

4.6 Newly Emerging Xenobiotics

New compounds are being developed continuously. Life Cycle Analysis (LCA) is an important feature in this development, but still no guarantee for environmental safety. In the marine environment, compounds are still being found that should have been eliminated in waste water treatment plants. Diffuse application is an uncontrollable source of many compounds. The need for ever more effective compounds and their great economic importance still results in powerful pollutants ending up in the environment. In this section, some compounds/groups of high political priority are described for the first time in a QSR Wadden Sea.

4.6.1 Brominated Flame Retardants (BFRs)

BFRs are widely produced and used throughout the world to reduce the flammability of materials, mostly synthetic polymers. Flame retardants (FRs) slow down the initial burn rate, thereby increasing the time span to 'flash-over', the moment that the generated heat sets all combustible materials on fire instantly.

The compound group belongs to the (halogenated) flame retardants ((H)FRs) and can be split into four different types (BSEF, 2000):

- Tetrabromobisphenol-A (TBBPA)
- Hexabromocyclododecane (HBCD)
- Polybrominated Biphenyls (PBBs)
- Polybrominated Diphenyl Ethers (PBDEs)

As BFRs are considered to be the most cost and performance effective, they constitute 25–39% of the global application of flame retardants, and are mainly used in construction materials (e.g. foams), electronics (e.g. circuit boards, plastic housing) and electrical isolation materials. Other groups of FRs are also in use, where the choice depends on the type of application. On the world market (1998) BFRs have a share of 39% (BSEF, 2000).

DeCarlo (1979) was the first to report on BFRs in environmental samples, but only recently have BFRs been recognized as an environmental problem by policy in the Water Framework Directive. Nearly 20 years later, BFRs were found in sperm whales (*Physeter physeter*) (de Boer *et al.*, 1998). Here, a parallel to the story of PCBs is apparent. Due to their high lipophilicity and bioconcentration the compounds HBCD, TetraBDE (BDE 52–81), PentaBDE (BDE 82–104) and HexaBDE (BDE 128–169) are considered to pose an environmental problem. Both lipophilicity and bioconcentration are determined by the bromination level, where molecular weights greater than 700 are highly lipo-

philic but have no tendency to bioconcentrate in fish (Hardy, 2004). Deca-BDE (BDE 209) is supposed to be one of these non-bioconcentrating BFRs, due to either a low uptake rate (Hardy, 2004; BSEF, 2000), or a rapid metabolism (Boon *et al.*, 2002). Recently, however, WWF (2004) showed by far the highest BFR levels in human blood serum for Deca-BDE. Since cases of bioaccumulation were all found in lung-breathers, the uptake of this group of compounds may be faster than the metabolism and/or excretion.

4.6.1.1 Inputs

Few data are available on riverine, atmospheric or point source inputs of BFRs. In a recent study at near-Wadden Sea locations, BFRs in wet precipitation were below detection limits (Peters, 2003).

In Europe two BFR manufacturing plants are located near the borders of the North Sea, *viz.* GLCC (Aycliffe, UK) and Dead Sea Bromine (Terneuzen, NL), and thus through sea currents connecting to the Wadden Sea. At the latter location high concentrations of HBCD were found in wet precipitation (Peters, 2003).

4.6.1.2 Concentrations in sediment

Historical data about BFRs in sediment of the Dutch Wadden Sea is shown in Figure 4.6.1. Deca-BDE (BDE 209) was by far the dominant BFR (emerging between 1965 and 1978) at a 10 to 20 times higher concentration than Tri-BDE (BDE-28), Tetra-BDE (BDE-47) and Penta-BDE (BDE 99).

Sediment concentrations in the Dutch North Sea coastal zone and Wadden Sea were reported by Åkerman *et al.* (2004) and Klamer *et al.* (2002). In both reports BFRs show highest maxima of BDE209 and HBCD in the Wadden Sea and off Terschelling both in sediments and suspended matter (Figure 4.6.2). Only the Western Scheldt at Hansweert (close to the Dutch-Belgian border) had

