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**Review of oceanographic equipment and sensors
for the detection and measurement of pollutants**

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ABSTRACT <p>This Report was prepared as a contribution towards the work of the Committee on the Assessment of Ocean Environmental Issues of the International Towing Tank Conference. While suitable sensors exist for many physical parameters, many of those for chemical and biological parameters lag behind. The sensing problem is often difficult; measuring a specific parameter in seawater in the presence of many other substances is a challenge.</p> <p>For the pollutants considered in this study the situation may be summarised as follows:</p> <ul style="list-style-type: none">• For CO₂, spilled oil and the major nutrients (nitrate, phosphate, silicate) instruments and sensors exist, are in routine use by research and environmental laboratories but they are costly. Standards exist for calibration and for analytical procedures. The same holds true for oil present in produced water.• There exists a tremendous challenge for instruments and sensors that can measure and monitor the presence of biota in ships' ballast water on a routine basis. Aspects of the IMO's GLOBALLAST research programme are directed towards tackling this problem.• For marine debris and seabed litter there are serious problems providing quantitative unbiased observations. Cost is a major issue in obtaining information on the distribution and abundance of seabed litter in the deep oceans. <p>This report examines the technology options available, including recent developments in research that may offer improved performance or performance at lower cost.</p>	
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Review of oceanographic equipment and sensors for the detection and measurement of pollutants

A Review for the ITTC Committee on the Assessment of Ocean Environmental Issues

4 October 2004

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1. INTRODUCTION

Progress in ocean science has always greatly on observations. Instruments and sensors have been developed for many of the physical, chemical and biological parameters relevant to the study of ocean pollution. These sensors and instruments include those deployed *in situ* within the oceans, and those deployed remotely, for example on aircraft or satellites. While suitable sensors exist for many physical parameters, many of those for chemical and biological parameters lag behind. The sensing problem is often difficult; measuring a specific parameter in seawater in the presence of many other substances is a challenge.

For the pollutants considered in this study the situation may be summarised as follows:

- For CO₂, spilled oil and the major nutrients (nitrate, phosphate, silicate) instruments and sensors exist, are in routine use by research and environmental laboratories but they are costly. Standards exist for calibration and for analytical procedures. The same holds true for oil present in produced water.
- There exists a tremendous challenge for instruments and sensors that can measure and monitor the presence of biota in ships' ballast water on a routine basis. Aspects of the IMO's GLOBALLAST research programme are directed towards tackling this problem.
- For marine debris and seabed litter there are serious problems providing quantitative unbiased observations. Cost is a major issue in obtaining information on the distribution and abundance of seabed litter in the deep oceans.

This report examines the technology options available, including recent developments in research that may offer improved performance or performance at lower cost.

2. EQUIPMENT AND SENSORS FOR DETECTING AND MEASURING POLLUTANTS

2.1 Spilled Oil

Spilled oil is just one manifestation of petroleum inputs into seas and oceans. The US National Research Council best estimate in 1985 for the global input of oil into the sea was 3.2 million tonnes, comprising 3 million tonnes from anthropogenic sources and 200 thousand tonnes from natural seeps. Detecting and monitoring oil, as a class of substances, can be achieved in a number of ways, several of which are described in this section. Oil, or petroleum, is a complex and variable mixture of substances, with different environmental impacts, toxicity and lifetimes. Oil mostly comprises straight chain alkanes (C_nH_{2n+2}), together with cycloalkanes, olefins (unsaturated hydrocarbons) and aromatic compounds (at least one benzene ring). The latter class of compounds are particularly persistent in the environment; some compounds may be toxic and or carcinogenic. Aromatics may be present at concentrations of several percent in light crudes, but at less than 1 % in heavier oils. Polyaromatic hydrocarbons and compounds containing elements such as sulphur, nitrogen and oxygen "have the most serious environmental effects" (NRC, 2003:20). Polyaromatics may comprise from 0.2 to 7% of a crude oil. Therefore, for a true assessment of the environmental impact of spilled oil, the composition of the oil needs to be known or determined.

2.1.1 *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 with the long-wavelength UV optics option, or they can now be made *in situ*, e.g. using 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 (Figure 1). 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 (Figure 2). Thus real-time 2-D maps of dissolved hydrocarbon distributions can be obtained. Excitation is at 239 nm using a xenon lamp followed by a filter, with a 26 nm bandwidth at half maximum. Emission at 360 nm is detected with a photomultiplier. Depth rating is to 600 m in the standard instrument, but a 6000 m version is available. The detection limit of the sensor is 1 ng l⁻¹ of carbazole, with an upper limit of 10µg l⁻¹.



Figure 1 Spill Sentry buoys for in situ detection and measurement of hydrocarbons. Courtesy of Applied Microsystems Ltd.



Figure 2 (Left) UV Aquatracka installed on an ROV for hydrocarbon detection work. (Right) a close up of the instrument (Courtesy Chelsea Technologies Ltd.)

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 (Figure 3), 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 l⁻¹ to 10 µmol 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.



