape Ferret, Bay of Biscay	850-1,450	16.53	1,653
Meriadzec Terrace, Celtic Sea	2,200-2,400	14.86	1,486

3.6 Testing and Certifying Procedures

There is still no standard or protocol on how to test or certify tools and equipment relating to marine litter and debris.

3.7 Cooperation with other Organizations

Organizations which have been involved with marine litter issues are listed as follows:

- Korea Research Institute of Ships and Ocean Engineering / Korea Ocean Research and Development Institute (KRISO/KORDI)
- French Research Institute for the Exploitation of the Sea (IFREMER)
- Regional Seas Programme, United Nations Environment Programme (UNEP) - relating to establishment of global management regime on the marine litter issue.

4. CO_2

4.1 Introduction

Hoffert et al. (1979) estimated using their box diffusion model that if 90% of fossil fuels in the earth were depleted by 2100, the partial pressure of CO_2 (pCO_2) in the atmosphere would settle at an equilibrium of 1150ppm between the atmosphere and ocean in about 3000 years. The reason why it takes so long to reach equilibrium is because the ocean water is almost completely divided into two layers, surface and deep waters, by a thermocline. According to Hoffert et al. (1979), before the equilibrium, we would face a maximum pCO_2 of 2800ppm temporarily at the end of the 21st century, if we do not pay attention to the reduction of CO_2 emission (the so-called business-as-usual case) and continue to inject CO_2 into the atmosphere. This will be disastrous in many aspects, such as desertification of fertile lands, raising the sea surface level, and imposing impacts on marine life in the surface water.

4.2 Pollutant Characteristics / Pollutant Problem

The Intergovernmental Panel on Climate Change (IPCC) reported pCO_2 in the atmosphere in the range from 550ppm to more than 1000ppm at the end of the 21st century (IPCC, 2001). However, Thornton and Shirayama (2001) pointed out that even the pCO_2 of 560ppm causes nontrivial damage to benthos such as sea urchins in continental shelf waters. This implies that even the IPCC's most conservative scenario may not be sufficient for the sustainability of marine ecosystems on the continental shelves. More recently, the data from three international research projects, the World Ocean Circulation Experiment, the Joint Global Ocean Flux study, and Ocean-Atmosphere Carbon Exchange Study, were analysed by Sabine et al. (2004) and Feely et al. (2004), who claimed that the ocean has absorbed half of the anthropogenic CO_2 since 1880, and the rest remains in the atmosphere. As Takahashi (2004) noted, this means that the land plants have been neutral for atmospheric CO_2. To avoid catastrophic overrun of atmospheric pCO_2, and to avoid direct impacts of pCO_2 in the surface ocean, we need an energy alternative to fossil fuel, and means to sequester CO_2.

CO_2 ocean storage may be categorised into two methods, namely, direct injection (Marchetti, 1977; Liro et al., 1992; Ohsumi, 1995; Broecker, 1997) and ocean fertilisation (Martin, 1990; Jones and Otaegui, 1997; Suzuki et al., 2003). Both need further research, partly because the efficiency by which the particulate organic carbon sinks into the deep ocean (the so-called biological pump) has not been examined in any field experiment[7]. If there is not such a pump, CO_2 absorbed in increasing phytoplankton may be recycled only in the upper waters and not sequestered in the ocean. Therefore, we focus on technologies necessary for direct injection here. One of the uncertainties in this option is its impact on marine organisms near injection points before CO_2 is diluted widely in the ocean (Herzog et al., 1996; Auerbach et al., 1997; Caufield et al., 1997; Sato and Sato, 2002; Herzog et al., 2003). Therefore, collecting data on biological damage by CO_2 is a pressing need in the marine biological society (e.g. Kita and Ohsumi, 2004; Portner et al., 2004; Riebesell, 2004; Ishimatsu et al., 2004; Kurihara et al., 2004; Kikkawa et al. 2004; Sato, 2004).

4.3 Technology for Management, Control and Recovery

Currently, there are two methods of direct injection of CO_2: middle-depth dissolution and deep bottom storage. Since the density of liquid CO_2 (LCO_2) is larger than that of seawater below the depth of about 3000m, the injection

[7] www.cslforum.org

depth across 3000m gives different storage concepts.

In the former case, LCO_2 is discharged at depths of less than 3000m in the form of droplets, which dissolve during their rise. The technologies for dilution are required to minimise biological impacts. As hydrate is formed at the interface between LCO_2 and seawater under high pressure and low temperature conditions, it is necessary to know the dissolution rate through the hydrate film (e.g. Teng et al., 1996; Hirai et al.; 1997, Aya et al., 1997; Rehder et al., 2004). By using the dissolution rate and the rise velocity of a droplet with some diameter and density, it is possible to calculate the distance for the complete dissolution of the droplet. To obtain large dilution, it is planned to use a ship towing a pipe more than 2000m long (Ozaki, 1997).

The formation of hydrate should be considered. Masutani et al. (1997) examined the morphologies of LCO_2 droplets emitted from nozzles with various diameters and materials under the various conditions of temperature and pressure. Some practical designs for the nozzle were suggested by Minamiura et al. (2004) and Yamasaki et al. (2004). Hydrate gives rise to another difficulty in the injection system: the flow of LCO_2 may be blocked in the pipe or the nozzle when seawater comes in, even though a non-return valve is used. Some practical methods to exchange LCO_2 and other liquid like LN_2 at the start and end of the operation should be examined in laboratory-scale pressure vessels.

In the case of deep storage, LCO_2 droplets injected below 3000m sink and stay at the seabed hollows to form CO_2 lakes, which are covered with hydrate film. Since the hydrate suppresses the dissolution rate of CO_2 into the seawater and the current in the boundary layer near the deep seabed is normally slow, LCO_2 can be expected to remain in the lakes for some time period (Brewer et al., 1999). Although the ecosystems directly in the lakes are extinguished, the lakes are unevenly distributed. However, it is necessary to investigate the biological impacts caused by the dissolved CO_2 near and downstream the lakes (Omerod and Angel, 1996), because there is still dissolution from the surfaces of the lakes. The same discussion on the biological damage by CO_2 arises as that in the case of the middle-depth dissolution.

4.4 Numerical and Experiment Modelling Techniques

Numerical models for predicting CO_2 transfer in the ocean are classified in three spatial scales: near field (100-1000m), meso-scale (10-100km), and ocean scale (1000-10000km). The near field models are based on two-phase flow with mass and heat transfers. Alendal and Drange (2001), Sato and Sato (2002), and Chen et al. (2003) investigated the behaviours of LCO_2 droplet plumes and the diffusion of dissolved CO_2. The results were compared as ensemble studies and resulted in a proposal for standardisation of empirical models for some important physical parameters in the 7th Technical Committee Meeting of the International Collaboration Project on CO_2 Ocean Sequestration in Cairns in 2001.