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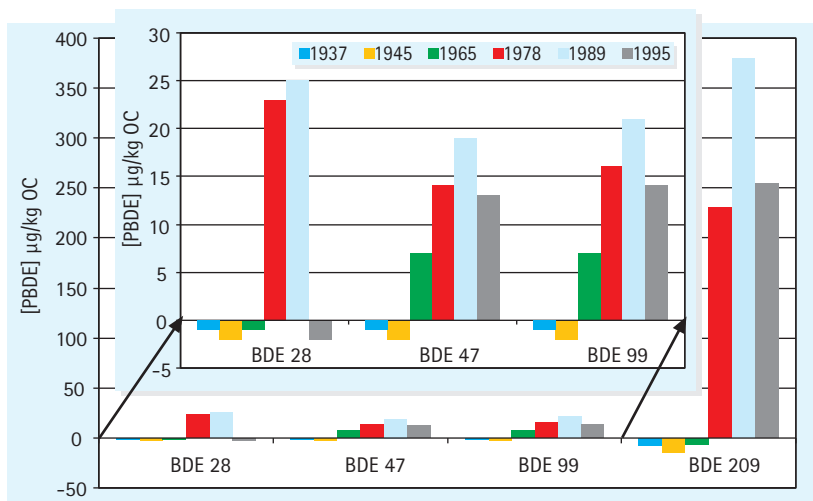
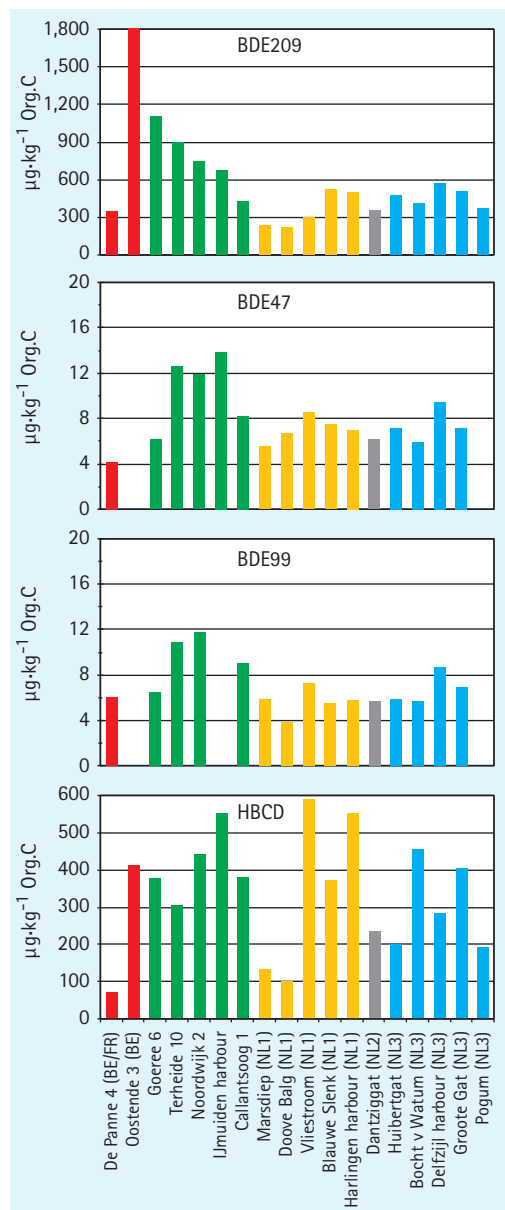


Figure 4.6.1: PBDE concentrations ($\mu\text{g kg}^{-1}$ organic carbon) in dated layers of a sediment core acquired at the western Dutch Wadden Sea. The insert shows the values of BDE 28, 47 and 99 at an enlarged scale. Concentrations below the detection limit are shown as negative values (source: Zegers *et al.*, 2003).

Figure 4.6.2: Contents ($\mu\text{g}\cdot\text{kg}^{-1}$ organic carbon) of poly-bromo-diphenylethers (PBDEs 209, 47, 99) and hexa-bromocyclododecane (HBCD) in suspended matter and along the Dutch and Belgian coast (BE), in the Dutch Wadden Sea and Ems estuary in 2003. Number following location name indicates the distance off the coast (km), (source: Åkerman *et al.*, 2004).



higher levels (data not shown). In 2003, BDE209 levels ranged from $25 \mu\text{g}\cdot\text{kg}^{-1}$ in suspended matter to $200 \mu\text{g}\cdot\text{kg}^{-1}$ in sediments. HBCD levels ranged from $30 \mu\text{g}\cdot\text{kg}^{-1}$ in suspended matter to $45 \mu\text{g}\cdot\text{kg}^{-1}$ in sediments (all levels normalized at 5% organic carbon).

4.6.2 PerFluorinated Octane Sulfonates (PFOS)

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) belong to the group of perfluorinated chemicals (PFCs), in which fluorine is strongly bonded to variable lengths of carbon chains (e.g. Teflon). PFOS and PFOA are synthetically produced or (PFOA) the break-down product of PFCs. The heat stable, persistent and both hy-

dro- and lipophobic properties of these compounds have found extensive application in repellents and coatings. The largest producer in the USA (3M) announced to phase out PFOS and PFOA in May 2000, due to revealed wide distribution of these compounds in wild life and humans (WWF, 2004).

4.6.2.1 Concentration in sediment and biota

In 2003, PFOS and PFOA were found in sediments of all Dutch freshwater and estuarine/marine locations investigated (Schrap *et al.*, 2004; Åkerman *et al.*, 2004). In Wadden Sea sediments PFOA was below the limit of detection of the not yet fully validated analytical procedure. PFOS contents ranged from $1.5\text{--}0.4 \mu\text{g}\cdot\text{kg}^{-1}$ (at 5% organic carbon).

In 2003, first data on presence of PFOS and PFOA in blue mussels (*Mytilus edulis*) and flounder (*Platichthys flesus*) were all below the limit of detection (Schrap *et al.*, 2004). These compounds do however occur in humans. In the Detox campaign of the World Wildlife Fund, PFOS and PFOA were analyzed in human whole blood (WWF, 2004). Seven to eight perfluorinated acids were found, in which PFOA and PFOS were predominant.

4.6.3 IRGAROL

The compound N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine (IRGAROL 1051) is used as the active ingredient of anti-fouling agents and paints. Its application is world wide and the compound is found in coastal and estuarine waters and sediments. Few measurements on IRGAROL are available. IRGAROL is not recognized as a 'chemical of priority action' (OSPAR, 2002) nor subject to 'ecotoxicological assessment criteria' (OSPAR, 2003).

