

Papers published in *Ocean Science Discussions* are under open-access review for the journal *Ocean Science*

Detecting marine hazardous substances and organisms: sensors for pollutants, toxins, and pathogens

O. Zielinski¹, J. A. Busch¹, A. D. Cembella², K. L. Daly³, J. Engelbrektsson⁴, A. K. Hannides⁵, and H. Schmidt⁶

¹Institute for Marine Resources, Bremerhaven, Germany

²Alfred Wegener Institute for Polar- and Marine Research, Bremerhaven, Germany

³College of Marine Science, University of South Florida, St. Petersburg, FL, USA

⁴Department of Chemistry, University of Gothenburg, Sweden

⁵Department of Fisheries and Marine Research, Nicosia, Cyprus

⁶Institute for Optics and Atomic Physics, Berlin Institute of Technology, Germany

Received: 29 April 2009 – Accepted: 4 May 2009 – Published: 14 May 2009

Correspondence to: O. Zielinski (oliver.zielinski@imare.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

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Marine environments are influenced by a wide diversity of anthropogenic and natural substances and organisms that may have adverse effects on human health and ecosystems. Real-time measurements of pollutants, toxins, and pathogens across a range of spatial scales are required to adequately monitor these hazards, manage the consequences, and to understand the processes governing their magnitude and distribution. Significant technological advancements have been made in recent years for the detection and analysis of such marine hazards. In particular, sensors deployed on a variety of mobile and fixed-point observing platforms provide a valuable means to assess hazards. In this review, we present state-of-the-art of sensor technology for the detection of harmful substances and organisms in the ocean. Sensors are classified by their adaptability to various platforms, addressing large, intermediate, or small areal scales. Current gaps and future demands are identified with an indication of the urgent need for new sensors to detect marine hazards at all scales in autonomous real-time mode. Progress in sensor technology is expected to depend on the development of small-scale sensor technologies with a high sensitivity and specificity towards target analytes or organisms. However, deployable systems must comply with platform requirements as these interconnect the three areal scales. Future developments will include the integration of existing methods into complex and operational sensing systems for a comprehensive strategy for long-term monitoring. The combination of sensor techniques on all scales will remain crucial for the demand of large spatial and temporal coverage.

1 Introduction

The quality of marine environments is influenced by a range of anthropogenic and natural hazards, which may adversely affect human health, living resources and the general ecosystem. The focus of this review is on biological marine hazards, including

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6, 953–1005, 2009

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those produced by- or the organisms themselves, and on chemically mediated deleterious effects, rather than on physical hazards (rogue waves, tsunamis, storm surge, meteorological effects, etc.). Major components of such bio-hazards are typically endogenous to marine systems, but may also be contributed from freshwater aquatic and terrestrial habitats via run-off and coastal erosion. Identification of types of hazards and their temporal and spatial scale are crucial for an analysis of the associated risks. In this review, we address the assessments of ecological status and the protection and restoration of ecological potential of habitats. These issues are regulated by law under global, regional or national statutes, such as the EU Water Framework Directive (WFD) (2000/60/EC), the EU Marine Strategy Framework Directive (MSFD) (2008/56/EC), and the US Federal Water Pollution Control Act (Clean Water Act) of 1948 and its amendments (33 U.S.C. 1251–1376).

One goal of the marine science community has been to detect hazardous substances and organisms and to monitor related parameters in the ocean to improve understanding of critical processes and to prevent and mitigate adverse effects. Significant advances in the detection and analysis of hazards have been achieved in recent years, in particular in expanding the temporal and spatial scales of observational technologies and in improving resolution. These monitoring techniques are, in most cases, complementary to methods applied to discrete point-source samples. A close cooperation between remote- and in situ disciplines has also emerged, if somewhat belatedly. During the last decade, a range of global and regional monitoring programs have been developed to protect human- and environmental health and prevent economic losses caused by marine hazardous substances in an integrated manner. Amongst these programs are the following: 1) Global Ocean Observing System (GOOS, 2008), 2) Global Ecology and Oceanography of Harmful Algal Blooms (GEOHAB, 2008), 3) Harmful Algal Bloom Forecasting System (NOAA, 2008a), 4) CoastWatch (NOAA, 2008b), and 5) United Nations Environment Program (UNEP) on Global Monitoring for Persistent Organic Pollutants (POPs) (UNEP, 2004).

To tackle extant and emerging environmental problems, flexible approaches and



methodologies must be linked with decision-making strategies of managers. Ecological risk assessment is currently undergoing a shift from the evaluation of particular health impacts, often on a small scale in a specific environment, towards more complex assessments of whole populations and communities across ecologically meaningful landscapes on larger scales (Landis, 2003; Hope, 2006). This conceptual approach was designed primarily with terrestrial “landscapes” in mind, but it is no less valid for consideration of “seascapes”, albeit that the fluxes, dynamics, and community structures are somewhat different in the sea. Increasingly, remote observations will be performed on an operational basis from a variety of in situ platforms and enabling technologies, including profiling moorings and floats, autonomous underwater vehicles (AUVs), gliders, drifters, ships-of-opportunity, and nodes attached to cable networks. Since successful remote ocean operations for marine hazards fundamentally depend on the sensing techniques, we have to examine the state-of-technology and derive demands for upcoming methodologies, sensors, and sensor systems.

Sensors may be generally characterized as devices that capture and transduce a signal related to the presence and/or concentration of a compound or organism, including related physical properties, which can then be stored or transmitted to a receiver at a different location. The captured signal can then be related to biological, chemical, or physical processes affected by or affecting the compounds or organisms detected. “Smart sensors” additionally comprise the ability of the sensor to process and evaluate the captured signal to yield information upon which the receiver or the sensor platform can directly respond.

A variety of platforms are needed to support sensing systems in the ocean, including multiplex and integrated observational technologies. Fixed-point profiling moorings are essential to resolve a wide range of temporal variability (short-lived episodic events, subtle changes over decades, etc.) of physical, chemical, and biological processes that occur between the sea surface and the sea floor. Mobile platforms (floats, gliders, AUVs) with appropriate sensors provide measurements of spatial variability to complement the fixed sites. Satellites can yield broad spatial synoptic measurements of the

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surface ocean, but are of limited use in the vertical dimension.

A vast number of articles have been published on the detection of hazardous substances and organisms. A recently published comprehensive volume on observational technologies for coastal ecosystems, with a focus on Harmful Algal Blooms (HABs) (Babin et al., 2008) is illustrative of the rapid advancements in such fields. The coverage of all hazards and upcoming technologies in this vivid field of development would have to be accomplished separately. Rather than providing a detailed review of all groups of hazardous substances and organisms, including all possible sensors, here we restrict our purview to advanced techniques for detection of marine pollution, toxins, and pathogens in the ocean, with a focus on sensors applicable for remote deployment.

2 Marine health hazards

Hazardous substances and organisms in marine waters may derive from anthropogenic or natural sources. In this review we distinguish between man-made marine pollution (MP), natural marine toxins (MT), and pathogenic agents (PA) (Fig. 1). Unfortunately these categories are not so clear cut – formation of many marine pollutants is facilitated by the combination and transformation of anthropogenic components with naturally occurring substances. Furthermore, hazardous “natural” occurrences of toxic organisms (e.g., HABs) or bacterial and viral pathogens may be stimulated by human activities, such as sewage inflow and eutrophication or long distance human-mediated transport, as in ship ballast water. Finally, natural pathogenic organisms can be enhanced in diversity and biogeographical extent through human interventions such as agricultural run-off and improper sewage treatment. It is, therefore, unwise to treat these phenomena as unrelated events for observational and management purposes.

By consensus MP is perceived to be derived exclusively from human activities. The term pollution is defined by GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection, 1983) as:

“... the introduction by man, directly or indirectly, of substances or energy into the

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marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance of marine activities, including fishing, impairment of quality of use of seawater, and reduction of amenities.”

According to the EU WFD and the US CWA, priority substances that represent a significant risk to or via the aquatic environment range from toxic metals, to organic contaminants, such as persistent hydrocarbons, organochlorine compounds and pesticides, as well as organometallic compounds. In this review of marine sensing technologies, we examine the broad range of MP divided into sub-categories: heavy metals, including cadmium, mercury, lead, copper, and radionuclides; petroleum hydrocarbons, also referred to as oils or polycyclic aromatic hydrocarbons (PAHs), dispersed in water or as a surface layer; persistent organic pollutants, such as polychlorinated biphenyls (PCBs), tributyltin (TBT), pesticides, dioxins and furans; and also nutrients, such as nitrate, ammonia, and phosphate. These nutrients occur naturally in the ocean and are critical to ecosystem function, but are considered pollutants when land-based nutrients entering watersheds and estuaries exceed natural levels, and stimulate excessive primary productivity – a process termed eutrophication (GESAMP, 1990). An additional class of pollutant is constituted by hormones, such as estradiol, estrone, and ethinylestradiol, contributed largely from agricultural sources as feed to farm animals to enhance growth, milk production or meat yield, or from human sources added to domestic sewage and run-off from waste originating as hormone supplements or birth control agents. High concentrations of certain hormones in aquatic systems are responsible for developmental anomalies, e.g., change of sex in fish (Christiansen et al., 2002).

