

A note concerning “novel pollutants” and cetaceans.

M.P. Simmonds¹, P. A. Johnston² and G. M. Troisi³

1. Whale and Dolphin Conservation Society, Alexander House, James St. West, Bath BA1 2BT UK.
2. Greenpeace Research Laboratories, University of Exeter, Exeter EX4 4PS UK
3. Wildlife & Human Toxicology Unit, School of Life Sciences, Kingston University, London, UK

Abstract.

In this paper we consider some “novel” organic compounds (meaning those that are not routinely analysed for in cetaceans), provide a brief update on what is known about them and discuss their potential importance. Three classes of novel compounds appear to be of particular concern: the brominated flame retardants; the polyaromatic hydrocarbons and the organotin. However, there is also a range of other important environmental contaminants that have been little investigated in cetaceans.

The relationship of these “novel pollutants” compounds to ongoing pollution studies is considered and vigilance with respect to novel pollutants is recommended.

Background

In 1996, Colborn and Smolen highlighted the threat posed by organochlorines to marine mammals. On the basis of an extensive review of the literature, they found evidence that some 16 species had experienced population instability, major stranding episodes, reproductive impairment, endocrine and immune system disturbances, organ damage, general health decline and serious infectious diseases since 1968. They also reported a “relative lack of information on contaminants in whales and in particular, baleen whales” and that “attempts at determining contaminant concentrations in individual species have been limited primarily to total PCBs... and total DDT and its metabolites...”. Nonetheless, they also reported that a “growing” list of organochlorines had been reported from marine mammals – i.e. chlordane, dieldrin, mirex, lindane, HCB. Some limited data were identified for the coplanar-PCBs, dioxins and furans. Colborn and Smolen did not mean their list to be exhaustive but, even so, this “standard suit” of organochlorines regularly features in the cetacean literature (e.g. Reijnders *et al.*, 1999).

The IWC’s 1995 “Workshop on chemical pollution and cetaceans” also considered “exotic compounds” and produced a list identifying three categories of priority compounds “to be tested for in cetaceans” (Reijnders *et al.*, 1999):

- Category One – chemicals already monitored on a routine basis;
- Category Two – chemicals that presently require specialist analyses; and
- Category Three – compounds for which only limited information is available but for which it was suggested that bioassays should be carried out to determine if further action should be taken.

The 1995 Workshop recommendations were further developed through a series of meetings into a resulting “core” programme of investigation known as “Pollution 2000+” (see Reijnders *et al.*, 1999). This programme seeks to correlate a range of biological indicators (e.g. indicators of immune function) with certain pollutants. The pollutants chosen were the organochlorines, particularly the PCBs (IWC, 1999). These were selected because their origin is anthropogenic, they are found at extremely high tissue concentrations in some cetacean populations, and they have recognised impacts upon wildlife.

In this brief review, we consider other organic compounds that may be of importance to cetaceans. These are selected from two sources – i.e. those recently reported from marine mammals and those that have been listed as “chemicals for priority action” (see Annex 1) by OSPAR (OSPAR, 2000).

1. The Polybrominated Biphenyls and Polybrominated Diphenyl Ethers.

The polybrominated biphenyls (PBBs) were recognised by the IWC workshop as Category Two compounds and they are also listed by OSPAR. In fact, the analysis of these compounds is increasingly becoming routine, although requiring specialist sample preparation techniques in common with many of the chlorinated hydrocarbons of concern. They are amongst several classes of compounds (including the chloroparaffins discussed later) that have been used as flame retardants. At one time, this also included the PCBs, however brominated compounds have proved to be more useful in this respect than chlorinated ones (Bernes, 1999).

Bernes (1999) commented that “the use of brominated flame retardants could continue for a number of years. At present, no suitable substitutes are available, and the possible environmental effects of these chemicals has been regarded as less significant than the increased fire risk that would arise if we were to refrain from using them”. Thus, whilst environmental levels of PCBs can be expected to fall following the cessation of their manufacture, PBBs are still in use and still moving into aquatic systems, including the top predators.

De Boer *et al.* (1998) recently issued a warning concerning polybrominated compounds following their discovery in sperm whales and other marine mammals. They commented that “the presence of PBBs (polybrominated biphenyls) and PBDEs (polybrominated diphenyl ethers) in sperm whales, the high levels of particularly PBDEs in seals and dolphins, and the ongoing industrial production of these compounds suggest that an environmental problem may be on its way”.