4.6.3.1 Input

Anti-fouling paints containing IRGAROL were introduced on the European market around 1985, being solely produced by Ciba Specialty Chemicals Inc. (Rasenberg and van de Plassche, 2002). Main sources of environmental contamination are located at maintenance sites (shipyards) and harbors (leaching). IRGAROL leaches out of the paints at about $2.6\text{--}5 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$. In comparison, TBT leaches at a rate of $4,000\text{--}5,000 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$ (Rasenberg and van de Plassche, 2002).

4.6.3.2 Concentrations in water, sediment and biota

In the few measurements available, IRGAROL ranges from 28 (in marinas) to 0.2 (open Dutch Wadden Sea) $\text{ng}\cdot\text{l}^{-1}$ in water and was not demonstrat-

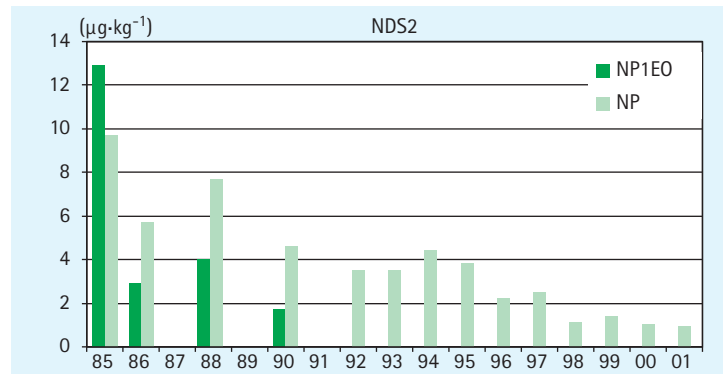


Figure 4.6.3: Contents of nonylphenol (NP) and nonylphenol monoethoxylate (NP1EO) ($\mu\text{g kg}^{-1}$ wet weight) in blue mussels in the Jade Bight (NDS2) (source: Environmental Specimen Bank, Wenzel *et al.*, 2004).

ed in sediments (Bellert and van de Ven, 2003). Ecotoxicological effects are not expected at concentrations of up to $0.24 \text{ ng}\cdot\text{l}^{-1}$ (van Wezel and van Vlaardingen, 2001), implying that IRGAROL exceeded this upper limit by a factor of more than 100. Although IRGAROL is considered as hardly biodegradable, bioaccumulation does not occur due its quick elimination and low $\text{Log } K_{ow}$.

4.6.3.3 Ecotoxicological risks

IRGAROL acts on the photosynthetic capacity by blocking the photosystem II (Holt, 1993), implying main toxicological risk to algae, macrophytes and photosynthetic bacteria. Scarlett *et al.* (1997) reports 50% effect levels (EC50) on photosynthetic activity of the green alga *Enteromorpha intestinalis* at $2.5 \text{ }\mu\text{g}\cdot\text{l}^{-1}$. Chronic toxicity on growth of the diatom *Skeletonema costatum* was reported at concentrations higher than $0.14 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ (Jongbloed and Luttik, 1996).

4.6.4 Alkylphenols

Alkylphenols (APs, *a.o.* octylphenol, nonylphenol) and their ethoxylates (APEs, *e.g.* Triton X-100) are used as additives in plastics and as the active ingredient in industrial non-ionic detergents and emulsifiers. Octyl- and nonylphenol isomers are most commonly used (>90%), being the world's second largest class of non-ionic surfactants (Metcalf *et al.*, 1996). Environmental sources are cleansing applications (textile, tapestry, bulk tanks) and agricultural pesticide emulsions (Maguire, 1999). APs are moderately water soluble, while APEs are more soluble.

Alkylphenols are of environmental concern due to their hormonal disruptive action (xeno-estrogens). Maguire (1999) concluded that initial breakdown of parent NPEs occurs readily in sewage treatment plants, resulting, however, in metabolites more persistent in the environment and toxic to aquatic organisms. Nonylphenol is such a breakdown product, showing acute or chronic toxicity at about 20 or $4 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ respectively, in fish,

invertebrates and algae (Servos, 1999). Municipal effluents in The Netherlands in 1999 had alkylphenol concentrations up to $1.5 \text{ }\mu\text{g}\cdot\text{l}^{-1}$, compared to up to $39 \text{ }\mu\text{g}\cdot\text{l}^{-1}$ in untreated industrial waste. The effluent solids, however, contained up to $70 \text{ mg}\cdot\text{kg}^{-1}$ dry weight nonylphenoethoxylate and $3.4\text{--}12 \text{ mg}\cdot\text{kg}^{-1}$ dry weight nonylphenol (Vethaak *et al.*, 2002). The number of ethoxylate units and water solubility of APEs is inversely related. Nonylphenol is poorly soluble in water and tends to adsorb to sediment and bioaccumulate, as shown by its octanol-water partition coefficient ($\text{Log } K_{ow}$) of 4.3 (Maguire, 1999). This explains the observations in the municipal effluents.

4.6.4.1 Input

APs and APEOs in wet precipitation mainly consisted of nonylphenoethoxylate (NPE) and its parent nonylphenol (Peters, 2003). Around the Dutch Wadden Sea, the concentrations were at minimum, ranging $0.03\text{--}0.04 \text{ }\mu\text{g}\cdot\text{l}^{-1}$.