When considering man-made marine pollutants, the issue of waste disposal and long degradation periods for discarded plastics is of increasing concern. Plastics absorb PCBs in aqueous media (Endo et al., 2005; Rios et al., 2007). A correlation between ingested plastic and PCBs has already been detected over two decades ago in great shearwaters *Puffinus gravis* (Ryan et al., 1988). Plastic particle uptake has also been observed in holothurians (i.e., sea cucumbers) (Graham and Thompson, 2009), there-

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fore leading to accumulation in the food web. Plastic particles could conceivably also influence the spreading of indigenous HABs as a vector for microalgal dispersal (Masó et al., 2003).

Health hazards with a natural origin comprise both MT and PA, although recent observations indicate an increased prevalence and distribution due, at least partially, to anthropogenic influences on the marine environment (Anderson et al., 2002). A large number of marine animals from many different phyla, including certain snails, jellyfish, sea anemones, sea urchins, sponges, and fish, etc. produce highly bioactive substances, including potent toxins and venoms for prey capture or defence. These substances can also be hazardous to human health. Because the effects are extremely localized and the toxins themselves cannot usually be monitored with in situ or remote sensors, they are not dealt with in detail in this review.

An exception should be made for toxic jellyfish (medusae and comb jellies), which can be potentially monitored by optical sensors when present as mass occurrences (“jellyfish blooms”). Swarms of poisonous and nuisance jellyfish species are responsible for world-wide seasonal beach closings, power plant shut-downs, and even fish-farm cage destruction (e.g., Graham et al., 2001; Mills, 2001). Although the exact reasons for jellyfish blooms are incompletely understood, these mass occurrences are likely to continue unabated in the future and to pose the same if not increasing hazards to many human activities, especially in the coastal zone.

Our focus here on MT comprises biotoxins synthesized by living organisms, with emphasis on toxins produced by microorganisms, such as microalgae, fungi, and bacteria, including cyanobacteria. These MTs are widely associated with contamination of seafood. The most widespread classification of these microorganism-derived toxins linked to seafood poisoning is based on associated toxin syndromes (Campás et al., 2007), e.g., okadaic acid and dinophysistoxin analogues causing diarrhetic shellfish poisoning (DSP); saxitoxin and related derivatives causing paralytic shellfish poisoning (PSP); domoic acid associated with amnesic shellfish poisoning (ASP); brevetoxins causing neurologic shellfish poisoning (NSP); azaspiracids causing azaspiracid shell-

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fish poisoning (AZP); ciguatoxin and maitotoxin analogues linked to ciguatera fish poisoning (CFP); and tetrodotoxin causing pufferfish (*fugu*) poisoning (Geistdoerfer and Goyffon, 2004; Campas et al., 2007). Human illness caused by marine toxins can also be divided into their primary transvectors – those associated with seafood consumption, and those due to exposure to water (or aerosols) containing toxins. These human health effects are highly diverse, ranging from mild to acute (even fatal) especially when neurotoxins are involved, and can include nausea, neurological disturbances, paralysis, short term memory loss, fevers, ear and eye irritation, and pulmonary consolidation, and may be associated with longer term kidney- and liver damage even resulting in carcinogenesis and tumour promotion (for references see Codd et al., 2005).

Most toxins associated with marine microorganisms are naturally produced by microalgae, including the prokaryotic cyanobacteria (“blue-green algae”). There are also occasional reports of mycotoxins in the marine environment, such as those of the toxic fungus *Aspergillus fumigatus*, which can accumulate in mussels (Grovel et al., 2003). Toxins of algal origin (phycotoxins) may be transferred through the food chain via the consumption of toxic microalgae and then can accumulate in higher trophic levels (fish, marine mammals, seabirds) with devastating consequences, as well as in seafood with a risk for human consumers. Phycotoxins in the marine environment regularly lead to restrictions on commercial and recreational shellfish harvesting and negatively impact tourism and public health resulting in high economic losses each year. Cyanobacterial toxins in fresh and brackish water are another critical and emerging problem, with evidence of effects on marine ecosystems related both to toxicity and high biomass production.

The term Harmful Algal Bloom (HAB) is often applied operationally to algal occurrences that cause harm through the production of toxins and/or by excessive accumulation of biomass – but not all HABs meet both criteria (Anderson et al., 2002; Másó and Gárces, 2006). Blooms are generally characterized by development, maintenance, and decline phases. The detection of such events occurs mainly during later development and maintenance stages when significant biomass and/or toxic effects are present;



early warnings of impending events are thus rare and bloom prediction and modelling remains a major challenge that is being addressed in only a few key areas (e.g., the Gulf of Maine, reviewed by Anderson et al., 2005). High biomass accumulation alone may lead to environmental damage, such as hypoxia, anoxia, and harmful shading of underlying vegetation, such as seagrass beds and corals. Furthermore, certain toxins, including some from cyanobacteria, can persist in the water phase after extracellular release (Lawton et al., 1994), thus the absence of the bloom does not necessarily indicate absence of toxins.

A pathogenic agent is defined as “any organism, which in living on or within another organism (the host) causes disease in the host” (FAO, 1998). Agents of waterborne diseases include viruses, bacteria, and protozoa (Gerba, 1996). Although many species of cyanobacteria (“blue-green algae”) and some free-living marine protists (eukaryotic microalgae and protozoa) are responsible for waterborne diseases associated with the production of phycotoxins, they are not intrinsic pathogens to mammalian hosts and, therefore, will be considered under the HAB topic for purposes of this review. Nevertheless, there is evidence of correlations in the occurrence of algal blooms and viruses, stressing the need of process monitoring and cross-linking fields of research.

Some pathogens, such as the cholera bacterium, *Vibrio cholera*, occur naturally in marine waters, whereas others, e.g., from fecal contamination sources, may have only limited survival periods in the marine environment. Generally, the survival of bacteria depends on factors such as water quality, nutrient supply, salinity, exposure to sunlight (ultraviolet radiation) (Johnson et al., 1997), as well as grazing pressure (Worden et al., 2006). Human exposure pathways include head or face immersion, swallowing water, entering water up to or beyond waist level (WHO, 2001), as well as the consumption of contaminated seafood. Increasing evidence is given for a proportional increase of associated infection rates to the level of pollution (Cabelli et al., 1982; Cheung et al., 1990; Corbett et al., 1993; Kay et al., 1994). Consequences of pathogen-contaminated waters include human health problems, frequently gastroenteritis (WHO, 2001). Further symptoms and syndromes associated with pathogenic bacteria and protozoa may

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include: skin rashes, fever, and acute febrile respiratory illnesses (AFRI) (Fleisher et al., 1996a), salmonellosis, meningo-encephalitis, cryptosporidiosis, and giardiasis (Prüss, 1998). The risk of infection is determined by type of exposure, as well as type and concentration of pathogen. There are also economic losses due to the closure of shellfish fisheries and recreational areas. The recommended indicator for human pathogens in marine waters and gastrointestinal symptoms are faecal streptococci/enterococci (WHO, 2001). However, there is no worldwide agreement on best indicators of public health risks – the US monitors enterococcus or coliforms, and Hong Kong tracks *Escherichia coli*, whereas the UK monitors fecal streptococci. Unfortunately, indicator bacteria do not generally mirror the human enteric virus or bacterial distribution in seawater (Jiang et al., 2001).

3 Detection of health hazards: status and developments

The health hazards described above can be classified based on source of origin: a) point sources, such as discharges from urban waste waters, oil spill, or aquaculture; b) diffuse sources, like losses from agriculture or leakages; and c) spread sources, such as the atmospheric deposition on water bodies. This areal dependence on the origin of the potential hazards introduces a spatial dimension that can also be transferred to the corresponding sensing technologies. However, there is a reciprocal relationship in the spatial coverage of a research area of interest and the information depth with the majority of sensor methodologies associated to the level of areal coverage (Fig. 2). The coverage of a large area is of importance as well as precise measurements of a smaller “pixel”. Subsequently, we review the state-of-technology for the detection of marine hazards following this area-approach, from large to small scales.

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3.1 Status of sensor techniques with decreasing spatial coverage

3.1.1 Detection on a large scale: remote sensing

Remote sensing techniques are required to obtain broad spatial synoptic coverage of the ocean surface. Remote sensing in general is the detection and identification of phenomena at a distance from the object of interest using human capabilities or special sensors. Modern remote sensing instruments are normally based on optical, electronic or, less frequently, chemical techniques. During the last few decades, many improvements have been achieved in the development of new sensors and in the improvement of existing sensors and their application (Bonn agreement Aerial Surveillance Handbook, 2007).

Remote sensing of the ocean on a larger scale is commonly, though not exclusively, applied from above the water surface via satellite or aircraft. Most wavelengths for optical or radio-sensing techniques are strongly attenuated in seawater, which prohibits a deep penetration of the water column, and, thus, are limited to sensing the surface layer of the ocean. Satellites can detect marine surface films, for example those generated by oil-spills; however, any sub-surface blooms, such as those of harmful algae, remain undetected, if low water transparency prohibits upwelling radiation from being detected at the relevant depths.