Polybrominated flame retardants (PBBs and PBDEs) are structurally very similar to the PCBs. In the case of PBBs, their 3-dimensional structure is identical to PCBs except that bromine atoms are present instead of chlorine. Accordingly, certain PBB isomers have a planar configuration enabling them potentially to interact with the aryl hydrocarbon receptor (*AhR*), as do other planar hydrocarbons such as coplanar PCBs, dioxins and PAHs. This leads to induction of cytochrome P450 1A isozymes and dependent mixed function oxidases (e.g. benzopyrene hydroxylase; BaPOH) resulting, *inter alia*, in the formation of carcinogenic free radical metabolites that can interact with DNA.

PBDEs share a common structure to PCBs and PBBs but with added oxygen. The more polar nature of these molecules allows potentially significant interactions with intracellular proteins.

2. Dioxins and Dibenzofurans

Both PCB products and organochlorine pesticides are often contaminated with small quantities of other chlorinated compounds. This includes the polychlorinated dibenzo-p-dioxins and dibenzofurans. These occur in the form of a large number of congeners, some of which are extremely toxic (Bernes, 1999). Dioxins and furans have never been intentionally manufactured but can form as byproducts when chlorinated compounds are produced or burnt. One of the dioxins (2,3,7,8-TCDD) is “often described as the most poisonous substance ever created by humankind” (Bernes, 1999).

Not surprisingly, the 1995 IWC workshop recognised these compounds as Category One (i.e. “routine”) – although it might also be noted that they are relatively expensive to analyse - and they are also, of course, listed by OSPAR.

The toxicity of these compounds is generally considered (along with twelve dioxin-like PCBs) via the Toxic Equivalency approach. This system has now been developed and refined (van den Berg *et al.* 1998) to account for the broad differences in toxicological response to these compounds between birds, fish and mammals. Accordingly, three different scales have been devised to apply to each of these groups.

Brominated and brominated/chlorinated dioxins and furans have been identified in ash from municipal incineration (Schwind *et al.* 1988), in car exhausts (Hutzinger & Fiedler 1989) and in the residues after house fires, or when items such as cars or televisions are burned (Zelinski *et al.* 1993 & 1994). Of the theoretically possible 1700 dioxins and 3320 furans with bromo-, chloro- or bromo-/chloro-

substitution, 351 dioxins and 667 furans are 2,3,7,8-substituted and therefore of particular toxicological concern (Fiedler *et al.* 1990). Their toxicity has been estimated to be of the same magnitude as that of the chlorinated congeners on a molar basis (Schwind *et al.* 1988.), but a recent review found that certain congeners (particularly 2,8-Br₂-3,7-Cl₂-dibenzo-p-dioxin) can be even more biologically active than 2,3,7,8-TCDD (Weber & Greim 1997).

Simmonds *et al.* (2000) reviewed the development of Toxic Equivalency assessment for humans and its recent application to wildlife, particularly marine mammals, and compared it with other methods of toxicological hazard evaluation.

In relation to the dioxins, it may be concluded that:

- The toxic equivalency approach has the potential to be a valuable tool in marine mammal health risk evaluation. In its favour are the facts that (1) TEQs can be used in addition to other approaches such as those using single groups of chemicals (e.g. PCBs); and (2) it allows the toxicity of the important Dioxin Group to be assessed in samples.
- However, the methodology is an emergent one that still has limitations. There remain a number of problems with the calculation and application of TEQs. For example, they can only be calculated where appropriate data have been generated (Colborn and Smolen, 1996) and such analyses are very expensive. Moreover, TEQs cited in the literature may not be strictly comparable. (For example, the new WHO TEFs will result in an approximate 10% increase compared to both the I-TEFs and the original WHO TEFs (van Leeuwen *et al.*, 2000)).
- The major contribution made by PCB compounds to TEQ values in recent studies of cetaceans, supports their choice by the IWC (Reijnders *et al.*, 1999) as an important and practical indicator group for contaminant impacts.
- It is by no means clear that the TEQ scales which have been devised fully account for the sensitivity of cetaceans to these compounds.
- The TEQ system at present does not formally account for the brominated and mixed-halogenated dioxins which are known to be emitted from a number of sources and may be of equal or greater toxicological significance to the chlorinated isomers.