Figure 3 The METS methane sensor (left) in its titanium pressure housing and (right) a simplified schematic. Courtesy Capsum at http://www.capsum.de/capsum_online/mets.html

2.1.2 Remote sensing technologies

Airborne and satellite remote sensing have the potential to become capable and practical tools for detecting and monitoring oil spills in coastal and open ocean environments. The advantages of remote sensing over in situ techniques include the rapid area coverage, with the ability to map spills. The simplest 'remote sensing' technique is also the most used – visual observation by human observers, although most authorities do not consider visual observation to be remote sensing. However, this is predominantly a daytime only approach, and there are limitations at times of poor visibility, for example, due to rain or fog. Passive automatic optical remote sensing techniques such as scanning multi-spectral radiometers share these limitations, while all-weather techniques such as microwave radar backscatter are more demanding in the interpretation of the results. Active optical sensors are not restricted to daytime operation, but, used alone, such instruments may not have the sufficient specificity to uniquely determine the presence of oil on the sea surface against similar effects produced by other factors, such as patterns of different roughness caused by wind gusts ('cats paws'), modulation of the surface roughness by internal waves, by brackish runoff in coastal waters, by silt and suspended sediment and by biological patchiness due to seaweeds or algae. Combinations of sensors can lead to increased specificity, for example by adding measurements of fluorescence spectra to optical imaging. Combined sensors have also been developed to estimate the thickness of oil patches as well as their horizontal extent.

Remote sensing of oil spills has been a goal of a joint programme between the US Department of the Interior, Minerals Management Service and Environment Canada and many techniques have been investigated. Brown et al. (1995) and the references therein provide a summary of several systems. The following are examples of systems being developed or in service:

- **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. Broadly, with these systems the exciting radiation is in the UV (typically 300-355 nm) and detects oil fluorescence between 400 and 550 nm, peaking at 480 nm. Interference from

biogenic organic matter, which fluoresces with a broad peak at 420 nm, and chlorophyll, which appears as a sharp peak at 685 nm, can be filtered out.

The LEAF instrument (Laser Environmental Airborne Fluorosensor) was a joint development between the Minerals Management Service of the US Department of the Interior, Environment Canada, the Canadian Petroleum Association and others (see www.mms.gov/tarprojects/161.htm). The instrument has been used in an aircraft over Chesapeake Bay; in connection with the 'Irving Whale' oil barge incident and recovery and off the coast of California. 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 instrument that could estimate the thickness of oil spills as well as their extent. The complete instrument was to be a dual-frequency microwave radar operating in the Ka band (27-40 GHz) and the W band (75-110 GHz) where the difference in emissivity at the two frequencies would be related to the thickness of the spill. 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 first laser determines the surface position. The second laser generates a high power, short pulse to heat the surface of the oil air interface (e.g. a 100 ns pulse at 200 mJ from a CO₂ laser). The resulting thermal pulse produces a pressure wave (or sound, with a bandwidth of some 15 MHz) that propagates into the oil layer until a partial reflection at the oil water interface occurs resulting in a back-propagating wave that causes a disturbance of the oil air interface. The time taken for this disturbance to occur is a function of sound velocity in the oil and the thickness of the layer. A third laser, configured as a confocal Fabry-Pérot interferometer could detect the high frequency disturbance of the oil air interface, Choquet et al. (1993). 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 (Figure 4) while changes in thickness could be

estimated (Byfield, 1999). What were not possible at the time were measurements of actual thickness, discrimination of cargo oil from fuel oil and quantitative estimates of the dispersed oil.

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

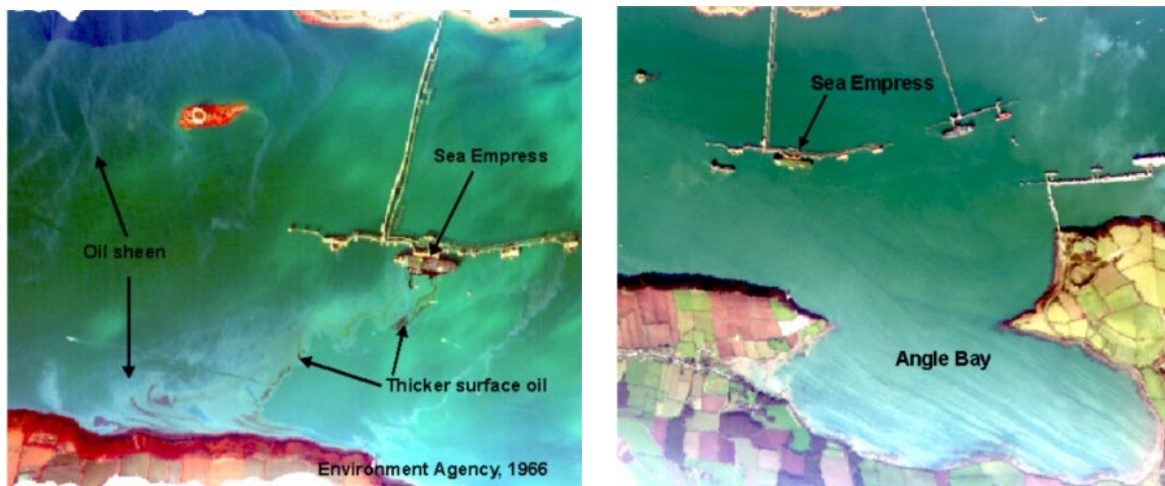


Figure 4 These images, obtained by the Environment Agency show (left) oil still from the ship on 22 February 1996. Thicker streaks of oil appear dark, medium oil is brown and sheen blue in this false colour image that assigns red to the 750 nm channel. On 27 February (right) oil is no longer leaking, but streaks of oil may still be seen in Angle Bay, as alternate dark and bright lines (from Byfield, 1999).