Ocean scale simulations have been conducted by Dewey et al. (1997) and Wickett et al. (2003), the latter of which used an ocean circulation model with a 1° mesh. The purpose of this type of simulation is to predict the time period of sequestration and mixing volume (the dilution ratio) within hundreds of years. The results largely rely on the vertical eddy diffusivity, the measurement of which is also one of the urgent research topics.

There have been many kinds of experimental studies so far with respect to the direct injection of CO_2, the objectives of which vary widely. The following list of such experiments excludes biological impacts and field measurements.

- Nozzle assembly and morphology of hydrate formation in a high-pressure vessel (Masutani et al. 1997; Minamiura et al. 2004; Yamasaki et al. 2004).
- Droplet plume behaviour in a channel of circulating stratified water (Socolofsky et al. 2000; Sato and Sato 2001).
- Turbulent wake of a pipe in a towing tank (Tejima et al. 2004).

4.5 Equipment for Detection and Measurement of Pollutants

The challenge in measuring oceanic CO_2 is not in the measurement itself, but in obtaining robust estimates of the net flux given its variability in space and time and the sparseness of the *in situ* sampling programmes.

To properly interpret the role and fate of carbon dioxide entering the oceans it is necessary to measure carbon as different inorganic species, namely:

- As dissolved carbon dioxide:
  $CO_{2gas} \Leftrightarrow CO_{2aq}$
- As aqueous carbon dioxide:
  $CO_{2aq} + H_2O \Leftrightarrow H_2CO_3$ (8 μmol kg^{-1} surface ocean)
- As the bicarbonate ion:
  $H_2CO_3 + H_2O \Leftrightarrow H_3O^+ + HCO_3^-$ (1617 μmol kg^{-1} surface ocean)
- As the carbonate ion:
  $HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$ (268 μmol kg^{-1} surface ocean)

However, at the present state of analytical systems available to oceanographers, the concentrations of the individual species in seawater cannot be determined directly and in isolation. The methods employed to make measurements that include two or more of the species include:

TCO_2: Is determined in discrete water samples as $C_T = [CO_{2aq}] + [HCO_3^-] + [CO_3^{2-}]$, obtained by acidifying the sample and measuring the amount of carbon dioxide gas that is evolved. In the standard protocol developed for the US Department of Energy CO_2 measurement programme this is done using a UIC Inc. model 5011 CO_2 coulometer on the research vessel (Dickson, 1997 – SOP2).

Alkalinity: Dickson (1997) has described total alkalinity (A_T) as 'a mass-conservation relationship for the hydrogen ion'. The shipboard laboratory measurement uses an automated, temperature controlled closed cell potentiometric titration. A_T is calculated from the sample volume and e.m.f. data as described in the Annex to SOP3 in Dickson (1997).

pH: The approximation that pH = -log $[H^+] = [H^+]_F + [HSO_4^-]$ holds for sea water at pH > 4 and is obtained from a sequence of measurements of the e.m.f. of a cell comprising a reference electrode, concentrated potassium chloride solution, the sample, and a glass electrode. The sample in turn will be a buffer solution of known pH and the seawater sample to be measured. Resolution to 0.001 pH units can be achieved if the temperature is known to better than 0.1˚C and the sample arrangement avoids exposure of the sample to atmospheric CO_2 (Dickson, 1997 – SOP6).

Fugacity of CO_2 Gas in Equilibrium with a Seawater Sample $f(CO_2)$: Is calculated from the partial pressure of the CO_2 gas, corrected for the non-ideal behaviour of the gas as determined from its equation of state (Dickson, 1997 – SOP24).

Measurement of any two of the above four quantities can provide a full description of the CO_2 system in seawater, although the errors differ depending on the combination of actual measurements used. It is usual to measure more than two of the parameters to reduce uncertainty. The full procedures are described in the Annex to SOP2 in Dickson (1997).

Reference Standards: Certified reference standards for total dissolved inorganic carbon and for total alkalinity are available from Dr A.G. Dickson at the Scripps Institution of Oceanography, San Diego. Uncertainties in the certified samples are ±1.5 μmol kg^{-1} in C_T and ±2 μmol kg^{-1} in A_T, over a 3 year period (Dickinson, 2001).

Automated measurements of pCO_2 can be made from a vessel when underway using an infrared gas analyzer or gas chromatographic analysis of the CO_2 concentration within an air sample that has equilibrated with the seawater sample. This technique has been extended to automated measurement from a moored buoy (Friederich et al., 1995) using a Licor LI-6252 CO_2 analyzer. While suitable for sea surface use, this technique would not easily be adaptable for use beneath the surface. Degrandpre et al. (2000) describe an *in situ* fibre optic CO_2 sensor based on multi-spectral optical absorbance measurement after the CO_2 diffusing through a gas-permeable membrane reacts with a sulphonephthalein indicator. The depth rating of the instrument is primarily determined by the gas permeable membrane. Degrandpre has recently commercialised the instrument, and a version to 1500 m is available[8].

Distinct from the dissolved carbon discussed above is particulate organic carbon (POC). Information from optical transmission measurements can shed light on POC concentrations (Bishop, 1999). Bishop has now implemented this technique on autonomous drifting floats[9], capable of operation down to 2000 m.

Knowledge of the atmospheric CO_2 concentration is needed to interpret fully the oceanic data, as it is the difference between atmospheric and oceanic concentration (and wind speed) that drives the air-sea exchange of CO_2. Atmospheric CO_2 measurements are usually carried out using infrared gas analyzers (IRGA).

4.6 Testing and Certifying Procedures

Hydrate tests in pressure vessels are possible candidates for test guidelines. However, forming CO_2 hydrate is still not easy compared with methane, even though we know its phase equilibrium conditions. For tests using pressure vessels, there are already some regulations made by other organisations.

4.7 Cooperation with other Organizations

IEA is the main organisation to lead the CO_2 ocean storage. National bodies active in the issue include NIVA in Norway, RITE and NMRI in Japan, and MBARI in USA. The Carbon Sequestration Leaders Forum (CSLF) provides funds for inter-governmental research projects.