There still seem to be very few studies that have considered dioxins and furans in cetaceans. Ross *et al.* (2000) have recently reported on pollutants, including dioxins and furans, in several Pacific communities of orcas. They found that whilst PCB concentrations were very high compared with other marine mammals studied, dioxins and furans did not appear high in any community. This was despite near-by historical sources of such compounds.

3. Polyaromatic Hydrocarbons (PAHs)

The occurrence of PAHs is largely unknown in most populations of cetaceans, despite the fact that they are a chemical group of particular concern because some of their metabolites have carcinogenic and mutagenic potential (Law & Whinnett, 1992). The IWC workshop listed PAH-metabolites as Category Two Compounds and they are also on the OSPAR list.

Detailed consideration has been given to the exposure of the beluga whales (*Delphinapterus leucas*) of the Gulf of St Lawrence to PAHs. This population is exposed to many industrial contaminants but the high prevalence of cancers in the population has been related specifically to PAHs (e.g. Martineau *et al.*, 1988). PAH levels have also recently been determined for harbour porpoises (*Phocoena phocoena*) from UK waters (Law & Whinnett, 1992).

PAHs in the environment can come from a number of sources, including waste incineration, wood burning, forest fires, petroleum spills, urban run-off and various industrial activities, such as aluminium smelting operations (Ray *et al.*, 1991). Very high concentrations may come from industrial and urban effluents and, unlike some other pollutants, PAHs are not evenly distributed in the environment but remain concentrated relatively close to their source. They, thus, tend to be localised in rivers, estuaries

and coastal marine waters (Neff, 1985). Nevertheless, PAH contamination can be detected in marine sediments from remote and uninhabited areas distant from inputs and sources of these chemicals..

The Saguenay Fjord, a tributary of the St Lawrence estuary, is known to have received up to 10 tonnes/year of the highly toxicologically significant PAH - benzo(a)pyrene (BaP) - a potent carcinogen. This has led to heavy contamination of sediments (Ray *et al.*, 1991) and some biota (see Beland & Martineau, 1988).

PAH emissions from aluminium smelters in this region have been causally related to bladder cancer in humans (Theriault *et al.*, 1984) and, thus, when a transitional cell carcinoma was discovered in the bladder of a beluga whale, it was, not surprisingly, related to the presence of high environmental concentrations of PAHs (Martineau *et al.*, 1985). Only one neoplasm had previously been reported from a cetacean.

The link between PAHs and cetacean cancers remains controversial. Both fish and odontocete cetaceans possess inducible enzyme systems capable of metabolising aromatic hydrocarbons and the small quantities of PAHs sometimes detected in body tissues (for example muscles) may represent only that proportion of PAHs that has escaped metabolism (see Law & Winnett, 1992).

Indeed, in common with some other ubiquitous environmental contaminants, the detection of PAHs presents complex problems of analysis and interpretation. These compounds are rapidly taken up from the environment by invertebrates and fish but are also readily degraded and excreted by many fish and mammals. PAH excretion may be enhanced in animals also exposed to other pollutants in their environment and which also induce the enzyme systems that degrade xenobiotics (NRCC, 1984). PAH concentrations in tissues are thus likely to be depressed in relation to expected accumulation at a given ambient environmental concentrations when certain other pollutants are also present, as, for example, is the case for the St. Lawrence belugas.

PAHs and their metabolites can, however, form covalently bonded adducts with the cellular genetic material DNA, which can be detected and used as indices of exposure in organisms. Measuring such adducts is therefore generally regarded as an index of potential carcinogenic impacts.

Geraci *et al.* (1987) criticized the link that had been made between PAHs and the beluga bladder tumour, noting that many "confounding variables" would be present and suggesting that PAHs were not particularly high in the environment concerned. In their response, Beland & Martineau (1988), reviewed the contaminant evidence, noting that studies "unequivocally indicate that there are large amounts of PAHs in the Saguenay fjord, in the heart of the habitat of the resident population of beluga whales". They also reported that the belugas could live for 30 or more years and have a varied diet of pelagic, demersal, and benthic organisms, sometimes even ingesting sediments. The animals are therefore highly exposed to PAHs. The researchers also reported that whilst benzo(a)pyrene (BaP) had not been detected in the whale with the bladder cancer (and that analysis may thus have been inadequate in this animal), more recent analyses had found BaP adducts in the brains of three other St Lawrence beluga whales. Adducts were not, however, found in the brains of a control sample of belugas from the Arctic. This provided "incontrovertible evidence" of exposure to BaP and that it had been metabolized in the St Lawrence animals to the "ultimate carcinogenic" form. Beland & Martineau (1988) concluded that the link they had made might indeed be "simple" but that it was also "appropriate and logical".

