

Monitoring organic microcontaminants in the marine environment: principles, programmes and progress

Patrick Roose, Udo A.Th. Brinkman

Monitoring trace organic microcontaminants in the marine environment has been on-going for several decades. However, the compounds considered in most programmes are still mainly the 'old' organochlorines, the polynuclear aromatic hydrocarbons, several metals and metal-containing compounds. However, the marine environment is threatened by a much larger suite of organic microcontaminants. In recent years, European and other international organisations have been moving towards extending their lists of priority hazardous substances. Simultaneously, there have become available novel analytical techniques that offer new possibilities for monitoring in the marine environment.

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Abbreviations: ACME, Advisory Committee on the Marine Environment; AEPS, Arctic Environmental Protection Strategy; AMAP, Arctic Monitoring and Assessment Programme; BSC, Black Sea Commission; CEMP, Coordinated Environmental Monitoring Programme; COMMPS, Combined monitoring-based and modelling-based priority setting; DYNAMEC, Dynamic selection and prioritisation mechanism; EAA, European Economic Area; ED, Esbjerg Declaration; EMMA, European Marine Monitoring and Assessment; EMS, European Marine Strategy; EPA, Environmental Protection Agency; FAO, Food and Agricultural Organisation; GEF, Global Environment Facility; GESAMP, Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection; GIWA, Global International Waters Assessment; GPA, Global Programme of Action; HELCOM, Baltic Marine Environment Protection Commission or Helsinki Commission; IAEA, International Atomic Energy Agency; ICES, International Council for the Exploration of the Seas; IMO, International Maritime Organisation; IMW, International Mussel Watch; IOC, Intergovernmental Oceanographic Commission; JAMP, Joint Assessment and Monitoring Programme; JMP, Joint Monitoring Programme; MEDPOL, Programme for the Assessment and Control of Pollution in the Mediterranean Region; MON, OSPAR Working Group on Monitoring; NGO, Non-Governmental Organisation; NOAA, National Oceanic and Atmospheric Administration; NST, National Status and Trends programme; OSPAR, Oslo and Paris Commission; OSPARCOM, OSPAR Commission; PHS, Priority hazardous substance; POP, Persistent organic pollutant; PTB, Persistent, toxic and bioaccumulating; QSR, Quality status report; QUASIMEME, Quality Assurance of Chemical and Biological Effects Measurements in Marine Environmental Monitoring; RSP, Regional Seas Programme; SGO, Strategic goals and objectives; UNEP, United Nations Environment Programme; UNESCO-IOC, United Nations Educational Scientific and Cultural Organisation - Intergovernmental Oceanographic Commission; WFD, Water Framework Directive; WGSAM, ICES Working Group on Statistical Aspects of Environmental Monitoring; WHO, World Health Organisation; WMO, World Meteorological Organisation

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1. Introduction

After the Second World War, modern society rapidly evolved through a technological progress that seemed to open virtually unlimited opportunities, with the chemical industry delivering new products at a breathtaking pace. Unfortunately, the growing economy also caused increasing and widespread pollutant emissions, a problem that was previously mostly limited to the immediate vicinity of

emission sources. The general awareness of the huge risks of large-scale contamination increased, as a number of incidents gave global prominence to the inherent danger of this evolution. In Minamata, Japan, in 1961, a crippling, sometimes fatal, disease was found to be related to industrial mercury discharges. Scientists discovered that, even in the open ocean, big fish sometimes contained high concentrations of mercury. At about the same time, the pesticide DDT proved to be responsible for the decline of bird of prey populations, such as the bald eagle in North America [1] and the white-tailed eagle in the Baltic [2].

Aided by novel analytical techniques, such as gas chromatography (GC), scientists started investigating their environment for the presence of DDT and its degradation products. In 1966, Sören Jensen [3], while measuring DDT, identified a number of unknown peaks in his chromatograms as polychlorinated biphenyls (PCBs). The same compounds were found to be the agents in the Yusho incident in Japan, in 1968, where a massive accidental exposure of humans to PCBs and trace levels of polychlorinated dibenzofurans (PCDFs) occurred, caused by ingestion of a commercial brand of rice oil contaminated with these chemicals. As a result, about 1800 patients showed clinical symptoms such as acneiform eruptions, pigmentation of the skin, nails, and conjunctivas, increased discharge from the eyes, and numbness of the limbs [4]. Later work showed that these, and many other, xenobiotics are present in all compartments of the environment, even in regions far away from known sources, such as the Arctic and Antarctic [5]. In this way, it became apparent that these modern chemicals, their breakdown products and by-products generated during their production can threaten the marine environment.

Realisation of the potential danger of certain or rather many chemicals resulted in a call for not only measures to regulate their input into the seas, but also long-term monitoring. National and international workshops and study groups were convened to discuss monitoring and assessment of microcontaminants and to outline strategies for terrestrial and aquatic pro-

grammes [6]. Monitoring has now been going on for several decades and has revealed the ubiquitous presence of trace organic microcontaminants and heavy metals in all compartments of the environment. Table 1 gives an overview of some well-known, long-term, marine monitoring programmes and the principal contaminants that are being measured. They will be discussed in greater detail below.

Although heavy metals are important contaminants of the marine environment, in the present article, we will primarily discuss organic micropollutants (OMPs). OMPs are still a major cause of concern for the marine environment, despite the measures that have been taken to reduce their input and/or use. For example, in the OSPAR Quality Status Report 2000, Region II Greater North Sea [7], next to fisheries and nutrients, OMPs are considered a first-priority human pressure on the North Sea. Although the concentrations of some pollutants are decreasing, an increasing number of xenobiotics can be detected [7]. However, there is a general lack of data on the presence of organic hazardous substances in the marine environment. The report recommends that steps should be taken to close the gaps in knowledge "...in particular regarding the occurrence and effects of hazardous substances in the marine environment". Knowledge of the occurrence of OMPs is patchy, mainly because:

- (1) most projects focus on just a single group of chemically related pollutants;
- (2) all relevant compartments within a study area are not always investigated;
- (3) selection of sampling sites is not coordinated in most monitoring programmes; and,
- (4) analytical methods are not always developed to the level that allows measurement of the target compounds in marine field samples at suitably low concentrations [7,8].

This article aims to give an overview of the monitoring activities that have been carried out in the framework of marine pollution by organic compounds. We discuss the programmes, their efforts, their successes and their shortcomings. We mainly focus on monitoring activities

Table 1. Overview of major long-term monitoring programmes, and the contaminants and matrices measured

Organisation or programme	Start of the programme	Parameters ^{2,3}	Sample type
AMAP	1978	HM, PCBs, PAHs, OCPs	biota, sediment, water
HELCOM	1979	HM, PCBs, PAHs, OCPs, OTINs	biota, sediment
NS&T	1986	HM, PCBs, PAHs, OCPs	biota, sediment
IMW ¹	1965	HM, PCBs, PAHs, OCPs	biota (molluscs)
OSPAR	1978	HM, PCBs, PAHs, OCPs, OTINs	biota, sediment

¹IMW started in 1991-92, but data were already available from earlier programmes with a different name as early as 1965.

²Not all parameters measured during entire period.

³HM, Heavy metals; PCBs, Polychlorinated biphenyls; PAHs, Polycyclic aromatic hydrocarbons; OCPs, Organochlorine pesticides; OTINs, Organotin.

in the northeast Atlantic and, more specifically, the North Sea. Where appropriate, we will discuss other areas.

2. Monitoring programmes for the marine environment

We do not intend to give an exhaustive overview of all monitoring programmes for OMPs that are currently active, but to briefly describe a number of major programmes (see Table 1 and Fig. 2) and to consider common aspects and differences. We discuss the programmes that are relevant for the northeast Atlantic and the North Sea in greater detail. In essence, monitoring is about gathering information that allows authorities tentatively to assess the quality of the environment, to recognise threats posed by human activities and to assess whether earlier measures have been effective. It is precisely here that the challenge for a monitoring programme lies: Will the data that have been obtained be practically useful?

2.1. Monitoring programmes for the North Sea area

2.1.1. The Oslo and Paris Commissions and the Joint Assessment and Monitoring Programme. In 1974, the 1972 Oslo Convention – also called the Convention for the Prevention of Marine Pollution by Dumping from Ships and Airplanes – entered into force. The Convention regulated dumping operations involving industrial waste, dredged material and sewage sludge [9]. The Paris Convention – or Convention for the Prevention of Marine Pollution from Land-Based Sources – was established in 1974 and came into force in 1978. Its principal aim was to prevent, reduce and, if necessary, eliminate pollution of the Convention area from land-based sources, which are discharges from rivers, pipelines and the coast, but also offshore installations and the atmosphere.

The tasks set forth in both Conventions were originally handled by two individual commissions, the Oslo Commission and Paris Commission. In 1978, both Commissions established a Joint Monitoring Programme (JM), obliging contracting parties to initiate monitoring activities for a number of parameters in their water bodies. [9].

In the eighties, the policy of the Oslo and Paris Commissions evolved with the general evolution of environmental policy in Western Europe, voiced at the Ministerial Conferences for the Protection of the North Sea [10]. It was soon recognised that the existing Oslo and Paris Conventions did not adequately control some of the many sources of pollution, and that a revision was warranted. This resulted, not in a revision of the initial conventions, but more importantly, in the merger of both Commissions into the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) [11].

The new Convention was opened for signature at the Ministerial Meeting of the Oslo and Paris Commissions, in September 1992. The convention area is shown in Fig. 1. The key objective of the strategy is the cessation of discharges, emissions and losses of hazardous substances by 2020 with the aim of achieving concentrations in the marine environment close to background values for naturally occurring substances and close to zero for man-made synthetic substances.

To monitor environmental quality throughout the north-east Atlantic, a Joint Assessment and Monitoring Programme (JAMP) has been established, which has recently been revised [12].

2.1.2. The European Commission and the Water Framework Directive. In 1997, the EC proposed a European Parliament and Council Directive establishing a framework for Community action in the field of water policy, the Water Framework Directive (WFD). The Directive, which was adopted in September 2000 (2000/60/EC), should “contribute to the progressive reduction of emissions of hazardous substances to water”, the ultimate aim being “to achieve the elimination of priority hazardous substances (PHS) and contribute to achieving concentrations in the marine environment near background values for naturally occurring substances” [13].

In order to achieve this, pollution through the discharge, emission or loss of PHSs must cease or be phased out. The WFD foresees that the development of water quality should be monitored by the member states on a systematic and comparable basis. Technical specifications should therefore be laid down in order to assure a common approach (e.g., the standardisation of monitoring, sampling and methods of analysis). Although the WFD is designed for surface water and groundwaters, transitional (bodies of surface water in the vicinity of river mouths that are partly saline in character but mainly influenced by freshwater flows) and coastal (roughly the first mile of territorial waters) waters are also included. The WFD will therefore start playing a major role in the field of marine environmental monitoring. Although the Directive aims at making its contribution to earlier approved agreements, such as OSPARCOM, HELCOM and MEDPOL (see below), it imposes its own demands for monitoring on member states.

2.1.3. European marine strategy. In October 2002, the EC published a Communication to the Council of the European Union (EU) and the European Parliament entitled “Towards a strategy to protect and conserve the marine environment” (COM(2002) 539), which sets out objectives and related actions [14]. The communication is the first step in the incremental development of the European Marine Strategy (EMS) for the protection and conservation of the marine environment.

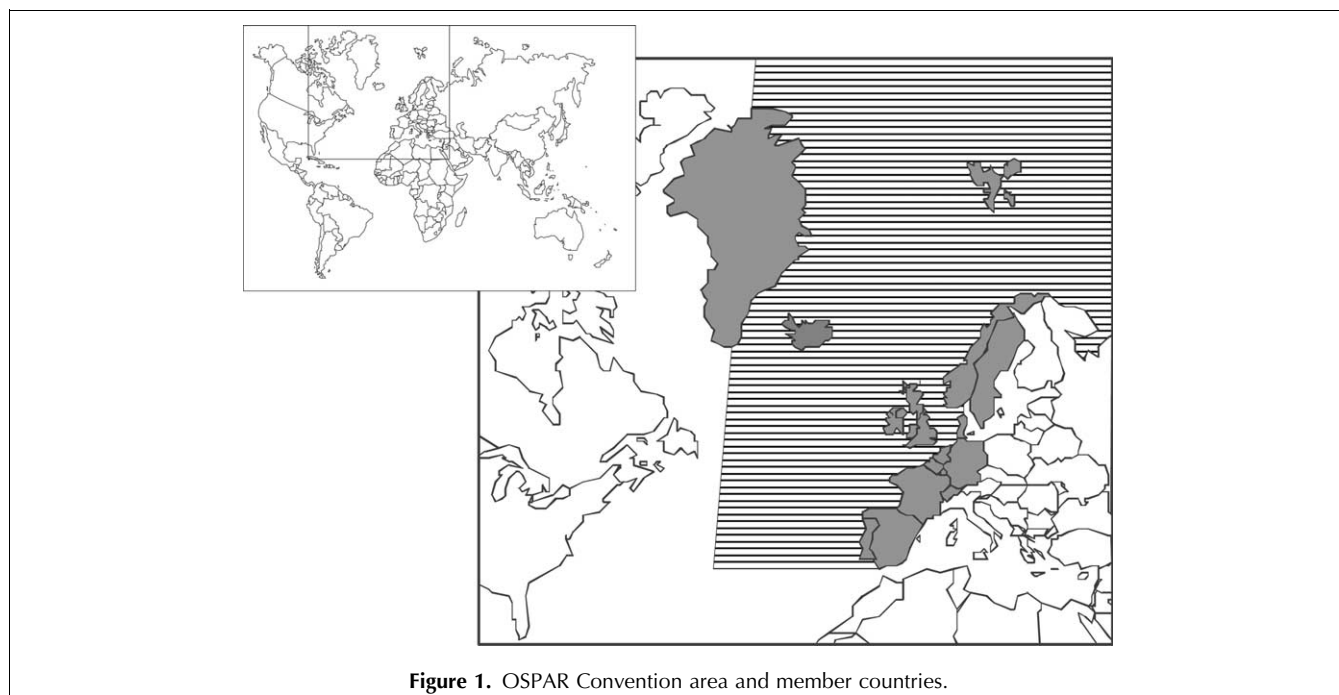


Figure 1. OSPAR Convention area and member countries.

The Commission's intention was to develop the EMS in close cooperation with member states, candidate countries, the European Parliament, European Economic Area (EEA) States (Norway and Iceland), the various, mainly regional, international organisations engaged in different sectoral aspects of the marine environment (such as OSPAR, ICES and IMO (International Maritime Organisation)), and with environmental non-governmental organisations and various sectoral industry associations.

It is expected that the Council will reach conclusions in the very near future, thereby establishing the EU political framework for the further development of the EMS and the implementation – in coordination with the regional marine conventions, such as OSPAR (see Fig. 2) – of actions to achieve the objectives already identified in the Commission Communication of 2004 [15].