5. NUTRIENTS

5.1 Introduction

Nutrients such as nitrogen and phosphorous are essential for the growth of the marine ecosystem but eutrophication is thought to be the main reason for declining quality of sea water in coastal seas and enclosed bays near cities. Nutrients are discharged as industrial effluent and waste waters of human activities. Particulate organic matter in waste waters is usually removed by sewage treatment but the inorganic matter is not removed. Nutrients discharged into seas in the past years might be taken by phytoplankton in primary production and transformed into organic matter and accumulated in water and bottom sediments in enclosed bays. The chemical and biological processes are very important in the marine ecosystem. At the same time, the transport and diffusion of nutrients is also important because the water flow is not simple in coastal estuaries.

[8] http://www.sunburstsensors.com/index.htm
[9] http://www-ocean.lbl.gov/NOPP.html

Regarding countermeasures against eutrophication, the regulation of total emission of nutrients from land is one way, but it may be difficult to dissolve the eutrophication in a short time because a large amount of the total emission in the past may be accumulated in waters and in the bottom sediment. To solve these complicated problems, ecosystem models have been developed using numerical calculations considering the flow and diffusion in coastal estuaries. An ecosystem model is expected to be a reliable prediction method for the outbreak of phytoplankton bloom or red tide, and the generation of oxygen deficient waters which cause significant damage to fisheries.

5.2 Pollutant Characteristics / Pollution Problem

Eutrophication may cause phytoplankton bloom or red tide under some weather conditions. Red tide may cause damage to marine creatures in two ways: one is due to the toxicity of the phytoplankton; the other is caused by the generation of hypoxia waters. Furthermore, the dead bodies of red tide plankton accumulated on bottom sediment may consume the dissolved oxygen near the bottom in the process of bacterial decomposition. Then, the oxygen deficient waters near the bottom layer may cause the generation of hydrogen sulphide and methane in the decomposition of organic matter by anaerobic bacteria in bottom mud. Moreover, if the bottom mud becomes oxygen deficient and is reduced, nutrients in mud become easy to elute into water, which may be another cause of eutrophication of the sea.

The main pollution problems by nutrients are summarized as follows:

- Hypoxia waters, which is toxic and harmful to organisms such as fish, crustacea and shellfish.
- Algal blooms, which may be toxic, harmful, unsightly and odours.
- Changes in population and reduced species diversity.
- Changes in phytoplankton leading to bleaching of coral reefs.

5.3 Technology for Management, Control and Recovery

Nutrients from land are mainly supplied through rivers. The total amount of nutrients depends on the forest area, population, livestock numbers, amount of applied fertilizer, the industrial effluent and the method of sewage treatment. The problems of nutrients on land are not considered in this report.

There are several kinds of artificial method to control nutrients in the sea. Tidal energy is used to control nutrients in enclosed bays by stimulation of tidal exchange so the circulation of water is enhanced to flush nutrients out to the ocean. For this purpose, some civil engineering works, such as dredging, may be needed to improve the geometry of the bay. Some people propose the introduction of pumps to enhance the circulation of waters in the bay. The pumps may be driven by wave power, solar power, or electricity.

To suppress the elution of nutrients from bottom sediment, sand banking is sometimes used, but the effects cannot be expected to continue for a long time.

An indirect means to control nutrients is by using sea plants, such as sea lettuce, which can absorb nutrients during their growth. Similarly, a project has been proposed to grow mussels in eutrophied bays to improve the water quality.

5.4 Numerical and Experimental Modelling Techniques

There are two main routes of nutrients in seawater. One is brought by the direct discharge of rivers and another is the decomposition of organic matter by bacteria in seawater. Therefore, the total amount of nutrients varies unsteadily depending on the activity of the ecosystem. Nutrients from land may be absorbed by phytoplankton in photosynthesis. They will transform into particulate organic matter or dissolved organic matter after the death of the phytoplankton. Organic matter accumulated on the bottom sediment may be decomposed into nutrients by aerobic bacteria, and they may return to the water column. To describe those complicated routes of the material circulation, some ecosystem models have been proposed.

Figure 5.1 shows the block diagram of the ecosystem model proposed by Nakata (1993). A box in Fig. 5.1 shows a state variable in the ecosystem. Six compartments are considered: phytoplankton (P), zooplankton (Z), particulate organic matter (POM), dissolved organic matter (DOM), phosphates (PO4) and three kinds of inorganic nitrogen (NH4, NO2, NO3). The variation of these compartments is described by partial differential equations including the advection and diffusion terms.

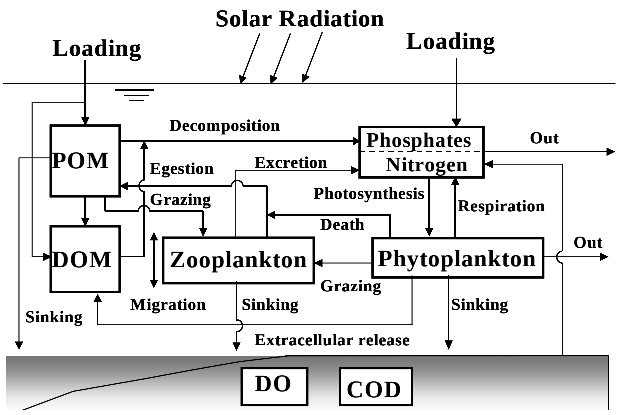

Figure 5.1- A marine ecosystem model.

One or more phytoplankton for dominant species in the sea can be taken in the model. The rate of growth of phytoplankton (P) is calculated by the production of photosynthesis, which depends on the intensity of light, water temperature and concentration of nutrients. On the other hand, the rate of decrease of phytoplankton is calculated by the extracellular release, respiration, grazing by zooplankton and benthos, mortality and sinking.

Similarly, the rate of zooplankton (Z) is given by the grazing of phytoplankton and particulate organic matter (POM), egestion, excretion, natural death, preyed by benthos and the diurnal vertical migration. Two kinds of organic matter (POM) and (DOM), phosphates (PO4) and three kinds of nitrogen (NH4, NO2, NO3) are formulated considering the material transport in the ecological food chain. The dissolved oxygen (DO) and the chemical oxygen demand (COD) are the passive compartments calculated from the values of the above compartments.

Detailed ecosystem models can include many compartments, not only the pelagic ecosystem, but also the benthic ecosystem. Kitazawa et al. (2003) developed such a model with the pelagic and benthic sub-models.

One of the problems of ecosystem modelling is the parameters between compartments. More than 100 parameters are needed for a simple ecosystem model in Fig. 5.1. The parameters depend on not only the physical environment, such as water temperature, salinity and flow velocity, but also chemical and biological effects due to the activity of bacteria. Consequently, the parameters strongly depend on the sea area, although empirical values are generally used in the present models. The development of databases for ecosystem parameters is very important.

