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Monitoring of Pollutants: A Historical Perspective for the North-East Atlantic Region

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1.1 INTRODUCTION

The general public had, until the mid 1950s, little or no idea about the ‘environment’; it was just there, as it had always been. It was there to be used and exploited. That chemical products entering the sea could be hazardous to man became shockingly apparent in 1956 when in Minamata Bay (Japan) people suffered from a neurological syndrome as a result of eating methyl mercury-contaminated tuna and swordfish. Rachel Carson published *Silent Spring* in 1962 (Carson, 1962). In this book she focused attention on the environment itself by discussing the biological effects of pesticides. It is considered the start of the environmental movement.

In March 1967 the *Torrey Canyon*, a 120 000 tons oil tanker, was wrecked on Seven Stones off the Isles of Scilly (UK). Two years later, in 1969, there was a blow-out on Union Oil’s Platform A in the Santa Barbara Channel 9 km off the Californian coast (USA). Similar to the April 2010 disaster with BP’s Deepwater Horizon in the Gulf of Mexico, the environmental effects were huge in all these accidents. In contrast to many pollutants that are dissolved in water or adsorbed to particles, and thus unseen by the naked eye, crude oil and its biological effects are very visible, also to the public. Newspapers reported on these and other pollution events with evident biological effects, like fish kills in the River Rhine and massive bird mortality in Scotland, also in 1969. Public opinion did help to create a climate in which effective legislation was possible and scientific activities in research and monitoring were encouraged. Environmental laws, like the implementation of ‘Statement of environmental effects’, or banning of chlorinated pesticides were imminent. The US Environmental Protection Agency (EPA) was founded within 2 years after the Santa Barbara blow-out (1970).

Scientific research had started to get better information on the input, transport, fate (sinks) of pollutants and of their biological effects (Pearce, 1998). In response to this and to ‘help coordination of research by rapid dissemination of information relating to pollution of the sea’, the first issue of *Marine Pollution Bulletin* was published in January 1970. It intended to be an information bulletin (‘spreading news of pollution’) rather than a scientific journal, and clearly aimed also to inform policy (Anon, 1970).

1.1.1 Definition of Monitoring

In 1977 the International Council of Scientific Union’s (ICSU) Scientific Committee on Problems of the Environment (SCOPE) defined ‘monitoring’ as (Holdgate and White, 1977):

the collection, for a predetermined purpose, of systematic, inter-comparable measurements or observations in a space–time series, of any environmental variables or attributes which provide a synoptic view or a representative sample of the environment (global, regional, national, or local). Such a sample may be used to assess existing and past states, and to predict likely future trends in environmental features.

This definition still seems valid today. Monitoring is thus a systematic method of collecting data needed for environmental problem solving; it is linked to environmental policy. (National) monitoring in this sense started in most areas not before the early 1970s.

Very often, monitoring programmes are understood as linked to the concentration of harmful substances only. However, for a proper assessment, different variables shall not only include measuring of levels of pollutants (in various compartments, including biota), but also include physical attributes (e.g. salinity, turbidity, fluxes) and biological effects (possibly at several biological organization levels). Species distribution and density have been measured for over a century for fundamental biological research; although in the past the objective was never ‘monitoring’ (at most surveys), today these biological variables are the corner stones of describing the biodiversity of a region.

Basic reasoning for monitoring changed over the years. In the mid 1970s it was argued that the first concern was to avoid hazards to human health. It was considered of no importance to monitor, for instance, Hg in coastal waters unless it presented an unacceptable hazard to human health or produced an ecological change. Reduction in the monitoring effort to the barest essentials was thus advocated (Anon, 1975). Today, reasoning stems from a more holistic approach. The concern is reaching – in Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD) terminology (see Chapter 3) – Good Environmental Status (GES) and the focus is on the environment. Evaluation and assessment of biological and chemical status and trends have become key environmental management tools.

In this chapter, the centre of attention will be on the historic development of marine monitoring, with a focus on the situation in the North-East Atlantic Ocean, including the North Sea and Baltic seas. This will relate to the definition and purpose of monitoring, relevant international treaties, the context and developments in international institutions, and general concepts like monitoring of different environmental compartments and the need for quality-assured data.

Because of the limited space available, this contribution had to be restricted to the monitoring of hazardous substances in water, sediment and biota. Other fields, such as biological effect monitoring or monitoring of species richness (biodiversity), are not included. As an example for many other groups of pollutants, long-term trends for selected trace metals will be briefly discussed, also in view of the improvement of analytical methods.

1.1.2 Stockholm Conference 1972

The United Nations Conference on the Human Environment (Stockholm, 5–16 June 1972) is considered a landmark in (marine) monitoring. A Declaration and an Action Plan were adopted. According to the Declaration (Principle 7):

States shall take all possible steps to prevent pollution of the seas by substances that are liable to create hazards to human health, to harm living resources and marine life, to damage amenities or to interfere with other legitimate uses of the sea.

The Action Plan (Recommendation 73) ‘recommended that governments actively support, and contribute to international programmes to acquire knowledge for the assessment of pollutant sources, pathways, exposures and risks’ (UNEP, 1972).

The 1972 Stockholm Conference strengthened the partially existing efforts of environmental (marine) monitoring in national and international programmes. Many international organizations, all (becoming) active in the marine monitoring field, each with their own objectives and plans and possibly afraid of competition, used the outcome to better harmonize and structure future monitoring plans and activities.

1.2 INTERNATIONAL CONVENTIONS

Supra-national policies were required to allow combating pollution of the world's oceans and seas to become successful. Hence, a number of international treaties were drafted, subsequently signed and ratified. Focusing mainly on the European situation, the following lists a number of these conventions, that would become instrumental in environmental protection, and that would install monitoring programmes to monitor status and trends of the marine environment.

1.2.1 London Dumping Convention

In 1972 the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (1972, in force 1975), in short the London Dumping Convention (LDC), now called London Convention (LC 72), was signed. This treaty intended to cover the world's oceans and seas. It followed a 'black list/grey list' approach to regulate ocean dumping: Annex I (black) chemicals were banned (unless in trace amounts), Annex II (grey) listed chemicals for which dumping was restricted. A permanent secretariat is hosted by the International Maritime Organization (IMO).

1.2.2 Oslo and Paris Conventions, OSPAR Convention

The same year the Convention for the Prevention of Marine Pollution by Dumping from Ships and Aircraft, the Oslo Convention (1972, in force 1974), was signed. The area covered consists of the North-East Atlantic and part of the Arctic Ocean, but excluding the Baltic seas. There was a distinction between 'black' and 'grey' list chemicals. The limitations of the Oslo Convention by not including land-based sources were taken away 2 years later, when the Convention for the Prevention of Marine Pollution from Land-based Sources, the Paris Convention (1974, in force 1978), was signed. It covered the same marine area as the Oslo Convention. The Oslo Commission (OSCOM) and the Paris Commission (PARCOM) shared a joint secretariat in London (OSPARCOM) (OSPAR, 1984).

The Convention for the Protection of the Marine Environment of the North-East Atlantic, or OSPAR Convention (1992, in force 1998), is the current legislative instrument regulating international cooperation on environmental protection in the North-East Atlantic. It combines and updates the 1972 Oslo Convention and the 1974 Paris Convention, but decisions and other agreements adopted under those conventions remained applicable unless they are terminated by new measures adopted under the OSPAR Convention. Work carried out under the convention is managed by the OSPAR Commission. The developments of the Oslo and Paris Commissions over the first 25 years (and their relationship with the North Sea Ministerial Conferences) were detailed by Tromp and Wieriks (1994). The OSPAR Convention now regulates (for its geographic region) European standards on marine biodiversity, eutrophication, the release of hazardous and radioactive substances into the seas, the offshore oil and gas industry and baseline monitoring of environmental conditions.

1.2.3 Helsinki Convention

In 1974 the Convention on the Protection of the Baltic Sea Area, the Helsinki Convention (1974, in force 1980), was adopted. It employed the 'black' and 'grey' lists of hazardous substances. The Helsinki Commission (or HELCOM: Baltic Marine Environment Protection Commission), located in Helsinki, is acting as its governing body. Also, in the light of political changes in the late 1980s, a new Helsinki Convention was signed in 1992 (in force 2000). Its first 20 years were reviewed

by Helsinki Commission (1994). The convention now covers the whole of the Baltic Sea area, including inland waters and the water of the sea itself and the sea-bed. Measures are also taken in the whole catchment area of the Baltic Sea to reduce land-based pollution.