Other limitations of remote sensing are its dependency on the radiative transfer within the atmosphere, which is especially important for optical sensors. This critical feature also highlights that calibration and validation exercises are imperative. Another limitation is the restricted availability of remote optical sensing data due to cloud cover and orbital path and temporal coverage in the case of satellite-borne systems. Similar constraints may also affect the availability of airborne remote sensing data, which depends on the range, technical status, and obligations of the carrier platforms (Zielinski et al., 2001).

Remote ocean sensors, in general, require a change in the absorption, scattering, and/or reflection of water for a given wavelength, using either natural (denoted as pas-

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sive sensing) or artificial (active sensing) illumination sources. Airborne sensors basically draw on the same techniques developed for satellite observations, reducing the atmospheric influences by operating at lower altitudes, but concurrently reducing their aerial coverage. The increased flexibility and mobility of airborne sensors makes them a prominent choice for surveillance tasks and supporting actions, e.g., to complement shipboard observations. Here we examine satellite and airborne sensors as remote sensing systems and discuss existing approaches being used to address the classes of marine hazards described in the first section.

Marine pollution (MP)

MP such as caused by heavy metals and radionuclides is not directly detectable in seawater from satellite or airborne remote sensing instruments, since the pollutants are low in concentration and the known detection methods are not transferable to these remote platforms. Nevertheless, other matrices including sewage effluents can serve as indirect indicators of certain MP at large scales, whereby optical detection is achieved, e.g., by increases in turbidity or coloured dissolved organic matter (CDOM) concentrations. This also holds true for most of the persistent organic pollutants, except for petroleum hydrocarbons, for which highly specific wavelength-dependent remote sensing equipment has been developed, especially for airborne oil-spill surveillance.

During the last two decades, airborne remote sensors have evolved into common instruments for the operational surveillance of oil pollution. The most common sensor arrangements include a SLAR (side-looking airborne radar) and an IR/UV (infrared/ultraviolet) line scanner. Whereas the former sensor is used for far-range detection of pollution, the latter is especially designed to locally characterize oil spills. In addition to this standard there are newer sensors, such as the laser fluorosensor (LFS) or the microwave radiometer (MWR) that allow an advanced analysis of oil spills for the remote identification of oil species and the estimation of film thickness (Hengstermann and Reuter, 1990; Grüner et al., 1991; Zielinski, 2003; Zielinski et al., 2006a). In addition, the laser fluorosensor may be used for hydrographic measurements of chlorophyll

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or CDOM (Browell, 1977; Hoge and Swift, 1983; Zielinski et al., 2001).

Satellite detection of oil spills is mainly based on radar/microwave observations, although both optical and laser induced illumination technologies have been applied (Gade, 2006). The optical properties of nutrients such as nitrate or ammonia are not accessible in the visible or infrared spectra and, therefore, not detectable directly from satellites. Again, as a guide for large-scale monitoring of certain MPs, the effects of excess nutrient concentrations contributed by sewage and river runoff in coastal areas leading to algal blooms can be detected remotely via increased chlorophyll-, or other pigment-linked biomass as a proxy for high nutrients.

Marine toxins (MT) and mass occurrence of toxigenic organisms

The presence of toxins in the water column or within marine organisms is not detectable by remote sensing since their concentrations and optical properties do not provide significant changes neither in ocean colour nor in other electromagnetic features. However, remote sensing provides for detection of mass aggregations (blooms or swarms) of biotoxin-bearing organisms. For example, the location and mass characteristics of large aggregations of the jellyfishes, *Rhizostoma octopus*, *Cyanea capillata*, and *Chrysaora hysoscella*, have been identified via aerial surveys (Houghton et al., 2006). Such successful applications of remote detection methods provide a means of monitoring potential primary transfectors of toxins.

Whereas toxins do not change the optical properties of seawater, algal blooms certainly do so and are, therefore, potentially detectable by remote sensing. Passive remote sensing takes advantage of the distinct absorption characteristics of chlorophyll *a* in microalgae and the corresponding influence on ocean colour. Both airborne and satellite-based optical remote sensing systems have been widely applied for monitoring the magnitude and distribution of algal blooms, both benign and harmful. In HAB research and monitoring, remote sensing offers the possibility to track mass-surface aggregations based upon pigment spectral signatures (although not toxins). In cases where the species identification and toxic or otherwise harmful potential has been es-

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5 established by independent means, such as in situ sampling or access to historical data on bloom characteristics, remote sensing is a valuable method of conducting broad scale synoptic surveys. For example, remotely sensed chlorophyll data have been used as a proxy for abundance of the Florida red-tide dinoflagellate, *Karenia brevis*, from which the cell abundance estimates can serve as a proxy for the brevetoxins produced during blooms (Tester et al., 2008). Further successful development of other remote sensing techniques to detect and track *K. brevis* blooms on the west Florida shelf are now being implemented (Carder and Steward, 1985; Hu et al., 2005, 2008). Recently, a novel classification approach combining high chlorophyll-low backscatter measurements allowed improved satellite detection of *K. brevis* (Cannizzaro et al., 2008).

15 We emphasize that it is not possible to discriminate toxic species or populations from non-toxic ones by large-scale remote sensing. It is, however, possible to identify anomalies and typical situations with high probabilities for HAB events that can be used as triggers to enable countermeasures for aquafarming or tourism (Stumpf, 2001; Stumpf et al., 2003, Reinart and Kutser, 2006). Aircraft observations can be automated with optical equipment, such as still- and motion-cameras, mounted on light-weight platforms such as Unmanned Aircraft Systems (Patterson and Brescia, 2008). In regions where jellyfish swarms or HABs constitute a common interference with marine enterprises and activities, such as tourism, aquaculture, navigation, etc., protocols could be developed for aerial observatory operations or satellite-based systems to detect, enumerate, and predict the development and distributional pattern of such events.

Marine pathogenic agents (PA)

25 In addition to those occurring naturally in marine waters, pathogens are carried into waterways after defecation/urination/shedding from human or animal hosts, e.g., via sewage effluent, agriculture and storm water runoff, sewage from ships, recreational aquatic activities, industrial processes, wildlife, septic tanks near the shore, and urban development (WHO, 2001). Many pathogenic agents are of terrestrial origin, but can

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be carried by river discharge into marine coastal areas. The detection of pathogens via remote sensing is only possible through the detection of these source pathways. The relationship between risk of pathogens and pathways is influenced by many factors that can change rapidly, such as weather conditions, land use, redirection for agricultural or power generation purposes, and, therefore, there is a need for frequent validation through ground-truthing.

The large-scale data provided by remote sensing techniques are a valuable resource, providing information on health hazards either directly or indirectly, e.g., by ocean colour or temperature gradients. Several marine hazards are not detectable from air-borne or satellite-based sensors, including marine toxins, pathogens, and heavy metals and, thus, must be dealt with by in situ sensing techniques for ground-truthing and validation.

3.1.2 Detection on intermediate scales: in situ platforms

Assessing processes on intermediate temporal and spatial scales, including transient events, requires even higher resolution of measurements than for large-scale remote sensing. Long time-series stations and ocean observatories need hardened, reliable instruments for long duration deployments (Dickey, 2001; Daly et al., 2004). Sensors must have sampling rates high enough to detect the development of transient events and operate over time scales at least comparable to those of physical processes (and physical sensors for conductivity, temperature, and pressure). To give an illustration: the application of an optical nutrient sensor on a winch onboard a ship produces a nearly one-dimensional data set (a depth profile) without any sample preparation on board. As part of an undulating tow-fish or a glider, the same sensor can even yield quasi two-dimensional information. The point of this example is that the dimensions of the area that can be probed depend on the capabilities of the mobile platform in combination with sensor characteristics (e.g., sampling rate). Of course the integrated sampling area will be smaller than the vast areas covered by satellites or aircraft remote-sensing, but larger than that covered by discrete shipboard water sam-

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pling from fixed depths, which often require sophisticated (non-real-time) laboratory analysis to generate results.

With respect to the recent development of mobile platforms such as floats, gliders, or AUVs, the intermediate scale is also the most relevant scale for sensor applications and development. We therefore review the portable in situ sensor technologies for the marine health hazard classes defined in the first section.

Marine pollution (MP)

Among the laboratory devices for heavy metals, colorimetric, polarographic, and ion-selective electrode devices can most easily be made portable for field detection (Bundy et al., 1996). Polarography is an electroanalytical voltammetric method that can be adapted to perform trace level analysis with speciation capability. Several modifications of basic laboratory methodology, including changes in power supply, data acquisition, experimental control, and methods of metal extraction from test samples, are needed, however, to produce a practical, portable polarographic field sensor. Voltammetric instruments are a promising tool for in situ measurements of trace metals (Howell et al., 2003). A commercially available voltammetric in situ profiling system (VIP) (Tercier et al., 1998; Tercier-Waeber et al., 1999) has been successfully applied for autonomous, continuous monitoring in estuarine and coastal marine waters for up to one week (Tercier et al., 1998; Howell et al., 2003) with detection limits for dynamic fractions of Cu(II), Pb(II), Cd(II), and Zn(II) at ppb level, for Mn(II) at ppt level. Based on the VIP, Tercier-Waeber et al. (2005) have presented a Multi Physical-Chemical Profiler (MPCP) based on gel-integrated voltammetric microsensors and a multi-channel voltammetric probe as well as advanced microprocessor. The MPCP includes commercially available detectors for various parameters and is constructed for the simultaneous in situ autonomous monitoring of major fractions of Cu, Pb, and Cd, as well as CTD, pH, oxygen, redox E, turbidity, and chlorophyll.