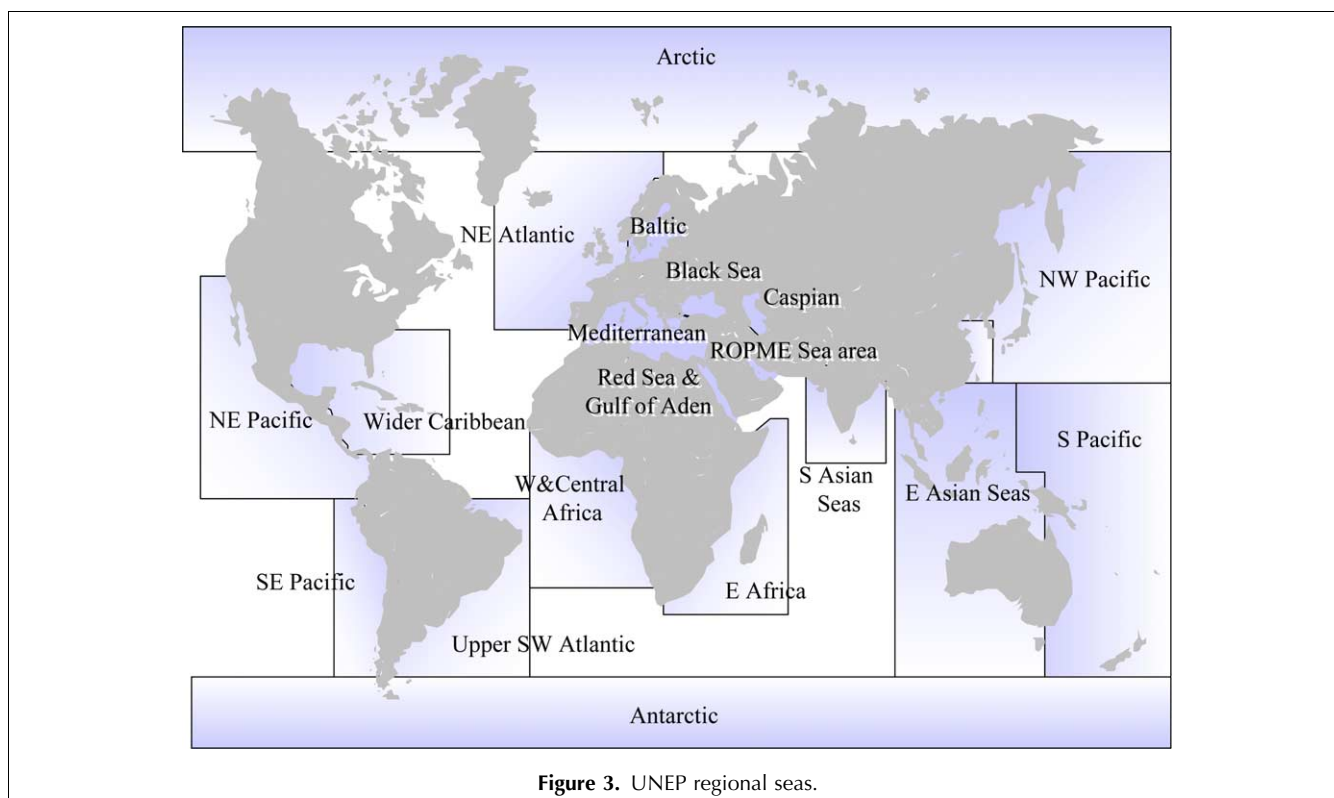
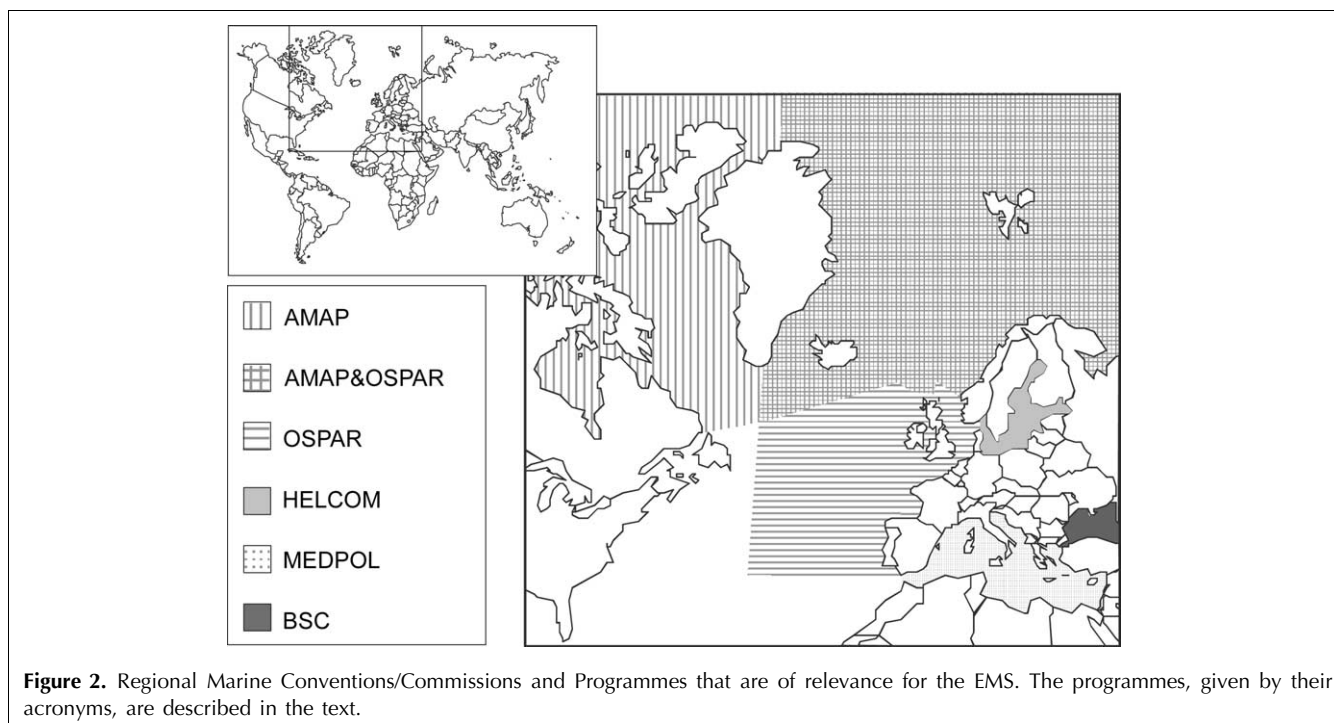
2.2. Other global and regional monitoring programmes

2.2.1. United Nations Environment Programme. Monitoring activities on a global scale are inevitably linked to the United Nations Environment Programme (UNEP), which was established as a follow-up to the 1972 Stockholm Conference on the Human Environment [16]. UNEP has several water-related programmes. For example, the Regional Seas Programme (RSP), initiated in 1974 as a global programme, includes 15 regions and more than 140 coastal states and territories (Fig. 3). It is an action-oriented programme and focuses on both the causes and the mitigation or elimination of the consequences of environmental degradation. The focus has gradually shifted from protecting the marine

environment from pollution to striving towards sustainable development of the coastal and marine environment through integrated management.

The Stockholm Convention (2001) is a global treaty to protect human health and the environment from persistent organic pollutants (usually called UNEP POPs), which has been signed by 151 governments. In implementing the Convention, governments will have to take measures to eliminate or to reduce the release of POPs into the environment [17]. POPs are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the (generally fatty) tissue of living organisms and are toxic to humans and wildlife. POPs circulate globally and can cause damage wherever they travel. The Stockholm Convention has identified a somewhat outdated list of 12 priority POPs – aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, PCBs, polychlorinated dibenzodioxins (PCDDs), PCDFs and toxaphene. The Stockholm Convention on POPs and other international agreements state that monitoring activities should be established to verify the effective implementation of the Convention and the decrease of environmental levels of POPs. Some monitoring activities are already in place but, as different methodologies are used, comparison of the data is often very difficult.

2.2.2. Other regional monitoring programmes. The Arctic Monitoring and Assessment Programme (AMAP) was established in 1991 to implement certain parts of the Arctic Environmental Protection Strategy (AEPS),



primarily “providing reliable and sufficient information on the status of, and threats to, the Arctic environment, and providing scientific advice on actions to be taken in order to support Arctic governments in their efforts to

take remedial and preventive actions relating to contaminants” [18]. AMAP was conceived as a programme that integrates monitoring and assessment activities in relation to pollution issues and provides

information and reports on the state of the arctic environment. The AMAP Trends and Effects Monitoring Programme is designed to monitor the levels of pollutants and their effects in all compartments of the Arctic environment.

The Baltic Marine Environment Protection Commission or the Helsinki Commission (HELCOM) is the governing body of the Convention on the Protection of the Marine Environment of the Baltic Sea Area, signed in 1992 [19]. HELCOM's main goal is to protect the marine environment of the Baltic Sea from all sources of pollution, and to restore and safeguard its ecological balance. The set-up is very similar to that of OSPAR, and many of the principles – such as the 'best environmental practices', 'best available technologies' and 'the polluter pays' – are adopted and applied by HELCOM.

The Programme for the Assessment and Control of Pollution in the Mediterranean region (MEDPOL) was initiated in 1975 in Barcelona as the environmental assessment component of the Mediterranean Action Plan (MAP) and is now in Phase III [20]. Its task is to assist Mediterranean countries in implementing pollution-assessment programmes (marine pollution trend monitoring, compliance monitoring and biological effects monitoring) directly contribute to implementing the Land Based Sources (LBS) and Dumping Protocols.

The Black Sea Commission (BSC) or the Convention on the Protection of the Black Sea Against Pollution was signed in Bucharest in April 1992, and ratified by the legislative assemblies of all six Black Sea countries in early 1994 [21]. The Convention aims to

- (1) control land-based sources of pollution;
- (2) control dumping of waste; and,
- (3) establish a framework for joint actions in the case of accidents, such as oil spills.

2.3. Conclusions

The above overview focuses on organisations and programmes immediately relevant for Europe as a whole and, specifically, the North Sea. There are various other regional and international monitoring programmes, such as the National Status and Trends (NST) monitoring programme of the National Oceanic and Atmospheric Administration (NOAA), which has been going on since 1986 and covers the Atlantic, Pacific and Gulf coasts of the USA, and the International Mussel Watch (IMW) programme that covers Central and South America, including Mexico and the Caribbean [22].

A global overview of the regional programmes, their common points of interest and interactions can be found in GESAMP [23]. In essence, the various programmes all recognise that organic micropollutants are an important threat to the marine environment, which should be carefully monitored. As a minimum, the programmes share the following two goals:

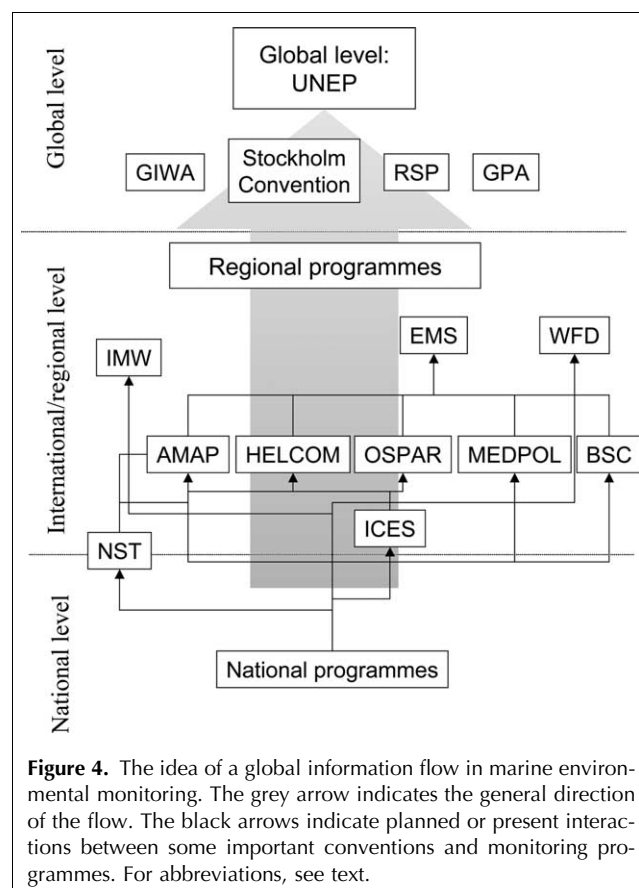


Figure 4. The idea of a global information flow in marine environmental monitoring. The grey arrow indicates the general direction of the flow. The black arrows indicate planned or present interactions between some important conventions and monitoring programmes. For abbreviations, see text.

- (1) to study the status of the marine environment with regard to contaminants; and,
- (2) to detect trends in concentrations.

As a positive development, there is a tendency to make the various programmes mutually supportive rather than competitive. Fig. 4 illustrates the current idea of information flow starting from national programmes, feeding into international/regional and, finally, global programmes.

There is also a general awareness that the data that are produced should be of high and, specifically, well-defined quality. The emphasis on quality assurance and quality control (QA/QC) is therefore omnipresent and has gained considerable importance in recent years. Amongst other things, this implies the obligation of laboratories to participate in international intercalibration exercises and to use clearly described methodologies in the form of standard operating procedures [23].

3. Current state of marine environmental monitoring

The previous section showed that several monitoring programmes are currently active and/or have been so for many years or even decades. All early programmes dealt with the industrialised northern hemisphere. The output

of these programmes was used to identify areas or regions of concern, estimate the hazards caused by OMPs to man and the marine environment and assess the effectiveness of the measures taken.