- **Satellite remote sensing** has both attractions and difficulties for oil spill detection and monitoring. Optical sensors on satellites share the same limitations as optical sensors on aircraft. Then there is the issue of the frequency of overpasses. In the visible region the positive detection of oil is difficult because, although the reflectivity of oil is higher than that of water, there is a lack of structure in the spectrum from 400-700 nm making discrimination difficult. Brown et al. (1995) have reviewed optical techniques, including thermal infra red (8-14 μm), near infra red (2.5-3.1 μm) and UV. Lack of specificity is a general problem. For example, while oil is highly reflective in the UV, such that layers of less than 10nm can be detected, wind slicks, sun glint and naturally occurring biogenic films also produce high reflection. Writing in 1995, Brown et al. noted that it took researchers over 2 months to find the signature of oil on the sea surface in satellite imagery of the *Exxon Valdez* spill. The introduction of Synthetic Aperture Radar (SAR) onto satellites has changed the situation. SAR has proven to be an effective tool for oil spill detection and monitoring. Oil films damp the very short capillary-gravity waves on the sea surface, reducing the radar backscatter signal (Figure 5 (a,b,d)). The technique is most effective at wind speeds of 2.5-15 m s^{-1} . In a now famous case, evidence from SAR on the ERS-1 satellite helped lead to the prosecution in a marine oil spill case in Singapore (Chen, 2000) . What is less common than this point source detection is the use of SAR to assess oil spill pollution over large areas of open ocean. Partly,

this may be because discrimination between oil slicks and similar patterns of low backscatter due to other causes (Figure 5 (c)) requires careful analysis of each image. Lu et al. (1999) examined 5029 scenes from the ERS-1 SAR in a region of South-East Asia between longitudes 90° and 120° E and 10° S and 20° N between 1995 and 1998. They found that 45.6% of the scenes showed evidence of oil slicks, with 60% of the slicks between 1 and 10 km in length, and 10% over 10 km, Figure 5(e).

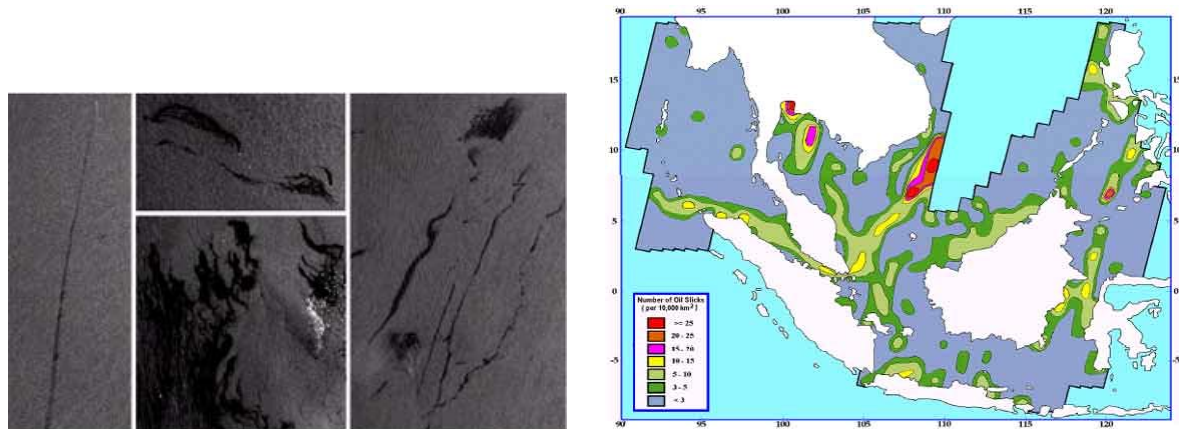


Figure 5 From Lu et al. (1999): (Left) examples of oil slicks on ERS SAR images: (a) long linear slick from a moving ship, (b) slicks from offshore oil rigs, (c) slicks probably from natural seepage, (d) slicks along a major shipping route and (right) (e) map of the average oil pollution occurrence intensity in the Southeast Asian waters, where red represents the worst oil pollution and blue the lowest.

2.1.3 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 MV Braer off Shetland on 5 January 1993 (the 11th 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, in this case by the Fisheries Research Services of the Scottish Executive, 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.

2.2 Carbon dioxide

As a result of human activity some 7 Pg (7×10^{15} g) of carbon dioxide is being released into the atmosphere each year. Some 3 Pg of this CO₂ remains in the atmosphere, while some 4 Pg is transferred to the terrestrial biosphere and the oceans (Feely et al., 2001). The partition of the 4 Pg between the terrestrial biosphere and the oceans is a matter of debate. Estimates of annual oceanic uptake of CO₂ vary from 1.0 Pg to 3.0 Pg, from Table 1 in Feely et al. (2001). This is for the net flux of *anthropogenic* CO₂, for the natural carbon cycle in the ocean involves the far larger stores of carbon – dissolved inorganic carbon at some 38,000 Pg and dissolved organic matter at ‘roughly 685 Pg’ (Hansell and Carlson, 2001). The challenge in measuring oceanic CO₂ 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: $\text{CO}_{2\text{gas}} \rightleftharpoons \text{CO}_{2\text{aq}}$
- As aqueous carbon dioxide: $\text{CO}_{2\text{aq}} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ (8 $\mu\text{mol kg}^{-1}$ surface ocean)
- As the bicarbonate ion: $\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-$ (1617 $\mu\text{mol kg}^{-1}$ surface ocean)
- As the carbonate ion: $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ (268 $\mu\text{mol kg}^{-1}$ 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:

- **TCO₂** – is determined in discrete water samples as $C_T = [\text{CO}_{2\text{aq}}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$, 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 CO₂ measurement programme this is done using a UIC Inc. model 5011 CO₂ 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’ of the form $A_T = \Sigma [\text{proton acceptors with dissociation constant} < 10^{-4.5}] - \Sigma [\text{proton donors with dissociation constant} > 10^{-4.5}]$. 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 $\text{pH} = -\log [\text{H}^+] = [\text{H}^+]_F + [\text{HSO}_4^-]$ holds for sea water at $\text{pH} > 4$ 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 CO₂ (Dickson, 1997 – SOP6).
- **Fugacity of CO₂ gas in equilibrium with a seawater sample $f(\text{CO}_2)$** – is calculated from the partial pressure of the CO₂ gas, corrected for the non-ideal behaviour of the gas as determined from its equation of state (Dickson, 1997 – SOP24):

$$f(\text{CO}_2) = x(\text{CO}_2) * p \left(\exp \frac{-123.2 \times 10^{-6} + 2 \cdot (1 - x(\text{CO}_2))^2 \cdot 22.5 \times 10^{-6} * p}{RT} \right)$$

Where $x(\text{CO}_2)$ is the measured partial pressure, p the standard atmospheric pressure (Pa), R the gas constant and T the absolute temperature.

- Measurement of any two of the above four quantities can provide a full description of the CO₂ 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 $\pm 1.5 \mu\text{mol kg}^{-1}$ in C_T and $\pm 2 \mu\text{mol kg}^{-1}$ in A_T , over a 3 year period (Dickinson, 2001).

Automated measurements of the partial pressure of CO_2 ($p\text{CO}_2$) 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 operating at a wavelength of $4.26 \mu\text{m}$. Measurements with a precision of 1-2 μatm were achieved. 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 multispectral optical absorbance measurement (at 434, 620 and 740 nm) after the CO_2 diffusing through a gas-permeable membrane reacts with a sulphonephthalein indicator. The ratio of absorbance at 620 nm to 434 nm and the absolute absorbance values are used in order to achieve better long-term stability. A blank measurement, made every two days, was also used to reduce drift. 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 (the SAMI-1500, details at <http://www.sunburstensors.com/index.htm>).



Figure 6 Infra Red gas analysers for CO_2 measurements, (left) the LI-COR 6262 closed path system and (right) the LI-COR 7500 open path analyser. Courtesy LI-COR Inc.

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, capable of operation down to 2000 m (see <http://www-ocean.lbl.gov/NOPP.html>). The range is 200-600 μatm with a resolution of 1 μatm .

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 analysers (IRGA). Closed path IRGA systems (e.g. the Licor LI-6262, Figure 6) use a pump to draw the gas being sampled into a tube through which IR radiation is passed, and from the spectral absorption measurement the concentration of CO_2 and water vapour can be determined. A second tube contains a reference gas as a standard. Open path analyzers (e.g. the Licor LI-7500, Figure 6) do not use a

sample tube but a folded optical path in free air. Instead of a separate reference tube an absorption measurement is made well away in wavelength from the absorption of CO₂ and water vapour to correct for absorption by dust or contamination on the optical surfaces.

2.3 Nutrients

The key nutrient elements for which anthropogenic inputs are a factor in altering marine ecosystems are nitrogen and phosphorous. These elements may be discharged into coastal estuaries, seas and oceans as organic wastes or as inorganic minerals. As most marine ecosystems are limited by the depletion in naturally occurring nutrients associated with plant growth, anthropogenic additions tend to increase the production of phytoplankton and alter the balance of species within the ecosystem. Silica, although an important nutrient, has almost no anthropogenic source, and consequently is not considered further. See www.pewoceans.org for a recent review of the causes and consequences of an oversupply of nutrients to the sea. Consequences of elevated levels of nutrients may include:

- Hypoxia (oxygen depletion to $< 2 \text{ mg.l}^{-1}$ leading to increased stress of organisms such as fish and crustacea).
- Algal blooms, which may be toxic, harmful or unsightly (e.g. foaming on beaches). However, an oversupply of nutrients is not the only cause of harmful algal blooms.
- Changes in population and reduced species diversity.
- Changes in phytoplankton leading to bleaching of coral reefs.

Most measurements of nutrients in seawater are on captured samples. Detailed procedures for the chemical analyses and the preparation of reagents, the avoidance of interfering species and detection limits can be found in EPA (1996). If the analysis cannot be done immediately after sampling, the samples should be filtered and frozen. The key substances that need to be measured to provide a comprehensive picture of the state of nutrients in seawater are:

- **Nitrogen as nitrate and nitrite:** Nitrate concentrations may vary from below current detection limits ($<< 0.1 \mu\text{M.l}^{-1}$) in the surface waters of oligotrophic gyres (e.g. the Sargasso Sea) to over $100 \mu\text{M.l}^{-1}$ 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. Filtered samples are passed through a heated copper cadmium reduction column to convert nitrate to nitrite. The concentration of reduced nitrate and original nitrite nitrate is determined by reaction with sulphanilamide and with N-1-naphthylethylenediamine dihydrochloride to form a coloured dye. Filtered samples that bypass the reduction column provide the nitrite concentration and nitrate is obtained by subtracting nitrite from the total nitrite+nitrate value. 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 take 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 Alchem Autoanalyser (Figure 7). The analyser contains the necessary fluidics and optical components to process three channels simultaneously (e.g. for nitrate+nitrite, phosphate and silicate).



Figure 7 An Alchem three channel autoanalyser, as would be used on a research vessel for the determination of nitrate, nitrite, phosphate and silicate. Courtesy USGS (wwbrr.cr.usgs.gov/projects/SW_inorganic/alp.jpg).