The application of a wet-chemical analyzer for determining the presence and concentration of dissolved iron(II) or manganese(II) in the water column (Prien et al., 2006)

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shows promise for field deployment for detecting metal pollutants. The analyzer is based on unsegmented continuous flow analysis, whereby the sample stream is inoculated with a reagent, the combined solutions are mixed and pass into a cell where the intensity of colour is determined by an LED light source and a photodiode coupled to a frequency converter as a detector. This type of in situ analyzer employs a series of valves that switches the system from pumping samples to a blank solution and a known standard. Thus, “onboard” two-point calibrations (standard and blank) can be carried out during deployment. This has the advantage that a correction for any effect that pressure and/or temperature may have on the colorimetric system can be applied to the data. The specificity for either iron or manganese is achieved through different chemical reagent regimes, but the physical instrument is the same for both analytes. Special emphasis on a fast reaction time of the analyzer (ca. 8 s between independent measurements) offers potential for deployment in profiling mode with concurrent CTD measurements or as payload on AUVs.

A gamma-radiation probe has been developed for radionuclide detection within a stationary monitoring network for radioactive contamination in the marine environment (German BSA, Federal Maritime and Hydrographic Agency). This detector system is based on a NaI-scintillator with a fully integrated spectrum analyzer. An interfaced processing unit measures gamma-spectra over preset observation intervals as well as integral counting of fixed gamma-energy regions. Under field conditions, this in situ method delivers comparable results to chemical analysis for nuclide mixtures originating from accidents (Wedekind et al., 1999). A specific complex energy spectra analysis of nuclides is not possible due to the relatively poor energy resolution of NaI-detectors. The KATERINA system, similar to that of the German BSA, has been developed by the Hellenic Center for Marine Research in Greece, and which incorporates a NaI(Tl) detector for the measurement of marine radiation (Tsabaris et al., 2008a, b). The system has been tested on a Remotely Operating Vehicle (ROV) (Tsabaris et al., 2008a) and integrated with fixed platforms (i.e., moorings) of the POSEIDON system. The output is configured to be transmitted via satellite to the base station (Tsabaris et al., 2008b).

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An alternative submersible program-controlled gamma-spectrometer based on an HPGe detector with 38% efficiency for monitoring radionuclides by volumetric activity in water in near-real time is also available (Gostilo et al., 2000).

Petroleum hydrocarbons (included as polyaromatic hydrocarbons [PAHs]) can be observed in situ with multispectral sensors or by detection at selected wavelengths of different optical properties of oil, among them fluorescence, reflection and absorption (see e.g., Zielinski and Brehm (2007) for a recent application and Arst (2003) for a general review). The oil groups can be classified based on fluorescence emission due to fixed wavelength excitation in the ultraviolet range, similar to the detection of oil on the water surface in airborne remote sensing (Hengstermann and Reuter, 1990). Laser induced fluorescence of oils and the effect on humic substances has been analyzed for example by Zimmermann et al. (1999). Nevertheless, the results of this technique can be strongly influenced by other substances in the water.

Surface-enhanced Raman scattering (SERS) is another spectroscopic method for the detection of PAHs suitable for in situ measurements. Schmidt et al. (2004) applied SERS to detect six PAH species with a flow through system at concentrations as low as a few nanograms per liter. The high specificity and fingerprinting characteristics of Raman spectra allow for substance identification in mixtures (Nguyen, 2004). The Raman measurement takes only 3–10 s and, therefore, is well suited for rapid in situ measurements. In harbour water, PAHs were found using the Multiparametric in-situ Spectroscopic Measuring Platform for Coastal Monitoring (MISPEC) including a SERS system (Kronfeldt et al., 2004). Currently, temporal and spatial resolution are limited by the adsorption kinetics of the sensor surface, with a timescale on the order of minutes (Murphy et al., 2000). This sensor is suited for stationary measurements, but improvements of the response time can be addressed with new sensor surfaces. This would make SERS a promising tool also for profiling. Other issues are to further decrease the limit of detection and to reduce weight and power consumption of the instruments.

An in situ ultraviolet spectrophotometer (ISUS) for the measurement of nitrate, bromide, and bisulfite, is capable of measurements at a sampling rate of 1 Hz (Johnson

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and Coletti, 2002). The same principle is applied in the in situ process photometer (ProPS), for measuring highly resolved profiles and transects from nutrient-poor to nutrient-rich waters (Zielinski et al., 2007). Both instruments are suitable for high-resolution and long-term monitoring. For nitrate measurements, Johnson et al. (2006) quote an accuracy of $\pm 2 \mu\text{M}$ and a detection limit of $1.8 \mu\text{M}$ for measurements at 1 Hz for a 2.5 year deployment. Accuracy and long-term stability of this approach can be further improved if the degrees of freedom within the algorithms are reduced by externally measured temperature and salinity information (Sakamoto et al., 2009). In comparison, the detection limits of the commercial submersible wet-chemical analyzers are about 40 nM, but the deployment times are limited by reagent consumption and degradation to less than ten weeks (Prien, 2007).

In the Spectrophotometric Elemental Analysis System (SEAS), a liquid core waveguide and long path lengths yield shipboard profiles at 0.4 to 0.75 Hz at nanomolar levels of nitrate and phosphate using reagent chemistry (Adornato et al., 2007). Real-time communication with SEAS will allow control of ascent/descent rates for improved measurements at specific features. The SEAS instrument can also accurately measure pH (± 0.0014 units) at 0.5 Hz (Liu et al., 2006). In addition, simultaneous surface measurements of pH, CO_2 fugacity, and total dissolved inorganic carbon concentrations can be obtained with an autonomous spectrophotometric flow-through system (Wang et al., 2007).

Marine toxins (MT) and mass occurrence of toxigenic organisms

Toxin- and taxon-specific detection

The identification of marine biotoxins, either phycotoxins or those produced by marine macrofauna (e.g., jellyfish, sea snakes, cone snails), at the intermediate scale from deployable systems is (with a couple of notable exceptions) not yet realizable. One of these exceptions is the detection of the phycotoxin domoic acid produced by several species of toxigenic pennate diatoms, *Pseudo-nitzschia* spp., based upon a specific antibody method for the toxin (G. Doucette, NOAA Marine Biotoxins Program,

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Charleston, SC, USA, personal communication) and integrated into the moored Environmental Sample Processor (ESP) developed at the Monterey Bay Aquarium, Monterey, California (see detailed description in Scholin et al., 2008). The ESP system was originally designed for in situ near real-time detection of harmful algal taxa based upon their unique ribosomal DNA signatures. The molecular probes can be multiplexed for simultaneous detection of many putatively harmful species and can be hierarchically designed to reflect the closeness of target affiliations (class, order, genus, species, geographical population, etc.). Hybridization of compatible rRNA from in situ cells extracted on-line in the “sandwich hybridization assay” can be detected optically by either fluorescence or photometric sensing, which also provide a semi-quantitation of total hybridizable rRNA as a proxy for target cell number. This ESP system is now past the advanced prototype stage, and in the latest configuration has been deployed over several months on moorings in Monterey Bay, California and the Gulf of Maine, USA. Commercial production is expected to follow within the near future.

Since most marine toxins are non-volatile compounds they are not readily amenable to certain chemical analytical techniques, such as gas chromatography coupled with mass spectrometry (GC-MS) without derivatization. Current applications of liquid chromatography with mass spectrometry (LC-MS) to marine biotoxin analysis are limited to laboratory extracted and serially injected discrete samples (Quilliam, 2003) and do not include in-water profiling or moorage deployment. The successful deployment of an advanced coupled tandem mass spectrometer (LC-MS/MS) with linear ion-trap (ABI SCIEX 4000 with Q-trap) for shipboard measurements of marine phycotoxins harvested from the water column particulate fraction in the North Sea (Krock et al., 2008) is an example of transitional analytical technology for intermediate temporal and spatial scales. In precursor ion scan mode, a wide array of putative phycotoxins belonging to different structural grouping can be assessed qualitatively and quantitatively from a single injection in <1 h run time, providing quasi-synoptic spatial coverage in near-real time for these toxins while underway (Krock et al., 2009). This on board laboratory technique provided the chemical signal for the identification of the organismal source of

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azaspiracid toxins (Tillmann et al., 2009) – previously a mystery and major issue for shellfish toxins monitoring programs. It would of course be significantly advantageous if LC-MS systems were available for in situ applications (Marr et al., 1992) and recent developments towards miniaturization of both LC and MS technology (Taylor et al., 2001) indicate that in situ toxin analysis directly from seawater may be feasible in the not too distant future.