All these conventions aimed and aim at the regulation of inputs, to carry out baseline studies (present status), to monitor for trends and to carry out inter-calibrations between contracting parties to warrant quality data.

1.2.4 Bonn Agreement

Focused on discharges of oil and other substances into the North Sea region in 1969 is the Agreement for Co-operation in Dealing with Pollution of the North Sea by Oil, the Bonn Agreement (1969, in force 1969). This treaty was superseded by the Agreement for Cooperation in Dealing with Pollution of the North Sea by Oil and other Harmful Substances (1983, Bonn Agreement, in force 1989). Now parties were required to jointly develop and establish guidelines for joint action and to provide information on pollution incidents. Developments were discussed on the occasion of its 40th anniversary (Bonn Agreement, 2009). One of the implementation instruments of the Bonn Agreement is the ongoing aerial surveillance programme, which started in 1986 to monitor and assess trends in levels of oil inputs into the marine environment (Carpenter, 2007).

1.2.5 MARPOL

Recognizing the threat of pollution of the seas by oil from shipping, in 1954 the UK organized a conference on oil pollution which resulted in the adoption of the International Convention for the Prevention of Pollution of the Sea by Oil, the OILPOL Convention (1954, in force in 1958). It primarily addressed pollution resulting from routine tanker operations. The Intergovernmental Maritime Consultative Organization (IMCO, since 1982 the IMO) organized in 1973 the International Conference on Marine Pollution in London, which led to the International Convention for the Prevention of Pollution from Ships, MARPOL (1973, which did, however, not get into force). In 1978, it was revised by the MARPOL Protocol, and the combination of the convention and protocol led to the MARPOL 73/78 treaty (1978, in force 1983). Its worldwide objective was to preserve the marine environment through the complete elimination of pollution by oil and other harmful substances and the minimization of accidental discharge of such substances. The initial focus on oil was expanded in later years with the inclusion of other substances: noxious liquid substances carried in bulk, harmful substances carried in packaged form, sewage, garbage and air pollution.

1.2.6 Other Conventions

The concept of the Oslo and Paris Conventions was used as a basis for developing a framework for the protection of other (European) sea areas. In 1976, the Convention for the Protection of the Mediterranean Sea against Pollution, the Barcelona Convention (1976; in force 1978) was adopted. In 1992, the Convention on the Protection of the Black Sea against Pollution, the Bucharest Convention (1992, in force 1994) was signed.

1.3 INTERNATIONAL INSTITUTIONS

In the years before the 1972 Stockholm Conference, quite a number of international institutions started to take initiatives related to environmental protection and to 'monitoring of the environment'.

A certain competition was apparent, as several sought to take the lead in international monitoring. The Organization for Economic Co-operation and Development (OECD) already in 1965 developed a plan to coordinate and programme pollution research. From 1966 onwards, the International Council for the Exploration of the Sea (ICES) formalized work on marine pollution (see below). In 1967, the Biologische Anstalt Helgoland (BAH) organized the symposium 'Biological and hydrographical problems of water pollution in the North Sea and adjacent waters'. The UN Food and Agriculture Organization (FAO) convened a 'Technical conference on marine pollution and its effects on living resources and fishing' in 1969. In the same year, a joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), co-sponsored by IMCO, FAO, the United Nations Educational, Scientific and Cultural Organization (UNESCO) and the World Meteorological Organization (WMO) met for the first time. The purpose of GESAMP was to advise the various agencies and subsidiary bodies within the UN that were concerned with marine pollution. Later, the World Health Organization (WHO), the International Atomic Energy Agency (IAEA), the UN and the UN Environmental Programme (UNEP) were added, thus totalling eight organizations (Windom, 1991). Much later, in 2005, GESAMP would produce a strategic vision on the scientific aspects of marine environmental protection (GESAMP, 2005).

The Scientific Committee on Problems of the Environment (SCOPE) was established by the ICSU in 1969. The Commission on Monitoring of SCOPE published a report 'Global environmental monitoring' (SCOPE, 1971) as input for the Stockholm Conference. In this report it was argued that, for the marine area, a strong coordination should be built between a marine pollution monitoring system and the Integrated Global Ocean Station System (IGOSS) then under development by the Intergovernmental Oceanographic Commission (IOC) for monitoring the physical conditions of the oceans. Studies, limited to monitoring of water, top sediments and biota for the levels of a few critical substances, were proposed to be conducted in selected pilot areas, such as the North Sea, Baltic, Mediterranean and Puget Sound (USA). The organisations considered best to handle the development and implementation were considered in the report to be the IOC (policy aspects) and the Scientific Committee on Oceanic Research (SCOR), representing international science. For global monitoring, suitable (national) data should be collected by a monitoring office, and for coordination purposes a central monitoring co-ordinating unit should be set up. The ideas were further worked out in the Action Plan for Phase I of the Global Environmental Monitoring System (GEMS) (Munn, 1973), and priority pollutants were defined (Andersen *et al.*, 1988).

1.3.1 ICES

ICES, founded in 1902, has been an internationally recognized player in the many scientific aspects dealing with the northern Atlantic Ocean (Griffith, 2003). Initially, ICES mainly focused on fish and fisheries, but a task also included the production of 'standard seawater' for calibration of salinity measurements (Culkin and Smed, 1978). Went (1972), reviewing the first 70 years of ICES, hardly touched the subject of monitoring, an indication that the subject was nearly ignored in the period 1902–1972. This changed considerably in the third quarter of ICES' existence, as detailed by Rozwadowski (2002) and Griffith (2003). The great experience and science network of ICES was considered beneficial at the time for setting up monitoring work (ICES, 1974c).

In 1965 the Organization for Economic Cooperation and Development (OECD) mentioned to ICES leaders its intention to coordinate an ambitious plan to programme pollution research. ICES, fearing dominance by an institution with limited practical oceanographic experience, sought a broader scope, which led in the end to a common ICES–IOC–OECD cooperation. The ICES Fisheries Improvement Committee (FIC) was established in 1966 (from which in 1978 the Marine Environmental Quality Committee (MEQC) was formed). Despite its name, their tasks included

marine pollution (biological effects) issues. Soon, there was a need for more specialized working groups (WGs), and in 1968 the ICES WG on Pollution of the North Sea convened for the first time; it was followed in 1971 by the ICES/SCOR joint WG on the Study of the Pollution of the Baltic.

Practical surveys were initiated by ICES in carrying out baseline studies, a kind of precursor to regular monitoring programmes. The first was carried out in the North Sea in 1972 for trace contaminants in fish and shellfish (as potential hazard to human health) (ICES, 1974a). A few years later, in 1974, a similar study was coordinated in the Baltic (ICES, 1977a) and, upon a request from the Oslo Commission, in 1975 extended towards the northern Atlantic Ocean (ICES, 1977b). After the North Sea baseline study, annual North Sea monitoring was initiated in 1974 (ICES Coordinated Monitoring Programme; ICES, 1977c); the Baltic monitoring programme started in 1979.

In 1973 ICES established the Advisory Committee on Marine Pollution (ACMP). Amongst its early activities the ACMP, together with the ICES Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA), developed guidelines on the sampling, sample preparation, analytical procedures and data reporting required to obtain good-quality data. It paid particular attention to the various designs of sampling programmes to meet different monitoring objectives – public health assurance, environmental protection or trend monitoring. ACMP reported annually until 1992, when it was transformed into the Advisory Committee on the Marine Environment (ACME), again producing annual reports until 2003.

In support of the exchange of scientific information, method development and intercalibration exercises, ICES installed WGs, several of which have influenced monitoring studies; for example, the Marine Chemistry WG (1978), the Marine Sediments WG (1980) and the WG on the Biological Effects of Contaminants (1986).

From 1984 onwards, the data from the (OSPAR) Joint Monitoring Programme (JMP; see below) are compiled and quality checked by ICES; HELCOM data have been submitted to the ICES database since 1998.

Thus, ICES has been (and is) instrumental in the development of monitoring programmes, initially in the North Sea, later extending towards the North-East Atlantic and the Baltic. Although ICES coordinated the early baseline surveys, it recognized that (being essentially a science oriented organization) the actual monitoring would be better in the hands of the users of monitoring data: policy. Today, it is the responsibility of the respective national governments (contracting parties to OSPAR and HELCOM) to carry out the monitoring work, including the sampling and analyses. They report their annually collected data to ICES, who, after a quality check, makes them available to OSPAR and HELCOM for reporting purposes.