Most organisations have published status reports that evaluate the quality of the, mostly regional, marine area that they consider. These have provided a basic idea of the geographical distribution of OMPs in regions, such as

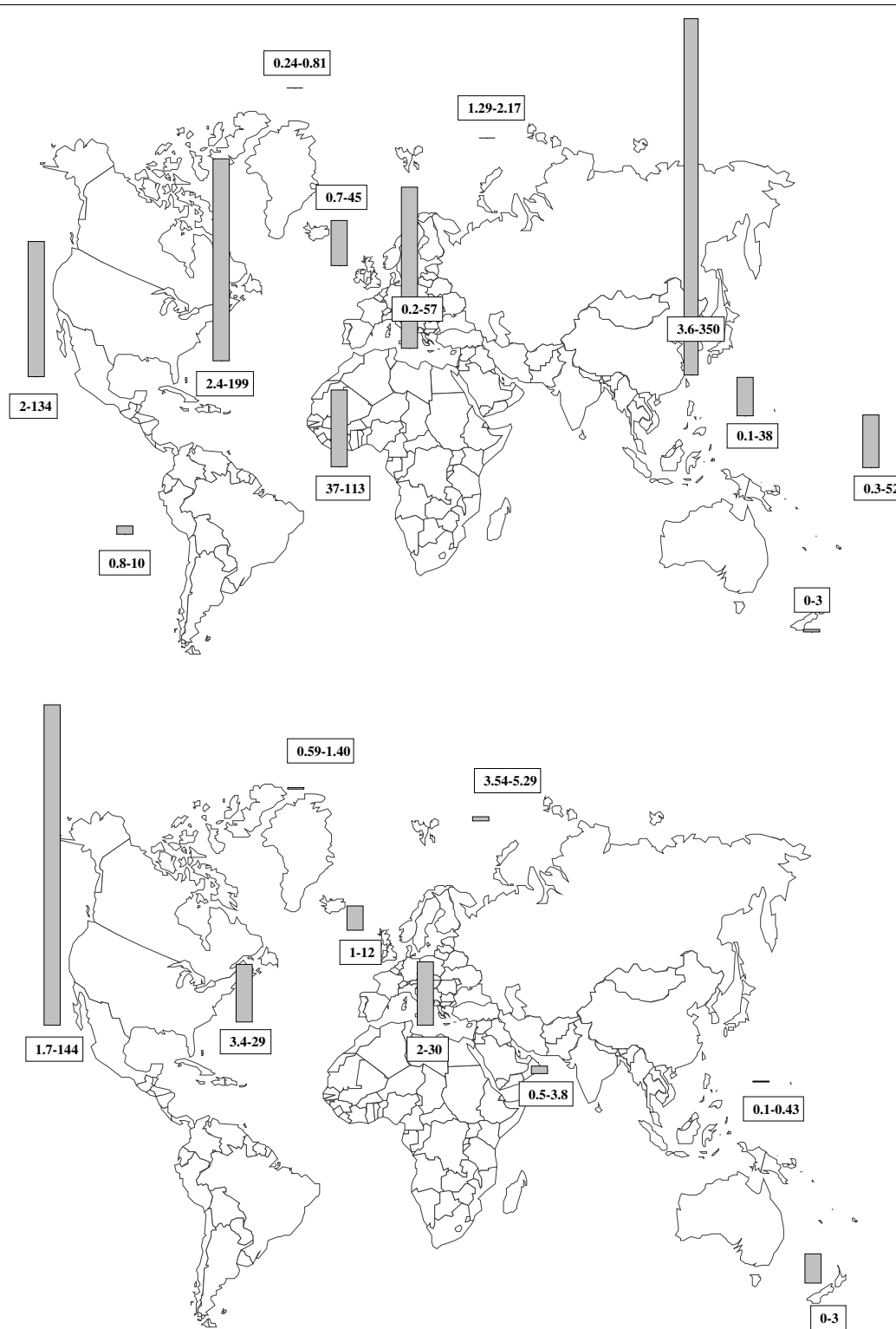


Figure 5. Concentration ranges of DDTs (top) and PCBs (bottom) in bivalves (µg/kg ww) reported during the 1990s (source: UNEP Chemicals [28]).

the Arctic [24], the Baltic [25,26] and the North Sea [10,13], and the Atlantic and Pacific coasts of North America [22,27]. These regional programmes also contributed significantly to an estimate of the global distribution of OMPs. The UNEP assessment of the worldwide presence of persistent toxic substances has, for the marine environment, greatly benefited from the information provided by these regional programmes [28]: sources, pathways and concentration ranges for the various compartments (water, sediment/soil, organisms) of both the terrestrial and the aquatic environment (marine and freshwater) are considered on a global scale.

In general, the highest concentrations have been reported for DDTs (mostly DDE), PCBs (as the sum of individual congeners) and PAHs, with concentrations that are up to five to six orders of magnitude higher than, e.g., PCDDs/Fs (ng/kg concentrations). Most other OMPs, such as HCB, lindane, the PBDEs, toxaphene and modern pesticides, have concentration levels in between ($\mu\text{g/kg}$ concentrations) [28]. As an illustration, the global concentration ranges of PCBs and DDTs in bivalves reported in the 1990s are given in Fig. 5.

Long-term monitoring programmes also demonstrate changes in the levels of OMPs in the marine environment. For example, monitoring in the Baltic, which started in the late 1960s, clearly showed the decline of several OMPs following actions to prevent their release [29,30]. Decreasing PCB concentrations were cited in the 1993 North Sea Quality Status Report for several species and various locations [9]. In the 1998 OSPAR assessment of trends of contaminants in organisms, significant downward trends were reported for HCB, γ -HCH, PAHs, CBs, DDTs and dieldrin [31]. Assessment of the data collected through NST and IMW [34] (see above) showed a general decrease in total DDT concentrations in molluscs for the northern part of the Gulf of Mexico, presumably as a result of the ban on DDT in the USA in 1972. Decreasing concentrations were also found for PCBs, but not for PAHs. Brown et al. [32] found similar results for the Pacific coast of the USA, following a seven-year study during the National Benthic Surveillance Project of NST; PCBs and DDT concentrations were decreasing in fish and sediment, but PAHs showed no significant downward trend.

Despite the interesting results of the various programmes quoted above, some prudence is called for when interpreting the data. For example, in their status reports, most organisations tend to combine the contaminants in groups rather than to present the concentration of individual compounds. In the examples given above (Fig. 5), the sets of target PCBs and the DDTs were not specified. Particularly for the PCBs, it is well known that, on the one hand, the concentrations of the individual congeners are widely different while, on the other hand, the non-ortho and mono-ortho congeners are much more toxic than all other congeners [33]. In

addition, for most other classes of micropollutants, much less information is available and is, moreover, essentially limited to North America, the western half of Europe, Australia and Japan in virtually all instances. This problem was duly recognised in the 2003 UNEP assessment [28]. In other words, DDTs and PCBs are virtually the only pollutants for which it is possible to attempt making temporal and geographical comparisons [34]. This does not mean that there are no data available for other chemicals or for less developed parts of the world. However, in regions where surveillance networks are not operational, the information is generally the result of one-off surveys and more patchy. In addition, the information in the open literature is strongly targeted on the “classical” pollutants, such as PCBs, DDTs, PAHs, OCPs and PCDD/Fs.

Fortunately, the threat posed by other contaminants is increasingly being recognised by the scientific community and governmental bodies. For example, Muir et al. [35] recently noted that there is an overall lack of data on PTSs (Persistent and Toxic Substances) in North America. To quote an example, for most of the 100 priority chemicals listed by the Canadian Government, there is very limited information on their current environmental levels, persistence and/or bioaccumulation. Quite a number of them have not been studied at all. Obviously, selection of a significantly wide range of relevant chemicals for the marine environment has a high priority. We discuss this topic – which is receiving increasing attention in recent programmes and updates of older programmes – in the next section.

4. Selection of priority hazardous substances

4.1. Introduction

Monitoring was initially limited to compounds entered on a “red” list after a catastrophe or selected after their – sometimes accidental – detection in the environment (see above). In other words, in the absence of well-directed and/or targeted programmes, most chemicals were, and will be, “missed”. However, it will be clear that it is impossible to determine concentrations of the approx. 250,000 man-made chemicals – the so-called chemical universe – in the marine environment [36]. Over the years, this awareness led to the development of criteria that allow the prediction of which chemicals could be of concern for the marine environment. We briefly discuss these selection criteria below.

4.2. Selecting priority substances

In 1990, the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection and Advisory Committee on Protection of the Sea (GESAMP) [37] made a selection based on criteria such as the octanol/water partition coefficient or bioconcentration potential,

acute toxicity, persistence, production volume and use of a chemical compound. The resulting list of potentially harmful substances contained mainly low-molecular-weight (MW) (C_1 - C_3) chlorinated alkanes, such as chlorinated methanes (e.g., dichloromethane, chloroform and tetrachloromethane), chlorinated ethanes (e.g., 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane), chlorinated ethenes (e.g., 1,1,2,2-tetrachloroethylene and 1,1,2-trichloroethylene), and medium-MW compounds, such as chlorinated benzenes, phenols and toluenes, PCBs and PCDDs/Fs. In addition, an extensive list of compounds was identified for which insufficient data were available. In other words, next to the three most important characteristics – persistence, bioaccumulation and toxicity – the production volume and use were also taken into account. This resulted in the selection of chemicals such as dichloromethane. The same or similar approaches were also used in more recent assessments, as exemplified below.

The threat of hazardous substances was recognised at the Third International Conference on the Protection of the North Sea [38], which resulted in a list of 38 priority substances (Annex 1A) and an additional list of 170 potentially hazardous substances (Annex 1D) [38].

The Fourth International Conference on the Protection of the North Sea or Esbjerg Declaration (ED) identified the need for further development of criteria for defining and prioritising hazardous substances, which require action [39]. In addition, the need to develop risk-assessment methods and measurement programmes for hazardous substances in the marine environment – specifically risk-assessment methods for complex mixtures of substances and endocrine disrupters – was recognised.

OSPAR's activities on hazardous substances are of special relevance to the North Sea Conference work, as the OSPAR Convention is an instrument to implement the ED targets. OSPAR's strategy with regard to hazardous substances was revised and implemented in 1998 in the so-called Sintra Statement [40].

In response to its strategy concerning hazardous substances, the OSPAR Commission developed a dynamic selection and prioritisation mechanism, DYNAMEC, to select priority substances [36]. The entire process is illustrated in Scheme 1.

Hazardous substances are defined as (groups of) compounds that are persistent, toxic and liable to bioaccumulate (PTB), or give rise to an equivalent level of concern (e.g., through synergistic effects or degradation into hazardous substances [36]).

During the initial selection, the following criteria were used:

- highly hazardous properties resulting in a general threat to the aquatic environment;
- strong indications of risks for the marine environment;

- widespread presence in one or more compartments of the marine environment;
- potential threat to human health via consumption of seafood; and,
- presence of various pathways or a diversity of sources to the marine environment.

After the initial selection, a ranking based on a ranking algorithm was made. Final selection of substances for priority action was done by a group of experts. As with the GESAMP criteria quoted above, the selection relied heavily on the PTB criteria. However, in addition, data on direct and indirect effects and production volumes and use were also taken into account. Calculated exposures and monitored concentrations were also considered.

The initial selection led to a total of 80 substances or groups of substances, divided into five categories; 15 were selected as substances for priority action and another 12 as candidates for prioritisation [36]. The list of substances was updated in subsequent years. After the recent additions of perfluorooctane sulfonate (PFOS), and the (pentabromo)methyl ester of 2-propenoic acid, the list now contains 47 chemicals for priority action [41]. The entire list of OSPAR's priority substances is given in Table 2. Of these, 14 have a lower priority, although they have rankings in terms of persistency, bioaccumulation and toxicity that are of equal concern to those for the other substances on the list. However, because they are used exclusively as intermediates in closed systems in the production of other substances or because there is no current production or use in the OSPAR states, they have a lower priority (Table 2).

The OSPAR list played an important role during the selection of priority substances for the WFD. The basic procedure for the WFD was the Combined Monitoring-based and Modelling-based Priority Setting (COMMPS) procedure [42,43]. Similar to OSPAR, hazardous substances mean "substances or groups of substances that are toxic; persistent and liable to bioaccumulate; and other substances or groups of substances that give rise to an equivalent level of concern". During the initial step of the COMMPS procedure, priority substances were again selected from among the list of hazardous substances, based on evidence regarding the intrinsic hazard, widespread environmental contamination and other proven factors that may indicate the possibility of widespread contamination, such as production or use volume. Next, exposure indices – based both on surface-water monitoring and on modelling data – and effect indices were calculated, which finally led to a risk-based priority index, essentially by multiplying both previous indices. This list was then submitted to expert judgement for the selection of priority substances. Interestingly, "historic pollutants", such as PCBs, were eliminated in this step [43]. Finally, the list was checked against the OSPAR list, other lists from EC regulations

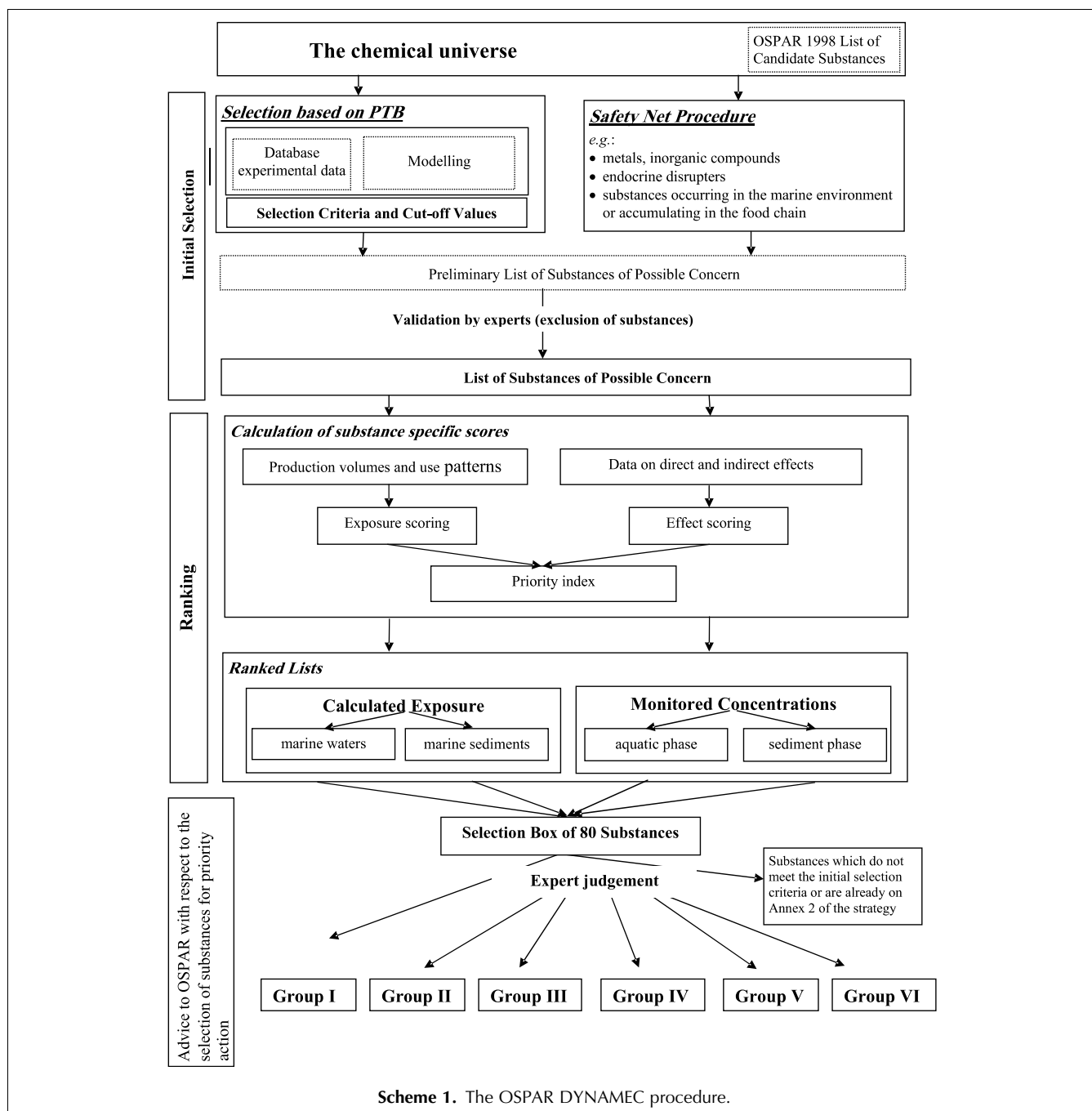
and lists resulting from international agreements (e.g., the Stockholm Convention on POPs) [44]. The procedure resulted in a list of 33 priority hazardous (groups of) substances and an additional 10 priority (groups of) substances [45] (Table 2).