- *In situ* versions of this wet-chemical determination of nitrate and nitrite have been produced, e.g. the NAS-2E from Envirotech LLC, Figure 8. 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 (<http://www.subchem.com/prod01.htm>), 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, by measuring the absorbance at 220 nm with reference to 235 nm, where there is little absorption by the halides or nitrate, nitrate concentration can be determined at a sampling rate of 1 Hz over a range of 0.1 to 100 $\mu\text{M.l}^{-1}$ (Clayson, 2000). Practical UV absorption nitrate sensors have been made by SOC and by the German company TriOS.



Figure 8 (Left) the NAS2E in situ nutrient analyser from Envirotech LLC, (Centre) an UV absorption nutrient analyser from TriOS and (Right) the UV dissolved nitrate sensor from SOC.

- **Nitrogen as ammonia:** Ammonia concentrations in open coastal waters may range from 1 to 5 $\mu\text{mol.l}^{-1}$ 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 (Figure 9). The method is based on the reaction of ammonia with orthophtaldialdehyde and sulphite, has a detection limit of 1.5 nMol l⁻¹ and uses UV excitation at 370 nm and an emission band of 418 nm to 700 nm, with the emission peak at 425 nm. The sensor has been included in the AquaLab instrument from Envirotech LLC.



Figure 9 *In situ* ammonia sensor. Courtesy SOC.

- **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 (PO₄³⁻) 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 chemistry) have become available (e.g. the NAS-2 from Envirotech LLC see <http://www.n-virotech.com/products/nas.htm>).
- **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.

2.4 Produced water

Measurement of oil and grease in produced water is an essential part of compliance with environmental regulations. For example, the US EPA requires produced water from oil production should not contain more than 29 ppm oil and grease averaged over a 30 day period, and that the daily

maximum should not exceed 42 ppm. For the North Sea, the permitted monthly average is 40 ppm, although in recent years the actual annual figure has been 22 ppm (1998), from NRC, (2003). The current laboratory measurement protocol is EPA Method 1664A, which was introduced in 1999 to replace a procedure that depended on Freon-113 (EPA, 1999). The protocol is not suitable for petroleum fuels that are volatile below 85°C. In summary, this gravimetric procedure (EPA, 1993) takes a one litre sample, acidified to a pH of less than two and serially extracted three times with n-hexane, before being dried over sodium sulphate. The next stage is distillation, to remove the n-hexane solvent (hence the 85°C limit for volatiles, leaving the remaining substance to be desiccated and weighed. Where the need is to remove polar compounds from the substance under test, silica gel is added to the distillate, n-hexane added and redistilled.

Hand-held and on-line analytical techniques and instruments are also available that measure oil and grease in produced water. While these methods claim to correlate with the approved gravimetric protocol, they do not substitute for the laboratory chemical analysis. Recent developments in hand-held UV fluorescence instruments, for example the Turner Designs TD500, which can perform an analysis in less than 4 minutes, has a detection limit of less than 1 ppm and an upper limit in excess of 1000 ppm (Turner Designs, 2003). On-line monitors, such as the Turner Designs TD-4100 (Figure 10a) employ infra red spectral absorption to provide a continuous analysis. Infra red absorption enables all of the oil in the water to be measured. That is, the measurement is of dispersed, emulsified and dissolved oil.

Oil in water can also be estimated from light transmission and scattering, for example the Inventive Systems Inc. BA-200 (Figure 10b). However, sensors that rely on light scatter may have difficulty in differentiating between suspended matter and oil droplets, and there is a debate on how effective they are when the oil is emulsified or dissolved.

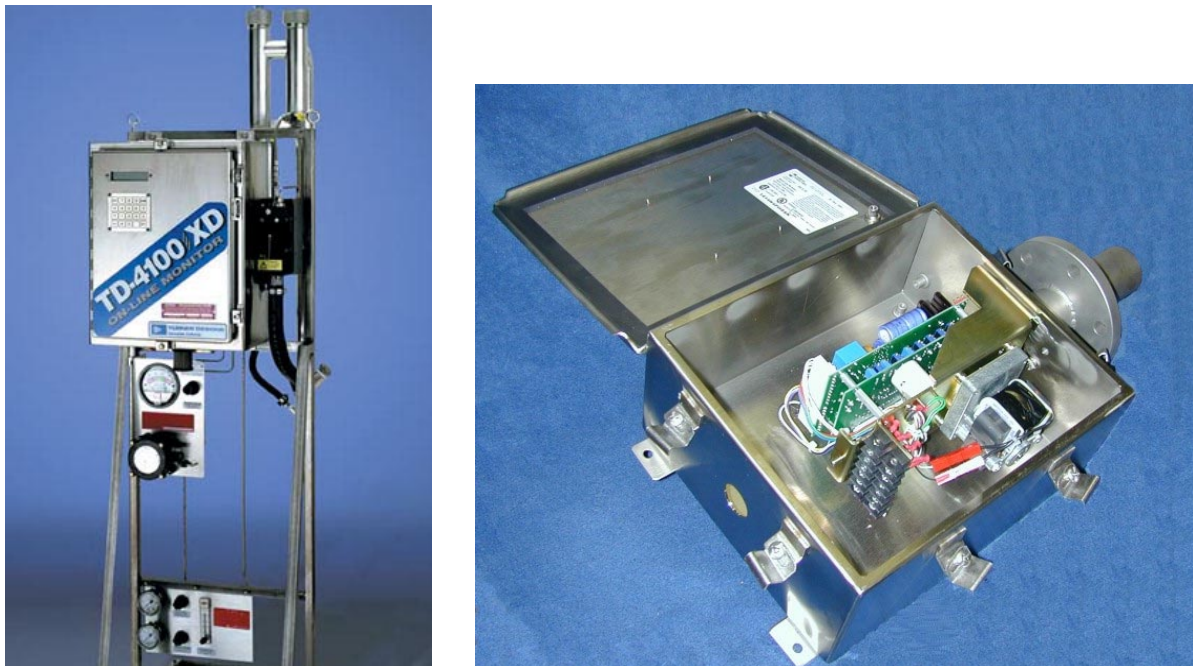


Figure 10 a) the Turner Designs TD-4100 on line infra red oil in water analyser and b) the internal arrangement of the Inventive Systems BA-200 instrument that relies on light transmission and forward scatter, from <http://www.oilinwater.org>