1.3.2 UNEP

The United Nations General Assembly decided in 1972, as a follow up of the Stockholm Conference, to establish UNEP to serve as a focal point for environmental action and coordination within the United Nations system. The Governing Council of UNEP chose ‘oceans’ as one of the priority areas. At the onset, UNEP’s tasks involved the assessment and control of marine pollution. As resources initially were limited, the initial plans were considered rather ambitious (Birnie, 1974). Recognizing that pollution of the marine environment is generally most severe in coastal areas and semi-enclosed seas, efforts were concentrated on promoting regional marine pollution monitoring, leading to the initiation of its Regional Seas Programme in 1974. Most of these regions are located in the less-developed areas of the world, but partner programmes, like the Baltic (HELCOM) and the North-East Atlantic (OSPAR), are members of the Regional Seas family. In 1975, 16 Mediterranean countries and the European Community adopted the Mediterranean Action Plan (MAP). The MAP was the first-ever plan adopted as a Regional Seas Programme under UNEP; currently,

MAP Phase IV (2006–2013) is operable (www.unepmap.org). The Regional Seas Programme's approach and strategy includes a regional environmental assessment, and involves the development and implementation of regional seas monitoring programmes (Gerges, 1994). In 1984, UNEP published its 'Prospects for global ocean pollution monitoring' report. A first observation was that there was no demonstrated need for open ocean monitoring. In addition, since levels of contaminants were very low, biological effects were considered impossible to identify (UNEP, 1984). Considering the logistical problems related to true open ocean monitoring (e.g. by using WMO ocean weather ships as a monitoring platform) and the associated costs of such a programme, it is not surprising that it never materialized.

1.3.3 IOC

Established in 1960, the IOC of UNESCO promotes international cooperation and coordinates programmes in marine research, services, observation systems, hazard mitigation and capacity development in order to learn more and better manage the nature and resources of the ocean and coastal areas. In response to the recommendations of the Stockholm Conference (1972) the IOC in 1974 developed the Programme of Global Investigation of Pollution in the Marine Environment (GIPME), co-sponsored by UNEP and IMO. Its objectives were: to provide authoritative evaluations of the state of the marine environment at both regional and global levels, to identify the requirements for measures to prevent, or correct, marine pollution and to develop/implement procedures for assessing and improving compliance and surveillance monitoring of conditions and effects in the marine environment. Its operational regionally based Marine Pollution Monitoring System (MARPOLMON, since 1979) was to provide information on contamination in the marine environment which ideally would lead to an assessment of pollution. The developments and implementation of the Comprehensive Plan for GIPME (MARPOLMON) have been detailed by Kullenberg (1986). MARPOLMON constitutes a marine chemical component of GEMS (Andersen *et al.*, 1988), and incorporated the Marine Pollution (Petroleum) Monitoring Pilot Project (MAPMOPP, 1974–1979). Important GIPME priorities were the baseline studies (status) and the standardization of methods and techniques. A great deal of emphasis has been placed on developing, testing and calibrating methodologies to ensure the quality of data for the major classes of contaminants measured in a variety of marine compartments and to attempt to determine fluxes in the marine environment (Dawson *et al.*, 1988).

The day-to-day work within GIPME is conducted by three expert scientific groups: the Group of Experts on Methods, Standards and Intercalibration (GEMSI) deals with the assessment and methodology for measuring levels and flux of contaminants; the Group of Experts on the Effects of Pollutants (GEEP) deals with the biological effects of contaminants, pollution assessment and indicators of biological and ecosystem condition in the marine environment; the Group of Experts on Standards and Reference Materials (GESREM) deals with the assurance of data quality and comparability of measurements (Ibe and Kullenberg, 1995).

1.3.4 European Union

In 1972 the European Economic Community (EEC) formulated its first formal environment policy, with the associated Programme of Action of the European Communities on the Environment being adopted the following year. The current Sixth Community Environment Action Programme, 'Environment 2010: Our Future, our Choice', provides a strategic framework for the EEC's environmental policy for 2002–2012 and is the central environmental component of the EEC's sustainable development strategy.

The European Union (EU) is not involved in operational monitoring activities, neither in the planning nor in the execution. It is the task of the member states to implement the legal frameworks, such as directives, in their national laws and to take care of their implementation. Already from the 1970s there were legal instruments to limit pollution (such as the Council Directive on Pollution Caused by Certain Dangerous Substances Discharged into the Aquatic Environment of the Community, Directive 76/464-EEC). The EU WFD is a combination of (and replaces) a number of such older directives. It was adopted in 2000 (European Commission, 2000). Although its main purpose is to establish a framework for the protection of inland surface waters and ground waters, the WFD explicitly also covers surface 'transitional waters' (like estuaries) and coastal waters, generally extending to one nautical mile from the coastline. Monitoring of these waters has been addressed by Ferreira *et al.* (2007). Member states shall ensure the establishment of programmes for the monitoring of water status in order to establish a coherent and comprehensive overview of water status, including its ecological and chemical status. Amending Annex X of this directive, the Decision 2455/2001/EC established a list of 33 priority substances in the field of water policy. This list was further elaborated in the 'Directive on Priority Substances' (Environmental Quality Standards, EQS Directive 2008/105/EC; European Communities, 2008a) which sets in its Annex I the limits on concentrations of these 33 priority substances and an additional nine substances in surface waters. Its Annex III lists substances subject to review for possible identification as priority substances or priority hazardous substances. Interestingly, this directive allows member states to apply EQS for sediment and/or biota instead of water.

The EU Directive 2008/56/EC, the MSFD, was signed in 2008 (European Communities, 2008b). Under this directive each member state should develop a marine strategy for its marine waters. Marine strategies should culminate in the execution of programmes of measures designed to achieve or maintain GES by the year 2020 at the latest. For coastal waters there is some overlap with the WFD. Under the MSFD, provision should be made for the preparation of an appropriate framework, including marine research and monitoring operations. Member states should undertake an analysis of the features or characteristics of, and pressures and impacts on, their marine waters. On the basis of such analyses, member states should determine for their marine waters a set of characteristics for GES. Achieving GES should be underpinned by the establishment of environmental targets and monitoring programmes for ongoing assessment. The MSFD recognizes a regional approach and defines regions that are covered by existing organisms: the Baltic Sea (HELCOM), the North-East Atlantic Ocean (OSPAR), the Mediterranean Sea (Barcelona Convention) and the Black Sea (Bucharest Convention). The interplay between OSPAR, North Sea conferences and MSFD policies was discussed by Skjærseth (2006) and Borja (2006).

1.4 MONITORING IMPLEMENTATION

In the 1960s, and even earlier, surveys were conducted to investigate the distribution of nutrients, trace metals and selected organic pollutants. Regular monitoring started in the early 1970s, primarily as a national activity. National governments installed national water acts in support of pollution prevention and national monitoring programmes, usually in the form of surveys or surveillance programmes. For example, in the Netherlands, surveys of the water quality of the Wadden Sea started in 1971 and of the North Sea in 1975. The earliest surveys of the Western Scheldt estuary had already begun in 1964 (Beukema *et al.*, 1986). National monitoring strategies were developed and grids of monitoring stations and sampling frequencies were defined. The strategies were usually ambitious, and over the years the number of locations and the frequencies were reduced, mainly because governments realized the high costs involved, but (in the 1990s) also because of the tendency to apply modelling 'we have measured enough' was an issue already raised in the mid 1970s (Anon, 1975). Such changes in (the number of) monitoring locations and frequencies continue to pose problems for the statistical (trend) assessment of the data (Nicholson and Fryer, 1992).

It became evident that the results of national monitoring programmes for areas subject to different national policies – as is the case for the North Sea – were very difficult to interpret without sharing information and without harmonization of strategies, methods and data reporting. Thus, initiatives were taken to combine efforts; for example, in the Oslo, Paris and Helsinki conventions areas.

1.4.1 OSPAR

The Oslo and Paris Commissions recognized their duty to examine the condition of the sea covered by the conventions. Hence, the Commissions established a permanent Joint Monitoring Group (JMG). After asking ICES for advice and guidance for monitoring aim status and trends, the two Commissions set up a JMP in 1978 (OSPAR, 1984). OSPARCOM adopted many of the principles of the ICES programme in defining the JMP. The monitoring programme of JMG had four main objectives (Portman, 1986); i.e. the assessment of:

1. possible hazards to human health;
2. harm to living resources and marine life;
3. the existing levels of marine pollution (spatial distribution); and
4. the effectiveness of measures taken for the reduction of marine pollution within the framework of the conventions (temporal trend assessment).