Part of Martineau and Beland's case clearly rests on the absence of BaP adducts in the Arctic beluga whales but a subsequent study (Ray *et al.*, 1991), which measured levels of aromatic DNA adducts in liver tissues of beluga whales from the Canadian Arctic and St. Lawrence Estuary, actually determined similar concentrations in both areas. One explanation for this may, however, rest in the different methodologies used in the two studies and differences in the tissues examined. As a result, some of the "adducts" diagnosed in the animals may be the result of processes other than PAH exposure. In wild fish, for example, Kurelec *et al.* (1989) have reported that background levels of adducts may completely overwhelm any pollution-related adducts.

Whatever the explanation is, the plight of the St. Lawrence belugas is certainly not limited to a single case of bladder cancer. There is a remarkably high level of tumors in the population (40%); 53% of

animals examined show lesions in the digestive system and 45% (of adult females) in the mammary glands. Pregnancy rates and survivorship are far lower than for Arctic belugas (Beland *et al.*, 1991).

A recent study of PAHs in cetaceans reported on concentrations in the muscle tissues of harbour porpoises from around the UK (Law & Whinnett, 1992). Concentrations were similar to those reported for Canadian marine mammals. Similar concentrations were found in all ages, so accumulation was assumed to be low. The authors also noted that of the 27 harbour porpoises examined between 1988 and 1991 and for which post mortem examination had provided a likely cause of death, only in one case was this considered to be a cancer. Whether or not the incidence is increasing is impossible to determine in the absence of earlier data for the populations concerned. Holsbeek *et al.* (1999) recently detected low levels of the 1-4-ring PAH compounds in sperm whales that stranded in the North Sea. The researchers commented that “It is generally considered unlikely that PAHs affect marine mammals, with a few individual exceptions...”.

Interpreting the significance of these, and other, PAH concentrations in cetaceans as illustrated by the St Lawrence belugas, will remain difficult. Consideration of cause and effect is even more difficult for PAHs than for some other classes of pollutants. In particular, the rapid transformation of PAHs into unstable metabolites and their excretion, combined with the lag time between exposure and a potential resultant physiological effect (e.g. a cancer), are certainly confounding.

Law and Whinnett (1992) chose to conclude their paper by drawing attention to bycatch, the more obvious cause of death and decline in the animals that they were considering (i.e. "UK" harbour porpoises). However, the scale of this impact could be obscuring the potential impact of PAHs and, especially if few porpoises presently live long enough to exhibit resulting effects, such as gross tumours, a factor that may affect many other inshore populations. In the fullness of time, the removal of one acute problem (i.e. bycatch) may allow another more chronic, but potentially equally threatening (i.e. pollution), to be recorded. Clearly, the threat to marine wildlife from PAHs deserves to be closely monitored.

4. “Organotins”

The IWC workshop recognised some organotin compounds as being of importance (i.e. Category Two – “non-routine”). Similarly, OSPAR lists “Organic tin” compounds. In addition, Tanabe (1999) has recently commented that butyltins “may pose a considerable toxic threat to some coastal species of cetaceans”.

Certainly, they are to the forefront of the “novel compounds” that have been increasingly identified in the tissues of cetaceans. The most important source of organotin compounds to the marine environment is from their use in “anti-fouling paints” – i.e. coatings that allow the “controlled” release of organotin compounds (typically as tributyltin) used to keep boat hulls and other marine structures free of fouling organisms such as seaweeds and barnacles (Simmonds, 1986).

The first report of butyltin compounds in marine mammals came from animals sampled in Japan (Iwata *et al.*, 1995). Butyltins were detected in finless porpoises, *Neophocaena phocaenoides*, Dall’s porpoises, *Phocoenoides dalli*, a common dolphin, *Delphinus delphis*, a spinner dolphin, *Stenella longirostris*, and a killer whale, *Orcinus orca*. The highest concentrations were found in the liver, and the lowest in the blubber. The authors noted that immunotoxicity has been emphasised as one of the toxic effects of such compounds and that this was the first report to identify such compounds at “potentially hazardous levels in marine mammals”. Kim *et al.* (1996) similarly reported on butyltin compounds in a sample of 42 Risso’s dolphins, *Grampus griseus*, collected off Taiji, Japan in 1991. Tanabe *et al.* (1998) and Tanabe (1999) provide helpful recent reviews about organotin contamination in marine mammals.