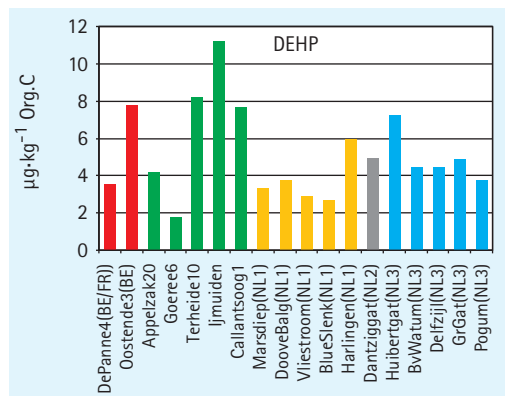
Major input of alkylphenols into the environment originates from agricultural applications where there is no possibility for sewage treatment. In The Netherlands, agriculture is responsible for 77% of the NPE input into the environment, whereas it uses only 35% of the total NPE consumption (Groshart *et al.*, 2001b).

4.6.4.2 Concentrations in sediment and biota

In the Dutch Wadden Sea and Ems estuary, concentrations of NP and NPE in sediment and suspended matter were 34 and $33 \text{ mg}\cdot\text{kg}^{-1}$ DW, respectively. NPE concentrations in flounder (*Platichthys flesus*) were low ($0.1 \text{ mg}\cdot\text{kg}^{-1}$ wet weight) and below the detection limit in blue mussels (*Mytilus edulis*) (Vethaak *et al.*, 2002).

In the German Wadden Sea (NDS2), the concentrations of NP and NPE in blue mussels (*Mytilus edulis*) have decreased strongly since the 1980s after the production was stopped completely in Germany (Figure 4.6.3) (Wenzel *et al.*, 2004).

Figure 4.6.4:
Content of di(2-ethylhexyl)phthalate (DEHP; mg kg⁻¹ organic carbon) in suspended matter of the Belgian-Dutch North Sea coast, in the Dutch Wadden Sea and Ems estuary in 2003. DEHP-free sampling equipment was used. (source: Åkerman *et al.*, 2004).



4.6.5 Bisphenol-A

Bisphenol-A (BPA) is an important intermediate in the production of epoxy resins, polycarbonate and flame retardants. The global production of BPA increased from 1.1 million ton in 1993 to an estimated 2,6 million ton in 2002. Its chemical properties make BPA relatively hydrophilic (Groshart *et al.*, 2001a).

BPA is toxic to fish and invertebrates (at 1–10·10³ µg·l⁻¹) and readily degradable (Staples *et al.*, 1998). Toppari *et al.* (1995) report estrogenic potential, which is why BPA is included in the list of suspect endocrine disruptors (see section 4.7.1).

4.6.5.1 Input

Major emission sources to surface waters estimated by Groshart *et al.* (2001a) are thermal paper recycling (~72 %) and production of plastics (PVC, Phenoplast, ~21 %).

4.6.5.2 Concentrations in water, sediment and biota

Vethaak *et al.* (2002) report high concentrations of BPA (100–320 ng·l⁻¹) in surface water of the Dutch Wadden Sea and Ems-Dollard estuary in 1999. These high concentrations may be related to the industrialized area of Delfzijl, and compare to levels in polder ditches and rivers Rhine and Meuse. In comparison, concentrations found in other Dutch coastal waters range from below detection limit (North Sea) to 80 ng·l⁻¹ (Western Scheldt) (Vethaak *et al.*, 2002).

BPA was not found in sediment of the Dutch locations investigated (Vethaak *et al.*, 2002), but BPA did occur in Wadden Sea flounder (*Platichthys flesus*) muscle tissue (1.2–2.6 µg·kg⁻¹ wet weight [24% dry weight]) and blue mussel (*Mytilus edulis*) tissue (18–22 µg·kg⁻¹ wet weight [~20% dry weight]) (Vethaak *et al.*, 2002).

4.6.6 Phthalates

Phthalates are a large group of 'softeners' widely used in many plastics. In some plastics, such as flexible PVC, phthalates constitute 50% of the total weight. Alternative applications are phthalate additions to heat-exchange fluids, ink, paint, adhesives, pesticides (Vethaak *et al.*, 2002). About 2.7·10⁹ kg·y⁻¹ of phthalates are produced globally (van Wezel *et al.*, 1999), the major part of which is used in PVC (WWF, 2004).

In the marine environment Di (2-ethylhexyl) phthalate (DEHP) is predominant. Due to its high hydrophobicity ($K_{ow} = 7.5$; Staples *et al.*, 1997) DEHP adsorbs to sediments and suspended matter (Furtmann, 1999) and bioaccumulates. Due to their bi-polar structure phthalates may form micelles in water, increasing their apparent solubility (Staples *et al.*, 1997).

Biodegradation of phthalates occurs, with a reported half-life of 20–40 days for DEHP. DEHP, however, is found in North Sea sediments in high concentrations (Åkerman *et al.*, 2004).

Due to the wide spread use of phthalates, specifically of DEHP, in plastics, uncontaminated sampling is a tedious job.

4.6.6.1 Input

Vethaak *et al.* (2002) report high levels of DEP and DEHP in Dutch sewage sludge of up to 15 mg·kg⁻¹ dry weight to 50 mg·kg⁻¹ dry weight respectively. Most input is from diffuse sources and thus not well documented.

4.6.6.2 Concentrations in sediment, suspended matter and biota

In fluvial sediments and suspended matter, concentrations of DEHP were found to be up to 50 times higher than in marine sediment and suspended matter (Vethaak *et al.*, 2002).