The JMP was to be based on the national programmes of the contracting parties, with their national laboratories responsible for the sampling and analyses. To ensure comparability of data, calibration of methods should be supported by participation in (e.g. ICES) interlaboratory comparison studies. The actual monitoring programme started in 1979, and was initially limited to mercury and cadmium in seawater and in organisms, and polychlorinated biphenyls (PCBs) in organisms. In the early 1980s a strategy was developed to set sampling frequencies according to monitoring objectives. For purpose (1), in organisms the frequency was set at every second year (implemented in 1984) and for sediments every 5th year (≥ 1985). Purpose (3) had frequencies for organisms and seawater (per 5 years, ≥ 1985), while for objective (4) the frequencies were defined annually for organisms and seawater (≥ 1983) and sediments (≥ 1986) (Portman, 1986). Since 1984 the JMP data are compiled by ICES in their database (and checked for validity).

In 2003 the Ministerial Meeting of the OSPAR Commission adopted a strategy for the Joint Assessment and Monitoring Programme (JAMP), a combination of the national monitoring programmes of the contracting parties. This provided a framework for work to prepare and produce a series of thematic assessments (quality status reports, QSRs). Thus, OSPAR is coordinating repeated measurement and assessment of the marine environment over a decadal time frame. The organizational structure of OSPAR changed in 1995. Monitoring and assessment became a task of the Assessment and Monitoring Committee of OSPAR (ASMO). Monitoring has since been split into several domains in several WGs under ASMO, such as the Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME), WG INPUT, dealing with atmospheric inputs (via the Comprehensive Atmospheric Monitoring Programme (CAMP) and riverine inputs and discharges (via the Comprehensive Study of Riverine Inputs and Direct Discharges (RID)), and WG MON, e.g. via CEMP, the Co-ordinated Environmental Monitoring Programme (de Jong, 2006).

1.4.2 North Sea Conferences

The baseline studies, other surveys and surveillance programmes and serious concern at the political level led to a series of North Sea conferences starting with the First North Sea Conference in 1984 (Bremen). Assessments were made, not only on the status and trends of pollutants, but also on the use of the seas as a resource for human activities. In later years several international North Sea conferences were organized in London (1987), The Hague (1990), Esbjerg (1995) and Bergen (2002) (Skjærseth, 2006).

In support of these North Sea conferences and OSPAR ministerial meetings, QSRs were prepared. Implementing the ecosystem approach, these reports provide an integrated assessment of the cumulative and relative impact of all human pressures on the marine environment, identifying where action needs to be taken. Marine pollution is one of the pressures for which monitoring provides the factual information. QSRs are compiled contributions by experts, usually from the respective governmental institutions of the different states bordering the region concerned (initially the North Sea, later the North-East Atlantic). The 1st QSR served the Bremen (1984) conference (Carlson, 1986).

One of the outcomes of the Second North Sea Conference in 1987 and QSR 1987 was the recognition that, despite the large number of contaminants measured, the spatial coverage of the North Sea was rather limited. As a result, the North Sea Task Force (NSTF) was set up in 1987, co-sponsored by OSPARCOM and ICES. The objectives of NSTF included to advise on research, to plan, develop and implement a quality-assured monitoring programme and to develop the next QSR for the North Sea (Hoogweg *et al.*, 1991). The aims of the NSTF Monitoring Master Plan were to enhance scientific knowledge and understanding of the North Sea environment, and to overcome shortcomings in data on the distribution of contaminants (Reid, 1990). An assessment of the North Sea area, the QSR 1993 was subsequently published as input to the Third North Sea Conference (NSTF, 1993). NSTF existed from 1988 to 1994 and its approach was then incorporated into ASMO.

The QSR 2000 (OSPAR Commission, 2000) was based on the combined efforts of JMP and JAMP. The geographic coverage was expanded to a larger area, the North-East Atlantic (the OSPAR convention area) which was subdivided into five regions (Arctic waters, Greater North Sea, Celtic Seas; Bay of Biscay and Iberian Coast, and the Wider Atlantic). For each region a separate report was prepared, as well as a holistic synthesis report for the entire area. QSR 2010, the most recent report, was published on the occasion of the Ministerial Meeting of the OSPAR Commission in Bergen (2010). Again, a regional approach was followed in a printed and electronically available version (<http://qsr2010.ospar.org>), albeit in one volume (OSPAR, 2010).

1.4.3 HELCOM

For the period 1974–1980, when the Helsinki Convention entered into force, a WG referred to as the Interim Commission (IC) was installed. It established a Scientific Technological Working Group (STWG), which had as one of its tasks ‘monitoring and assessment of the state of the marine environment’ (BSEP56; HELCOM, 1994). Since 1979, the Baltic Sea Environment Proceedings (BSEP) report series has been published (list and pdf files at www.helcom.fi/publications/bsep/en_GB/bseplist/).

Under the Helsinki Convention, monitoring of physical, chemical and biological variables of the open sea started in 1979 (of radioactive substances in 1984), but was considered a national obligation. It was called the Baltic Monitoring Programme (BMP) and was revised several times. The first pilot period covered 1979–1983; the second phase (1984–1988) had a larger coverage.

The third stage started in 1989. For political reasons, the coastal areas of the sea were only poorly covered by the BMP, and the programme focused on the open sea. The aim of the BMP was to monitor the long-term changes of selected indicators in the Baltic ecosystem. In support of these programmes, several guidelines were published, such as for the BMP second stage (BSEP12, 1984) and in 1988 for the BMP third stage on, for example, physical and chemical determinands in sea water (BSEP27B) and harmful substances in biota and sediments (BSEP27C).

Under the revised 1992 Helsinki Convention, the Cooperative Monitoring in the Baltic Marine Environment (COMBINE) was instituted in 1992. The HELCOM monitoring system consists of several complementary programmes: PLC-Air and PLC-Water to quantify inputs to the sea via water and air; COMBINE, to quantify the state, impacts and changes in the various compartments (water, biota, sediment); and MORS, to quantify the sources, inputs and state of artificial radionuclides in these compartments.

A first ministerial meeting was organized in 1984, at the occasion of the 10th anniversary of HELCOM; a second meeting was held in 1988. At the 1990 Prime Ministers Meeting (Ronneby) it was suggested to install a HELCOM Programme Implementation Task Force (PITF), active since 1992. A first task for PITF was the preparation of the Baltic Sea Joint Comprehensive Environmental Action Programme (JCP), projected to last for 20 years (1993–2012) (BSEP48).

In 1981 an ad hoc Group of Experts on the Assessment of the Marine Environment of the Baltic Sea (GEA, later to become GESPA) was installed. Their task was to compile the first periodic assessment report. A series of such 'Periodic Assessment of the State of the Marine Environment of the Baltic Sea Area' reports was published. The first, covering 1980–1985 (BSEP17A-B), was issued in 1986. A second periodic assessment covered 1984–1988 (BSEP35A-B, 1990), followed by a third assessment for 1989–1993 (BSEP64A-B, 1996) and the fourth for 1994–1998 (BSEP82AB, 2002). The 'ecosystem approach' adopted by the Joint HELCOM/OSPAR Ministerial Meeting in 2003 led to a different type of assessment. The objective now was to assess the pressures of human activities and the resulting impacts on, and state of, the marine environment. For the Stakeholder Conference held in Helsinki in 2006, thematic assessments were published on six issues. Next to thematic assessments for eutrophication, maritime transport, climate change, ecological objectives, and biodiversity and nature protection, the hazardous substances report gives evidence on status, trends and strategies for monitoring of the Baltic (www.helcom.fi). The HELCOM Baltic Sea Action Plan (BSAP) was adopted in November 2007 (Krakow, Poland) by the HELCOM Extraordinary Ministerial Meeting.

1.5 MONITORING OF WHAT?

1.5.1 Selection of Compartments

When monitoring started, fish and shellfish (biological tissue) were the matrix of interest. This clearly stemmed from the focus on potential hazards to human health from the consumption of this seafood. The initial North Sea, Baltic and North Atlantic baseline studies, in the early 1970s, exclusively used these compartments for their assessment. The concept of 'Mussel Watch' was presented by Goldberg (1975) as a method to assess the health of the ocean. Bivalves are sedentary organisms; they concentrate many pollutants in their tissue to a level where they are in equilibrium with the surrounding water. He argued that by utilizing *Mytilus edulis* and similar species from coastal and open ocean sites they could be annually analysed for their concentrations of halogenated carbons, transuranics, heavy metals and petroleum. Since then the Mussel Watch approach has been implemented in the USA under the NOAA National Status and Trends programme and in many other countries around the world (O' Connor *et al.*, 1994). Concentrations of trace metals and other pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and PCBs, are routinely monitored in the OSPAR and HELCOM areas.