The OSPAR and EU approaches, which clearly show mutual influence, provided the basis for priority setting under HELCOM [30]. As a result, a very similar list of 42 (groups of) substances was identified (and is included in Table 2). For further comparison, the Stockholm Con-

vention or UNEP list of POPs, which contains 12 (groups of) chemicals, is also shown in Table 2.

4.3. Comparing the lists

Comparison of the lists discussed above clearly shows that there is much overlap, but there are also several striking differences. Most surprisingly, not a single compound appears on all four lists. To facilitate further discussion, the priority substances of Table 2 have been sub-divided into several categories.



Categories of priority hazardous substances and cut-off values for PTB criteria according to the OSPAR DYNAMEC procedure

Group	Description	Applied PTB cut-off values	Examples
I	Substances of very high concern (i.e. POP-like substances or substances with PTB profile, selection I) and indication of production, use or occurrence in the environment	P: not inherently biodegradable <i>and</i>	2,4,6- <i>tris</i> (1,1-dimethylethyl)-phenol, dicofol, endosulphan, methoxychor, octylphenol, EPN, tetrasul, miconazole nitrate, diosgenin, trifluralin, clotrimazole
		B: $\log K_{ow} \geq 5$ or $BCF \geq 5000$ <i>and</i> T_{aq} : acute $L(E)C_{50} \leq 0.1$ mg/l, long-term $NOEC \leq 0.01$ mg/l <i>or</i> $T_{mammalian}$: CMR or chronic toxicity	
II	Other initially selected substances (with less severe PTB profile) and indication of use or exposure	P: not inherently biodegradable <i>and</i>	hexamethyldisiloxane, 1,2,3,4,5,5-hexachloro-1,3-cyclopentadiene, TBBA, 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, 1-(1,1-dimethylethyl)-4-methyl-benzene, cyclododecane, triphenylphosphine, isododecane, chlorpyrifos
		B: $\log K_{ow} \geq 5$ or $BCF \geq 5000$ <i>and</i> T_{aq} : acute $L(E)C_{50} \leq 0.1$ mg/l, long-term $NOEC \leq 0.01$ mg/l <i>or</i> $T_{mammalian}$: CMR or chronic toxicity	
III	Substances of very high concern (i.e. POP-like substances or substances with PTB profile, selection I) with <u>no</u> indication of use or exposure	P: not inherently biodegradable <i>and</i>	heptachloronorborene, flucythrinate, PCNs
		B: $\log K_{ow} \geq 5$ or $BCF \geq 5000$ <i>and</i> T_{aq} : acute $L(E)C_{50} \leq 0.1$ mg/l, long-term $NOEC \leq 0.01$ mg/l <i>or</i> $T_{mammalian}$: CMR or chronic toxicity	
IV	Other initially selected substances with no indication of use or exposure	P: not readily biodegradable <i>and</i>	fenitrothion, isodrin, pentachloroanisole, fenpropimorph, diazinon
		B: $\log K_{ow} \geq 5$ or $BCF \geq 5000$ <i>and</i> T_{aq} : acute $L(E)C_{50} \leq 1$ mg/l, long-term $NOEC \leq 0.1$ mg/l <i>or</i> $T_{mammalian}$: CMR or chronic toxicity	
V	Substances with PTB properties but which are heavily regulated or withdrawn from the market	P: not readily biodegradable <i>and</i>	DDTs, chlordane, PCTs, aldrin, HCB, toxaphene, nitrofen, heptachlor
		B: $\log K_{ow} \geq 5$ or $BCF \geq 5000$ <i>and</i> T_{aq} : acute $L(E)C_{50} \leq 1$ mg/l, long-term $NOEC \leq 0.1$ mg/l <i>or</i> $T_{mammalian}$: CMR or chronic toxicity	
VI	Endocrine disrupters which do not meet P or B criteria or natural hormones	P: not readily biodegradable <i>and</i>	estradiol, estrone, diethylstilbestrol, 17-ethynylestradiol, butylphenol
		B: $\log K_{ow} \geq 5$ or $BCF \geq 5000$ <i>and</i> T_{aq} : acute $L(E)C_{50} \leq 1$ mg/l, long-term $NOEC \leq 0.1$ mg/l <i>or</i> $T_{mammalian}$: CMR or chronic toxicity	

P, Persistence; B, Bioaccumulation; T_{aq} , Aquatic toxicity with $L(E)C_{50}$ the lethal (L) or effect (E) concentration that affects 50% of the population; NOEC, No observed effect concentration; $T_{mammalian}$, Mammalian toxicity; BCF, Bioconcentration factor; CMR, Carcinogenicity, mutagenicity and adverse effects on reproduction.

Scheme 1. (continued)

PCBs, OCPs (e.g., DDTs, aldrin and dieldrin) and PCDD/Fs are considered as the “old” organochlorines and are also referred to as the “old” contaminants [46]. The entire UNEP POP list comprises these substances, so it is somewhat outdated; they are also priority substances for OSPAR and HELCOM. They have been the

subject of extensive study and international regulation in recent decades. It is specifically because of the international attention that they are not on the WFD list (with the exception of hexachlorobenzene and HCHs). Although the initial COMMPS selection procedure included most of them (even as top-ranking substances), they

Table 2. Overview of (groups of) substances selected by four international organisations				
(Groups of) substances	OSPAR	WFD	HELCOM	UNEP POP
“Old” organochlorines				
Aldrin			X	X
Chlordane			X	X
DDTs			X	X
Dieldrin			X	X
Endosulphan	X	X ²		
Endrin			X	X
Heptachlor			X	X
Hexabromobiphenyl			X	
Hexachlorobenzene		X ²		X
Hexachlorocyclohexane isomers (HCH)	X	X ²	X	
Isodrin	X ¹		X	
Mirex			X	X
PCBs	X		X	X
PCDDs	X		X	X
PCDFs	X		X	X
PCNs	X ¹			
Polychlorinated terphenyls			X	
Toxaphene (OSPAR: heptachloronorbornene)	X ¹		X	X
“New” pesticides				
Acrylonitrile			X	
Alachlor		X	X	
Aramite			X	
Atrazine		X ²		
Chlordecone			X	
Chlordimeform			X	
Chlorfenvinphos		X		
Chlorpyrifos		X ²		
Dicofol	X			
Diuron		X ²		
Ethyl O-(p-nitrophenyl) phenyl phosphonothionate (EPN)	X ¹			
Flucythrinate	X ¹			
Fluoroacetic acid and derivatives			X	
Isobenzane			X	
Isoproturon		X ²		
Kelevan			X	
Methoxychlor	X			
Morfamquat			X	
Nitrophen			X	
Pentachlorophenol (PCP)	X		X	
Quintozone			X	
Simazine		X ²		
2,4,5-T			X	
Tetrasul	X ¹			
Trifluralin	X	X ²		
VOCs				
1,2,3-Trichlorobenzene	X	X ²		
1,2,4-Trichlorobenzene	X	X ²		
1,2-Dibromomethane			X	
1,2-Dichloroethane		X		
1,3,5-Trichlorobenzene	X	X ²		
Benzene		X		
Dichloromethane		X		
Trichloromethane		X	X	
PAHs				
Anthracene	X	X ²		
Fluoranthene	X	X		
Naphthalene	X	X ²		
Polyaromatic hydrocarbons	X	X ²	X	

(continued on next page)

Table 2. (continued)				
(Groups of) substances	OSPAR	WFD	HELCOM	UNEP POP
"New" organohalogenes				
Brominated flame retardants				
(WFD: polybrominated biphenyls only)	X	X ²		
1,3,5-tribromo-2-(2,3-dibromo-2-methylpropoxy)-benzene	X ¹			
Hexachlorobutadiene		X ²		
Hexachlorocyclopentadiene (HCCP)	X			
Pentabromoethylbenzene	X ¹			
Pentachloroanisole	X ¹			
Pentachlorobenzene		X ²		
2-Propenoic acid, (pentabromo)methyl ester	X ¹			
Short-chain chlorinated paraffins (SCCPs)	X	X ²	X	
Tetrabromobisphenol A (TBBP-A)	X			
Endocrine disruptors				
Nonylphenol/ethoxylates (NP/NPEOs) and related substances	X	X ²	X	
Octylphenol	X	X ²		
Phthalates: dibutylphthalate, diethylhexylphthalate (DEHP)	X	X ²	X	
Other organic chemicals				
1,5,9-Cyclododecatriene	X ¹			
2,4,6-Tri- <i>tert</i> -butylphenol	X			
3,3'-(ureylenedimethylene)bis(3,5,5-trimethylcyclohexyl)-				
Diisocyanate	X ¹			
4-(dimethylbutylamino)-Diphenylamin (6PPD)	X			
4- <i>tert</i> -Butyltoluene	X			
Clotrimazole	X			
Cyclododecane	X ¹			
Diosgenin	X			
Hexamethyldisiloxane (HMDS)	X			
Musk xylene	X		X	
Neodecanoic acid, ethenyl ester	X			
Perfluorooctanol sulphonic acid and its salts (PFOS)	X			
Triphenyl phosphine	X			
Metals and related compounds				
Cadmium	X	X ²	X	
Lead and organic lead compounds	X	X ²	X	
Mercury and organic mercury compounds	X	X ²	X	
Nickel and its compounds		X		
Organic tin compounds	X	X ²	X	
Selenium and its compounds			X	
¹ Lower priority in OSPAR because of exclusive use as intermediates in closed systems or no current production and/or use in the OSPAR area.				
² First-priority hazardous substances.				

were not considered as priority substances because of the fact that there is no current production or usage, or use is strictly regulated or forbidden. Exclusion is therefore not based on toxicological properties and/or presence in the environment. By contrast, organisations such as OSPAR and HELCOM consider them as priority substances, precisely because of their presence in the environment, which seems a sounder approach.

The CBs are a particularly good example of this category. They have been a major cause for concern since their discovery in the environment by Jensen [3]. Large amounts of technical mixtures of CBs were manufactured by companies in the USA, Japan and several

European countries between 1930 and 1983 when their production (e.g., approx. 36,000 tonnes in Europe alone in the period 1981–84) was discontinued in most countries [47]. During this period but, also, more recently, large quantities of CBs reached the environment (e.g., through large-scale disposal, leakage, evaporation and accidents) [48,49]. Since the early 1980s, CBs have been routinely monitored in a variety of marine samples, specifically, organisms and sediments.

Most monitoring programmes require or suggest the analysis of individual congeners such as the "ICES 7" (CBs 28, 52, 110, 118, 138, 153 and 180). However, in the 1980s, it had already become clear that several CB

congeners showed a dioxin-like toxicity [33], particularly non-ortho, but also mono-ortho, CBs able to form a planar configuration and therefore bind to the Ah receptor in a way very similar to dioxins. Their toxicity is generally expressed by means of a toxic equivalent factor (TEF: ratio of toxicity of congener and 2,3,7,8-TCDD (tetrachlorodibenzodioxin)) [50]. Total toxicity is then calculated as Toxic Equivalent Quotients (TEQs), where $TEQ = \sum TEF_i \times c_i$, for all congeners, i , of interest.

Although the concentrations of these CBs typically are 1000-fold less than those of the so-called indicator CBs, their toxicity is some 1000-fold higher [8]. Nevertheless, neither non-ortho nor mono-ortho CBs are part of most monitoring programmes and are, therefore, not routinely monitored, although their importance is recognised (e.g., by WHO, OSPAR, HELCOM, QUASIMEME (Quality Assurance of Chemical and Biological Effects Measurements in Marine Environmental Monitoring) and the EU). One exception is the AMAP Trends and Effects Programme where, next to e.g., DDTs, planar CBs are recognised as “essential” in contrast to “recommended” parameters for certain matrices, such as sediment cores, fish liver and blubber of marine mammals [51].

The “old” contaminants remain a cause of concern because of their persistence and because of continued releases and transport through the atmosphere of significant quantities of these chemicals or their transformation products (e.g., p,p' -DDE as a transformation product of p,p' -DDT) [23,39,46].

There has long been concern over sub-lethal effects of long-term, low-level chemical exposure, particularly about the possibility of immunosuppression in mammals from both acute and chronic low-dose exposures [23]. Also, sub-lethal effects should be located at the level of critical biological processes, such as reproduction, development and growth, which are mostly hormone driven. Recent concern about endocrine-disrupting chemicals (EDCs) has led to significant new research on the hormonal effects of persistent (and some non-persistent) chemicals, amongst which are most of the 12 UNEP POPs [23]. Moreover and controversially, the fact that chemicals have for a long time been recognised as important contaminants does not necessarily mean that their presence in the marine environment has been amply demonstrated. This is particularly true for the CDD/Fs. Quite recently, OSPAR's QSR highlighted the lack of data for these compounds in the marine environment [7], mainly due to costs involved in their ultra-trace level determination.

PAHs also belong to the group of “old” contaminants. It is quite surprising that they are not on the UNEP POP list, since they are recognised as priority hazardous substances by OSPAR, WFD and HELCOM. Also, Law [52] estimated that approx. 230,000 tonnes of PAHs reach the marine environment every year and are dis-

tributed worldwide. For the OSPAR area, this is estimated to be around 8000 tonnes/year for the “Borneff 6” [53]. In the marine environment, PAHs tend to adsorb to particulate material as a result of their hydrophobic nature and to be deposited into the underlying sediments [54]. They are quite persistent, particularly in anaerobic sediments, and can accumulate to high concentrations [55]. The highest concentrations are generally found in coastal areas and in estuaries, with total PAH concentrations of up to 8.5 µg/l for the water phase and up to 6 mg/kg (dry weight) for sediments [53]. As a result of their high persistence and potential carcinogenic and mutagenic effects [56,57] PAHs should be considered as high-priority environmental pollutants [53]. In North Sea sediments, the most carcinogenic PAH, benzo(a)pyrene, has been detected at concentrations up to 0.24 mg/kg [7]. PAHs have been routinely monitored since the 1970s. As is evident from Table 2, most major programmes identify specific individual PAHs and/or include them as a class. The most commonly used list of individual PAHs is that of the US EPA and contains 16 parent PAHs. However, OSPAR has a list of only 10 target PAHs, while AMAP has an additional 23 (groups of) alkylated PAHs over and above the 16 EPA PAHs.

The other categories included in Table 2 – with the exception of metals, which are not considered here – can be considered “new” or emerging contaminants. A prominent group are the “modern” pesticides. Again, there is much discrepancy between the lists and not a single pesticide is on all of them. Phenylurea pesticides diuron and isoproturon, triazines atrazine and simazine and anilide alachlor all belong to the group of semi-polar pesticides. With one exception, alachlor, they show up on only the WFD list. Much less polar and, typically fat-soluble pesticides include chlorpyrifos, chlorfenvinphos, trifluralin and dicofol. Their adverse PTB characteristics make them environmental hazards. Production volumes can be quite high (e.g., trifluralin, a dinitroaniline herbicide used to control a wide spectrum of annual grasses and broadleaf weeds in agriculture, has an annual production volume of 6000 tonnes in the EU and worldwide production of 24,000 tonnes [58]). They have been detected in concentrations of up to 20–60 µg/l in seawater, but little is known about their presence in sediments, fish and marine mammals.