Not only have these now been shown to accumulate in a range of cetacean species but they have been found in cetacean brain tissue, indicating that they can pass through the blood-brain barrier, possibly (as in the case of methylmercury) by binding to sulphhydryl residues (Law *et al.* 1998). Organotins may have a wide variety of toxic effects, including immunosuppression (Tanabe, 1999). Tanabe (1999) commented that “unlike organochlorines, comparable residue levels of butyltins were found in male

and female marine mammals...[which] suggests that butyltins are less transferable through gestation and lactation...”.

5. Short Chained Chlorinated Paraffins

The chlorinated paraffins form a chemical group that may include a larger number of isomers and congeners than any other (Stringer and Johnston, 2001) and they are recognised in the OSPAR list and in IWC Category Three. They have been little researched and little is known of their occurrence and behaviour in the environment. Despite this, over 200 different technical mixtures have been manufactured and they have a wide variety of applications – e.g. they are used in high pressure lubricants/cutting agents for metal working, vinyl coatings and in sealants (Stringer and Johnston, 2001).

The shorter-chain chlorinated paraffins are the more toxic. Some or all chlorinated paraffins accumulate in the intestine, adipose tissue, liver, kidney, ovary, CNS and adrenal cortex (Stringer and Johnston, 2001). Their impact on the endocrine system is unclear, as are other aspects of their toxicology. There is evidence that these compounds do not biomagnify to as great an extent as other POPs, since seals have been found to have concentrations similar to, or lower than, fish.

6. Others.

There are a number of other classes of compounds that may be of concern and either listed in the report of the IWC workshop (Reijnders *et al.*, 1999) or by OSPAR.

For example, the IWC workshop (Reijnders *et al.*, 1999) discussed the insecticide “toxaphene”, noting that, although not routinely analysed for, it had a similar global production to the PCBs and that the biomagnification from mackerel to cetaceans in the North Sea was at least one order of magnitude greater than that of the PCBs.

Another class of ubiquitous contaminants, the phthalates (phthalic acid esters or benzenedicarboxylic acid esters), are plasticisers and represent some 69% of plasticisers used in the US, 92% in western Europe and 81% in Japan (Stringer *et al.*, 1999). Releases of phthalates during their manufacture, use and disposal of PVC and other products has caused these chemicals to become ubiquitous in the global environment. Two phthalates were recognised to be of potential concern by OSPAR (see annex 1). One significant potential source of human exposure to plasticisers has recently been shown to be plastic toys (Stringer *et al.*, 1999).

Nonylphenol is another plasticiser and a persistent compound that has oestrogenic activity (Stringer *et al.*, 1999). It has recently been noted that ubiquitous plastic pellets (used as feed stock by the plastics industry) may be a significant source of nonylphenol to marine wildlife if ingested (Mato *et al.*, 2001). Mato *et al.* (2001) also show that these pellets accumulate PCBs and DDTs. They may therefore be an important source of a variety of pollutants.

Many, if not all of the compounds recognised by OSPAR are, of course, well known in terms of wildlife toxicology (see, for example, Peterle, 1991) even if not specifically known yet from marine mammals. For example, pentachlorophenol (PCP), which is used as a wood preservative, defoliant and herbicide; endosulfan a broad spectrum non-systemic insecticide; and dicofol a non-systemic acaricide.

On the other hand, some further novel compounds are now being reported directly from marine mammals. Tris (4-chlorophenyl) methane (TCPMe) and tris (4-chlorophenyl) methanol (TCPMeOH), in particular, have, for example, recently been reported from a Baltic Sea food web that includes harbour porpoises (Falandysz *et al.* 1999). Both compounds bioaccumulate and biomagnify to a higher degree than DDT, and under environmental conditions seem more persistent contaminants than DDT or its analogues. Binh Minh *et al.* (1999) provide a helpful table showing TCPMe and TCPMeOH levels reported in marine mammals around the world (16 populations to date). Their own work showed high levels in hump-backed dolphins, *Sousa chinensis*, and finless porpoises in Hong Kong waters. The IWC workshop put TCPMe and TCPMeOH in Category Three.