In the compartment water, notably trace metals (since the late 1970s) and nutrients (from 1990 onwards) were routinely monitored under the ICES and HELCOM programmes. The (third-stage) BMP in 1988 routinely monitored heavy metals, petroleum hydrocarbons and chlorinated hydrocarbons in seawater.

The OSPARCOM JMP started routine sediment monitoring in 1982. Although many organic pollutants have as a measure of hydrophobicity an octanol–water partition coefficient higher than 10^5 ($\log K_{ow} > 5$, e.g. hexachlorobenzene, HCB), indicating that they are predominantly present in sediment and suspended particulate matter, those with a $\log K_{ow} < 3$ (e.g. atrazine) are preferably analysed in water. This has been recognized by, for example, the WFD amendment EQS Directive, which states that hydrophobic compounds may be monitored in water and/or biota (instead of water).

1.5.2 Selection of Compounds

At the beginning of environmental protection the now common ecosystem approach was yet to be developed. At the first GESAMP meeting in 1969, a ‘list of substances carried as cargo’ might be selected, as if disasters at sea were the only input route for pollution of the marine environment. Chemicals were rated on the basis of human toxicity, aquatic toxicity and aesthetic effect (GESAMP, 1969). This was refined at a later stage when GESAMP reviewed the harmful substances which may have deleterious effects on human health and on economic and cultural activities in the marine environment and coastal areas, and with regard to (harm to) living resources in the sea as a major source of protein-rich food (GESAMP, 1976). Important pollutants, for which restrictive or preventive measures were recommended, were domestic sewage, pulp and paper mill wastes, organochlorine pesticides, PCBs, mercury and its compounds, organo-lead compounds, elemental phosphorus, silver and several organic chemicals, often solvents.

ICES, with its background in fisheries research, in its initial monitoring days limited their monitoring activities to toxicants in fish and shellfish (at first primarily being foodstuff for humans, but later also related to the health of the marine environment; i.e. higher trophic levels). Initially, the compounds selected were the heavy metals Cd and Hg and selected organochlorine pesticides and PCBs accumulated in a few indicator species, such as mussels, herring, cod and plaice. For the North Atlantic baseline study, as well as the research programme for investigations of the Baltic Sea, the number of substances had increased, although subject to analytical capabilities: ‘whenever it seems feasible with the present sensitivity of methods’ (ICES, 1974b). Nearly the same lists of compounds were used: organohalogen compounds (HCB, PCBs, pesticides such as the DDTs, dieldrin, chlordane and hexachlorocyclohexane (HCH) isomers), the metals Hg, Pb, Cu, Cd, Cr (replaced by As for the Baltic) and Zn, petroleum hydrocarbons and nutrients (nitrogen compounds and total phosphorus), a list that formed the basis for HELCOM’s pilot-phase BMP. The second-phase BMP listed, next to basic oceanographic variables, nutrients, heavy metals and petroleum and chlorinated hydrocarbons in seawater, and heavy metals and chlorinated hydrocarbons in fish and shellfish (HELCOM, 1983). At about the same time, ICES’ ACMP reviewed the occurrence and effects of (new) contaminants, like Hg, Pb, Cd, Zn, PCBs, toxaphene, hexachloro-1,3-butadiene, polychlorinated terphenyls (PCTs), alkyl-tin, furans and dioxins in the marine environment (McIntyre, 1985).

Gradually, as more chemicals were identified as being harmful to the (marine) environment, more and more chemical compounds became part of routine monitoring programmes. Examples include many more pesticides, organo-tin compounds (like tributyltin (TBT), affecting oysters and marine gastropods) and brominated compounds (flame retardants).

The EU Directive on Priority Substances (Environmental Quality Standards Directive) supports the WFD and applies to the member states’ coastal waters. It defines the limits on concentrations of

33 priority substances and nine other pollutants in EC surface waters, including the coastal waters (European Communities, 2008a). The list includes trace metals (Cd, Hg, Ni, Pb, TBT), different pesticide groups, seven PAHs, (chlorinated) solvents and other compounds such as nonylphenol and brominated diphenylether.

Focusing solely on the marine environment, OSPAR priority groups of chemicals currently include trace metals (Cd, Pb, Hg), organometals (of Pb, Hg and Sn), organohalogens (including short-chained chlorinated paraffins (SCCPs), perfluorooctane sulfonates (PFOSs), polychlorinated dibenzodioxins and dibenzofurans (PCDDs, PCDFs), PCBs, brominated flame retardants and other polybromodiphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A)). Furthermore, seven pesticides are included, such as endosulfan, HCH isomers (including lindane), pentachlorophenol (PCP) and trifluralin. Other groups include phenols, phthalates (such as DBP and DEHP), PAHs, pharmaceuticals and personal care and other substances (OSPAR, 2010).

Usually in support of biological research, nutrients have been analysed since the beginning of the 20th century (Brandt, 1927), albeit initially not always of high analytical quality. Nutrients, mainly the nitrogen compounds nitrate, nitrite and ammonia, and phosphorus, are not considered as hazardous substances, but their enrichment may lead to adverse effects upon the marine environment. Monitoring of nutrients in the OSPAR area started rather late. As a result of decisions to reduce nutrient inputs to the OSPAR area by 50%, OSPARCOM's JMP, NSTF and NUT (Nutrient Working Group, under the Oslo/Paris Commissions) agreed to start a mandatory monitoring programme in 1990. Results would provide input to the QSR (de Jong, 2006).

1.5.3 Background Concentrations

Heavy metals are natural and, subject to the hydro-geological situation, are present in lower or higher concentration; thus, this background concentration may vary from place to place. Pollution may add to this background concentration, creating harmful concentrations in the environment. Background concentration is subject to many debates; for example, for the correct implementation of environmental quality standards. For man-made compounds, like PCBs and TBT, the background concentration is zero. For a few groups of compounds, such as PAHs, some occur naturally; others are anthropogenic.

Owing to the regional differences, global averages will not work, and attempts have been made to define regional (North Sea) background concentrations for metals in water sediment and biota (Kersten *et al.*, 1994). OSPAR, in 2005, agreed on background concentrations for contaminants in seawater, sediments and biota (OSPAR, 2005). In view of the new demands by the WFD, Tueros *et al.* (2008) discussed ways to define background concentrations for trace metals in coastal seawater.

1.6 QUALITY OF DATA

During the early 1970s there was increased concern about the quality of the analytical results from monitoring programmes. Within the laboratories one was confident about one's own data, but data sets from different laboratories often did not match. Interlaboratory comparisons were organized to investigate this. They showed that, for example, the results for the analysis of seawater for trace metals differed by two or even three orders of magnitude. Quality data will lead to quality information. Hence, Goldberg and Taylor (1985) argued that only validated data should be included in databases. In order to avoid expensive environmental management actions, monitoring data should not be published without demonstrable evidence of quality practices in all aspects of the monitoring exercise (Batley, 1999).

Several instruments were developed to improve the quality of monitoring data. They include the building up of the laboratory's quality assurance (QA) measures and a continuous analytical quality control (QC) programme. This included the development and implementation of guidelines on sampling, analysis and QA/QC, the implementation of quality control by the use of certified reference materials (CRMs) and QC materials (QCMs) in the analytical process, and the participation in laboratory performance studies (proficiency tests, PTs). Within-laboratory QC and between-laboratory QC shall be demonstrated throughout the monitoring programme (Nicholson, 1989).

Recently, European policies recognized the need for quality data from monitoring programmes. The European Commission Directive 2009/90/EC (European Community, 2009) underpins the WFD in laying down technical specifications for chemical analysis and monitoring of water. It establishes minimum performance criteria for methods of analysis to be applied by member states when monitoring water status, sediment and biota, as well as rules for demonstrating the quality of analytical results for other directives dealing with monitoring. It explicitly addresses QA and QC, and makes it mandatory that laboratories demonstrate their competences by participation in proficiency testing programmes and analysis of representative reference materials.

1.6.1 Interlaboratory Comparisons

The initial interlaboratory comparison studies aimed at demonstrating that sufficient agreement was present to enable intercomparison of monitoring results by different laboratories from different countries. The studies showed that, for nearly all analytes and matrices, insufficient agreement was present and considerable work was to be done to arrive at these objectives. Interlaboratory comparisons thus started to become a training tool for improvement of laboratory skills.