Most target pesticides are on the WFD list but, surprisingly, dicofol is on only the OSPAR list. This can be explained by the selection procedures. Although the initial selection was in all cases based on PTB (see above), the individual procedures tended to emphasize different criteria in their final selection. For example, WFD applies a monitoring-based exposure scoring but relies exclusively on the freshwater aquatic environment for this – and mainly on the water column [43]. Many of the above compounds are indeed already monitored in

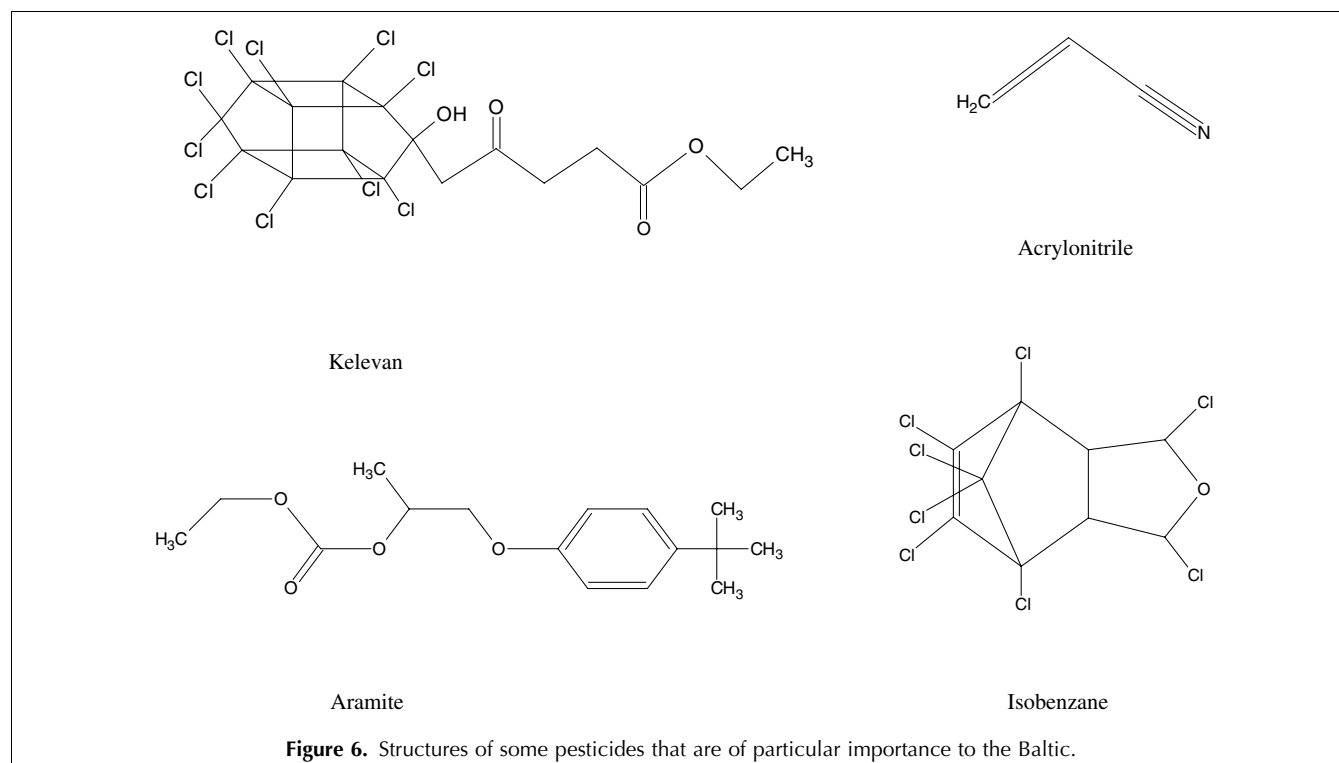
the freshwater environment, hence their selection. This particular criterion is not applied by either OSPAR or HELCOM, which should explain the differences. Methoxychlor, which is on only the OSPAR list, is another good example. Although there is no hard evidence on current production and use in the OSPAR area, the pesticide is persistent, bioaccumulates and is very toxic to aquatic organisms. It also has potentially endocrine-disrupting properties. Because of this, it was included by OSPAR in the List of Chemicals for Priority Action in 2000 [59].

Most of the pesticides mentioned above are well known and much research on them has been conducted in the field of freshwater studies. However, compounds such as acrylonitrile, aramite, isobenzane and kelevan (Fig. 6) all taken from the HELCOM list, will appear somewhat exotic to most readers. Again, the selection procedure has to be consulted. For its prioritization procedure, HELCOM self-evidently took the situation in the Baltic into account, which is not done by either DYNAMEC or COMMPS, which are not region specific. In the Baltic, there are certain physical, chemical and biological features that (may) increase the vulnerability of this ecosystem to anthropogenic chemicals, and that differ from the marine or freshwater environments addressed in the OSPAR and EU framework [60]. For example, the Baltic is a semi-enclosed sea with a large catchment area, which will have obvious implications (e.g., for trapping chemicals, stocking up chemicals in anoxic, deep sediments, the occurrence of stable hot-spot sedimentation areas and a high input of hazardous substances). There are also socio-

economic factors that may contribute to market occurrence and use of hazardous substances and that differ significantly from those on the EU market (e.g., the chemicals market and stocks of outdated hazardous chemicals in the Baltic countries, Poland and Russia). One example is the use of acrylonitrile in synthetic soil blocks as a grain fumigant and a pesticide; it was banned in Estonia in only 1999 [60]. The same is true for aramite, an extremely efficient miticide/acaricide used in the protection of fruits, vegetables and non-food plant crops from predation by mites (IRPTC). For insecticides isobenzane and kelevan, essentially no information is available concerning production, marketing and use – a situation typical for the Baltic area.

Good examples of “new” organohalogens are the polybrominated flame retardants (BFRs) that have attracted increasing interest from the community of environmental scientists in the past five years [61,62]. BFRs comprise compounds such as PBDEs, TBBP-A and brominated cycloaliphatic compounds such as HBCD. The annual world production of PBDEs has been estimated at 40,000 tonnes [63]. The use of PBDEs in the EU in 1994 was estimated at 11,000 tonnes [63] with a 75% contribution of deca-BDE. In 1999, over 9,200 tonnes of HBCD were used in the EU [63]. BFRs are persistent, bioaccumulate and are often transported over considerable distances. So far, most efforts in this field have been dedicated to the BDEs.

Concentrations in the various compartments of the marine environment are at least an order of magnitude lower than those of the CBs. However, most of the BDEs



are still being produced and concentrations in the environment are reported to be increasing (e.g., in human milk, Beluga whales, guillemot eggs, marine mammals and sediments) [63,64]. A recent survey of marine sediments in estuaries discharging into the North Sea showed deca-BDE concentrations from less than 0.5–1700 µg/kg dry wt. The highest level was detected in the Mersey Estuary, at a site formerly used for dumping sewage sludge and an area with much textile industry. The next highest level, 200 µg/kg, was detected in the Scheldt Estuary [63], close to a production site. In marine mammals, such as the sperm whale, BDE concentrations of about 100 µg/kg were found in blubber, which indicates that these compounds have reached deep ocean waters [61] and supports the hypothesis of long-range transport.

In this category, one should also mention short-chain chlorinated paraffins (SCCPs). They are formed by the chlorination of *n*-paraffins with chain lengths of 10–30 C-atoms and a chlorination degree of over 48 wt% [65,66]. SCCPs are very persistent and adsorb strongly to sludge and sediments and rapidly accumulate and biomagnify in aquatic food chains [67]. They are therefore included on the OSPAR List of Chemicals for Priority Action and are classed as PHSs under the WFD. The 25th Adaptation to Technical Progress to the Dangerous Substances Directive 67/548/EEC has formally classified SCCPs as Category 3 carcinogens, and as dangerous for the environment. Releases of SCCPs to water from production or usage sites in the EU were estimated at some 1800 tonnes/year, 95% being from metal-working sites [66]. In past decades, SCCPs have mainly been produced for use in metal-working fluids (70%), but also as plasticisers (14%) and flame retardants (12%) [65,66]. In the mid-1990s, the annual production in Europe was of the order of 15,000 tonnes, but has been decreasing since then [66]. SCCPs have been found in a variety of water bodies and sediments, and also in fish and marine mammals [68–70]. However, generally speaking, there is a lack of environmental data on SCCPs, which reflects the lack of sensitive, quantitative analytical procedures. Most published methods are qualitative because even sophisticated capillary GC cannot create sufficient separation of the very many congeners. There also is a lack of suitable standards and, consequently, little information on relative response factors of individual congeners [70–72]. We address this problem further in Section 5 below.

In view of the current concern about EDCs, this category – which is recognised by all programmes except UNEP POP – also deserves some attention. Although many of the “old organochlorines” discussed above are also suspected to be EDCs, the alkylphenols have received specific attention in recent years. They are used to produce phenolic resins and alkylphenol

polyethoxylates for use as surfactants in cleaners, wetting agents and emulsifiers [73]. Pentachlorophenol (PCP) is mainly used as a biocide in the wood industry. In the EU, production of PCP and its sodium salt was terminated in 1992. Today, these chemicals are imported from the USA. Production figures of octylphenol (OP), nonylphenol (NP) and nonylphenol ethoxylates (NPEOs) were some 25,000, 75,000 and 120,000 tonnes/year, respectively, in the late 1990s [74,75]. Alkylphenols and short-chain alkylphenolethoxylates have fairly high $\log K_{ow}$ values (typically 4–6) and will therefore accumulate in sediment and, also, in marine biota [74–76]. OP was detected in water with concentrations of up to 13 µg/l in estuaries, but only up to 0.016 µg/l in coastal waters [74]. As for NPEOs, concentrations up to 9.5 mg/kg dry wt were found in the livers of river fish [75]. PCP has been detected in water, sediments and a large number of aquatic organisms. The Euro Chlor Risk Assessment for the Marine Environment showed that PCP concentrations are up to 0.8 µg/l for the North Sea, coastal waters and estuaries [77]. Recent literature shows that PCP concentrations in surface water and the marine environment of Western Europe are decreasing [78].

Although persistence and bioaccumulation are important factors in the selection process, these are not always decisive; Table 2 features many VOCs, such as benzene, 1,2-dichloroethane, dichloromethane, trichlorobenzenes and trichloromethane. These well-known atmospheric contaminants are mostly important industrial compounds with high annual production [79], which can be anywhere in the range from several hundred thousand tonnes (e.g. tetrachloromethane) to more than 10 billion tonnes for benzene [79–81].

The low $\log K_{ow}$ values of the VOCs – typically 1–2 – led to the general belief that bioconcentration should be considered insignificant [82]. As a consequence, and also because of the considerable problems associated with the determination of VOCs, specifically in biota, there is a general lack of information. However, recent studies showed the general presence of several VOCs in the tissue of marine organisms from different levels of the food chain [83] with concentrations in marine organisms that are up to 1000-fold higher than in the surrounding water. The bioconcentration factors calculated from these data were generally higher than those reported in the literature, possibly due to the continuous exposure of the organisms to (very) low levels of these compounds in the water column. Determination in the water column alone is therefore insufficient.

Finally, amongst the group of miscellaneous organic chemicals, which was generated entirely by the OSPAR DYNAMEC procedure, several entries do not appear to be obvious choices. Discussion of a few examples seems to be of interest:

- Clotrimazole is a pharmaceutical that is mainly used for treatment of dermatological and gynaecological fungal infections. It was selected by the OSPAR procedure on the basis of its resistance to biodegradation and its toxicity [84].
- Hexamethyldisiloxane (HMDS) is used as an intermediate in the synthesis (e.g., of polymers) and as an ingredient in personal-care products and solvents. In 2000, the total production of HMDS in the EU was 4025 tonnes [85]. The rather high production, and also the persistence of HMDS probably led to its inclusion in the OSPAR list. A recent assessment of the environmental risk of HMDS concluded that it poses no risk to the marine environment on the regional scale, but that there is a potential risk on the local scale [85].
- Finally, 4-*tert*-butyltoluene is used primarily as a raw material in the production of *p*-*tert*-butylbenzoic acid, which is utilised in the manufacture of unsaturated polyesters and alkyd resins [86]. The compound was selected on the basis of its ability to bioaccumulate and its persistence, although it shows low acute aquatic toxicity [86].

5. Monitoring: conclusions and trends

5.1. Future monitoring in the North Sea

There has been monitoring in the North Sea for a long time, and is still greatly influenced by OSPAR. This could easily lead to the conclusion that the OSPAR list mentioned above will constitute the list of compounds for future monitoring in this ecosystem. However, as the WFD list is legally binding for EU countries, many of which are contracting parties to OSPAR, and, as the European Marine Strategy (EMS), in a way, potentially extends the WFD into the open sea [87], the list proposed by the WFD will, in our opinion, be the main driving force for future monitoring in the North Sea. OSPAR has already studied the compatibility of its own monitoring programme with that of the WFD. It also has recently decided that it would like to let the EU take the lead in future decisions on prioritisation of hazardous substances [87]. Furthermore, the Stockholm UNEP POP Convention is a global convention and commitments made in this framework supersede all regional obligations. This means that the agreed list of 12 POPs (see Table 2) should become part of all national and regional surveys – or that, at the very least, information should be gathered concerning their presence in the environment.

In Table 3, we have tried to summarise the above by indicating which OMPs will probably be important for future monitoring of the North Sea. Our selection is primarily based on the WFD list but, in contrast to the conclusions of the WFD, some additional OSPAR pri-

ority substances and the “old” organochlorines are still included in our list, partly because they are on the UNEP POP list but also because of their environmental relevance. For most groups of compounds in this category, it still has to be decided which congeners or isomers will have to be monitored. Although several lists of congeners are currently accepted, they may need to be revised. For example, we have already mentioned that the selection of CB congeners is limited to a number of key CBs, such as the ICES 7, while the highly toxic planar CBs (non-ortho and mono-ortho CBs) are not included in most cases (see Section 4). We recommend that these congeners should become part of future monitoring activities, as is already the case for the Arctic.

A similar decision should be taken for the CCD/Fs – with the 17 2,3,7,8-substituted congeners being an obvious choice – and the PAHs, where the 16 EPA priority PAHs are a good set of candidates. More problems will no doubt be encountered with the PCNs and PBDEs. Analysis of these less exhaustively studied compound classes does not appear to be particularly difficult, but, until very recently, a lack of standards for the individual congeners and, more importantly, the paucity of PTB data prevented a well-founded choice being made. Toxaphene and the SCCPs – both comprising many thousands of congeners and isomers – require still more attention. In this case, adequate separation has, so far, met with dramatic problems (see Section 5.2).

As a consequence, the synthesis of properly selected congeners and an in-depth study of PTB characteristics are still in their infancy.