Elevated levels of oil may be found in the sediments, particularly within 200 m of discharges.

2.5 Ship discharges ballast water

The IMO's Marine Environment Protection Committee has been drafting, for the last few years, an International Convention on the Control and Management of Ships' Ballast Water and Sediments. The text of the Convention was put before a Diplomatic Conference and adopted on 13 February 2004. Because there are limited methods and technologies that are available now to treat ballast water, ballast water exchange (for oceanic water) will remain for some time. The Convention stipulates that such exchanges take place at least 200 nm from land and in water deeper than 200 m. In some regions, and for some ships, this would not be possible; in such cases the Convention requires that a risk assessment should be made.

Several concerns had been expressed on parts of the draft Convention; the following have been abstracted from a UK Maritime and Coast Guard Agency note (MCGA, 2003):

- Concerns have been expressed by the US that “there is insufficient knowledge of the inter-relationships among organisms and their environments at both the originating and receiving ports”.
- Performing a risk assessment would need knowledge of organisms present on any particular voyage. How would that knowledge be obtained?
- The UK line is that “a stringent standard needs to be set, and that ballast water exchange should be phased out and replaced by treatment”.
- There was debate on the appropriate allowable concentration of organisms in ballast water discharge.

The debate is illustrated in the options considered for the allowable discharge standards shown in Table 1 for particular categories of organisms. The Table also shows the standards adopted by the Convention.

Table 1 Allowable concentration of organisms in ballast water discharge from the IMO Convention for the Control and Management of Ships' Ballast Water and Sediments (2004).

Type of organism	Size	Proposed discharge standards from Regulation D-2
Viable organism	>50 µm	<10 per m ³ (<1 or <100 per m ³ were suggested)
Viable organism	>10 but <50 µm	<10 per ml (<1 or <10 or <100 per ml were suggested)
Toxic <i>vibrio cholera</i>		<1 colony forming unit (cfu) per 100 ml
Toxic <i>vibrio cholera</i>		<1 cfu per 1 g wet weight zooplankton
<i>E. coli</i>		<250 cfu per 100 ml (<250 or <500 per 100 ml cfu suggested)
Intestinal <i>Enterococci</i>		<100 cfu per 100 ml (<100 or <200 cfu per 100 ml suggested)

Being able to demonstrate compliance with a standard of <10 viable organisms in the range >10 µm but <50 µm is acknowledged as challenging for measuring instruments and is certainly ambitious. It is

the UK's view that "to set the standard on the basis of currently available or anticipated technology may not be effective in reducing risk" (MCGA, 2003). Recognising this, Article 6 of the Convention calls for "parties individually or jointly to promote and facilitate scientific and technical research on ballast water management and to monitor the effects of ballast water management in waters under their jurisdiction". In addition, Regulation D-5 allows for a review of the standards, "the review should include a determination of whether appropriate technologies are available to achieve the standard".

2.5.1 Technologies for identifying and quantifying organisms in ballast water

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 a 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 Multisize 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). The innovation at the heart of a flow cytometer was the use of a clean sheath fluid surrounding and coaxial with the sample stream, with the hydrodynamics so arranged as to force the cells in the sample stream into a single file. Cells therefore pass the measurement head one at a time. A typical measurement head consists of a laser to induce fluorescence and to size the cells, with detectors for the fluorescence emission wavelength(s) and for forward and side-scattered light, thus characterising cells by their fluorescence, size and light scattering. Furthermore, with on-line cell characteristic recognition, the stream of cells exiting the measurement head can be sorted into different sample tubes by deflecting the path of individual cells using, for example, an electrostatic field. A marine flow cytometer (Figure 11) 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.



Figure 11 The Cytobuoy flow cytometer for use within an AUV. The leftmost section contains the system for sheath fluid injection and recycling; the lower right section contains the optics while the upper right houses the control electronics (courtesy Glen Tarran, Plymouth Marine Laboratory).

- **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. A fluorochrome molecule (which can be detected by its fluorescence) may be attached to the oligonucleotide to ‘label’ the probe. The resulting molecular probe enters cells and binds to the complementary site on the target cells’ rRNA – the presence of the probe within the target cells being detected through fluorescence (Figure 12). Thus 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 bacteria and protozoa (see <http://www.chemunex.com/products/chemscan.htm>).

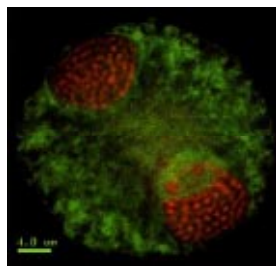


Figure 12 A fluorescence microscope image of a single *Alexandrium* showing in red the fluorescence from the molecular probes that have attached themselves to the cell’s rRNA, from Don Anderson’s laboratory at <http://www.whoi.edu/redtide>.