Following the development of the compounds and matrices that were monitored in the period 1970–1990s, the first ICES intercomparison was for trace metals (Hg only) and chlorinated hydrocarbons in biological tissue in 1972. Many would follow. For biological tissues, 9 exercises would be conducted for trace metals (1972–1989), 3 for hydrocarbons (1984–1990) and no less than 15 for organochlorine compounds (1972–1993). The second matrix tested was seawater, which spanned two decades for 11 interlaboratory comparisons on trace metal analysis (1976–1996), and 5 studies for nutrients (1989, 1993) (ICES, 1992). Sediment intercomparison studies started in 1980. There was one for hydrocarbons (1980) and two for chlorinated hydrocarbons (1980, 1993). For heavy metals in sediments there were nine studies (1983–1993).

In particular, the exchange of information at meetings where the outcomes of the tests were discussed proved beneficial, as experts could support each other on how to further improve their methods. Usually, the lower the concentration, the higher the variance in the analytical results, as postulated by Horwitz (1982): the 'Horwitz trumpet'. Still today, the variance (coefficient of variation, CV) between laboratories for groups of analytes follows $CV(\text{nutrients}) < CV(\text{trace elements}) < CV(\text{chlorinated hydrocarbons})$.

Several times (as, for example, in the case of chlorinated organic compounds in biological tissue) it initially proved too difficult to start with the matrix: analytical results varied too much. A holistic approach was followed by starting on a less complex analysis level, using calibration solutions and/or extracts that were centrally prepared. Only when harmonization could be shown for these samples were natural matrices reconsidered in the interlaboratory tests.

Although the ICES/SCOR Baltic WG joined the ICES intercomparison studies, HELCOM also organized interlaboratory comparisons, such as the biological intercalibration workshops which included a component on nutrients (first in 1979; second in 1982 (BSEP09) and third in 1990 (BSEP38)), and in 1981 on the analysis of hydrocarbons in seawater (BSEP06). In 1992, HELCOM reported on an interlaboratory comparison for airborne pollutants (BSEP41). Other organizations

coordinating interlaboratory comparisons were the IAEA, initially often for the analysis of radionuclides, but later including many other organic and inorganic compounds. The WHO/FAO/UNEP Joint Project MED POL, a concerted effort to monitor contaminants and to assess pollution in the Mediterranean Sea (since 1975, part of the Barcelona Convention) has been the cornerstone of the MAP and has been instrumental in developing the capabilities of the (Mediterranean) countries to measure and assess marine pollution (Carvalho and Civili, 2001). The IAEA Marine Environment Laboratory in Monaco acted as the analytical and training centre for MED POL.

In order to define the baseline concentrations for selected trace metals in open Atlantic seawater, IOC–GIPME conducted an intercalibration in 1990. One of the prerequisites was the mandatory use of CRMs (Landing *et al.*, 1995).

The role of (ICES) interlaboratory comparisons has been gradually taken over by the participation in PTs, such as the QUASIMEME programme (see below), which was a combined ICES/QUASIMEME exercise.

Since the implementation of QA/QC procedures in analytical laboratory activities, comparability of data has improved considerably. Although intercomparisons were not only devoted to the analysis itself, but also included, for example, trace metals sampling (Bewers and Windom, 1982) and filtration procedures (Bewers *et al.*, 1985), Kramer (1994) argued that most QA/QC procedures were limited to the activities within the laboratory, and that they should be extended to the activities before samples reached the laboratory, such as sampling, sample treatment and storage. This can be achieved by using written standard operating procedures, agreement on a specifically developed sampling plan and safeguarding full documentation at every stage of the operation, including unexpected events (Wagner, 1995). Davies and Wells (1997) concluded that QA and the interpretation of international marine monitoring programmes had improved considerably, in part as a result of the series of interlaboratory comparison studies and laboratory performance studies. There still was (and is) an urgent need for (certified) reference materials (CRMs, QCMs) as instruments for further improvement of the analytical quality.

1.6.2 Guidelines

Initially, national guidelines and standard operating procedures were implemented. When the JMP resulted in poor overlap in the respective results, there was a need for international guidance for sampling and analyses. Without trying to be complete, a few organizations that produced guidelines are discussed below.

Since its foundation, ICES has had a tradition in method development by its Central Laboratory. Already in the early 1970s, guidelines for sampling and analysis of physical, chemical and biological parameters had become available (e.g. ICES, 1972). In support of sampling and analysis for biological and chemical monitoring programmes, ICES started the series of publications ‘Techniques in Marine Environmental Sciences’ (TIMES) in 1987. Each issue treated a particular aspect related to a specific analytical procedure; for example, on sampling and storage methods for trace metals in seawater (TIMES 2; Yeats, 1987), good laboratory practice and QA (TIMES 6; Vijverberg and Cofino, 1987) or the review of methods for analysis of hydrocarbons in seawater, biota and sediments (TIMES 12; Ehrhardt *et al.*, 1991).

When OSPAR started to coordinate monitoring under JAMP it also started to produce monitoring guidelines. Monitoring guidance is regularly reviewed in collaboration with ICES. Where necessary, they are updated to take into account new developments, including the inclusion of new monitoring parameters in the CEMP. Examples of JAMP guidelines are the ‘JAMP Guidelines for Monitoring Contaminants in Biota (agreement 1999-2)’ or ‘JAMP Guidelines for Monitoring Contaminants in Sediments (agreement 2002-16)’ (latest updated versions are electronically available at www.OSPAR.org).

Similarly, HELCOM has published guidelines in support of its monitoring programme; for example, from the Baltic Sea Environment Proceedings series (BSEP27A-D): Harmful Substances in Biota and Sediments (HELCOM, 1988). Following new developments since the initiation of the COMBINE programme, the 'Manual for Marine Monitoring in the COMBINE Programme of HELCOM' is maintained up to date on the HELCOM website (www.helcom.fi), which includes, for example, the 'General guidelines on quality assurance for monitoring in the Baltic Sea'.

All three GIPME Expert Scientific Groups, already indicated above (GEMSI, GEEP and GESREM), supported the UNEP Regional Seas Programme by the publication of guidelines, in development and testing of reference methods, in preparation of reference materials, in QC of monitoring data, in the organization of intercalibration exercises and in QA/QC training (Ibe and Kullenberg, 1995).

1.6.3 (Certified) Reference Materials

'Standard seawater', used to calibrate chlorinity/salinity measurements, has been produced since the beginning of the twentieth century as a primary standard and is probably the first environmental reference material (Culkin and Smed, 1978). In support of pollution monitoring programmes, new materials were urgently needed. The National Research Council Canada (NRCC) was the first institution that recognized the need for a series of environmental CRMs to answer to the increasing needs of monitoring programmes. In support of trace metal analyses, they started their production with MESS-1 and BCSS (marine sediments, in 1981), NASS-1 (seawater, in 1982) and TORT-1 (lobster hepatopancreas, in 1984). For PCBs, poor agreement between laboratories for organochlorine compounds in matrix reference materials in those days forced laboratories to develop their methods; hence, standard iso-octane solutions were produced (CLB-1-A and -D, 1985) (Waldichuck *et al.*, 1987).

In Europe, the EC Community Bureau of Reference (BCR) was installed in 1973 (van der Eijk, 1977). It existed until 2003, when its activities were transferred to the JRC-IRMM (Quevauxviller, 2003) and BCR remained only a brand name. Also, the BCR recognized the monitoring needs and started CRM production; for example, for trace metals BCR-279 (sea lettuce, in 1987), BCR-277 (estuarine sediment), BCR-278 (mussel tissue), both in 1988, and BCR-403 (seawater, in 1991). In 1988, PCBs in cod liver oil (BCR-349) served to further improve analytical performance of the analytical laboratories. Only in 2001, when analyses were generally under control, did PCBs in a matrix CRM (mussel tissue, BCR-682) come on the market. Producers followed the trends in policy and monitoring practice, where more (and more complex) hazardous substances had to be analysed. As a result, CRMs for the analysis of methylmercury in tuna (BCR-463, in 1994) and of the antifouling agent TBT and other organotin compounds in mussel tissue (BCR-477) and in coastal sediment (BCR-462) were introduced in 1997 and 1998 respectively; CRMs for the analysis of brominated flame retardants (PBDEs) were introduced only recently.

Other early CRM producers were the Japanese National Institute for Environmental Studies (NIES), such as mussel tissue (NIES No. 6, 1984) and Sargasso seaweed (NIES No. 9, 1988), both for trace element analyses. Early IAEA marine reference materials produced by their Marine Environment Laboratory (Monaco) include IAEA-SD-N-2 (marine sediment, 1986) and IAEA-MA-B-3/RN (fish flesh, 1987), each for the analysis of radionuclides.