From Table 1, Section 1 and the discussion on monitoring programmes in Section 2, it is clear that a substantial number of the (groups of) compounds included in Table 3 are currently not being monitored routinely in the marine environment. However, this should not be taken to imply that suitable analytical methods have not been reported and/or that no survey-type information on these compounds is available. With respect to analytical methods, which are discussed in some more detail in Section 5.2, the right-hand side column of Table 3 clearly indicates that the number of problems is limited. As regards survey information, there have been several promising, but rather short-term studies conducted by specialized laboratories, for example on musk xylenes [88,89], on VOCs [83,90,91] and also on emerging pollutants, such as tri-(4-chlorophenyl)-methanol and tri-(4-chlorophenyl)-methane in flatfish [92]. The results of a survey of VOCs in eel [90] prompted the Flemish Government to consider including these compounds in its eel-monitoring programme, as well as heavy metals and CBs.

As for the list of matrices included in Table 3, our preference is based on both experimental evidence taken from the literature and, more simply, the generally

Table 3. List of OMPs expected to remain and/or become priority target compounds for the North Sea area		
(Groups of) substances	Preferred matrices	Analytical methods available*
“Old” organochlorines		
Aldrin	sediment, biota	GC-MS
Chlordane	sediment, biota	GC-MS
DDTs	sediment, biota	GC-MS
Dieldrin	sediment, biota	GC-MS
Endosulphan	sediment, biota	GC-MS, LC-MS
Endrin	sediment, biota	GC-MS
Heptachlor	sediment, biota	GC-MS
Hexachlorobenzene	sediment, biota	GC-MS
HCHs (e.g., lindane)	water, sediment, biota	GC-MS
Metoxychlor	water, sediment, biota	GC-MS, LC-MS
Mirex	sediment, biota	GC-MS
PCBs	sediment, biota	GC-MS, GC-ECD
PCDDs	sediment, biota	GC-MS, GC-ECD
PCDFs	sediment, biota	GC-MS, GC-ECD
PCNs	sediment, biota	GC-MS, GC-ECD
Toxaphene	sediment, biota	GC-MS**
“New” pesticides		
Alachlor	water, sediment, biota	GC-MS, LC-MS
Atrazine	water, sediment	GC-MS, LC-MS
Chlorfenvinphos	water, sediment	GC-MS, LC-MS
Chlorpyrifos	water, sediment	GC-MS, LC-MS
Dicofol	water, sediment	GC-MS, LC-MS
Diuron	water, sediment	LC-MS
Isoproturon	water, sediment	LC-MS
Simazine	water, sediment	GC-MS, LC-MS
Trifluralin	water, sediment	GC-MS, LC-MS
VOCs		
1,2,3-Trichlorobenzene	water, sediment, biota	GC-MS
1,2,4-Trichlorobenzene	water, sediment, biota	GC-MS
1,2-Dichloroethane	water, sediment, biota	GC-MS
1,3,5-Trichlorobenzene	water, sediment, biota	GC-MS
Benzene	water, sediment, biota	GC-MS
Dichloromethane	water, sediment, biota	GC-MS
Trichloromethane	water, sediment, biota	GC-MS
PAHs		
Priority set and/or individual PAHs	sediment, biota	GC-MS, LC-FLU or LC-MS
“New” organohalogenes		
BFRs: PBDEs, HBCD, TBBP-A	sediment, biota	GC-MS/LC-MS***
Hexachlorobutadiene	sediment, biota	GC-MS
Pentachlorobenzene	sediment, biota	GC-MS
SCCPs	sediment, biota	GC-MS**
Endocrine disruptors		
NP/NPEOs and related substances	water, sediment, biota	LC-MS
Octylphenol	water, sediment, biota	LC-MS
Dibutyl and diethylhexyl phthalate	water, sediment, biota	GC-MS***
PFOS	water, sediment, biota	LC-MS
*“MS” comprises all current techniques, primarily quadrupole, triple quadrupole, ion-trap and time-of-flight MS.		
**Adequate analysis is not yet possible.		
***Analysis has been described but there are still problems.		

observed accumulation of hydrophobic compounds in sediment (and biota). Here, it is also of some interest to note that the WFD is currently in the process of proposing the water column as the most appropriate matrix for its list. This is mainly because environmental quality

criteria (based on toxicological tests) are mostly available for the water phase and cannot be converted directly to sediment or biota. However, in our opinion, this is not a fortunate choice in view of the fact that many apolar compounds are listed in Table 3. Marine scientists have

amply demonstrated that sediments and biota are much more suitable sample types for such analytes, while water is a proper matrix for more polar compounds (e.g., the “new” pesticides, which are indeed frequently detected in coastal and estuarine waters).

5.2. Analytical procedures

Fig. 7 outlines the analytical strategy generally used to arrive at the desired outcome, the concentration data of the target analytes. The sampling process itself is not included in the flow chart. Suffice it to say that sampling at sea is very expensive and labour-intensive, frequently with a substantial reduction of the number of samples collected compared with that initially intended, owing to bad-weather conditions in the sampling area and/or technical difficulties. To quote an example, an estimated 9% of the intended data were not received for the Belgian

sediment monitoring programme in the North Sea in the period 1990–2003, because of the conditions at sea, but virtually none due to errors made during the analysis in the laboratory.

5.2.1. Sample preparation. As far as water samples are considered – and, consequently, the more polar analytes of Table 3, such as the modern pesticides and the NP/NPEOs – liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are essentially the only techniques in use. Rather large sample volumes of, typically, 5–20 l are collected and analyte extraction is done on board the ship to minimize analyte degradation and to facilitate transport.

Detailed information on a few selected procedures is presented in Table 4, taken from an extensive recent study by Steen [93]. One important aspect is that

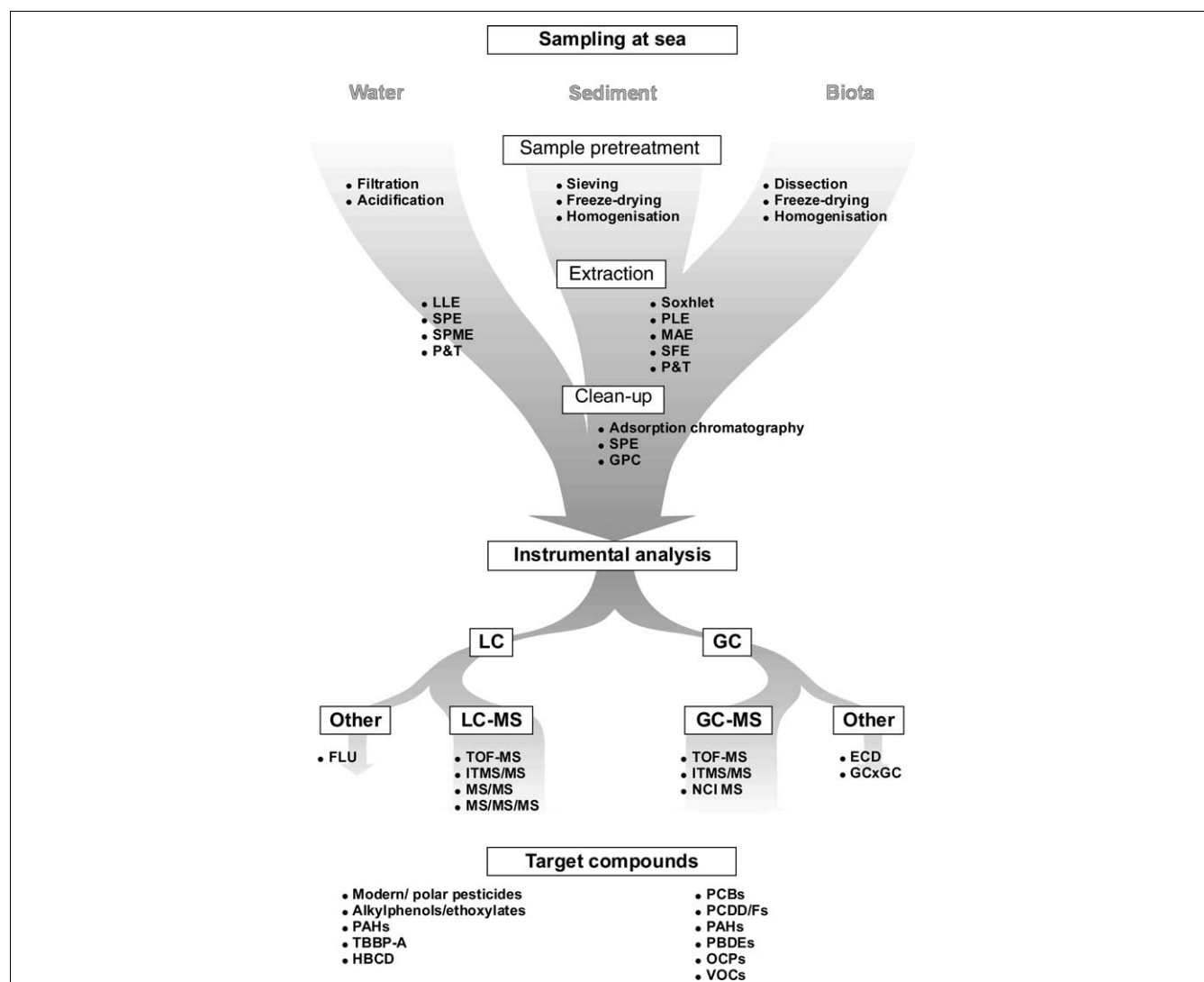


Figure 7. Analyte strategies for the determination of organic micro-contaminants in the main marine environmental matrices, water, sediment and biota.

Table 4. Examples of large-volume extraction methods for the determination of pesticides in river and marine waters from Steen [93]

Compounds	Water sample	Sample volume (l)	Extraction technique, solvent and/or sorbent	Analysis	LOD (ng/l)	Ref.
Acidic compounds	River	20	GLSE ^a ; DCM	GC-MSD	1–10	[94]
Model substances including pesticides	Sea	10	SPE; 2 g SDB-1 ^b	GC-ITDMS	0.1–0.7	[95]
Triazines, OPPs ^c , acetanilides	River/estuarine	10	SPE; stacked cartridges 2–4 g GCB ^d or 10 g C18	GC-MS	0.5–3	[96]
Triazines, OPPs, acetanilides, OCPs	Marsh	10	SPE; 90 mm C18 disks	GC-MS	0.05–2	[97]
Triazines	Sea	5	SPE; 47 mm C18 disks	GC-NPD or GC-MS (SIM)	0.02	[98]
Triazines	River/estuarine	5	LLE; DCM	GC-MS	0.1	[99]
Acidic herbicides, bentazone	Estuarine	5	SPE; 47 mm SDB disks	LC-DAD UV	50–100	[100]
Triazines, OPPs, acetanilides, TP ^e	River and simulated sea	4	SPE; 47 mm C18 disks	LC-DAD UV	10–20	[101]

^aGLSE, Goulden large-sample extractor.^bOn-line filtration-extraction with styrene-divinylbenzene copolymer (SDB).^cOPP, Organophosphorus pesticides.^dGCB, Graphitised black carbon.^eTPs, Transformation products.

on-line filtration and extraction of the target analytes from river and estuarine samples with high suspended-particulate-matter concentrations and DOC contents may well take 10 times as long as from relatively clear marine waters. This should be kept in mind, especially when consulting one or more recent reviews on sample preparation of aqueous samples for subsequent analysis by GC-mass spectrometry (GC-MS) (off-line and on-line) or liquid chromatography (LC)-MS (usually on-line); their focus generally is surface water and groundwater rather than water from estuaries or the open sea [102–105]. One should also consider that the limits of detection (LODs) that have to be achieved for the marine environment, are much lower – i.e. 1–5 ng/l – than the, typical values of about 100 ng/l quoted in such reviews.

The analysis of biota and sediments requires the use of extraction techniques that allow the release of the analytes from the matrix. Soxhlet extraction – including modifications, such as hot Soxhlet extraction, the use of binary non-polar/polar solvent mixtures and semi-automated Soxtec – is still the benchmark and is most commonly used for extracting virtually all (classes of) analytes in Table 3, even emerging contaminants, such as the PBDEs [8,105,106]. However, there have been numerous attempts to find alternative procedures that are less time-consuming, use less solvent and/or enable miniaturisation. Amongst these novel approaches are pressurized liquid extraction (PLE) and related sub-critical water extraction (SWE), microwave-assisted extraction (MAE), matrix solid-phase dispersion (MSPD) and ultrasound (US) extraction. Supercritical fluid extraction (SFE), an older and frequently less appreciated technique, should be added to this list because of its fat-removal potential.

Due to the low selectivity of most of the quoted techniques, the crude extracts usually contain a large number of interfering compounds – frequently in relatively large amounts – and further clean-up and/or fractionation is required. Conventional and well-documented procedures are solid-liquid adsorption in open columns packed with, e.g., Florisil, silica or alumina, and off-line or on-line SPE on a variety of bonded silicas or gel permeation chromatography. Specifically, when ultra-trace analysis at the low ng/kg level has to be performed – as, e.g., for planar CBs and priority CDD/Fs – carefully optimised multi-step procedures have to be applied [8,106–109].

To illustrate the general interest in introducing the novel techniques, a series of selected applications is summarised in Table 5. There is little doubt that modern extraction techniques will at least partly replace traditional methods, because they fulfil some of the demands mentioned above. However, a variety of techniques and different sets of optimum conditions will always be needed, because of the highly divergent analyte/matrix combinations that have to be considered. Consequently, there is little need to discuss the quoted, or other similar, examples in detail; it is the general trend in sample preparation that requires our attention. Even so, it is worthwhile to stress a few aspects of interest.

From among the techniques mentioned, PLE has – so far – been most successful, even though care has to be taken that no decomposition of thermolabile compounds occurs during extraction. Interesting modifications include in-cell clean-up of samples by blending them with, e.g., Florisil, alumina or a chemical used for extract purification in classical procedures [110], and using a small carbon column in the extraction cell, which selectively adsorbs dioxin-like compounds (subsequently isolated by back-flushing with toluene) [111]. PLE and

Table 5. Selected applications of novel extraction procedures for OMPs in solid matrices^{*,**}

Compounds	Matrix	Pre-treatment	Clean-up	Analysis	Ref.
PLE [110,114–116]					
PAHs	mussel	freeze-dry	GPC	GC-MS	[117]
PAHs	sediment	air dry, sieve		GC-MS	[118]
4-NP	sediment	freeze-dry, grind, sieve	Al ₂ O ₃	LVI-GC-MS	[119]
PCBs, OCPs	fish (CRM)	Na ₂ SO ₄	GPC	GC-MS	[117]
SCCPs	fish muscle	Na ₂ SO ₄	GPC, Florisil	GC-ECNI-MS	[120]
NP/NPEOs	marine sediment		SPE	LC-ESI-MS	[121]
PFOS	sewage sludge	freeze-dry	oxidative digestion, SPE	LC-MS and LC-MS ²	[122]
SWE [110]					
PAHs	marine sediment	dry, homogenise	In-cell SPE	GC-MS	[123]
PCBs	sediment	dry, sieve	SPME	GC-ECD	[124]
BFRs	sediment	dry, homogenize, sieve	On-line Tenax	LVI-GC-ECD	[125]
MAE [126]					
PBDE	marine mammals		GPC, SiO ₂	GC-MS	[127]
PCBs, HCHs,	fish tissue	freeze-dry	GPC	GC-MS	[128]
DDTs, toxaphene					
Trichlorobenzenes	fish tissue	homogenise	Al ₂ O ₃ , SiO ₂ , Na ₂ SO ₄	GC-ECD	[129]
US [112]					
Phthalates	river sediment			GC-MS	[130]
NP/NPEOs	estuarine sediment	drying	RP-LC	LC-ESI-MS	[131]
PAHs	sewage sludge				[132]
SFE [114,133]					
PBDE	sediment	drying, mixing and Cu		GC-MS	[134]
PCBs	harbour sediment (CRM)	Na ₂ SO ₄ and Cu		GC-MS	[135]
PCBs, DDTs	fish muscle	freeze-dry		GC-MS	[136]
NP/NPEO	mussels, sediment		SiO ₂	GC-MS	[137]
MSPD^{***} [138]					
Pharmaceuticals	river sediment		SPE	LC-ESI-MS ² and LC-APCI-MS ²	[139]
NP/NPEOs	fish tissue	homogenise		LC-FLU	[140]

*Step in-between pre-treatment and clean-up.