5.5 Equipment for Detection and Measurement of Pollutants

The key substances that need to be measured to provide a comprehensive picture of the state of nutrients in seawater are described below:

Nitrogen as Nitrate and Nitrite: Nitrate concentrations may vary from below current detection limits ($<<0.1\mu mol.l^{-1}$) in the surface waters of oligotrophic gyres (e.g. the Sargasso Sea) to over 100 $\mu mol.l^{-1}$ in upper parts of tidal brackish estuaries. Nitrite levels are usually lower in surface waters due to biological nitrification, unless oxygen is deficient. The standard wet chemical analysis procedure uses an automated colorimetric method for the determination of nitrite. This procedure is used for surface water samples and for samples captured using water bottles. It is inappropriate for rapid sampling as the reduction from nitrate to nitrite and the colour-forming reaction takes time, leading to a minimum sampling interval of about 30s.

A practical implementation of this wet-chemical protocol for nitrate and nitrite determination is found in the Alpchem Autoanalyser. The analyser contains the necessary fluidics and optical components to process three channels simultaneously (e.g. for nitrate+nitrite, phosphate and silicate).

In situ versions of this wet-chemical determination of nitrate and nitrite have been produced, e.g. the NAS-2E from Envirotech LLC. This instrument can operate unattended, at water depths down to 250 m, for periods of 1 week to 1 year. Multi-channel wet chemical analyzers have also been produced by SubChem[10] for nitrate and nitrite, but also with options of up to ten channels to include iron (II), iron (III), ammonia, urea, phosphate, silicate, copper and manganese (Hanson, personal communication). This instrument has been used intensively in moored applications. However, the sampling interval for wet chemical instruments remains too long for operation on a towed profiler, e.g. SeaSoar or in an Autonomous Underwater Vehicle. For such applications the rapid response of a measurement technique that does not rely on wet chemistry is needed. For dissolved nitrate, such a technique is UV absorption spectrophotometry. One difficulty with the method is that the halide ions in seawater provide interference. However, nitrate concentration can be determined at a sampling rate of 1 Hz over a range of 0.1 to 100 $\mu mol \cdot l^{-1}$ (Clayson, 2000).

Nitrogen as Ammonia: Ammonia concentrations in open coastal waters may range from 1 to 5 $\mu mol \cdot l^{-1}$ although higher values may be found in the upper reaches of estuaries. The standard wet chemical shipboard analysis procedure uses an automated colorimetric method where alkaline phenol and hypochlorite react with ammonia to form indophenol blue, the colour produced being proportional to the ammonia concentration. Sodium nitroprusside is added to produce a more intense colour.

Recently, an *in situ* measurement technique has been introduced based on fluorescence. Statham and co-workers at SOC (personal communication) have used the method of Kerouel and Aminot (1997) to produce an *in situ* sensor.

Nitrogen as Urea and Other Organic Compounds: An estimate of the dissolved organic nitrogen can be made by determining the total dissolved nitrogen and subtracting the inorganic fraction as determined using the methods for nitrate, nitrite and ammonia as described above. Total dissolved nitrogen can be determined using a persulphate oxidation technique under alkaline conditions where all forms of nitrogen are oxidized to nitrate. The nitrate concentration is then determined by colourimetric analysis as above.

Phosphorous as Phosphate and Orthophosphate: The orthophosphate form (PO_4^{3-}) dominates. Laboratory analysis is by automatic colourimetry where ammonium molybdate and antimony potassium tartrate react with the sample in an acidified solution to form an intensely blue-coloured antimony-phospho-molybdate complex. The intensity of the colour produced is proportional to the phosphate concentration present in the sample. Recently, *in situ* instruments based on this method (i.e. wet chemis-

[10] http://www.subchem.com/prod01.htm

try) have become available (e.g. the NAS-2 from Envirotech LLC[11]).

Phosphorous as an Organically-Bound Phosphate and Polyphosphates: Organically bound phosphates and polyphosphates cannot be measured directly. The sample is treated with an oxidizing agent (an alkaline persulphate) and autoclaved. This converts all the phosphorus compounds to orthophosphate. Total phosphate is then estimated as for orthophosphate above.

6. PRODUCED WATER

6.1 Introduction

As the environmental issues surrounding produced water discharges were determined by the Committee to be of relatively minor concern compared to the other pollutants dealt with here, only a brief summary is presented in this section. A more detailed account is given in Veitch (2005).

6.2 Pollutant Characteristics / Pollution Problem

Produced water is the most voluminous operational waste associated with the offshore petroleum industry. It includes formation water and injected water. Produced water can contain inorganic and organic compounds, naturally occurring radioactive materials, heavy metals, and hydrocarbons. The volume of hydrocarbons introduced to the ocean via discharges of produced water is relatively small compared to other anthropogenic sources.

6.3 Technology for Management, Control and Recovery

Produced water discharges are closely regulated in most jurisdictions and there is an array of technology for controlling the pollutants.

6.4 Numerical and Experimental Modelling Techniques

Models of produced water include hydrodynamic modelling of the fate of the discharge and the possible effects on ecological entities. There is a lot of uncertainty associated with such models, particularly in terms of effects on biota.

6.5 Equipment for Detection and Measurement of Pollutants

Instruments and sensors exist for the detection of oil in water. Standards exist for calibration and for analytical procedures.

6.6 Testing and Certifying Procedures

This is a relatively mature operational issue and equipment is typically governed by standards embodied in regulations. There is relatively little opportunity for the ITTC to contribute to this issue.

7. BALLAST WATER AND SEDIMENT

7.1 Introduction

Discharge of ballast water and sediment has been recognized as an important mechanism for the transportation, introduction, and distribution of non-indigenous aquatic species and pathogens into new ecosystems, including fresh water lakes and estuaries. Newly introduced

[11] http://www.n-virotech.com/products/nas.htm

species and pathogens may pose hazards to human health and the health of the native ecosystem. There is also potential risk to infrastructure, interference with traditional resource use, and subsequent economic and social disruption.

7.2 Pollutant Characteristics / Pollution Problem

It is difficult to characterize fully ballast water and sediments as a pollutant as there are so many species being transported world wide and their impacts, both potential and realized, are so diverse. Bacteria, invertebrates, eggs and larvae taken up as ballast in any part of the world have the potential to be introduced into and subsequently invade a new habitat. An estimated 3 to 5 billion tonnes of ballast water are transferred internationally annually, and about the same volume is transferred regionally within countries[12].

One example of an invasive species is the comb jelly fish, native to the east coast of the Americas and introduced to the Sea of Azov, and the Black and Caspian Seas. This has been a major factor in the collapse of fisheries as it has disrupted the food webs of regional ecosystems, causing substantial changes in habitat and severe economic and social dislocation.