Underwater mass spectrometers are available commercially (e.g., Applied Microsystems In-Spectr), although they are limited to analysis of very small molecules such as methane. Through the use of MEMS-based mass spectrometers (Taylor et al., 2001) the size and power demand of these systems could probably be reduced even further. On-chip or capillary LC with microfluidics would reduce the consumption of the mobile phase and the need for the vacuum pumps to remove large amounts of vapour from the interface, as well as improve sensitivity. The relatively low sample throughput (minutes to hours per sample) as well as power and space requirements of such a sensor system would likely make it best suited for larger/stationary platforms, short targeted deployments, or for ground-truthing of other sensors.

Detection of high biomass HABs

Profilers or moorage-based systems for detection of HABs are almost all based upon inherent- or apparent optical properties of the bloom and are hence generally both less sensitive and less specific than the techniques described for taxon- and toxin-specific sensors. Bloom detection with the former instrumentation, therefore, typically requires high biomass (or high concentration of a proxy parameter such as chlorophyll or phycobilin-pigments), while yielding only very low taxonomic resolution (Cullen et al., 1997). Such systems also perform best when the species composition is relatively well defined and where the bloom tends to be monospecific. For the continuous detection of microalgal blooms or particle concentrations on vertical and horizontal scales, a range of commercial in situ bio-optical instruments, such as fluorometers, transmissometers, or turbidometers, are commonly available (see also the review on optical tools in this

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5 volume, Moore et al., 2008). The discrimination of valid information on microalgae or bulk material in the water is mainly solved by the relatively large amount of information obtained over temporal and spatial scales. Commercial in situ bio-optical instruments use inherent optical properties (IOPs) of substances contained in seawater, such as the specific adsorption, attenuation, scattering, and backscattering, at an increasing number of wavelengths (Babin et al., 2005). The underwater IOPs range from bulk hyperspectral to miniature multispectral instruments, and are being deployed on all types of fixed and mobile in situ platforms, e.g., buoys, ROVs, AUVs (Mitchell et al., 2000; Bishop et al., 2002; Zielinski et al., 2006b).

10 Fluorometers with internal light sources are used as indicators for chlorophyll concentration, a proxy for phytoplankton abundance and humic/coloured dissolved organic matter (CDOM). A second group of optical instruments employ passive sensors, which measure the distribution of light in the water column (measurement of apparent optical properties – AOPs). Values of reflectance and diffuse attenuation can be derived, e.g., from the vertical gradient in irradiance, and inversion techniques can be used to derive IOPs and water constituents (Moore et al., 2008). Passive measurements are dependent on external light sources, such as daylight and are subject to potential sources of environmental variation and uncertainty. Recently, an increasing number of hyperspectral AOP sensors are being deployed enabling sophisticated spectral fitting algorithms that can be used to derive substance concentrations in complex water bodies, e.g., in coastal areas. However, discriminating harmful from non-harmful algae species is still an open challenge for optical sensors, except if the hazard is due to relatively high algal concentrations (Kirkpatrick et al., 2000).

25 The most advanced development of an optical plankton discriminator (OPD, also called the “Brevebuster”) has been successfully deployed to monitor and track blooms of the Florida red-tide organisms *K. brevis* (Kirkpatrick et al., 2000). Blooms of this red-tide species in Florida present a typically ideal suite of characteristics – high surface concentrations, high dominance and monospecific tendencies, plus an unusual pigment signature – that lends itself to optical detection systems. The “Brevebuster” uses

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5 a liquid waveguide capillary cell for the in vivo optical detection of the rare pigment, gyroxanthin-diester, which occurs in *K. brevis* in the eastern Gulf of Mexico and is in constant proportion to cellular chlorophylla (Millie et al., 1997). Comparing light absorption by particles in ambient water to the light absorption fingerprint characteristic of the unusual pigment signature provides a species-specific in situ detection system. The comparison yields a Similarity Index (SI) which is related to the fraction of phytoplankton community biomass contributed by *K. brevis*. Such OPDs are routinely deployed on underwater gliders to map subsurface *K. brevis* blooms on the west Florida shelf (Robbins et al., 2006). Further characterization of *K. brevis* multi-wavelength spectral properties should allow more sensitive detection with underwater spectrophotometers (Spear et al., 2009).

Marine pathogenic agents (PA)

15 As with the remote sensing of marine pathogens on a large scale, the rapid and high resolution detection of pathogens in situ is best approached by the determination of the pathways of introduction. By following the distribution of *E. coli* introduced to the marine environment from point-source measurements of inflow sources where the organisms are in high concentration, the potential pathogens can be effectively tracked on the mesoscale. An emerging development in the detection of microorganisms is the application of Raman spectroscopy (Rösch et al., 2005; Escoriza et al., 2006). Raman spectroscopy is a versatile technique to obtain fingerprints of the chemical composition of the organisms, which can then be used for identification and quantification. Field portable Raman spectrometers are commercially available from several manufacturers and there has also been some development in ocean-capable instruments, such as The Deep Ocean Raman In Situ Spectrometer (DORISS, Brewer et al., 2004).

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3.1.3 Detection on a small scale: in situ – point measurement

The application of highly accurate and precise methods is necessary to quantify specific harmful substances and associated organisms and to provide unambiguous identification of the toxic components and their affiliations with particular taxa. Most conventional approaches are constrained by a time delay in delivery of results, high implementation costs, the need for highly trained personnel, and the requirement for technologically advanced equipment and laboratories. For some toxic substances, the objectives of low cost and ease of use procedures can be partially attained by access to biochemical and biomarker assays (Wells et al., 2001; Cembella et al., 2003), which can often be run in parallel for additional time saving in high-throughput screening systems. Such assays can serve for toxicity testing from a variety of sample matrices including organisms and seawater, and can be configured to be highly specific for the analytes of interest. For most environmental monitoring, structural or functional assays, frequently supplemented with chemical analytical techniques for confirmatory analysis, have largely replaced testing with whole live mammals. The one major exception for marine hazards testing is the retention of the intraperitoneal mouse bioassay (AOAC, 1990; Fernández et al., 2003) for potentially phycotoxin-contaminated seafood by many regulatory agencies around the world. In addition to the well calibrated AOAC mouse bioassay for acute toxicity, many mammalian subjects are also sacrificed for long-term toxicity trials of marine hazardous substances for which alternative dose-response model systems are not available. Nevertheless, increasing concerns for animal rights, as well as the confounding disadvantages of mammalian test organisms, such as effect of age, gender, acclimation history, and natural variation, which can affect the reliability of bioassays strongly underscore the necessity of developing alternative detection methods for marine hazardous substances.

In recent years, there has been a tremendous expansion in the use of liquid chromatography with mass spectrometry (LC-MS), especially since the advent of atmospheric pressure ionization systems (API) in the late 1980s (Quilliam, 2003). In spite

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of the major breakthroughs in monitoring hazardous compounds by instrumental methods (LC with fluorescence or diode-array detection; LC-MS, etc.) or in vitro assays (immunological, biomarker, biochemical, etc.) most of these approaches remain confined to the laboratory. A few advances towards near real-time techniques suitable for field deployment have been made in attempts to transduce the signal from assays via sensors, thereby facilitating the transition from single-shot probing to continuous measurements. In the following section we focus on these sensor technologies, including biosensors and electrochemical, optical, and mass-sensitive sensors.

In addition, most of the sensor technologies for small scale detection still require validation with advanced analytical equipment and laborious laboratory analysis. The new methods, therefore, can be considered as an alternative or complementary to conventional laboratory methods, such as chromatography coupled with mass spectrometry, standard culturing and microscopic examination methods, immunoassays, etc, and not necessarily as complete replacements.

Marine pollution (MP)

Mass-produced sensors for quantitative detection of heavy metals are not generally available on a commercial scale, but test strips from several manufacturers are widely used for the semi-quantitative optical determination of a range of heavy metals. The majority of detection systems for heavy metals rely on optical and electrochemical transduction (Lieberzeit and Dickert, 2007). Optical detection of heavy-metal ions generally relies on reversible binding of the metal ions to optically active reagents, which provide both chemical selectivity and sensitivity. These can be either indicator dyes or ion-carriers which extract into a lipophilic phase on binding. The binding of heavy metal ions to these reagents is not usually specific, but rather the different ions have different affinity for the binding site. In order to provide selective quantification, arrays of different dyes or reagents can be used and the information be extracted by chemometrics. One example of electrochemical detection is stripping techniques, i.e., electrolytic accumulation followed by dissolution, and detection of the latter process. The response

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to a range of heavy metals instead of a specific one is described as one disadvantage of a biosensor by Liao et al. (2006), although this may be required for a range of objectives. Oehme and Wolfbeis (1997) recommend that a combination of spectroscopic methods, such as multi-wavelength spectrometry and measurement of decay time with chemometrics, is a good approach to quantify more than one analyte.

A prototype sensor for radionuclides has been described by Tarancón et al. (2005). Low-level active solutions of $^{90}\text{Sr}/^{90}\text{Y}$, ^{238}Pu , ^{134}Cs and ^{60}Co can be detected. This sensor has errors of $<10\%$ with a sensor based on a plastic scintillator receptor capable of continuous, on-time and accurate remote quantification of the activity of α , β and β - γ emitters. Grate et al. (2008) describe a minicolumn sensor for the detection of radionuclides with a sensing approach based on equilibrium in the columns.