**For recent reviews, one is referred to the references added to the sub-headings.

***MSPD, Matrix solid-phase dispersion.

MAE have the shared advantage over SFE that they are matrix-independent, which facilitates method development. Essentially, SWE is a PLE-type procedure with water as the extraction solvent. In contrast to PLE, pressure has no effect and only the temperature has to be optimised. Admittedly, SWE causes extracts to be rather diluted but, as water is the solvent, (on-line) combination with SPE, LC and/or solid-phase microextraction (SPME) opens interesting perspectives [110]. Recent years have seen increased use of US-based techniques for isolating analytes from solid samples. With most applications, extraction efficiency is fully satisfactory, and sonication time often is 30 min or less. Volatile and/or thermolabile compounds can be handled, since high temperatures are not used [112].

As far as sample preparation is concerned, VOCs are the only group of compounds in Table 3 that require a totally different approach. For these compounds, extraction is invariably based on their high volatility and

is, therefore, matrix independent. Dynamic headspace techniques, usually called purge-and-trap (P&T), have emerged as the leading technique for marine samples [91]. Other techniques, such as static headspace, SPME and membrane inlet mass spectrometry (MIMS), can also be applied, but, because of the low VOC concentrations (ng/kg range) in marine samples, LODs obtained when using these methods are generally not satisfactory. P&T has proved to be an exhaustive, reliable technique. Unfortunately, it is also labour-intensive and requires rather complex instrumentation [72,80,113]. However, if sample volumes can be kept small (<200 ml), partial automation of the procedure is possible. No clean-up is required and the P&T device can be coupled directly to GC-MS.

The only serious interference is caused by the considerable amounts of water vapour generated during purging. This is particularly so for solid samples, such as biota and sediment, where elevated temperatures (of up

to 70°C) are required to force the VOCs out of the sample. On-line water removal via a cold trap has then to be included. Under these conditions, foaming is regularly observed for biota samples. However, this drawback can easily be solved by adding some *n*-octanol to the sample [141].

5.2.2. Instrumental analysis. Although it may come as something of a surprise, there is little doubt that, for priority hazardous substances, such as those considered in Tables 2 and 3, GC-based analytical procedures will remain predominant in years to come. After all, most priority compounds have been selected on the basis of their PTB properties and are low-polarity compounds, which are ideally suited for analysis by means of GC-MS. One example was already mentioned above (viz on-line and automated P&T-GC-MS of sometimes up to 30–50 VOCs in sediment and biota [83,142,143]).

GC-MS is, of course, also the preferred separation technique for the “old” organochlorines as well as most “new” organohalogenes. However, here, the overall picture becomes somewhat more complicated. On the one hand, detection for screening purposes of, specifically, Cl-containing target analytes, is still most conveniently done with an electron-capture detector (GC-ECD). For identification and confirmation, next to conventional GC-MS, the use of ion-trap with its tandem MS (MS^2) option (ITMS²) – i.e., increased selectivity – is receiving increased attention. GC-ITMS is a less expensive alternative to high-resolution mass spectrometry (HRMS), which is commonly used to determine PCDD/Fs [144]. For the rest, GC-negative chemical ionization (NCI)-MS is a highly rewarding technique for organobromine compounds, toxaphene and organochlorines that contain more than five chlorine atoms. However, there are also several separation problems – sometimes primarily related to obtaining adequate resolution between analytes and matrix constituents, and sometimes to satisfactorily separating the analytes contained in a priority “group of substances” from each other. This aspect is briefly discussed in the following paragraphs.

Recent years have witnessed the emergence of so-called comprehensive two-dimensional gas chromatography (GCxGC) – a technique that can be used to considerably improve analyte/matrix as well as analyte/analyte separation. Briefly, a combination of a non-polar column and a (semi-)polar column is used, with a conventional 25–30-m long first dimension column, and a short, 0.5–1-m long, second-dimension column. The columns are connected via an interface called a modulator. The latter device serves to trap, and focus, each subsequent small effluent fraction from the first-dimension column and, then, to launch it into the second column. In order to maintain the integrity of the first-column separation, every peak should be modulated as three or four fractions. Consequently, the second-

dimension separation has to be very rapid – and therefore essentially isothermal – a process with a duration of, typically, 3–6 sec. The main advantages of the comprehensive approach are that:

- the entire sample (and not one or a few heart-cuts, as in conventional multidimensional GC [145]) is subjected to a completely different separation;
- the two-dimensional separation does not take any more time than the first-dimension run; and,
- the re-focusing in the modulator helps to increase analyte detectability.

A most interesting additional benefit is that structurally related compounds (e.g., PCB or PCDD/F congeners with the same number of Cl substituents) show up as so-called ordered structures in the two-dimensional GCxGC plane. A variety of published papers has shown that this is a powerful tool for the preliminary identification of unknowns [145]. The very rapid second-dimension separation requires the use of detectors with sufficiently high data-acquisition rates. Initially, only flame ionisation detectors (FIDs) could meet this requirement. However, today, there is also a micro-ECD (μ ECD) on the market, and it is widely used for GCxGC- μ ECD of halogenated compound classes. Even more importantly, analyte identification can be performed by using a time-of-flight mass spectrometry (TOF-MS) [146,147] or – with a modest loss of performance, but at a much lower price – one of the very recently introduced rapid-scanning quadrupole mass spectrometers [148,149].

Most studies on ordered structures in the field of organohalogen micro-contaminants deal with PCBs and (priority) PCDD/Fs [150–152]. One interesting observation is that, next to an ordering on the basis of the number of substituents, there is also – within each series of PCB congeners – an ordering due to the substitution pattern, with the non-ortho and mono-ortho congeners (i.e. the most toxic) ending at the top of the various lines. This provides a better separation from other analytes and facilitates their recognition. Very recently, GCxGC has helped to demonstrate the huge problems that still exist in the field of toxaphene and SCCP analysis, already referred to in Section 4.3. Partial unravelling of the composition of toxaphene – a technical mixture of, primarily, polychlorinated bornenes, but also bornanes, camphenes and camphanes – has for the first time unequivocally demonstrated the presence of series of pentasubstituted to undecasubstituted congeners, with a total number of individual constituents of over 1000 [153]. A typical GCxGC chromatogram is shown in Fig. 8 [153].

An even more complex situation is encountered with the SCCPs. On-going studies [154] show that what is usually an essentially unresolved large hump in one-dimensional GC now fans out into a large number of substructures. In this case, there is the additional complication that ordering occurs on the basis of both the

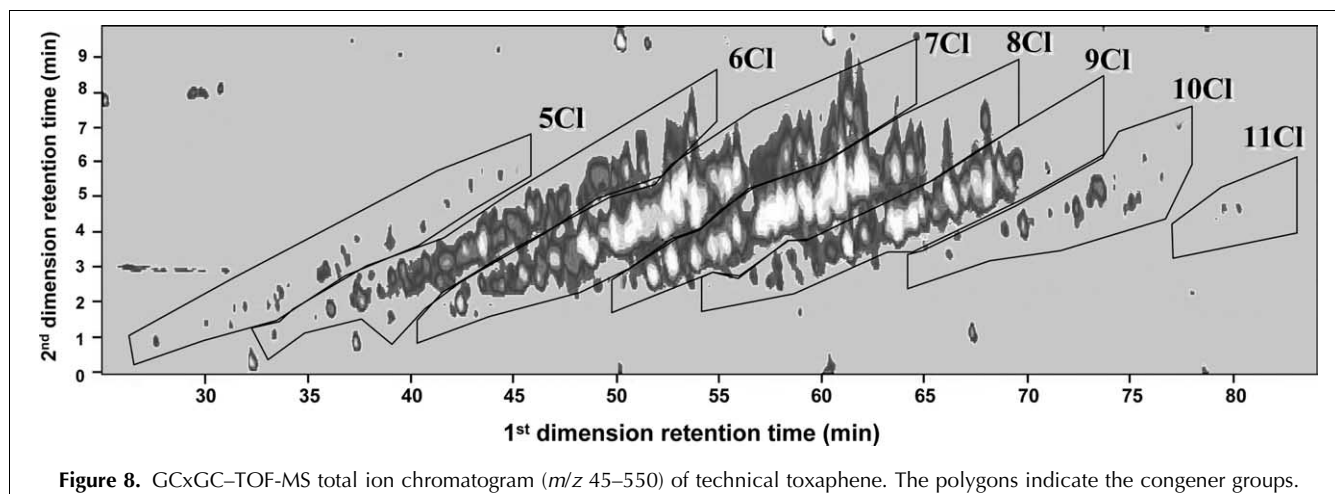


Figure 8. GCxGC-TOF-MS total ion chromatogram (m/z 45–550) of technical toxaphene. The polygons indicate the congener groups.

number of chlorine substituents and the carbon-skeleton length. In other words, whilst indicating that comprehensive separation techniques are demanded to solve analytical problems, as outlined here, the example also shows that more effort will be required to arrive at a satisfactory solution (viz the targeted analyses of the most toxic (groups of) congeners and isomers in such mixtures).

For most of the other (groups of) substances included in Table 3, there is less need to go into much detail. For example, as regards the majority of the modern pesticides, the phthalate esters and PAHs – which will also preferably be determined by means of GC-based procedures – ample ultra-trace level expertise is available from surface water, wastewater and estuarine water studies. Limiting ourselves for the sake of convenience to the pesticides, quite a number of papers show that these compounds have been detected down to ca. 1 ng/l concentrations in water form rivers and estuaries. LLE (off-line) and SPE (on-line and off-line) combined with GC-MS or more powerful GS-MS² are all suitable techniques and sample volumes can often be limited to 10–200 ml. A typical advantage of these analytical procedures – and this is also true for most of the LC-MS methods quoted below – is that they have been designed as multi-residue approaches. This means that if, in the near future, one or more related substances have to be added to the list, no further method development will be required, but only some (MS) parameter adjustment.

Today, the role of LC – almost exclusively reversed-phase LC – for monitoring and quantifying priority hazardous substances is still fairly modest, but rapidly becoming more important. One rather exceptional example is PAH analysis, where LC provides a more satisfactory overall separation of the target analytes than GC. An additional benefit is that LC-fluorescence (LC-FLU) detection is a highly sensitive and selective method of analysis for essentially all priority PAHs. With BFRs,

such as TBBP-A and HBCD, LC-MS is the preferred approach because the analytes of interest easily degrade in GC systems – mainly due to interaction with liners or column walls. In addition, GC cannot separate the three diastereomers of HBCD, while this separation is easily accomplished on a C₁₈ LC-column with a methanol/water gradient [155]. Unfortunately, there is a loss of detectability of about 1000-fold compared to GC-MS. At present, the method is therefore suitable for only highly polluted samples, such as fatty fish and sediments; for other applications, suitable trace-enrichment procedures will have to be applied. Further, from amongst the modern pesticides, phenylureas, such as diuron and isoproturon, have to be subjected to LC-MS or LS-MS² analysis because of their poor thermal stability and the unsatisfactory nature of most derivatisation procedures. Fortunately, published methods for these pesticides, as well as acetanilides, which use SPE combined with LC-ESI-MS², yield fully satisfactory LODs of 0.2–2 ng/l [93].

From among the fluorinated organic micro-contaminants, notably surfactants, PFOS is attracting most attention from environmental scientists. Initially, fluorinated surfactants were analysed by means of GC-MS after derivatisation. Today, direct analysis by means of LS-MS² in the electrospray ionization (ESI) mode is preferred [122,156]. The method has been used successfully, down to the low ng/g level, for biota, sediment and water samples. In seawater, PFOS and several related contaminants have even been determined down to the low pg/l level [157].

For another class of compounds, the alkylphenols and alkylphenol ethoxylates (OP, NP/NPEOs) a rather similar situation is encountered. Earlier GC-MS procedures required derivatisation for all but the most volatile target analytes (and, then, admittedly, sometimes yielded isomer separations not found in LC [106]), and are now being superseded by LC-ESI-MS and LC-ESI-MS² which

enables the direct determination of all analytes of interest. In this case, both normal-phase and reversed-phase LC are used; normal-phase LC allows the separation of the NPEOs according to the number of ethylene oxide units, whilst reversed-phase LC aims to distinguish the hydrophobic moieties (alkyl homologue separation) [106,158].

An interesting discussion of the huge polarity differences of the various types of analytes in the alkylphenol (ethoxylate) classes and the consequences for the preferred mode of MS detection (ESI vs. APCI; positive vs. negative ion mode) has been presented by Reemtsma [159,160]. As with the modern pesticides (see above), with the quoted multi-residue methods, structurally related compounds can be added to the list without need for further method development. Specifically, with the “emerging pollutants” discussed here, this is a major advantage.

5.3. Quality assurance

Quality assurance (QA) of analytical measurements is receiving increasing attention and will continue to be a most important aspect in the future. To quote an example, a few years ago – i.e. during the 1998 OSPAR assessment of trends in the concentrations of some metals, PAHs and other organic micro-contaminants in the tissue of various fish species and mussels – some 30% of the data had to be rejected because of a lack of, or the insufficiency of, QA information [31]. Fortunately, most marine laboratories now routinely look at procedural blanks, analyse reference materials and participate in intercomparison exercises. However, this does not

invariably mean that the analytical performance of those laboratories has increased in the past decade as much as one would expect.