The US National Institute of Standards and Technology (NIST) started the production of environmental matrix CRMs in the 1990s. In recent years they set a new trend by producing matrix materials certified for a wide range of analytes, thus serving the needs of laboratories that have to respond to the monitoring requirements, such as the US Environmental Protection Agency (EPA) and the EC WFD. Examples are the SRM-1944, a marine sediment certified for PAHs, PCBs, chlorinated pesticides and trace elements, or SRM-2974, a freeze-dried mussel tissue, certified for about the same set plus selected PBDE congeners. With these wide-range CRMs laboratories

may reduce costs, and the more frequent use of the CRMs for different analyses (thus earlier replacement) is considered beneficial.

Nutrient concentrations in natural seawater are not stable owing to the activity of microorganisms. This inherent stability problem was solved; and soon after monitoring of nutrients under the JMP became mandatory, a reference material for nutrients was developed (Aminot and Kéruec, 1991).

Several overviews of available marine CRMs were produced in the past (e.g. Cantillo, 1992; Kramer, 1998). Today, web-based databases are readily accessible, such as the Virtual Institute for Reference Materials (www.VIRM.net). Unfortunately, not all analytes in all matrices requested by monitoring programmes are fully covered. Notably, reference materials for organics in water are still lacking due to problems in production (stability of the analytes) (Wells, 1993).

1.6.4 Laboratory Performance Studies

Laboratory performance studies, also known as PTs, aim to verify the proficiency of a laboratory, namely its capability to analyse a given analyte in a given matrix with a sufficiently high accuracy and precision. This is usually done by coordinated sending out of samples with unknown composition to a large group of laboratories. Their analytical results are inter-compared and compared with a reference value and (accepted) deviation unit, and a measure of their proficiency (usually as a *z*-score) is confidentially reported back to the laboratory (Thompson *et al.*, 2006). A framework for PTs is guided by, for example, ISO/IEC 17043 standard (ISO/IEC, 2010), which replaces ISO/IEC Guide 43-1:1997.

In the early 1990s European laboratories were participating in marine pollution monitoring programmes, organized by the OSPARCOM JMG and the Intergovernmental NSTF. In order, for example, to prepare the QSR 1993 (NSTF, 1993) it was essential that data, collected by different countries, would match in one overview of the region concerned, the North Sea. Both NSTF and JMG, but also other international programmes conducting similar monitoring programmes in other regional seas, had expressed concern about data quality (Kullenberg, 1986; Topping, 1992). In view of developing a collaborative approach to serve these monitoring programmes in the (further) development of their QA and internal and external QC, the European Community funded the project Quality Assurance in Marine Monitoring in Europe (QUASIMEME), which started in 1992 (Wells *et al.*, 1993).

QUASIMEME was instrumental in the development of laboratory performance studies in support of monitoring of the (initially European) marine environment. A wide range of PTs was carried out, including nutrients in seawater, trace metals, PCBs and organochlorine pesticides in sediment and biological tissue, and PAHs in sediment (extract), thus covering nearly all analytes and matrices of monitoring interest (Wells *et al.*, 1997; Topping, 1998). Since the project has ended, the PT programme has continued as an independent sustainable activity. Today, other, sometimes commercial, parties also develop and implement PTs for specific analyte–matrix combinations in support of monitoring laboratories.

Other international organizations active in laboratory performance studies include the IAEA, for organic contaminants (PCBs, sterols) and trace metals, often including methylmercury (de Mora *et al.*, 2006).

Today, monitoring laboratories need to be accredited. They demonstrate their competence by internal and external QA and QC measures, complying with the ISO 17025 standard (ISO, 2005). All institutes/laboratories submitting data to OSPAR or HELCOM databases should participate in regular intercomparison exercises and proficiency testing schemes arranged, for example, under QUASIMEME, ICES, HELCOM and IAEA. They shall use CRMs and QCMs and new such reference materials as they become available; these should be used by all participating institutes or laboratories.

1.7 EXAMPLE: MONITORING OF TRACE METALS IN SEAWATER

Trace metals concentrations in seawater have been reported since the beginning of the twentieth century (As, Au, Cu, Fe, Hg) or even before (Ag, Zn), as reviewed by Johnston (1965). For elements at the nanogram/litre level, like cadmium and lead, earliest reported concentrations arrive in the late 1950s. Considering the low concentrations in seawater, sophisticated analytical methods were not available in the early periods. As a result of lack of attention to contamination control and QA/QC, concentrations tended to show a large variation. As a result of analytical improvements, this spread became smaller with time and concentrations dropped. Temporal trends of reported

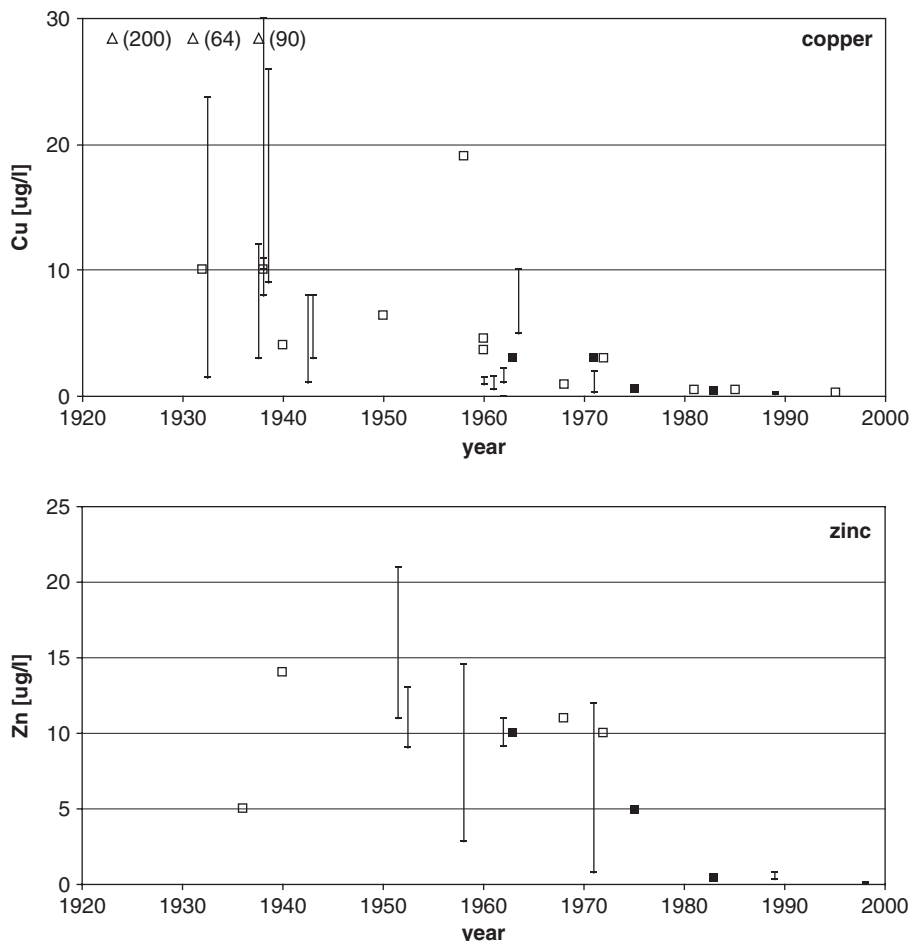


Figure 1.1 Concentration of dissolved copper (Cu) and zinc (Zn) reported for open sea waters since the 1930s. Closed symbols refer to the ‘accepted reference values’ (Goldberg, 1965; Riley and Chester, 1971; Brewer, 1975; Bruland, 1983). Data prior to 1963 are from Johnston (1965); later data are from Fabricand *et al.* (1962), Alexander and Corcoran (1967), Turekian (1968), Dutton *et al.* (1973), Ivanoff (1972), Brüggmann (1981), Bruland and Franks (1983), Kremling (1983), Balls (1985), Mart and Nürnberg (1986), Nolting and de Baar (1994) and Nolting *et al.* (2000).

concentrations (and concentration ranges) for open sea waters, e.g. copper and zinc, both since the 1930s, give (very) high observations with a large spread in results within data series until the mid 1970s; see Figure 1.1. Only after proper attention was given to the combat of contamination, also during sampling, and the implementation of QC procedures (see Section 1.6) did the results come to a closer agreement and the spread in results becomes much smaller. The 'accepted' average concentrations for seawater (Goldberg, 1965; Riley and Chester, 1971; Brewer, 1975; Bruland, 1983), identified by filled symbols in Figure 1.1, clearly demonstrate the advancement of analytical chemistry in monitoring programmes (such large decreases in concentrations for open sea waters are not expected to have resulted from a decrease in pollution). The 'typical' concentration values defined around 1980–1985 for the various trace elements in open sea water have hardly changed since.