In Figure 4.6.4 the latest data about DEHP in suspended matter of the Dutch Wadden Sea is shown, obtained from samples collected with a specially prepared centrifuge in order to minimize DEHP contamination (Åkerman *et al.*, 2004). Concentrations in suspended matter of the Wadden Sea locations ranged 150 – 350 µg kg⁻¹ at 5% organic carbon (3–7 mg kg⁻¹ org. C).

Vethaak *et al.* (2002) only report Di-ethylphthalate (DEP) concentrations in flounder (*Platichthys flesus*) of 10 µg·kg⁻¹ wet weight for the western Dutch Wadden Sea. In comparison, DEHP was the predominant phthalate present in the blood of 45 out of 47 members of the European Parliament, ranging from 37 to 1200 (median: 160) µg·kg⁻¹ whole blood (WWF, 2004).

4.6.7 Polycyclic musk fragrances

Polycyclic musk compounds such as Galaxolide (HHCB) and Tonalide (AHTN) are used as substitutes for the more expensive original musk in personal care products. In contrast to the original fragrance, synthetic musks are persistent in the environment and accumulate in aquatic organisms. Synthetic musk compounds are only slightly toxic but are long-term inhibitors of the cellular defense system (multixenobiotic resistance), which may aggravate adverse effects of other pollutants.

In Figure 4.6.5, HHCB and AHTN concentrations are shown for blue mussels since adverse effects of these substances on the cellular defense system have been demonstrated in this spe-

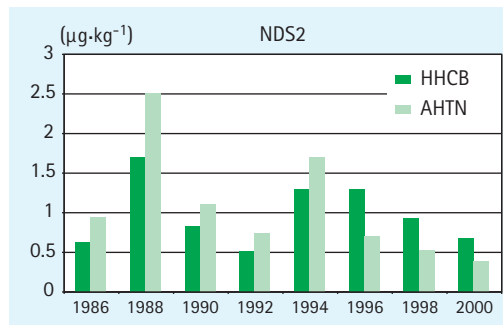


Figure 4.6.5: Contents of polycyclic musk compounds Galaxolide (HHCB) and Tonalide (AHTN) ($\mu\text{g kg}^{-1}$ wet weight) in blue mussels in the Jade Bight (NDS2) (source: Environmental Specimen Bank, Wenzel *et al.*, 2003).

cies. Perfume and consumer product companies began to phase out their use of polycyclic musks in Europe in the mid of 1990s, and a slow decrease in the concentrations in marine organisms can be observed (Wenzel *et al.*, 2003).

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4.7 New Developments

4.7.1 Xeno-hormonal disruption

OSPAR addresses substances with known or suspected potential endocrine disrupting effects under its Hazardous Substances Strategy, but has not (yet) addressed endocrine disruption as a selection criterion. OSPAR will await the outcome of appropriate test methodologies for endocrine disrupting effects in other international forums such as the OECD and the EC before deciding what criteria could be applied for such effects in the application of the DYNAMEC mechanism (OSPAR, 2003).

4.7.1.1 Reference to the 1999 QSR

In the 1999 QSR only limited attention was given to endocrine disruptors, *i.e.* substances that have a disrupting effect on hormonal processes in organisms including man. PCBs and Tributyltin (TBT) are examples of earlier endocrine disruptors, held responsible for reproductive failures in harbour seals (PCBs) and abnormal development of reproductive organs in marine snails (TBT). Since the 1990s, harmful effects of endocrine disrupting compounds in the aquatic environment have attracted the attention of scientists and water quality managers around the world. The Scientific Committee for Toxicity, Ecotoxicity and the Environment of the European Union reported on the impact of hormone disrupting substances in various species (SCTEE, 1999). The European Commission (CEC, 1999) announced a plan for follow-up actions including a list of potentially hormone disrupting compounds and the development of an international monitoring program. In 2000, the European Parliament accepted a resolution demanding that the precautionary principle be applied to hormone disrupting compounds.

4.7.1.2 Endocrine disrupting compounds

In The Netherlands, some 30 compounds were listed as most suspect of causing hormone disruption and relevant for the Dutch aquatic environment (Gezondheidsraad, 1999). A base-line study was conducted on the occurrence of natural and

synthetic estrogens in the aquatic environment (Vethaak *et al.*, 2002, 2005). Table 4.7.1 gives an overview of the compounds measured by this study in the Wadden Sea area. The study showed that almost all selected (xeno-)estrogens were found in municipal and/or industrial waste water. With the exception of three of the hormones, all of these compounds were detected in the aquatic environment. In general, no specific spatial pattern could be detected, except for high concentrations of polybrominated diphenyl ethers (especially BDE 209) in the Western Scheldt estuary (SW Netherlands). Bisphenol-A, alkylphenol ethoxylates and phthalates in particular were present both in fresh and marine waters, indicating diffuse contamination.

Levels of most (xeno-)estrogens in the Dutch aquatic environment were comparable to those reported for, for example, Germany and Denmark. Only phthalates in biota from the Wadden Sea were found in higher concentrations than in other countries. Also high concentrations of Bisphenol-A (up to 330 ng/l) were measured occasionally in the Dutch Wadden Sea. In this case, however, on the basis of the available ecotoxicological data and the measured concentrations, it can be concluded that Bisphenol-A alone does not seem to pose a threat to fish in the Dutch Wadden Sea (Belfroid *et al.*, 2002). On the other hand, recent experimental studies indicate that Bisphenol-A provokes negative effects in snails (Gastropoda) at far lower water concentrations than in fish (Oehlmann *et al.*, 2000).