A second example is the zebra mussel, native to the Black Sea and introduced to the Baltic Sea, Western Europe, and the east coast of North America, including the fresh water inland waterways. It impacts infrastructure and native habitat by fouling, for example vessels' hulls, water pipes, and irrigation systems. It has displaced native species and disrupted the food webs of regional ecosystems. Economic impacts of the zebra mussel in the US over the past decade have been estimated to be about $1B.

There are many other examples, including cholera and toxic algae, both of which have the potential to adversely affect human health[13].

7.3 Technology for Management, Control and Recovery

Regulations promulgated recently under the auspices of the IMO constitute an internationally recognized mechanism for managing the issues associated with ballast water and sediments. Specifically, the *International Convention for the Control and Management of Ship's Ballast Water and Sediment* was adopted in February 2004[14]. This convention requires all ships to implement a ballast water and sediments management plan. IMO has taken a major role in addressing the problems associated with ballast water, including a program called GloBallast (Global Ballast Water Management Program), which aims to provide technical support and guidance concerning best and emerging practices to support the convention's implementation. Practical guidance is offered in the *Guidelines for the control and management of ships' ballast water, to minimise the transfer of harmful aquatic organisms and pathogens* (IMO Resolution A.868(20)).

In broad terms, the guidance proposes means to reduce the risks associated with ballast water discharges. A brief summary of the means gives a sense of the level of sophistication incorporated in the guidance: minimise uptake and discharge of ballast water; avoid unnecessary discharge; clean ballast tanks regularly; exchange ballast water on the open sea; treat ballast water on board; discharge ballast water to shore facilities for treatment.

While ballast water exchange at sea is currently considered (by IMO) to be the best management option, it is limited by ship safety considerations. Ballast water treatment may

12 http://globallast.imo.org/

13 http://www.imo.org/home.asp

14 http://globallast.imo.org/

prove to be a better long term option, and considerable development work is underway to provide better treatment technology, whether through mechanical (filtration, separation), chemical (biocides), physical (sterilization), or other means. The convention provides for two routes to compliance: a performance standard based on shipboard monitoring and treatment, or other acceptable management strategy (based on risk assessment); and a prescriptive standard directed at ballast water exchange, which effectively requires that 95% of ballast water be exchanged during such operations. It also provides for the application of innovative treatment technology. There is concern that the degree of uncertainty surrounding the organisms and their possible impacts on new habitat renders risk assessment inadequate.

7.4 Numerical and Experimental Modelling Techniques

Re-ballasting at sea can be restricted by the ship design, its operating profile, and weather conditions. Amongst the issues identified as requiring immediate evaluation are operational procedures for re-ballasting safely, including weather restrictions, and human factors; and stability and ship strength considerations arising from heretofore unusual loading conditions, free surface effects, and sloshing. The IMO *Guidelines* include an appendix *Guidance on safety aspects of ballast water exchange at sea*, which gives a more detailed account of the safety issues and how they might be addressed. Classification societies are also engaged in these issues.

7.5 Testing and Certifying Procedures

The proceedings of the 1st International Workshop on Guidelines and Standards for Ballast Water Sampling provides a comprehensive survey of the different aspects of the global problem of organisms in ballast water (Raaymakers, 2003). In particular the proceedings spell out the different requirements and options for the four key tasks:

- Sampling methods and technologies for further scientific research into the issues concerning organisms in ballast water;
- Sampling methods that would be suitable for providing information for hazard analysis and risk assessment;
- Sampling methods that would be acceptable for monitoring compliance and enforcement of international standards;
- Sampling methods that provide information on the effectiveness of alternative methods of ballast water treatment.

A useful review of the state of the art in the analysis of single cell marine phytoplankton is the report of an EU sponsored Workshop in 2002 (Groben and Medlin, 2002). Techniques for the identification of organisms and possible toxins in ballast water include:

Particle counting provides information on the size, volume and surface area of particles, but no information on the species, and the technique cannot differentiate between living cells and mineral particles. The Beckman Coulter Multisizer 3 instrument can sample particles in the size range 0.4 to 1200 μm.

Flow cytometry, originally developed for the rapid, automated sampling and analysis of blood cells, has been adapted successfully for the analysis of marine phytoplankton (Yentsch, 1990). A marine flow cytometer may be useful for cell concentrations in the range 1 to 10^4 cells per ml at a sample throughput of 1 ml per minute.

Molecular probes are based on oligonucleotides (short chains of nucleic acid that are stable) chosen to be complementary to a part of the ribosomal RNA of a phytoplankton or bacteria under study. Specific species in a mixed population may be detected and counted. The challenge is to design a molecular probe for the specific organism (or groups of organisms) of interest. This technology has been applied to the study of toxic marine phytoplankton including *Alexandrium tamarense* (Anderson et al., 1999). The molecular probe technique can be combined with a laser scanner to provide an automatic cell identification and count system for micro organisms[15].

Optical imaging in its simplest form may use a microscope and digital camera to aid an operator to identify organisms to species and to measure characteristics such as length. The technique is applicable to zooplankton as well as phytoplankton. Recently, instruments have been developed by the research community to provide automatic on-line monitoring and recognition for organisms in the size range 10-200µm. Below 10µm flow cytometry is the preferred technique. The ‘Flowcam’ is one example of an optical imaging and recognition system (Sieracki and Viles, 1998).

Bulk fluorescence may be estimated using an on-line fluorometer to give an indication of the total chlorophyll *a*. The method is most reliable when calibration samples of phytoplankton are taken, their chlorophyll extracted and quantified, as fluorescence yield varies between species. Although the method can provide a rapid on-line measurement, there is no specificity – the species composition need to be determined using another method.

7.6 Cooperation with other Organizations

IMO has established itself as the leading international organization in this issue.

8. CONCLUSIONS

The Committee on Assessment of Ocean Environmental Issues (CAOEI) was tasked by the 23rd ITTC with investigating ocean environmental pollution problems caused by spilled oil, marine debris, seabed litter, and other chemicals. Under this last category, the Committee considered the following pollutants: CO_2, nutrients, ballast water discharges, and produced water discharges. In fulfilling its role, the CAOEI has acted as a filter, or interpreter, of broad ocean environment issues for the ITTC Members at large, with the aim of identifying opportunities for the ITTC community to make contributions.

The assessment of ocean environmental issues requires a holistic, multi-disciplinary approach. At a general level, involvement of the ITTC might include specific actions that aim to catalyze the formation and strengthening of ties between ocean engineers and naval architects with scientists. More specifically, spilled oil and CO_2 storage were identified as having particular relevance to the ITTC. Marine debris, seabed litter, ballast water discharges, and issues related to nutrients were considered to be of continued interest. While produced waters and nutrients from land-based run-off are important environmental issues, the consensus view of the Committee was that they are of marginal relevance to the ITTC.