- **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 10-200 μm . Below 10 μm flow cytometry is the preferred technique. The 'Flowcam', shown in Figure 13, is one example of an optical imaging and recognition system (Sieracki et al., 1998). A stream of sample fluid passes through a detection/measurement head that combines a fluorometer, LED flash and a digital camera. When the fluorometer detects a signal (from chlorophyll or phycoerithrin fluorescence) the LED flash backlights the sample and the digital camera takes an image. The image is stored together with the size and fluorescence data. In use, a bench-top unit with a x10 objective (providing one pixel per micron resolution) can sample at a flow rate of 1 ml per minute. Image recognition software can then be used to match images from the sample under test to images from a library of organisms.

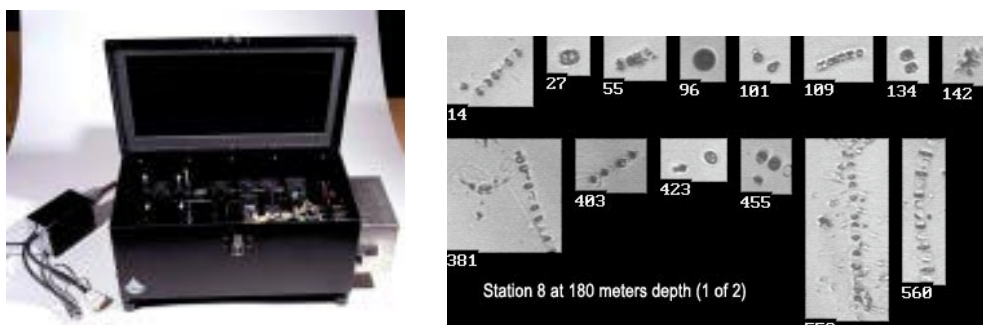


Figure 13 Flowcam system unit (left) and examples of shadowgraph images of various phytoplankton (right), from <http://www.bigelow.org/flowcam/>

- **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 would need to be determined using another method.

2.6 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) ... upstream of the end of the reverse tidal flow zone' (NRC, 2003:79).

The recommended sampling frequency was monthly (minimum of one sample per season) from the bottom, mid-water and surface. Such samples could be analyzed by any of the instruments and

methods described in 2.2.3 for the bulk oil concentration. Analysis for the concentrations of individual compounds would need to be done using a mass spectrometer, chromatograph or other similar instrument.

2.7 Marine debris

Marine debris remains an issue some 15 years after the adoption of Annex V of the MARPOL 73/78 convention that sets out strategies for the prevention of pollution by garbage from ships (IMO, 2003). It is now the requirement for garbage generated by ships to be either disposed of through facilities at ports or to be discharged at sea in accordance with the MARPOL regulations, recognising that in a number of geographical areas (currently the Antarctic, the Baltic and the North Sea) no discharges are allowed.

Marine debris can lead to large economic impacts. For example, in the addendum to the report 'Trends in US Coastal Regions 1978-90', NOAA(1999) the following examples were given of the economic impact of marine and beach debris:

- in 1992 the Japanese fishing industry spent \$4.1 billion dollars in boat repairs arising out of damage caused by marine debris (source not given);
- \$1.5 million is spent each year in New Jersey, USA to remove debris from beaches and coastal waters. This preventative measure is undertaken to reduce the risk of repetition of the 1987 and 1988 beach seasons when marine debris washed up on the state's beaches leading to an estimated \$2 billion reduction in tourist revenues. While in 1988 there were 855 beach closures, in 1998 there were none.

While vessels remain a source of marine debris, recent studies in the US have concluded that this source may contribute only about 20% to litter on beaches. The other 80 percent comes from those using beaches, street litter, waste receptacles that overflow, or overturn, landfills, and from sewer overflows. The fate of garbage dumped at sea is not easily predictable, leading to one statement in an authoritative review that "wash ups of some types of debris on beaches seem to defy logical explanation", NRC (1995:49). Persistent materials in the marine environment include *inter alia*: glass, cement, brick, metals, plastics, rubber, timber, hemp and cigarette butts. Many studies have shown that plastics form the largest class of marine debris, at least on beaches, from 75-98% in one US study (Cole et al., 1992 as reported in NRC, 1995:49).

Monitoring marine debris *at sea* is difficult, given its diversity and wide distribution. Recognising that part of an answer may be to use as many observers as possible, 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 that has been suggested (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, each 20 or 40 foot by 8 foot by 8 foot, vary 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 containers¹. 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 (Figure 14).

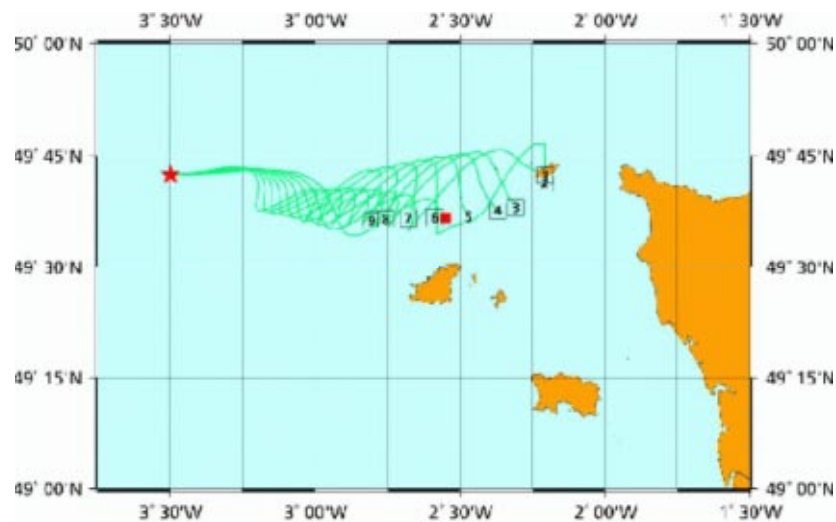


Figure 14 A Météo France simulation of the trajectory of containers lost at the position started off the NW coast of France. The simulated trajectories are shown for immersion depths of 10% to 90%. The red square represents the observed position of the containers, corresponding to about 60% immersion (see ¹).