Offshore oil/gas drilling platforms were identified as a possible source of the alkylphenols NPE and NP (Vethaak *et al.*, 2002, 2005). The high concentrations of these substances at such offshore locations have recently been confirmed by Jonker *et al.* (2004). It is not clear whether the actual source is drilling and production activities or shipping in the same area.

Newly emerging compounds suspect of endocrine disruption include polybrominated flame

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Category	Chemical group	Specific chemical
Estrogens	Natural estrogenic hormones	17 α -estradiol, 17 β -estradiol, estrone
Xeno-estrogens	Synthetic estrogenic hormones	17 α -ethynylloestradiol
	Alkylphenol (ethoxylates)	Nonylphenols Nonylphenol ethoxylates Octylphenols Octylphenol ethoxylates
	Bisphenol-A	
	Phthalates	DMP, DEP, DBP, DPP, BBP, DMPP, DCHP, DEHP, DOP
Thyroid-hormone disrupting compound	Brominated flame retardants	Polybromobiphenyls (PBBs) Polybromodiphenyl ethers (PBDEs)

Table 4.7.1: Overview of estrogens and xeno-estrogens measured in the LOES-study in The Netherlands (from: Vethaak *et al.*, 2002).

retardants, such as polybrominated diphenylethers (e.g. penta 2,2',4,4',5 BDE99), tri-Bromo-bisphenol A and hexabromo-cyclododecane, artificial musks and possibly perfluorinated surfactants (e.g. perfluoro-octylsulphonate, PFOS).

4.7.1.3 Estrogenic Biomarkers

Estrogenic effects in surface waters were estimated by measuring the concentrations of the yolk protein vitellogenin (VTG) in blood plasma of male fish. VTG concentrations in flounder from the Wadden Sea and Ems estuary were mostly low. None of the flounder had the intersex condition 'ovotestis', where female oocytes are found in male testis tissue. This contrasts to the VTG concentrations and ovotestis found in flounder in the estuaries of the polluted rivers Mersey and Tyne in Great Britain (see Vethaak *et al.*, 2005).

So far, there is little indication for estrogenic effects in fish in the Wadden Sea, which may be the result of the limited number of field studies on hormonal disruption in fish and invertebrates in these waters. In the UK and the southern Baltic Sea, such studies have provided clear evidence of endocrine disruption in a variety of fish species such as eelpout and sand goby (Allen *et al.*, 2002; Gercken and Sordyl, 2002).

4.7.1.4 Foodweb transport

Estrogenic activity in the estuarine and marine environment is strongly adsorbed on sediment particles (Allen *et al.*, 2002). Flounder and other species feeding on benthic invertebrates may obtain estrogenic exposure from sediments by their food. Accumulation of nonylphenol in estuarine copepods could be a source to higher trophic levels, such as juvenile fish (Scott *et al.*, 2004). Endocrine disrupting effects have recently been observed in the hyperbenthic crustacean *Neomysis integer* in the Western Scheldt. (www.vliz.be/projects/endis). It can be concluded that apart from TBT-induced effects in snails our knowledge of endocrine disruption in invertebrates in the Wadden Sea is generally very limited (Gezondheidsraad, 1999).

4.7.2 Biological effect assessment techniques

4.7.2.1 Bioassay assisted assessment

Bioassays are laboratory tests with organisms that are exposed to a compound, mixture or environmental sample and give information on the effects of chemicals, chemical mixtures or known and unknown pollutants present in the environment. These tests are used for risk assessment of surface water, effluents, sediments and dredged

material. Bioassays can be divided into *in vivo* and *in vitro* tests (Legierse, 2001). In *in vivo* bioassays organisms are exposed to compounds or samples under controlled conditions taking several days to weeks. They are used regularly for the ecological risk assessment of individual compounds and for the determination of environmental quality standards (Fan *et al.*, 1995; van Leeuwen and Hermens, 1995). Recently bioassays have been implemented in the assessment of environmental samples, such as dredged material (Stronkhorst *et al.*, 2003). *In vivo* bioassays can be subdivided into acute bioassays (short tests using criteria such as survival) and chronic bioassays (longer term tests, looking at more sensitive criteria such as reproduction, growth or behavior). Examples of commonly used marine and estuarine test organisms in bioassays are the bacterium *Vibrio fischerii* (MICROTOX Solid Phase), the amphipod *Corophium volutator*, the sea urchin *Echinocardium cordatum* and the polychaetous worm *Nereis virens*.

In vitro bioassays are quick tests (~28 hours) that use simple biological systems such as bacteria, cells or sub-cellular fractions. They are used as screening assays that provide an indication of possible detrimental ecological effects of compounds or mixtures. They can be subdivided into mechanism-based *in vitro* bioassays (reacting to a specific mode of action, such as the detection of endocrine disruption by binding to receptor sites) and broad-spectrum bioassays (reacting to different modes of action). Examples of commonly used toxicity mode of action assays are the general or acute toxicity (*Vibrio fischerii* in MICROTOX), dioxin-type toxicity (DR-CALUX), estrogenic activity (ER-CALUX) and genotoxicity (*Vibrio fischerii* in MUTATOX).