A summary of each pollutant investigated by the Committee is given in terms of the pollutant’s characteristics, technology used for its management, and numerical and experimental modelling. The status of equipment for detecting and monitoring the pollutant is noted, as is the status of testing and certifying procedures.

Should the ITTC wish to explore further its potential role in this area, it might maintain the Specialist Committee for a second term. Should the ITTC decide to expand its role in this area, it might consider establishing a more permanent Ocean Environmental Issues Committee, such as a working group reporting to the AC on specific issues of possible interest to the ITTC.

[15] http://www.chemunex.com/products/chemscan.htm

In order to lend clarity to the ITTC's nascent role in this area, ITTC Members should determine their current level of activity with respect to ocean environmental issues, their plans, and their in-house capabilities to address such issues.

At this early stage, it is premature for this Committee to take on the task of developing standards.

9. REFERENCES

Alendal, G. and Drange, H., 2001, "Two-phase, near-field modeling of purposefully released CO_2 in the ocean", J. Geophys. Res., Vol. 106(C1), pp. 1085-1096.

Amos, A.F., 1993, "Technical assistance for the development of beach debris data collection methods", Report to the US EPA TR/93-002.

Anderson, D.M., Kulis, D.M., Keafer, B.A. and Berdalet, E., 1999, "Detection of the toxic dinoflagellate *Alexandrium fundyense* (*Dinophyceae*) with oligonucleotide and antibody probes: variability in labeling intensity with physiological condition", J. Phycology, 35: 870-883.

Andrews, J., 1997, "Automated marine oil spill detection system development update", Marine Environmental Update, FY97(1), US Navy SPAWAR Systems Centre.

Auerbach, D.I., Caufield, J.A. and Adams, E.E., 1997, "Impacts of ocean CO_2 disposal on marine life", Environ. Modelling Assess., Vol. 2, pp. 333-343.

Aya, I., Yamane, K. and Nariai, H., 1997, "Solubility of CO_2 and density of CO_2 hydrate at 30Mpa", Energy, Vol. 22, pp. 263-271.

ASTM, 1999, ASTM Standards on Hazardous Substances and Oil Spill Response, 2nd Ed. USA.

ASTM, 2001, "ASTM F716-82 Standard Methods of Testing Sorbent Performance of Absorbents".

ASTM, 2002a, "ASTM F1084-90 Standard Guide for Sampling Oil/Water Mixtures for Oil Spill Recovery Equipment".

ASTM, 2002b, "ASTM F1778-97 Standard Guide for Selection of Skimmers for Oil-Spill Response".

ASTM, 2002c, "ASTM F1780-97 Standard Guide for Estimating Oil Spill Recovery System Effectiveness".

ASTM, 2003, "ASTM F1607-95 Standard Guide for Reporting of Test Performance Data for Oil Spill Response Pumps".

Bishop, J.K.B., 1999, "Transmissometer measurement of POC", Deep-Sea Research, 46(2): 353-369.

Brewer, P., Freedrich, G., Peltzer, E. and Orr Jr., F. M., 1999, "Direct experiments on the ocean disposal of fossil fuel CO_2", Science, Vol. 284, pp. 943-945.

Broecker, W.S., 1997, "Thermohaline circulation, the Achilles heel of our climate system: Will man-made CO_2 upset the current balance?", Science, Vol. 278, pp. 1582-1588.

Brown, C.E., Fingas, M.F., Fruhwirth, M. and Gamble, R.L., 1995, "Oil spill remote sensing: A brief review of airborne and satellite sensors", Presented at the SPOT Image 1995 User Group Meeting, Washington, D.C., U.S.A., August 24-25, 1995.

Byfield, V., 1999, "Monitoring oil pollution using airborne imaging spectrometers at visible and near-infrared wavelength", See http://www.soes.soton.ac.uk/research/groups/oil_monitor/oil.htm

Caufield, J.A., Adams, E.E., Auerbach, D.I., and Herzog, H.J., 1997, "Impacts of ocean CO_2 disposal on marine life: II. Probabilistic plume exposure model used with a time-varying dose-response analysis" Environ. Modelling Assess., Vol.2, pp. 345-353.

Chen, B., Song, Y., Nishio, M. and Akai, M. 2003, "Large-eddy simulation of double-plume formation induced by CO_2 dissolution in the ocean", Tellus, Vol. 55B, pp. 723-730.

Choquet, M., Heon, R., Vaudreuil, G., Monchalin, J., Padioleau, C., and Goodman, R.H., 1993, "Remote thickness measurement of oil slicks on water by laser-ultrasonics", Proc. 13th Biennial Conference on the Prevention, Behavior, Control, and Cleanup of Oil Spills, pp. 531-536, Tampa, Florida.

Clayson, C.H., 2000, "Sensing of nitrate concentration by UV absorption spectrophotometry", Chemical Sensors in Oceanography, M. Varney (ed.), Gordon and Breach, Amsterdam, pp. 107-121.

Coe, J.M., Anderson, S. and Rogers, D.B. 1997, Marine debris in the Caribbean region. Marine Debris: Source, Impacts and Solutions, D.E. Alexander (ed.), Springer, pp.15-24.

Degrandpre, M.D., Baehr, M.M. and Hammar, T.R., 2000, "Development of an optical chemical sensor for oceanographic applications: the submersible autonomous moored instrument for seawater CO_2", Chemical Sensors in Oceanography, M. Varney (ed.), Gordon and Breach, Amsterdam, pp. 123-141.

Dewey, R.K., Stegen, G.R. and Bacastow, R., 1997, "Far-field impacts associated with ocean disposal of CO_2", Energy Conv. Mgmt., Vol. 38, pp. 349-354.

Dickinson, A.G., 2001. "Reference materials for oceanic CO_2 measurements", Oceanography, 14(4):21.

Dickson, A.G., 1997, see http://andrew.ucsd.edu/co2qc/handbook.html.

Dicks, B., 1998, "The environmental impact on marine oil spills- effects, recovery and compensation", Proc. International Seminar on Tanker Safety, Pollution Prevention, Spill Response and Compensations, Rio de Janeiro.

Etkin, D.S., 2001, "Analysis of oil spill trends in the U.S and worldwide", Proc., International Oil Spill Conference, Tampa, pp. 1291-1300.

Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., Kleypas, J., Fabry, V.J. and Millwro, F.J., 2004, "Impact of atmospheric CO_2 on the $CaCO_3$ system in the ocean", Science, Vol. 305, pp. 362-366.

Friederich, G.E., Brewer, P.G., Herlien, R. and Chavez, F.P., 1995, "Measurement of sea surface partial pressure of CO_2 from a moored buoy", Deep-Sea Research I, 42(7): 1175-1186.

Galgani, F., Leaute, J.P., Moguedet, P., Souplet, A, Verin, Y., Carpentier, A. Goraguer, H., Latrouite, D., Andral, B., Cadiou, Y., Mahe, J.C., Poulard, J.C. and Nerisson, P., 2000, "Litter on the seafloor along European coasts", Mar. Pollut. Bull., 40: 516-527.

Galil, B.S., Golik, A. and Turkay, M., 1995, "Litter at the bottom of the sea: A sea bed survey in the eastern Mediterranean", Marine Pollution Bulletin, 30(1): 22-24.

Golik, A., 1997, Debris in the Mediterranean Sea: types, quantities, and behavior. Marine Debris: Source, Impacts and Solutions, D.E. Alexander (ed.), Springer, pp.7-14.

Griffiths, G., 2005, "Review of oceanographic equipment and sensors for the detection and measurement of pollutants", Southampton Oceanography Centre Research and Consultancy Report No.99, 24 pp.

Groben, R. and Medlin, L.K., 2002, "Analysis of single cells in the marine phytoplankton (ASCMAP)", Meeting report: EU Workshop, Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany, April 15-21, 2002, 153: 193-195.

Henry, C. and Roberts, P.O., 2001, "Background fluorescence values and matrix effects observed using smart protocols in the Atlantic Ocean and Gulf of Mexico", Proc. 2001 International Oil Spill Conference, pp. 1203-1207.

Herzog, H.J., Adams, E.E., Auerbach, D.I. and Caufield, J.A., 1996, "Environmental impacts of ocean disposal of CO_2", Energy Conv. Manage., Vol. 37, pp. 999-1005.

Herzog, H., Caldeira, K., Reilly, J., 2003, "An issue of permanence: Assessing the effectiveness of temporary carbon storage", Climatic Change, Vol. 59, pp. 293-310.

Hirai, S., Okazaki, K., Tabe, Y. and Hijikata, K., 1997, "Mass transport phenomena of liquid CO_2 with hydrate", Waste Mgmt., Vol. 17(5-6), pp. 353-360.

Hoffert, M., Wey, Y.-C., Callegari, A.J. and Broecker, W.S., 1979, "Atmospheric response to deep-sea injections of fossil-fuel carbon dioxide", Climatic Change, Vol. 2, pp. 53-68.

Ishimatsu, A., Kikkawa, T., Hayashi, M., Lee, K.-S. and Kita, J., 2004, "Effects of CO_2 on marine fish: larvae and adults", J. Oceanogr., Vol. 60(4), pp. 731-742.

IMO, 2003, "International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL 73/78)", Available at http://www.imo.org/Conventions/contents.asp?doc_id=678&topic_id=258

IPCC, 2001, "Climate change 2001: Working Group III: Mitigation", Pachauri, R. (ed.), www.grida.no/climate/ipcc_tar/wg3/.

Jones, I.S.F. and Otaegui, D., 1997, "Photosynthetic greenhouse gas mitigation by ocean nourishment", Energy Conv. Mgmt., Vol. 38, pp. 367-372.

Kang, C.-G., 1999-2003, "Report on the integrated management system for marine debris in Korea", KRISO/KORDI Project Report (in Korean).

Kawahara, F.K., Fiutem, R.A., Silvus, H.S., Newman F.M. and Frazar J.H., 1983, "Development of a novel method of monitoring oils in water", Analytica Chimica Acta, 151: 316-327.

Kerouel, R. and Aminot, A., 1997, "Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis", Marine Chemistry, 57:265-275.

Kikkawa, T., Kita, J. and Ishimatsu, A., 2004, "Comparison of the lethal effect of CO_2 and acidification on red sea bream during the early developmental stages", Mar. Pollut. Bull., Vol. 48, pp. 108-110.

Kitazawa, D., Fujino, M. and Tabeta, S., 2003, "A numerical tudy on change in the marine environment of Tokyo Bay in the latest 70 years", Proc. 22nd International Conference on Offshore Mechanics and Arctic Engineering, OMAE2003-37308.

Kita, J. and Ohsumi, T., 2004, P"erspectives on biological research for CO_2 ocean sequestration", J. Oceanogr., Vol. 60(4), pp. 695-704.

Kurihara, H., Shimode, S. and Shirayama, Y., 2004, "Sub-lethal effects of elevated concentration of CO_2 on planktonic copepods and sea urchins", J. Oceanogr., Vol. 60(4), pp. 743-750.

Laist, D.W., 1997, Impacts of marine debris: entanglement of marine life in marine debris including a comprehensive list of species with entanglement and ingestion records. Marine Debris: Source, Impacts and Solutions, D.E. Alexander (ed.), Springer, pp. 99-139.

Lehr, W.J., Goodman, R. and Molloy F., 2002, "Satellite remote sensing of heavy oil spills", Proc., 3rd R&D Forum on High-density Oil Spill Response, Brest, France, pp. 39-45.

Lentz, S.A. and Felleman, F., 2003, "Oil spill prevention: a proactive approach", Proc. International Oil Spill Conference, Vancouver, Canada, pp. 3-27.

Liro, C.R., Adams, E.E. and Herzog, H.J., 1992, "Modeling the release of CO_2 in the deep ocean", Energy Conv. Mgmt., Vol. 33, pp. 667-674.

Marchetti, C., 1977, "On engineering the CO_2 problem", Climatic Change, Vol. 1, pp. 59-68.

Martin, J.H., 1990, "Glacial-interglacial CO_2 change: The iron hypothesis", Paleoceanography, Vol. 5, pp. 1-13.

Masutani, S.M. and Nihous, G.C., 1997, "Rig techniques and experiments. In Ocean storage of carbon dioxide", Workshop 4: Practical and experimental approaches, Omerod, W. (ed.), IEA Greenhouse Gas R&D Programme, Cheltenham, pp. 37-48.

Minamiura, J., Suzuki, H., Chen, B., Nishio, M. and Ozaki, M., 2004, "CO_2 release in deep ocean by moving ship", Proc. 7th Greenhouse Gas Control Technol., (in press).

Moore, S.L. and Allen, M.J., 2000, "Distribution of anthropogenic and natural debris on the mainland shelf of the Southern California bight", Marine Pollution Bulletin, 40: 83-88.