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 Cunha group in the South Atlantic in the years 1984, 87, 88, 89 and 90. Despite the introduction of MARPOL Annex V in 1988 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 (r^2 of 0.96 compared to 0.92 for the exponential fit to the five data points). Communication with Dr Ryan has confirmed that constraints of logistics prevented a continuation of their survey of beach litter on Inaccessible Island. I consider this 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

¹ See http://www.meteorologie.eu.org/mothy/plaquette_en.html#Containers%20drift%20model

assessments undercounted by some 50%. In his report, the minimum suggested length of beach to be surveyed was 1 km, with the frequency determined by an analysis of the statistics related to the lifetime of debris on the beach.

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 microplastics from the seabed in coastal waters near Plymouth and 17 other beaches around the UK. The samples were analysed in the laboratory using Fourier Transform Infrared (FT-IR) spectroscopy, to separate plastics from natural particles via their absorption signature. Some one third of particles were identified as synthetic polymers. In an attempt to identify trends in microplastics 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 m³ in the 1960's to over 0.03 fibres per m³ in the 1980's and 90's. As this is the focus of recent research little is known on the biological impact of microplastics. Thompson et al. (2004) showed that zooplankton, worms and barnacles ingested microplastics, but did not attempt to show that toxic substances passed into the animals. More work is needed.

2.8 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 have examined the types and distribution of marine debris on the seafloor". Their study covered the Southern California Bight in the summer of 1994, from Point Conception in the north to San Diego in the south, including the waters off Los Angeles. The survey comprised a series of 113 trawl stations on the continental shelf at depths of 10 to 200 m. By extrapolation from their trawl stations, they concluded that anthropogenic debris was found over an area of 14% of the shelf in the Bight. Fishing gear debris dominated, followed by plastic and metal.

Stefatos et al. (1999) reported on the first survey of sea bed 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. In both cases the area surveyed was just less than 1.2 km². The catch was recorded as items per km², and grouped into 11 type categories and 7 use categories; 240 items per km² were found in the Gulf of Patras and 89 items per km² in Echinadhes Gulf. The difference was assumed to be related to the difference in population and the fact that more rivers and streams discharge into the Gulf of Patras. Plastic items dominated the numerical abundance at 79-83%. Fishing gear debris was a very low fraction at between 1.1 and 2%, even though fishing occurs in the area. This is in stark contrast to the findings of Moore and Allen (2000) in similar depths off the coast of Southern California. Although Stefatos et al. found that few items were date stamped "many of them were only two years old ... attest(ing) to the fact that the MARPOL regulations are not effective and more money must be spent in order to change public awareness".

An earlier seabed litter survey in the eastern Mediterranean (Galil, Golik and Turkay, 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. The depths at the sites varied from 194 to 4614 m. Litter was sorted into 13 categories. In this survey, the most common debris was paint chippings (44%) followed by plastics (36%). Numerical density varied from 200 items per km² on the shelves to 20 items per km² in deeper waters near shore or in shipping lanes to 1-8 items per km² in the deep waters outside shipping lanes.

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 (the extra category of wood included for the North Sea). Beam trawl estimates of debris density varied from 7 items per km² in the Bay of Seine, east of the Cherbourg peninsula to over 1900 items per km² in the NW Mediterranean. Observations from the submersibles *Cyana* and *Nautila* 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 km²). 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 km², 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.

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	<i>Estimated</i> items per km²
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

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. While Galgani et al. conceded that “the use of nets with otter boards ... probably underestimated the quantities present”, from their paper, they did not seem to have arranged a comparison at one site of the results from the submersible and from the trawl; for example, by surveying an area with the submersible, counting but not retrieving litter, followed by a trawl survey over the same area. It would be wise to check the reasonableness of the estimate of conversion from linear to areal density.

3. FUTURE DEVELOPMENTS IN SENSORS AND SYSTEMS FOR DETECTING AND MONITORING POLLUTANTS

The two areas where we foresee important future developments in sensors, instruments and systems for detecting and monitoring pollutants are:

- *in situ* detection and monitoring of a far wider range of chemical and biological parameters, with inexpensive instruments. Sensors, perhaps based on Micro Electro-Mechanical Systems, will become increasingly more capable and more specific. When applied to procedures such as flow cytometry, the result should be far less expensive systems, yet suitable for the analysis tasks required.
- Improved remote sensing techniques and analysis algorithms will lead to more efficient assessments of the pollution over large areas. Sensors on satellites and aircraft will become more capable. The challenge of remote sensing within the ocean will remain. Incremental improvements in optical and sonar systems for seabed monitoring are envisaged, but costs are likely to remain high. Improvements are likely in automatic detection and classification algorithms for objects on the seabed detected by sonar or optical systems. Advanced underwater instruments such as Laser Raman Spectrometers may become more common, aiding chemical analysis when underway from autonomous or remotely operated vehicles.

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