Bioassays of harbor sediments

In 1999–2000 a large number of harbors around the Dutch Wadden Sea were assessed for sediment quality (Stronkhorst *et al.*, 2003). The acute *in vivo* amphipod bioassay with *Corophium volutator* revealed that for 5 harbors the threshold of 24% mortality was exceeded (Table 4.7.2). This threshold is based on research experience and statistically based toxicity assessment criteria from the literature (e.g., McGee *et al.*, 1999). For *C. volutator* such information is limited to a study in the vicinity of a North Sea oil platform where lower infaunal species diversity was associated with a 50 % mortality response in the *C. volutator* acute bioassay (Roddie and Thain, 2001).

According to the acute *in vivo* sea urchin (*Echinocardium cordatum*) bioassay, more than half of the harbor sediment samples tested were signifi-

Harbour/bioassay	Number of samples	Test result	Percentage that exceed threshold of
Microtox Solid Phase		Average TU	48 TU
Delfzijl	13	32	31
Eemshaven	6	41	33
Lauwersoog	5	73	80
Wadden islands	13	31	31
Harlingen	18	50	50
Afsluitdijk	12	49	50
Den Helder	12	54	58
Corophium volutator		Average % mortality	24% mortality
Delftziyl	13	16	8
Eemshaven	5	23	40
Lauwersoog	1	13	0
Wadden islands	9	11	11
Harlingen	12	16	42
Afsluitdijk	6	13	0
Den Helder	5	8	20
Echinocardium cordatum		% Mortality	35% mortality
Delftziyl	13	51	62
Eemshaven	6	46	67
Lauwersoog	4	80	75
Wadden islands	13	43	54
Harlingen	18	53	78
Afsluitdijk	12	33	42
Den Helder	12	49	83

Table 4.7.2: Results of different bioassays on dredged material from harbors in the Dutch Wadden Sea in 1999–2000. TU = Toxic Units (see text) (from: Stronkhorst *et al.*, 2003).

cantly toxic compared to the lower threshold limit for sea urchin mortality (Table 4.7.2). These are strong indications that the harbor sediments along the coast of The Netherlands are still contaminated. Because sea urchins are not always readily available, and mortality differences among replicates cause statistical problems, research has been started to culture the species in order to improve the (statistical) performance of this bioassay.

The results of the *in vitro* Microtox Solid Phase test show that on average more than 50% of the samples exceed the threshold of 48 Toxic Units (Table 4.7.2). The use of this bioassay to classify the ecological risks of harbor sediments was discussed and the conclusion drawn that for this purpose the applicability of the test needs further elucidation.

Bioassays of sediments and suspended matter

In a survey in 1999/2000 sediments from different locations in the Dutch Wadden Sea (in and outside harbors) were assessed with *in vitro* bioassays (Microtox SP and DR-CALUX) and *in vivo* bioassays using *Corophium volutator*, *Crassostrea gigas*, *Brachionus plicatilis* and *Echinocardium cordatum* (van den Brink and Kater, 2000) and experimentally using *Nereis virens* (Kater *et al.*, 2000). Mortality thresholds in *C. volutator* and *N. virens* and average responses were exceeded at a number of non-harbor locations. The results showed no significant correlation with the contaminant levels of PAHs, PCBs and metals measured in these sediments. Only organic tin com-

pounds were significantly correlated with the Microtox SP and DR-CALUX response. Non-analyzed toxic compounds (*i.e.* mineral oil, organochlorine pesticides) or rather water soluble compounds might have shown better correlations.

Recently, *in-vitro* bioassay activity was measured in sediment or suspended matter extracts from locations along the Belgian-Dutch North Sea coast, the Wadden Sea and Ems estuary (Åkerman *et al.*, 2004). Some results presented in Figure 4.7.1 show relatively low estrogenic activity in the Wad-

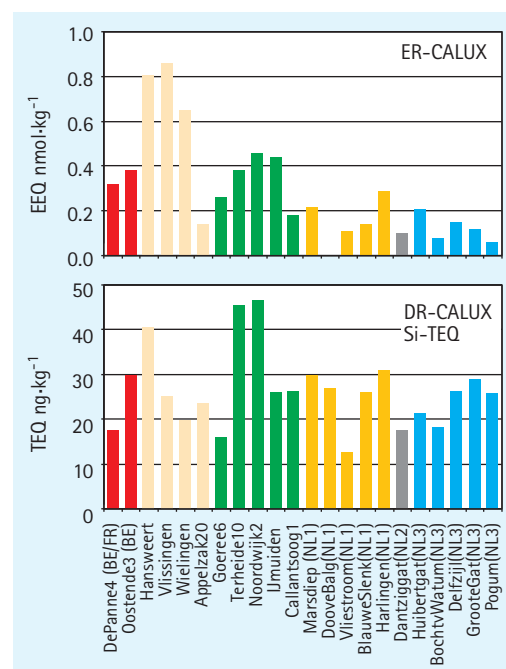


Figure 4.7.1: Typical Estrogenic activity (EEQ nmol kg⁻¹ dry weight) by the ER-CALUX assay (top panel) and dioxine-type toxicity (TEQ ng kg⁻¹ dry weight) by the DR-CALUX assay (lower panel) in suspended matter from the Belgian-Dutch North Sea coast, The Dutch Wadden Sea and Ems estuary, (source: Åkerman *et al.*, 2004).

den Sea and Ems estuary against high activity in the Western Scheldt. Dioxin-type toxicity does not show geographic differences.