Many toxic organic compounds can either be detected by enzymatic inhibition assays or via antibodies in immunosensors (Suri et al., 2002). A wide range of biosensors exists for the detection of pesticides (Solé et al., 2003), some of which can be classified as immunosensors. The amperometric biosensor Cellsense with *E. coli* (Farré et al., 2001) detects potentially toxic compounds such as phenol derivatives, non-ionic surfactants and benzene sulfonate compounds by measuring the electrical current produced by the bacteria's electron transport chain in wastewaters. One method for the detection of organotin compounds (TBT and DBT) is also based on a bacterial bioassay (Durand et al., 2003). Biosensors are also commercially available for the detection of nutrients, as described for nitrate and nitrite by Larsen et al. (1997) and for phosphate by Engbloom (1998).

Another relevant health hazard that is addressed by small-scale measurements are hormones and their metabolites, which can negatively affect endocrine systems, especially those of aquatic organisms. Endocrine-disrupting hormones may be natural or synthetic chemicals, such as pesticides, plasticizers, pharmaceuticals, cosmetics, household products and industrial chemicals, which interfere with hormonal systems or mimic hormones and block their function. The presence of these "hormone analogues" at only trace levels and their high similarity to naturally synthesized hormones

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produced by the organisms complicates the detection and measurement. Sensor development is in an early stage, but includes both biomimetic recognition systems and DNA microarrays (Sesay and Cullen, 2001; Asano et al., 2004; Tschmelak et al., 2005).

Marine toxins (MT) and mass occurrence of toxigenic organisms

5 As outlined before, the detection of many marine toxins via whole mouse assays, e.g., the AOAC intraperitoneal mouse bioassay for PSP toxins, remains a method in widespread use and is internationally accredited. For example, the mouse bioassay is still a EU reference method for detection of certain Phycotoxins in shellfish (Aune et al., 2007). For replacement in the current EU legislation, alternative methods need
10 to be validated according to an internationally recognised protocol. Such methodologies focus by now on laboratory methods, such as LC-MS (liquid chromatography-mass spectrometry (Alexander et al., 2008).

Several alternative in vitro assays, including in receptor binding assays, biochemical assays, immunoassays and electrochemical immunosensors have been developed and are increasingly applied in seafood toxin monitoring programmes (Cembella et al.,
15 2003; Fernandez et al., 2003). Chemical analytical methods such as chromatographic or electrophoretic techniques and mass spectrometry are now widely employed for the detection of marine toxins (Quilliam, 2003). The large variety of functional and structural assays for phycotoxin monitoring are unfortunately mainly targeted to a specific toxin or selected group of toxins and, therefore, do not provide a broad spectrum
20 screening (Rossini, 2005). Furthermore, interference by nonspecific matrix effects or limited availability of standard reference materials may also impair the application of these techniques for routine measurement (Campbell et al., 2007).

There is no ideal method for toxin determination and, therefore, methods that reliably
25 detect toxic substances in a rapid, low-cost and easy-to-use way are still required. Rapid developments are occurring in the jump from whole animal and tissue culture assays to biosensors, and from simple immunoassays (e.g., colorimetric or fluorometric ELISA) to sophisticated immunosensors (Campás et al., 2007). Biosensors also

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have potential as a partial alternative and/or complementary tool to long established technologies. For example, Campás et al. (2007) developed an amperometric immunosensor assay which was compared with the protein phosphatase inhibition (PPI) assay and conventional HPLC of cyanotoxins. The immunosensor proved its applicability as a screening tool for fast and reliable cyanotoxin detection. Given its success for detecting low level chemical contaminants in food, optical biosensors based on surface plasmon resonance technology also have the potential to be an alternative strategy for monitoring PSP toxins in seafood (Campbell et al., 2007).

Detection of high biomass HABs

The detection of HABs on the toxin- or species level is crucial for HAB monitoring, as the harmful effects are most often attributable to single species. In particular, sensors are needed to detect HABs at low, background concentrations to allow early warning of bloom development and possible mitigation strategies. Traditional observation techniques for algal species on a small spatial scale include light microscopy and laboratory analysis, which are labour-intensive methods that do not deliver real-time results or broad coverage (LaGier et al., 2007). Emerging techniques for near real-time monitoring of phytoplankton include the benchtop FlowCAM[®], combining microscopy and flow cytometry in measuring light-scattering and fluorescence from chlorophyll and phycoerythrin on individual particles larger than 5 µm coupled with image capture capabilities allowing for the recognition of species (Sieracki et al., 1998). The FlowCytobot is an automated submersible flow cytometer that has been used to analyze pico- and nanoplankton (Olson et al., 2003). Techniques depending on single cell analysis, however, may be inappropriate for the colonies or coiled filaments of cyanobacteria (Codd et al., 2005). Another autonomous in situ flow cytometer, the CytoBuoy, has been employed to quantify marine plankton, including the difficult HAB organism *Phaeocystis* spp., which tends to form amorphous gelatinous colonies (Rutten et al., 2005).

Molecular techniques also are being developed for in situ detection of HAB organ-

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isms. The moored Environmental Sample Processor (ESP) described above uses a rRNA hybridization approach (Scholin et al., 2008). In addition, the Autonomous Microbial Genosensor (AMG) (Paul et al., 2007) can collect and process molecular samples in the ocean. The AMG uses nucleic acid sequence-based amplification, with an initial configuration designed to detect *K. brevis*. This instrument is designed to be deployed on moorings and transmit data to shore in near real-time. Development of “phylochips” and DNA microarrays for selected taxa including harmful algal species are underway (Metfies and Medlin, 2008) but are not yet configured for in situ deployment.

Marine pathogenic agents (PA)

There is no universal method for the routine detection of all pathogenic agents of interest in one water sample. This is due to the physical differences between the major pathogen groups, co-concentrated inhibitors in the sample and standardizing a culture-independent endpoint detection method (Straub and Chandler, 2003). Such a universal method may be based on recent advances in sample collection, on-line sample processing and purification and DNA microarray technologies.

It is not possible to measure marine pathogens routinely, thus faecal indicator bacteria (e.g., faecal/thermotolerant coliforms, *E. coli*, enterococci/faecal streptococci) are used as indicators. For marine waters, the WHO (2001a) recommends faecal streptococci as an indicator for recreational use of marine waters, as these show a dose-response relationship for both, gastrointestinal illness (Kay et al., 1994) and AFRI (Fleisher et al., 1996b). One technique towards the detection and enumeration of waterborne pathogens comprises flow cytometry with autofluorescence/immunofluorescence (Parthuisot et al., 2000). A rapid biodetector in the form of a small surface plasmon resonance sensor (Spreeta[®] SPR) (Spangler et al., 2001) was employed to determine a detection range from 70 nm (6 µg/ml) toxin protein (MW 85 000 Da) to 600 nm (50 µg/ml) of *E. coli* enterotoxin in minutes.

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3.1.4 Coverage and gaps in hazard detection

Review of the state-of-technology reveals well established and proven, as well as not yet mature sensing approaches for marine health hazards on different spatial and temporal scales. Efforts to detect, monitor, track, and predict harmful substances and organisms by remote sensing techniques, in situ measurements with sensors and sensor systems, as well as fine-scale laboratory analysis, reveals that each methodology has advantages as well as limits to its range of implementation.

Remote sensing on a large scale is not a complete solution, but is useful for synoptically monitoring harmful substances or proxies. At the other end of the spectrum, dedicated laboratory measurements provide accurate and extensive measurements of a single water sample, but owing to the labour and time-intensive methods, they cannot yield higher spatial or temporal resolution within affordable budgets and resources. A combination of these applications, specifically an integration of large-scale quasi-synoptic data with high resolution surveys and laboratory in-depth analysis, can partly overcome the constraints of a single approach. This combination of scales will provide additional insight and decision making information. A gap remains for new sensing technologies, especially on the intermediate scale, where remote sensing and laboratory measurement intersect. The application of in situ sensors and sensor systems on moorings, ships of opportunity, etc. hold the possibility of combining some advantages of precise laboratory methods and remote sensing to address the demand for high resolution long-term data sets with broad spatial coverage.

Many sensors described herein still require research and development. Especially for detection of heavy metals, POPs, and pathogenic agents full commercialization has often not been achieved, whereas other devices (e.g., for detection of chlorophyll and nitrate) are already available often from multiple manufacturers (Table 1).

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4 Future demands and upcoming technologies

Some of the categories of health hazards are already addressed by a variety of commercialized sensor techniques. Whereas the areas where few sensors are available might be interpreted as an indication of critical immediate future needs, not all approaches are technically feasible or even recommended for the end-user community. For example, the demand for species identification via remote sensing from satellites or aircraft is simply not feasible as the required specifications typically exceed the laws of physics. In many cases, the analysis of marine hazard parameters has been approached by measuring what is easy (e.g., chlorophyll by fluorosensors or particle spectra and fluorescence of picoplankton by flow cytometry) merely because the technology is available, but not because it yields relevant results. Hope is, however, justified in the proposed adoption of the underlying principles of laboratory analytical measurements to be applied to the field. With respect to in situ technologies, there are grounds for optimism that many demands will eventually be satisfied, in spite of the technical and financial constraints in transferring laboratory prototypes to deployable sensor systems. The need for detection of certain substances may not yet be strong enough on all scales to catalyze the required efforts for technical development. Furthermore, the replacement of statutory laboratory methodologies by sensor technology is only possible if comparable (or better) sensitivity and selectivity towards the target analyte is accomplished and can be proven. Combining technology gaps with social demands will drive the needs and priorities for future development.