Discussion

It is apparent that the 1995 IWC Workshop's "priority list of compounds that should be tested in cetaceans" (and its three categories) was comprehensive. There is also already growing evidence that several of the groups of "novel" compounds identified above offer a significant potential threat to cetaceans, in addition to the more routinely analysed compounds.

The polybrominated compounds may prove to be a confounding variable in future toxicological studies of cetaceans focused on the standard suit of organochlorines (or just the PCBs) because they are so similar to the PCBs in terms of likely toxicological impacts. The worse case scenario might be that bioindicators show an impact that does not seem to correlate with low (or even falling) levels of PCBs. One way to ensure that this does not happen would be to occasionally check PBB levels in populations that are being studied.

The organotins could also have a confounding impact and it is interesting that their kinetics appear to differ from those of the organochlorines. This needs further consideration and, again, sampling to check for organotin compounds may help to deal with any confounding influences.

The polyaromatic hydrocarbons are perhaps a special case, as they do not usually bioaccumulate, and yet may have quite profound impacts. It would thus seem desirable to take the extent of PAH exposure of any population into account (particularly if there is any evidence of high levels of exposure, as in the case of the St. Lawrence belugas).

Perhaps because the short-chain paraffins do not biomagnify to the same extent as other POPs, they may be of less concern for cetaceans. However, this does not yet appear to have been rigorously investigated.

In some cases, the metabolites of compounds may themselves require monitoring. A case in point is the metabolites of PCBs, namely hydroxy PCBs and PCB methyl sulphones. These metabolites have a polar functional group which enables them to bind receptor proteins (transthyretin and uteroglobin / Clara cell secretory protein), displacing their endogenous ligands, thyroxine (thyroid hormone) and progesterone, respectively. This has adverse effects on immune function and fertility in marine mammals and mammals generally (see Brouwer *et al.*, 1989; Troisi *et al.*, 2001). Janak *et al.* (1998) reported on methyl sulfonyl polychlorinated biphenyls in gray seals and Karlson *et al.* (2000) recently reported on the methyl sulphone metabolites of PCBs and DDTs in various tissues of harbour porpoises from Swedish waters. The desirability of monitoring PCB metabolites was recognised by the IWC Workshop (which placed them in Category Two – non-routine).

The classes of chemical compounds considered here are those for which the data-base is already sufficiently developed for them to be acknowledged as of importance. There are many other chemicals whose properties cause them to be persistent in the environment and which have the potential to bioaccumulate. All such chemicals are of concern to marine top predators. Nonetheless, against a background of so many different kinds of contaminants entering the wider marine environment, the research in progress under the auspices of Pollution 2000+ - i.e. with a principal focus on correlating carefully chosen biomarkers with organochlorines (especially PCBs) – is a logical and pragmatic approach.

New knowledge about "novel" classes of compounds – including recently published reports of those found in marine mammals - does not alter this conclusion but reinforces the need to be vigilant and monitor "novel" compounds, as well as the better-known ones. This could be done by making further analyses of the samples already being collected or, if this is not adequate, by occasional studies of bycaught or stranded animals. Sampling other biota (for example fish or molluscs) may also help to investigate background levels of "novel" contaminants and establish whether there might be concerns relating to these compounds for particular cetacean populations or certain locations.

Acknowledgements

Thanks to David Santillo and Chris Parsons for their swift help in the production of this review.