Bioassays of water

Biological effect assessment of Dutch Wadden Sea water is reported by Åkerman and Smit (2003). In a pilot study with *in vitro* bioassays Microtox (for general toxicity), Mutatox (for genotoxicity) and ER-CALUX (for estrogenic activity) responses were found at several locations. The bioassays still need full validation for the water phase, but are considered a promising tool for the assessment of Wadden Sea surface water in the future.

4.7.2.2 TIE and EDA assisted assessment

Environmental anthropogenic contamination originates from numerous production, application and waste sources constituting a multitude of chemicals with intended or unintended effects on the biosphere. A relatively minute number of those chemicals, most of which have been recognized to be hazardous, are adopted in monitoring programs. From this view chemical monitoring alone is a poor approach for hazard assessment of the biosphere. This has been recognized in the Water Framework Directive, where the member states have to define both ecological and chemical targets. Not complying with either of the targets, however, does not elucidate the cause, and thus fails to indicate necessary measures in response. Nor does it shed light on the chronic risks from various anthropogenically elevated contaminant concentrations in the environment. Linking ecological effects and risk to chemical compounds is a prerequisite for establishing sustainable management of the environment. Effect Directed Analysis (EDA) offers functionality to link compounds to biological effects. This serves as a basis in the efforts to link (ecological) effects to their causative toxicants.

The principle of Effect Directed Analysis (EDA) and Toxicity Identification Evaluation (TIE) is to use the response in a biological (test) system to direct the chemical-analytical pathway towards identifying the compounds causing this response (Brack, 2003; Ankley *et al.*, 1991). The biological test systems are based on sets of bio-active structures responding to chemical compounds. At present they include tests with whole-organism *in-vivo* bioassays and cell-based *in-vitro* bioassays, and biochemical tests with biomarkers, biosensors and immunoassays, thus ranging from intact organisms to cell-free, bio-active cell components or molecules. Examples are described in section 4.7.2.1.

Ideally, a biological test system would respond to different (groups of) compounds, where the sequence of biological tests is sensitive enough to cover both a wide scope of biologically active chemical compounds as well as a wide range of pollution levels. Individual tests may, preferably, respond to a narrow range of compounds. In this way the EDA test battery and analytical sequence will respond to tracing back biological and ecological deteriorating effects due to its compound source. The chemical compounds identified by EDA can be denoted as 'key toxicants' and constitute the true priority compounds.

Additionally, the available chemo-analytical tools can, by concentrating the environmentally present compounds, boost the sensitivity of appropriate biological test systems to the level of ecological effect *prevention*.

In both aspects, hazard and risk, EDA is a useful tool in solving confounding factors in reaching the WFD targets such as 'good ecological status' from the key-toxicant view.

Once a biological response is recorded, indicating a potential or actual undesirable effect, the responsible compounds may be identified and counter measures designed. Measures derived this way should be more effective and thus more cost-effective than the current priority pollutant approach, which is usually based on correlation between effects and pollutant concentrations.

Several case studies of TIE and EDA reported in the literature were able to identify causative compounds with different degrees of certainty (Thomas *et al.*, 1999; Burgess *et al.*, 2000; Hollert *et al.*, 2002; Pessala *et al.*, 2003; Klamer *et al.*, 2004). Klamer *et al.* (2004) could attribute ~ 50% of the dioxin-type toxicity in Wadden Sea harbour sediment, assessed with the DR-CALUX assay (Aarts *et al.*, 1993; Murk *et al.*, 1996), to dioxin-like compounds.

4.7.3 Environmental quality and flood events

The Elbe flooding event during August 2002 was expected to cause an increased input of contaminants to the Wadden Sea and subsequent concentration changes in the environmental matrices. Unexpectedly, hardly any changes in Elbe river input or concentrations were observed (Nies *et al.*, 2003). Exceptions were some increased contaminant levels in bird eggs (see section 4.4), increased concentrations of hexachlorobenzene, DDD and DDE in blue mussels and of cadmium and hexachlorobenzene in liver of flounder (see section 4.2).

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4.8 Final Remarks

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4.8.1 Data management and quality assurance

Data management and quality assurance of chemical data (heavy metals and xenobiotics) in different matrices (except for bird eggs) is still a problematic issue in the Trilateral Monitoring and Assessment Program, which is rooted in existing national monitoring programs. On one hand, this ensures cost effectiveness, but on the other it hampers intercomparability of methods which were not well harmonized. During the preparation of this QSR problems were encountered regarding, for example, grain-size correction of concentrations in sediment, switched wet / dry weight data in blue mussels, and possible sample contamination.

It is therefore strongly recommended to regularly execute a thorough quality screening of Wadden Sea database data, based on the experiences of this QSR preparation and carried out by personnel trained to check chemical monitoring data.

4.8.2 Newly and politically emerging compounds

Newly and politically (e.g., Water Framework Directive) emerging compounds are not yet part of the TMAP, while certain matrices may efficiently be analyzed for some of those compounds.

It is recommended to update the TMAP by considering additional chemical analyses in bird eggs, mussels, flounder and sediment, especially organotins, brominated flame retardants and perfluorinated surfactants. In risk assessments, the apparent bio-magnification at the level of lung-breathing organisms should be taken into account. Of course, harmonization of sampling, preparation and analytical methods should be given proper attention.

The current organization of monitoring of contaminants in bird eggs ('one-lab-approach') could be a source of inspiration.

In the Water Framework Directive compound levels negatively influencing the chemical and ecological targets are of priority importance. This demands a different type of assessment of chemical monitoring data, e.g. by looking for those locations where contaminant levels deviate from the average.