Within the broad field of aquatic pollution, there is a large demand for sensors from the oil and gas industry. Petroleum hydrocarbons, such as oil or PAHs – on the water surface in dissolved form – are already addressed by a couple of commercial optical sensors on all scales. This underlines the high ecological and economic relevance of the observed processes and parameters. There is, however, a need for further improvements in detection, classification, and quantification of petroleum hydrocarbons, e.g., for the determination of leakages in pipelines or for the concentration in bilge wa-

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ter. Detection is required to be fast, reliable, and affordable to support monitoring- and alarm functions. UV-LED light sources and multispectral excitation-emission configurations are just two examples for the ongoing progress in these sensor technologies. Classification and quantification techniques for in situ application that have been available before only in a laboratory environment and at high costs include the combination of hyperspectral and time-resolved fluorescence sensors (Rohde et al., 2009), surface enhanced Raman spectroscopy, liquid waveguide capillary cells, and attenuated total reflection (ATR) spectroscopy using the evanescent field in coated fibres. The latter is especially suited for measurements in the presence of high amounts of suspended material (river mouths etc.) or high background absorbance.

The accumulation of heavy metals and persistent organic pollutants in the sediment involves a danger for the benthic ecosystem and the risk to bring out toxic components with time delay, e.g., pollutants can return to the food chain upon resuspension due to storms or floods. Algal toxins may be present in the water or accumulated in the food web after a bloom condition. Therefore, the detection of hazardous substances and organisms some time after an environmental stressor needs to be taken into account by coastal management and surveillance measures in the future.

For the assessment of the chemical status of marine ecosystems, as e.g., required for the European WFD, a variety of parameters need to be tracked over large temporal- and spatial scales in a rather precise resolution. Substances include chemical polluting elements as well as physio-chemical elements, such as nutrients. The WFD also requires the assessment of ecological status. Phytoplankton are included within the biological elements considered in the WFD. Established indicators in this respect are phytoplankton biomass, taxonomic composition and abundance, as well as the frequency of blooms (OJEC, 2000). The accurate and timely identification of harmful algal species and measurement of their toxins is fundamentally important to both HAB research and management. Mitigation could also be facilitated by early detection of toxic blooms. Cell counts of putatively toxic microalgae are often used as a proxy for inferring the presence of phycotoxins (Steidinger et al., 1999; Kirkpatrick et al., 2000), but

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these quantitative estimates are not very reliable because of large differences in cell toxin content among members of the same morphospecies and the ephemeral nature of the associated blooms.

A Florida State task force (Steidinger et al., 1999) identified six priority areas of study regarding HABs and their toxins, but this list is also reflective of global requirements: 1) determine the distribution of toxic and non-toxic strains, 2) develop epidemiological studies to determine public health risks, 3) develop economic impact studies to evaluate losses by location or industry, 4) determine the roles of nutrient enrichment and managed freshwater flow in blooms, 5) determine fate and effects of toxins in the food web, and 6) investigate control and mitigation methods, including hand-held and autonomous biosensors. The development and application of sensor methodologies would support the Member States of the EU in the WFD objective to reach a good surface water status by the year 2015.

Biosensors are a clear priority for detection of harmful algae and their respective toxins. Approaches such as membrane-ion channel biosensors, surface plasmon resonance-based biosensors (see Campbell, 2007), and molecular diagnostic procedures (e.g., immunoassays) must be further advanced to comply with the sensitivity requirements to replace the AOAC mouse bioassay.

For marine biotoxins, a single procedure covering multiple classes of toxins would provide the best standard for consumer protection (Rossini, 2005). Unfortunately such a method does not exist – the application of LC-MS/MS to toxin analysis comes closest, but has the major drawback of not directly measuring toxicity and cannot effectively screen for new classes of toxins without prior knowledge of chemical structure and evidence of toxicity. There remains a residual requirement for development of functional assays to determine toxin potency to at least partially replace whole animal bioassays. The range of biosensors for seafood toxicity screening allows detection of phycotoxins at adequate sensitivities, but their limited availability, primarily as research tools, hinders their broader utilization in monitoring programmes. Commercial exploitation could be enhanced by combining existing knowledge in interdisciplinary areas, such

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as nanoelectronics, bioelectronics, micromachining, and microfluidics (Campas et al., 2007). This would also contribute to the implementation of these devices on deployable measurement platforms.

Pathogen detection constitutes the least developed field of sensor development within the framework of this review. To fulfil the demands of the Bathing Waters Directive 2006/7/EC, continuous sensor devices to monitor the presence of fecal indicators and waterborne pathogens would form a clear advantage. Biosensors may form a solution for this demand.

A largely overseen hazard for marine ecosystems has been synthetic micro- and nanoparticles. Microparticles (<20 µm in diameter) are largely the by-product of fragmentation of larger plastic debris (Thompson et al., 2004). These particles are ingested by a variety of marine animals, and they have been shown to readily adsorb phenanthrene, a priority pollutant (Teuten et al., 2007). Nanoparticles (<0.1 µm in diameter) may be generated by further fragmentation of microparticles, but they may also be industrially mass-produced. The presence of nanoparticles in seawater may entail medical and environmental hazards, due to their ability to pass through cell membranes without cell wall disruption (Verma et al., 2008). The effects on the food web, human health, and the marine environment at large remain to be shown, but it is important to be aware of this issue. Further awareness will assist in foreseeing the capability to detect and enumerate synthetic micro- and nanoparticles in coastal areas where sources of hazardous pollutants such as PCBs are present and coincide with commercially important species, such as suspension-feeders (e.g., mussels).

The development of ecogenomic sensors is a future domain of investigation. Within this field, besides the definition of target compounds, methods for detection and signal transduction need to be established (see Scholin, 2009, this issue). In addition to biosensor and ecogenomic sensor-based applications, Raman and imaging-based techniques are promising tools to reach a higher sensitivity towards the target analytes and organisms. Although there has been some success in the application of Raman spectroscopy in the detection of health hazards (Brewer et al., 2002; Kron-

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feldt et al., 2004), this technique may be also regarded as an emerging technique for field deployment, due to the high potential for measuring inorganic and organic compounds even under extreme conditions (e.g., detection of leaking dumped ammunition or non-fluorescent CHCs is conceivable). In addition to conventional Raman scattering, sophisticated techniques such as SERS or resonance Raman can be employed to increase the sensitivity for specific compounds in a complex mixture, e.g., carotenoids and chlorophyll pigments in algae.

A different approach towards the aim of detecting hazardous organisms is the use of image forming devices. Systematic efforts in underwater imaging have been carried out since the 1970s (see Wiebe and Benfield, 2003, and references therein). Today digital technology allows sensing of object size classes below 100 μm and on spatial scales in the decimetre range. However, the required high magnification results in small volumes scanned per frame. Thus, particles with low abundances have a higher probability to remaining undetected until their number increases (Davis et al., 1992, Benfield et al., 1996). Another imaging system, the SIPPER, utilizes a high-speed linescan camera to continuously image all particles passing through a relatively larger volume of water (Remsen et al., 2004) and an image analysis software to measure and identify plankton (Luo et al., 2004). Recent research also is being conducted towards automatic species identification based on research platforms, such as the Lightframe On-sight Keyspecies Investigation method (LOKI) (Schulz et al., 2008). LOKI acquires images of objects in a defined volume and assigns them to environmental parameters. The challenging task is the reliability of the post-processing to ensure autonomous and proper identification of particles. In addition to standard parameters, like Hu-moments, Fourier-descriptors or texture analysis, the classification algorithms includes new form based feature extractions (Latecki and Lakämper, 2000, ISO/IEC TR 15938-8, 2002), increasing classification success.

In the future, progress in sensor technology is expected to depend largely on the development of small-scale laboratory sensor technologies with a high sensitivity and specificity towards the target analyte or organism. Deployable systems, however, must

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comply with platform requirements, as the latter connect the small – to the large scale. In any case, the combination of sensor techniques applicable to all scales will remain crucial for the coverage of all spatial and temporal dimensions.

5 Conclusions

5 In the past several decades, a large variety of measurement devices and sensing systems have been designed. This interdisciplinary field is characterized by a rapid technical development in disciplines such as science, systems engineering and field operation systems. We used the reciprocal relationship between the area coverage and the information depth obtained by the available sensors for these different spatial

10 dimensions to organize our review. From this status quo, a large window of opportunity is evident for the advancement of sensors in marine hazard detection on all scales. Ancillary requirements for monitoring and operational oceanography are improvements in the SWaP-factor (size, weight, and power consumption), biofouling prevention, handling, reagent free operation, real-time data availability, as well as simplified deployment and maintenance. Additional issues of stability and reliability and the testing of

15 techniques, e.g., in ring trials to reach comparable results of multiple users, must also be addressed. Current ocean-observation efforts are limited in scope and as yet do not have clear mechanisms for translating large-scale, international ocean experiments into long-term, operational observation efforts, or for transitioning emerging new ocean-observation technologies to operational use (NOAA, 2008c). This is particularly true

20 with respect to monitoring of (non-physical) marine hazards. The focus here should be on the operational oceanography aspects of in situ sensors with more precise measurements and integration with data via space- and air-borne systems, especially on the intermediate scale.