Increased attention to QA implies that analytical performance is under control and scientists can, consequently, identify problems and quantify the performance. However, when de Boer and Law [8] reviewed the analytical performance of laboratories for selected organochlorines and PAHs in the QUASIMEME Laboratory Performance Scheme (LPS) and other intercomparison exercises, they could not really observe the improvement in analytical performance expected because of the evolution of the various analytical techniques. This is illustrated in Fig. 9, in which the between-laboratory coefficient of variation (CV) is plotted against time for some typical OMPs. Even for a well-known compound, such as CB 153, the analytical performance has not greatly improved in the last decade and the situation is even worse for lindane. As is well known, there is an inverse relation between the concentration of the analytes and the CVs. de Boer and Law [8] therefore attributed the lack of improvement to a general decrease in the concentrations of micro-contaminants in the environment and, consequently, in the test samples. However, the question is: “Have concentrations changed all that much in the recent past?” [In our opinion, this is not so, as indicated by e.g. data on CB levels in cod, flounder, mussel and shrimp for the period 1983–93 [161] and in cod liver from the North Sea [162]].

de Boer and Law [8] also stated that, in the past, test samples were often not representative, as they had too

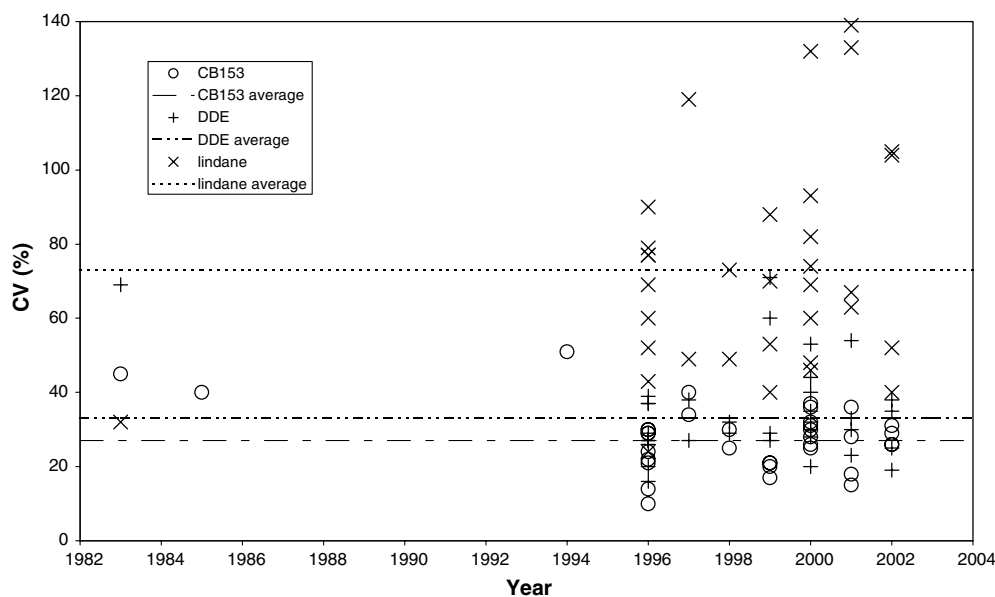


Figure 9. Plots of between-laboratory coefficients of variation (CVs) plotted against time for the determination of CB 153, DDE and lindane in various intercomparison exercises [8].

high concentrations and were therefore less difficult to analyse. For example, intercomparison exercises for CBs in biota were often run using fish oils that had much higher CB concentrations than fish tissue and were easier to process prior to analysis. This is a more valid argument because the QUASIMEME LPS has switched to real tissue samples in recent years. For lindane, this is indeed most probably the major factor contributing to the lack of improvement.

de Boer and Law [8] also mentioned that improved statistical methods, which reduce the effect of outliers, such as the recently developed Cofino statistics [163], may improve the picture. However, since marine scientists will continually be confronted with ever-smaller analyte concentrations, the QA requirements for many compounds included in Table 3 will certainly become more demanding.

5.4. Environmental variability

In addition to what has been said above about challenges in terms of sample treatment, instrumental analysis and method performance, there is one other item of interest that is, possibly, even more important. Future programmes will have to consider the interconnection between the frequency of sampling, the spatial distribution of sampling stations and the power of a programme to detect, often small, changes of concentrations – i.e. trends – in time and space. Specialized OSPAR, ICES and EU working groups are currently discussing these types of questions, but clear advice on, e.g., the desired degree of spatial and temporal distribution is still not available. However, such information is extremely important. For example, trend-detection programmes in OSPAR – and therefore also the statistics – are based on an annual sampling programme for a given region [164,165]. Nicholson et al. [166] studied the effect of both environmental and analytical variability on the possibility of detecting trends of contaminants in marine matrices. They estimated the performance of a temporal trend programme by calculating the detectable trend, i.e. the log-linear trend that would be detected after 10 years with a power of 90% using a test at the 5% significance level. [To quote an example, over a 10-year period a detectable trend of 10% corresponds with an increase of 146% or a decrease of 60%]. This is illustrated in Table 6 for what can be called low, medium and high environmental variability. The environmental variabilities in Table 6 were based on field data on mercury in fish liver for the OSPAR area and included the natural variability as well as variabilities caused by, e.g., the sampling programmes themselves.

Nicholson et al. concluded that, if the level of environmental variability is high, trend detection is poor, regardless of the level of analytical variability. It is instructive to see that, whilst improvement of the analytical performance has a significant effect on trend

detectability at low environmental variability, there is essentially no effect in the medium-to-high range. The medium environmental variability calculated here equals the median of that of the mercury data set in the OSPAR database, and it is safe to assume that very similar values will be obtained for most areas and most contaminants. Indeed, similar variabilities had already been calculated by de Boer and Brinkman [167] and could also be calculated in our work on Belgian monitoring data. As a result, one may well conclude that – even with excellent analytical performance characteristics – it will be difficult to detect trends of less than 10–15% over a 10-year period.

It is interesting to compare the above calculations with a very recent assessment by OSPAR of the data from its CEMP programme (see Section 2) for temporal trends and spatial distribution in organisms and sediments from the OSPAR area [168]. Two illustrative results are shown in Fig. 10, viz for CB 153 in biota and for fluoranthene in mussels; they are based on a 10-year monitoring study. In both cases, the outcome is seen to agree satisfactorily with the calculations, with the percentages of ca. 60% (less than 15%/year) and ca. 40% (less than 10%/year) for both analytes being somewhat better than expected. Since we know that the performance of the analytical procedures has not improved spectacularly in the recent past [62], one tentative conclusion might be that the environmental variability was “low” in a large part of the sampling area.

For the rest, there clearly is a need to study the environmental variability in more detail. From the literature [161,162,169], it is well known that cofactors (e.g., age, sex, fat content, grain-size distribution, organic matter content, seasonal variations and/or local situations) can all contribute to the total variability. In this context, it is slightly surprising that there is, in Fig. 10, so little difference between the data for CB 153, where data from different organisms were combined as “biota” and the data for the much more targeted study on fluoranthene, which was essentially for mussels only.

However, the beneficial influence of normalisation was clearly observed in the same OSPAR-CEMP assessment for, e.g., fluoranthene in sediments (Fig. 11). Fig. 11A shows that, as with the organisms, about 40% of the

Table 6. Trend detectability for varying degrees of analytical and environmental variability [166]

Environmental variability		Detectable trend (%) for analytical RSDs of:		
Group	RSD (%)	0%	12.5%	25%
Low	9.7	3.9	6.5	11.2
Medium	26.2	11	12	15
High	52.4	21	22	24

time series allows trends of less than 10% to be detected (again, a somewhat better result than expected on the basis of the data of Table 6). However, if the time series were normalised for the organic carbon content, C_{org} , and/or the fine fraction (FS) – i.e. the fraction $<63 \mu m$ isolated by sieving – the figures increased considerably, viz to ca. 55% (Fig. 11B and C). With the combined

C_{org} + FS normalisation, an annual trend of 15% or less can even be detected in three-quarters of all time series. To the best of our knowledge, this is the first time that environmental scientists have been confronted with sufficiently long and QA-assured time series collected over a wide area and in an international setting, which offer the possibility of studying the environmental vari-

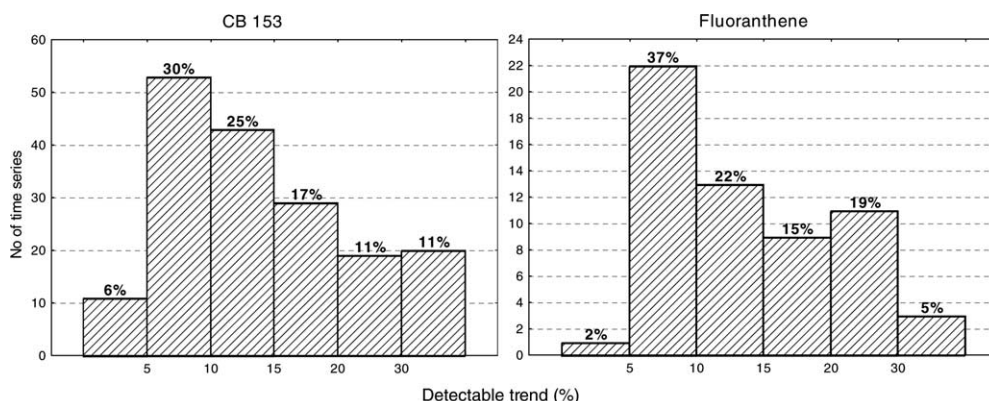


Figure 10. Detectable annual trend (indicated in bold) for the time series of CB 153 and fluoranthene in organisms (various fish species and mussels, respectively) from the OSPAR area, calculated for a 10-year dataset [168].

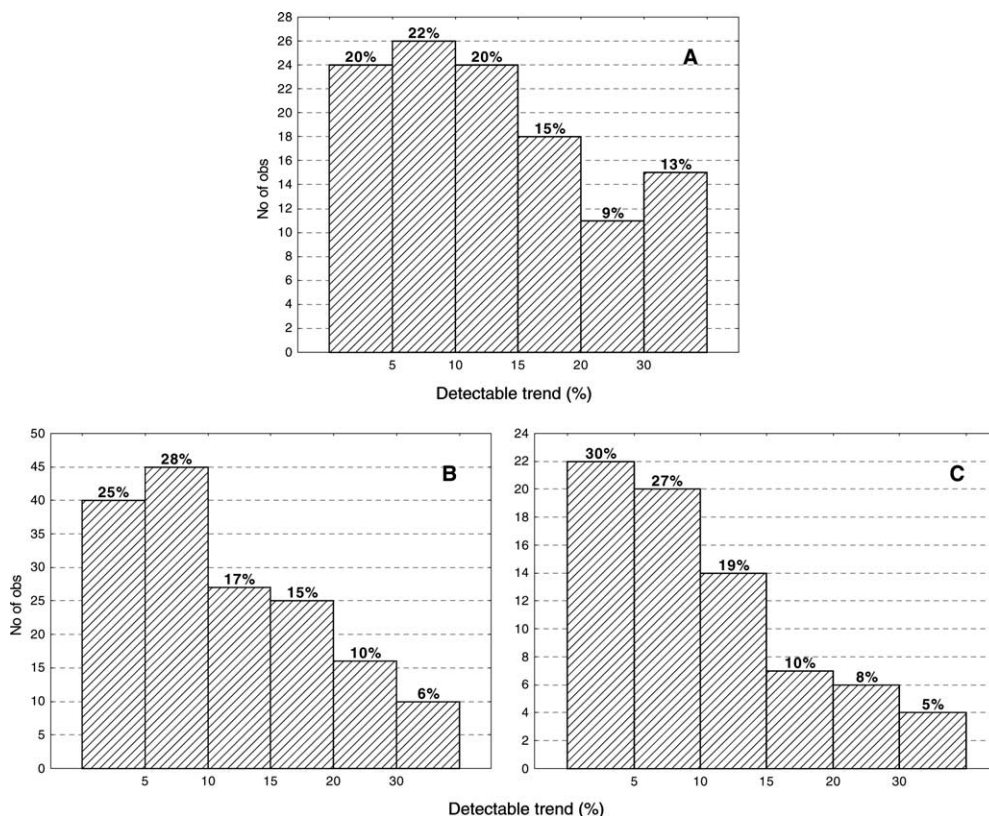


Figure 11. Detectable annual trend for the time series of fluoranthene in sediment; (A) not normalised; (B) normalised for C_{org} ; (C) normalised for C_{org} and FS all calculated for a 10-year dataset.

ability and the effect of normalisation in some detail [168]. Consequently, publication of the detailed report of the OSPAR assessment is eagerly awaited.

6. Conclusions

Today, there is a large – and, to the outsider, sometimes bewildering – number of international organizations, national, international, regional and sometimes global monitoring programmes, and increasing activity aimed at cooperation and quality assessment, which all deal with the study (primarily the monitoring) of OMPs in the marine environment. There is a tendency to move towards mutually supportive programmes, but implementation of this concept is still in its infancy.

Generally speaking, the (groups of) compounds considered priority hazardous substances in most programmes are the “old” organochlorines, the PAHs and several metals and their compounds. [For the organic pollutants, this emphasis can no doubt be explained on the basis of their adverse PTB characteristics]. In other words, long-term information is limited to these groups. Fortunately, in recent years, new and extended lists of OMPs have been published, with newly emerging organohalogens, a limited number of modern pesticides, VOCs, alkylphenols and alkylphenol ethoxylates, SCCPs and PFOS more prominent. An attempt at “harmonizing” several of such lists to arrive at a tentative OSPAR/North Sea area priority list is included in this review (see Table 3).

With respect to the trace-level determination of the various groups of target compounds in water, sediment and/or biota, a rapid search of the literature reveals that the number of pressing problems is limited. However, several aspects should be emphasized. While the pre-treatment of aqueous samples is essentially standardized (SPE or LLE approaches), there is much innovation in the field of solid-sample analysis (see Table 5) and further work in this area is recommended. Instrumental analysis is essentially limited to GC-MS (with GC-ECD as a robust alternative for screening of organohalogens) and LC-MS techniques. Specifically, the rapid progress in the field of MS-based detection – as manifest from the increasing use of ITMS, triple-quadrupole MS and TOF-MS – has helped to solve many analytical problems. Apart from the ultra-trace-level determination of the priority ortho- and mono-ortho CBs and CDD/Fs, the analysis of toxaphene (a mixture containing at least 1000 individual congeners and isomers) and the SCCPs will require special attention. In both substances, no known GC technique provides the required resolution and comprehensive GCxGC-TOF-MS will have to be used to arrive at something close to a satisfactory solution.

One positive aspect of the recent wish to start mutually supportive programmes and to pay more attention

to data quality, is that intercomparison exercises, QA and proper statistical evaluation of the experimental findings are highlighted in all current activities. As a spin-off, the effects of environmental variability on data interpretation, e.g., in trend analysis and for normalization purposes, are being studied more carefully.

Finally, government bodies, policy makers and experts involved in setting up programmes, as discussed in this review, should be aware that monitoring the marine environment is an expensive business. This is true because of the large cost of sampling at sea but, much more so, because calculations, as given above, indicate that, in order to detect an annual trend of 10% (a rather high figure in real life), a 10-year sampling programme is required. To add to the worries of those in office, the OSPAR-CEMP programme was conceived in the early 1990s as the result of a discussion that took several years – and it was based on an earlier programme that ran for more than a decade. The OSPAR-CEMP programme, which was modified several times over the years, has been running since then and has now yielded the extensive data set briefly discussed in Section 5. That inception phase of some 15 years is not unusual, as demonstrated by HELCOM. In this case, the convention was signed in 1974, but came into force only in 1980. Monitoring was then started immediately, but it required another seven years before, in 1987, the first assessment of the five-year period (1980–1985) could be made – 13 years after signing the convention.

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