Nakata, K., 1993, "Ecosystem model; its formulation and estimation method for unknown rate parameters", J. Adv. Marine Tech. Conf., Vol. 8, pp. 99-138.

NRC, 1995, Clean ships, clean ports, clean oceans, National Academies Press, Washington D.C., ISBN 0-309-05137-1.

NRC, 2003, Oil in the Sea III: Inputs, fates and effects, National Academies Press, Washington D.C., ISBN 0-309-08438-5.

Obe, I.C.W., 2000, "Oil spill response-experience, trends and challenges", Proc. International Oil Spill Conference, Darwin Australia.

Ohsumi, T., 1995, "CO_2 disposal options in the deep sea", Mar. Thechnol. Soc. J., Vol. 23(3), pp. 58-66.

Omerod, B. and Angel, M., 1996, "Ocean storage of carbon dioxide", Workshop 4: Environmental impact, IEA Greenhouse Gas R&D Programme, Cheltenham, pp. 37-48.

Ozaki, M., 1997, "CO_2 injection and dispersion in mid-ocean depth by moving ship", Waste Mgmt., Vol. 17(5/6), pp. 369-373.

Portner, H.O., Langenbuch, M. and Reipschlager, A., 2004, "Biological impact on elevated ocean CO_2 concentrations: lessons from animal physiology and earth history", J. Oceanogr., Vol. 60(4), pp. 705-718.

Raaymakers, S., 2003, "Report on the 1st International Workshop on Guidelines and Standards for Ballast Water Sampling", Globallast Monograph series No. 9, IMO, London, ISSN 1680-3078.

Rehder, G., Kirby, S., Durham, W.B., Stern, L. A., Peltzer, E.T., Pinkston, J. and Brewer, P.G., 2004, "Dissolution rates of pure methan hydrate and carbon-dioxide hydrate in undersaturated seawater at 1000m depth", Geochimica et Cosmochimica Acta, Vol. 68(2), pp. 285-292.

Ribic, C.A., Johnson, S.W. and Cole, C.A., 1997, Marine debris in the United States, 1989-1993. Marine Debris: Source, Impacts and Solutions, D.E. Alexander (ed.), Springer, pp.35-48.

Riebesell, U., 2004, "Effect of CO_2 enrichment on marine pyotoplankton", J. Oceanogr., Vol. 60(4), pp. 719-730.

Ryan, P.G. and Moloney, C.L., 1993, "Marine litter keeps increasing", Nature, 361: 23.

Sabine, C.L., Feely, R.A., Gruber, N., Key, R. M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.-H., Kozyr, A., Ono, T. and Rios, A., 2004, "The oceanic sink for anthropogenic CO_2", Science, Vol. 305, pp. 367-371.

Sato, T., 2004, "Numerical simulation of biological impact caused by direct injection of carbon dioxide in the ocean", J. Oceanogr., Vol. 60(4), pp. 807-816.

Sato, K. and Sato, T., 2001, "A study on bubble plume behaviour in stratification", J. Marine Sci. Tech., 6(2):59-69.

Sato, T. and Sato, K., 2002, "Numerical prediction of the dilution process and its biological impacts in CO_2 ocean sequestration", J. Mar. Sci. Tech., Vol. 6(4), pp. 169-180.

Sieracki, M.E. and Viles, C.L., 1998, Enumeration and sizing of micro-organisms using digital image analysis. Digital Image Analysis of Microbes, M. H. F. Wilkinson and F. Schut. New York, John Wiley & Sons, pp. 175-198.

Socolofsky, S.A., Crounse, B.C. and Adams, E.E., 2000, "Bubble and droplet plumes in stratification: 1. Laboratory studies", Proc. 5th Int. Symp. Stratified Flows, Vancouver.

Stefatos, A., Charalampakis, M., Papatheodorou, G. and Ferentinos, G., 1999, "Marine debris on the seafloor of the Mediterranean Sea: Examples from two enclosed gulfs in Western Greece", Marine Pollution Bulletin, 36(5): 389-393.

Suzuki, Y., Fujii, M., Casareto, B.E., Furuta, A. and Ishikawa, Y., 2003, "CO_2 sequestration and fate of organic matters within seagrass ecosystem", J. Chem. Engrg. Japan, Vol. 36(4), pp. 417-427.

Takahashi, T., 2004, "The fate of industrial Carbon Dioxide", Science, Vol. 305, pp. 352-353.

Tejima, T. Kamei, T. and Sato, T., 2004, "Three-dimensional aspects of vortices shed from an inclined cylinder", Proc. 2nd Asia-Pacific Workshop on Marine Hydrodynamics, Busan, pp. 103-108.

Teng, H., Yamasaki, A. and Shindo, Y., 1996, "Stability of the hydrate layer formed on the surface of a CO_2 droplet in high-pressure, low temperature water", Chem. Engrg. Sci., Vol. 51, pp. 4979-4986.

Tennyson, E.J., 1988, "Shipborne radar as an oil spill tracking tool", Proc. 11th Arctic and

Marine Oil Spill Program Technical Seminar, Vancouver, British Columbia, Canada, pp. 385-390, June 7-9, 1988.

Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D. and Russell A.E., 2004, "Lost at sea: Where is all the plastic?", Science, 304: 838.

Thornton, H. and Shirayama, Y., 2001, "CO_2 ocean sequestration and its biological impacts, III-1: Effects of CO_2 on benthic organisms", Bull. Japanese Soc. Scient. Fish., Vol. 67 (4), pp. 756-757 (in Japanese).

U.S. Coast Guard, 2003, "U.S. Coast Guard oil spill response research & development program, a decade of achievement", U.S. Coast Guard Research & Development Center Report No. CG-D-07-03.

Veitch, B., 2005, "Assessment of ocean environmental issues: produced water", Ocean Engineering Research Centre Report No. 2005-03, 13 p.

Wickett, M. E., Caldeira, K. and Duffy, P.B., 2003, "Effect of horizontal grid resolution on simulations of oceanic CFC-11 uptake and direct injection of anthropogenic CO_2", J. Geophys. Res., Vol. 108(C6), pp. 3189-3200.

Yamasaki, A., Tajima, H. and Kiyono, F., 2004, "Development of a new method of liquid CO_2 injection into the seawaters for the ocean sequestration", Proc. 24th Int. Conf. on Offshore Mech. and Arctic Eng., OMAE04-51283.

Yentsch, C.M., 1990, Environmental health: flow cytometric methods to assess our water world. In: Darzynkiewicz, Z and Crissman H A (eds) Methods in Cell Biology 33: Flow Cytometry. Academic Press, San Diego. pp. 575-612.