Another illustration of the temporal trend for the dissolved fraction of selected trace metals is given in Figure 1.2. The data shown are results of the Dutch national monitoring programme (MWTL) for one sampling location at the mouth of the Scheldt estuary (Vlissingen boei SSVH), taken from the DONAR database (Rijkswaterstaat, 2010). This location was selected because of the long time series available. Despite there being a few gaps in the copper and lead data, the data cover the period 1971–2009. At first sight there is an apparent decline in the concentration of all four metals shown (Cu, Zn, Pb, Cd), seemingly in line with the reduction of riverine inputs of the River Scheldt in the past decades. Again, there is an additional argument: improvement of the analyses. The period 1971–1982 is characterised by high concentrations for all metals with a large

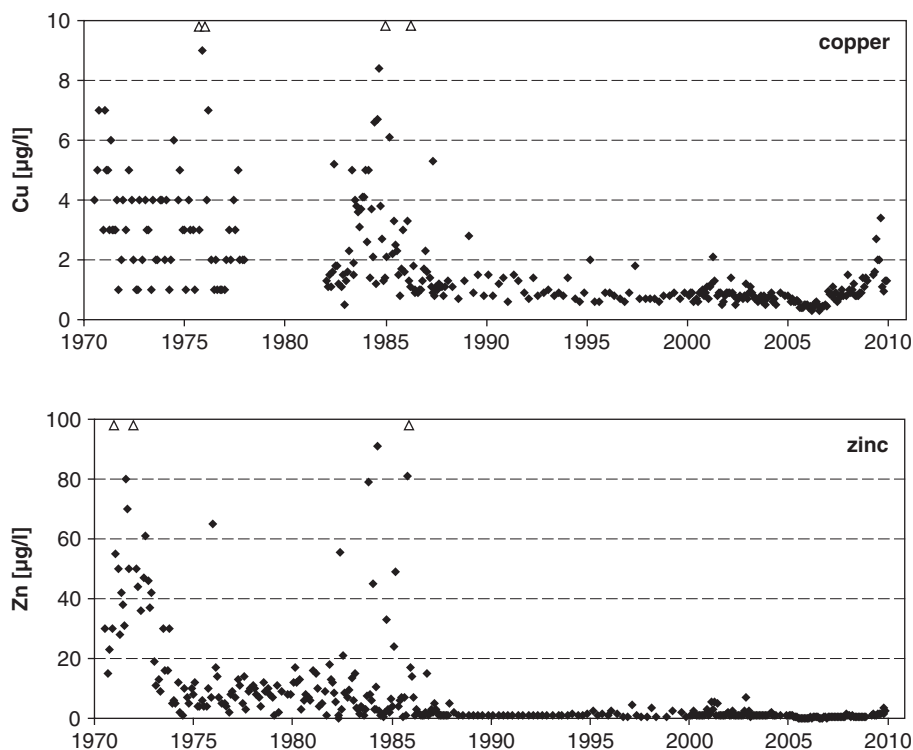


Figure 1.2 Concentration of dissolved copper (Cu), zinc (Zn), lead (Pb) and cadmium (Cd) for the same sampling station at the mouth of the Scheldt estuary (Vlissingen boei SSVH) for the period 1971–2009. Data <LoD were plotted at the LoD value. Data obtained from Rijkswaterstaat (2010).

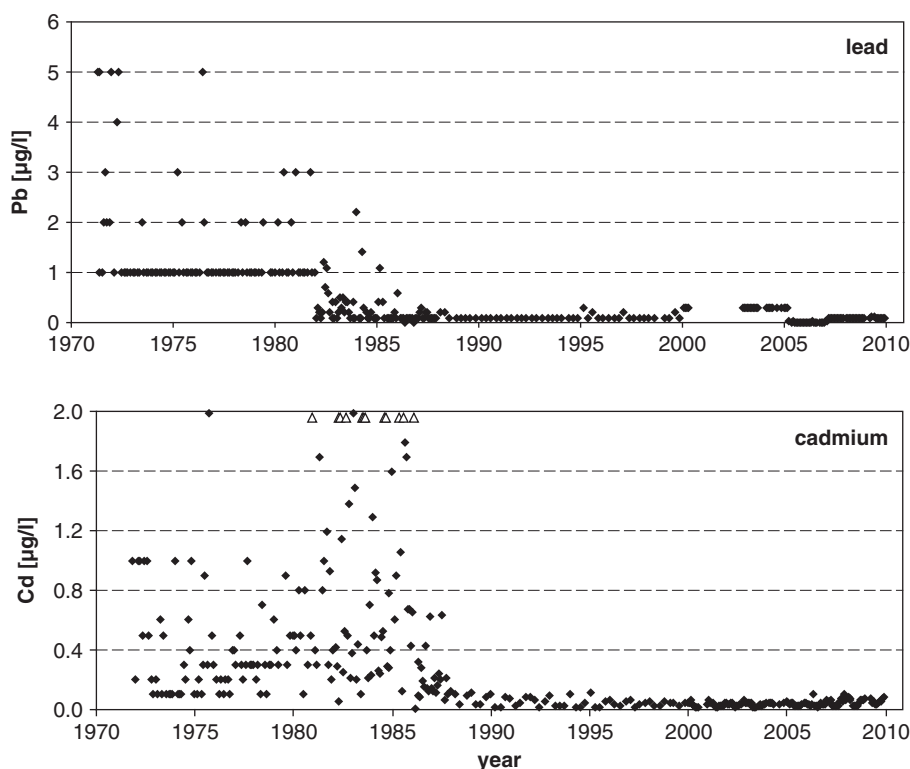


Figure 1.2 (continued)

(sometimes extreme) range in the results. This was the period before rigorous QA/QC methodologies were introduced. The analytical method (graphite furnace atomic absorption spectrometry (GF-AAS), direct in water samples) was not sensitive, as can be seen from the reported values: in this period results for dissolved Cu and Pb were presented in full digits only.

By 1982 the methods had improved and the results for these elements were now reported to one decimal place. In 1986 the laboratory introduced the metal complexation/extraction technique with subsequent analysis by GF-AAS. To ensure inter-comparability of the two methods, both techniques were applied for alternating samples for 2 years; from 1988 onwards, only extracts were analysed by GF-AAS, to be replaced by inductively coupled plasma mass spectrometry of water samples in 2005. Starting in 1990, values below the limit of detection (LoD) were identified in the database (in Figure 1.2, data <LoD are presented at the LoD value). Notably, the analyses for Pb often are subject to values reported <LoD, a value that in fact changes with time: 1990–1999: 0.1 µg/l; 2000–2005: 0.3 µg/l; 2005–2007: 0.01 µg/l; and from 2007: 0.1 µg/l.

Using all available data for different areas of the North Sea from the period 1980–1989, Scholten *et al.* (1998) found considerable differences in concentration between the first and second halves of this period and concluded this in line with the reduction in river inputs. Clearly, the improvements in analytical procedures have had an impact on the reported results, a factor complicating statistical trend analyses on long data sets. Because of the uncertainties in the ‘older’ analytical results, OSPAR, for example, in evaluating trends in riverine inputs, has used data since 1990 only. Even for the period 1990–2006, trend analyses proved cumbersome due to changes in analytical techniques and in LoDs (OSPAR, 2009).

1.8 CONCLUSION

This chapter focused mainly on the situation for the North-East Atlantic. As such, it is an example for developments in the rest of the world; albeit, the developments may not have taken place at the same time and/or at the same speed.

In response to public as well as policy awareness of the intrinsic quality of the (marine) environment in the late 1960s, international institutions started to focus on its protection. (Inter)national legal instruments were developed and implemented. The assessment of the status and temporal trends of, for example, harmful substances required the implementation and harmonization of international monitoring programmes.

Since routine monitoring started in the early 1970s, many developments have taken place. Early problems in the quality of the monitoring data have been solved by interlaboratory comparisons and rigorous implementation of QA and QC programmes. The initial use of fish and shellfish as a matrix for monitoring studies was soon expanded with monitoring of seawater and sediments. From monitoring only a few trace metals and PCBs, the list of hazardous substances has grown considerably, answering to the need to reduce the inputs of (often new and man-made) substances and to minimize their threat to ocean life.

Over the past 40 years the objectives of monitoring harmful substances in fish and shellfish as a potential hazard to human health have changed into an ecosystem approach where, in Europe under the WFD and MSFD, GES shall be reached. Monitoring is one of the management tools used for assessing the quality status and the temporal trends.

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