25 The future of ecological risk assessment will, according to Hope (2006), focus increasingly on larger spatial scales and the need for scientific, defensible, and implementable assessment tools beyond single organisms to large ecosystems. This will

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require a continued application and development of sensors to cover (spatially and temporally) an assessment of multiple stressors, including meta-data storage and analysis capacities.

Furthermore, improved communication amongst all decision makers, stakeholders, and lay audiences is required. This is beyond the scope of a sensor review paper. It is, however, important for the creation of data protocols, analysis tools, and for clear, effective management strategies and for the consideration of the socioeconomic consequences of marine hazards. The protection and restoration of habitats via improved detection and monitoring of hazardous substances, organisms, and linkages with associated critical processes, through sensors and sensor systems will contribute to the prevention and mitigation of adverse effects.

Acknowledgements. This work is based on the session “Health Hazards from the Ocean” of the OceanSensors08 workshop held 31 March–4 April 2008 in Warnemünde, Germany. The authors thank all participants of this workshop for their valuable discussion input and comments on the first draft of this work. We also acknowledge the efforts of T. Dickey, R. Prien, and G. Griffiths for their effort to concentrate and collect knowledge on the status quo of sensor techniques and development in this workshop and to make this information available to the public by means of this special edition in Ocean Science.

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Table 1. Compilation of commercially available in situ sensors for long-term applications in marine environments.

Target analyte	Sensor principle	Sensor	Company, location	Link	
Trace metals Cu(II), Pb(II), Cd(II) Zn(II) (ppt level); Mn(II), Fe(II) ppb level	Electro-chemical/ Voltammetric	Voltammetric in situ profiling system (VIP)	Idronaut, Italy	www.idronaut.it	
Pollution	Hydrocarbons, PAH	EnviroFlu HC	TriOS, Germany	www.trios.de	
	Hydrocarbons	Hydrocarbon Fluorometer	Sea & Sun, Germany	www.sea-sun-tech.com	
	Humic acids, amino acids, BTXE, PAH	HydroC™/PAH	Contros, Germany	www.contros.eu	
	Hydrocarbons	UViLux and UV AQUAtracka	Chelsea Technologies Group, UK	www.chelsea.co.uk	
	Crude oil	Optical	Cyclops-7 Submersible Sensors	Turner Designs, USA	www.turnerdesigns.com
	Nitrate, Nitrite	Optical	ProPs UV	TriOS, Germany	www.trios.de
	Nitrate, Nitrite	Optical	ISUS V3	Satlantic, Canada	www.satlantic.com
	Nitrate	Optical	SUNA (Submersible UV Nitrate Analyzer)	Satlantic, Canada	www.satlantic.com
	Nitrate	Ca Reduction/ Diazotization	9600 Nitrate Monitor	YSI, USA	www.ysi.com
	Sulphide	Amperometric	Submersible Sulphide/H2S Probe	Sea & Sun, Germany	www.sea-sun-tech.com
Nitrate, Nitrite, Phosphate, Ammonia	Chemical/ Optical	AFNA II	SubChem Systems, Inc., USA	www.subchem.com	
Ammonia	Chemical / Optical	MARCHEM	SubChem Systems, Inc., USA	www.subchem.com	
Nitrate, Nitrite, Ammonia, Phosphate, Silicate, Iron(II), Iron(III)	Chemical/ Optical	SubChem Pak Analyzer (with SubChemPak reagent delivery module and ChemStar absorption detector by WET Labs, Inc.)	SubChem Systems, Inc., USA	www.subchem.com	
Microalgae species composition	Optical	Multi-Exciter – in vivo multi-wavelength excitation fluorescence	JFE ALEC Co. Ltd., Japan	www.jfe-alec.co.jp	
Microalgae class composition/ Total Chl analysis	Optical	bbe FluoroProbe	bbe moldaenke GmbH, Germany	www.bbe-moldaenke.de	
HABs and Toxins	Chl	Optical	MicroFlu chl	TriOS, Germany	www.trios.de
	Phytoplankton	Optical	MicroFlu blue	TriOS, Germany	www.trios.de
	Chl	Optical	ECO BB2F	Wetlabs, USA	www.wetlabs.com
	Chl, rhodamine, fluorescein, phycocyanin, phycoerythrin, nephelometer	Optical	AQUAtracka III and UniLux/TriLux series	Chelsea Technologies Group, UK	www.chelsea.co.uk
	Chl-a in vivo, phycocyanin, phycoerythrin, cyanobacteria	Optical	Cyclops-7 Submersible Sensors	Turner Designs, USA	www.turnerdesigns.com

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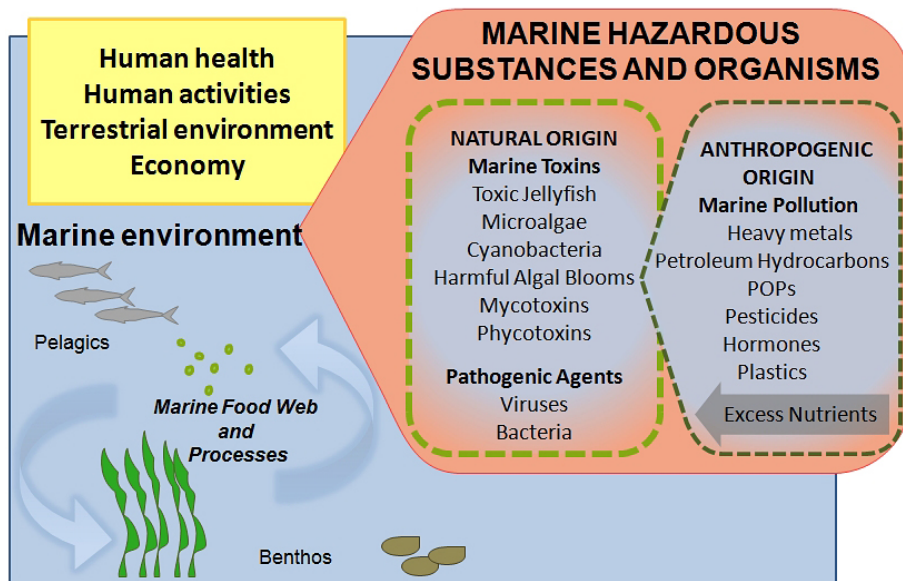


Fig. 1. Classification of marine hazards of anthropogenic and natural origin, as structured within this review, and schematic of marine and terrestrial systems imperilled by these harmful substances and organisms. Marine systems are sensitive to bioaccumulation in food webs.

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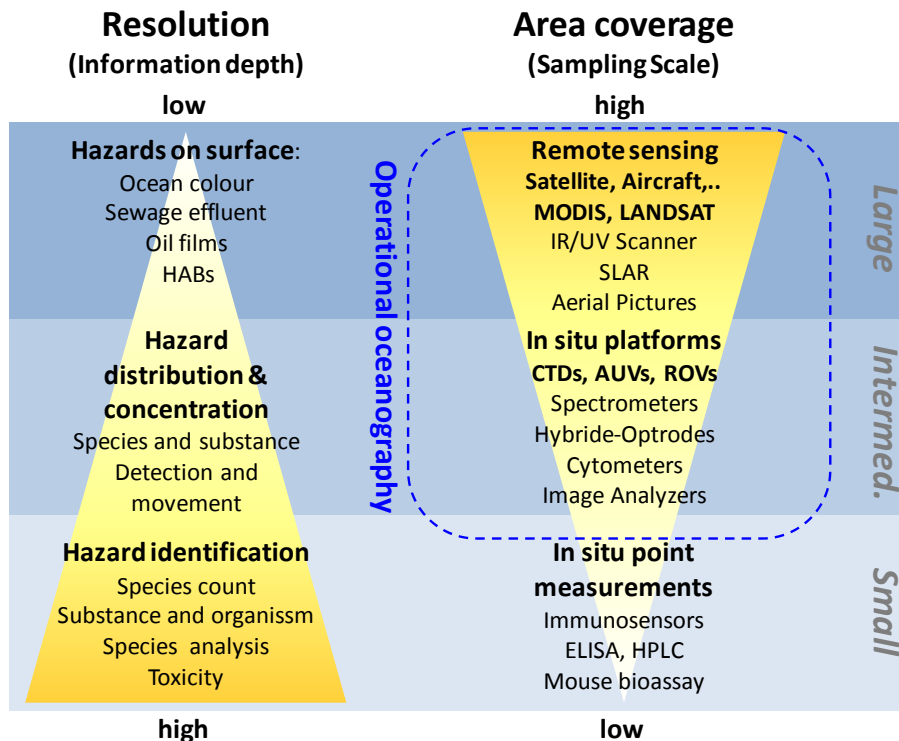


Fig. 2. The reciprocal dependency between sensor sampling resolution and sampling area influencing the extent to which information on hazardous substances and organisms in marine environments can be obtained on large-, intermediate-, and small-scales. Illustrative examples of technologies are provided.

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