References

- Beland, P. and Martineau, D. 1988. About carcinogens and tumours. *Can. J. Fish. Aquat. Sci.* 45, 1855-1856.
- Beland P., De Guise, S., Girard, C., Lagace, A., Martineau, D., Michaud, R., Muir, D., Norstrom, R., Pelletier, E., Ray, S. and Shugart, L. 1991. Toxic compounds and health reproductive effects in St Lawrence beluga whales. *Case-effects on St. Lawrence beluga whales. Case-effects Linkages II Conference, Traverse City, Michigan, USA, Sept 27-28.* 25 Pages.
- Bernes, C. 1999. Persistent Organic Pollutants – a Swedish View of an International Problem. *Swedish Environmental Protection Agency, Stockholm.* 152 pages.
- Binh Minh, T., Watanabe, M., Narkata, H., Tanabe, S. and Jefferson, T.A. 1999. Contamination by Persistent Organochlorines in Small Cetaceans from Hong Kong Coastal Waters. *Marine Pollution Bulletin*, 39, No.s 1-12, 383-392
- de Boer, J., Wester, P.G., Klamer, H.S.C., Lewis, W.E. and Boon, S.P. 1998. Do flame retardants threaten ocean life? *Nature.* 394:28-29.
- Brouwer, A., Reijnders, P.J.H., Koeman, J.H. 1989. Polychlorinated Biphenyl (PCB) – contaminated fish induces vitamin A and thyroid hormone deficiency in the common seal *Phoca vitulina*. *Aquatic Toxicology*, 15, 99-106.
- Colborn, T. and Smolen, M. 1996. An epidemiological analysis of persistent organochlorine contaminants in cetaceans. *Reviews of Environmental Contamination and Toxicology* 146: 91-172.
- Falandysz, J., Strandberg, B., Strandberg, L. and Rappe, C. 1999. Tris(4-chlorophenyl)methane and Tris(4-chlorophenyl)methanol in sediment and food webs from the Baltic South Coast. *Environmental Science and Technology.* 33(4):517-521.
- Fiedler, H., Hutzinger, O. and Timms, C.W. (1990) Dioxins: sources of environmental load and human exposure. *Toxicology and Environmental Chemistry* 29: 157- 234
- Geraci, J.R., Palmer, N.C. and St Aubin, D.J. 1987. Tumours in cetaceans: analysis and new findings. *Can.J.Fish.Aquat.Sci.* 44: 1289-1300.
- Holsbeek, L., Joiris, C.R., Debacker, V., Ali, I.B. Roose, P., Nellissen, J., Gobert, S., Bouquegneau, J. and Bossicart, M. 1999. Heavy Metals, Organochlorines and Polycyclic Aromatic Hydrocarbons in Sperm Whales Stranded in the Southern North Sea During the 1994/1995 Winter *Marine Pollution Bulletin* 38 (4)304-313
- Hutzinger, O. and Fiedler, H. 1989 Sources and Emissions of PCDD/PCDF. *Chemosphere* 18(1-6): 23-32
- Iwata, H., Tanabe, S., Mizuno, T. and Tatsukawa, R. 1995. High accumulation of toxic butyltins in marine mammals from Japanese coastal waters. *Environ. Sci. Technol.* 29:2959-2962.
- Reijnders, P.J.H., Aguilar, A. and Donovan, G.P. (eds). 1999. Chemical Pollutants and Cetaceans. *Journal of Cetacean Research and Management (Special Issue 1).* Cambridge, UK.
- Janak, K., Becker, G., Colmsjo, A., Ostman, C., Athanasiadou, M., Valtiers, K. and Bergman, A. 1998. Methyl sulfonyl polychlorinated biphenyls and 2,2-Bis(4-chlorophenyl)-1,1-Dichloroethene in gray seal tissues determined by gas chromatography with electron capture detection and emission detection. *Environmental Toxicology and Chemistry* 17(6): 1046-1055

- Jansson, A. and Bergman A. 1984. A new persistent contaminant detected in Baltic Wildlife: bis (4-chlorophenyl) sulfone. *Chemosphere*, 13, 33-41
- Karlson, K., Ishaq, R., Becker, G., Berggren, P., Broman, D. and Colmsjo, A. 2000. PCBs, DDTs and methyl sulphone metabolites in various tissues of harbour porpoises from Swedish waters. *Environmental Pollution* 110: 29-46
- Kim, G.B., Tanabe, S., Iwakiri, R., Tatsukawa, R., Amano, M., Miyazaki, N. and Tanaka, H. 1996. Accumulation of Butyltin compounds in Risso's dolphin (*Grampus griseus*) from the Pacific Coast of Japan: comparison with organochlorine residue pattern. *Environ. Sci. Technol.* 30:2620-2625.
- Kurelec, B., Garg, A., Krca S., Chaco, M. and Gupta, C. 1989. Natural environment surpasses polluted environment in inducing DNA damage in fish. *Carcinogenesis*. 10:1337-1339.
- Law, R.J., Blake, S.J., Jones, B.R. and Rogan, E. 1998. Organotin compounds in liver tissue of harbour porpoises (*Phocoena phocoena*) and Grey seals (*Halichoerus grypus*) from the coastal waters of England and Wales. *Mar. Poll. Bull.* 36:241-247.
- Law, R.J. and Whinnett, J.A. 1992. Polycyclic aromatic hydrocarbons in muscle tissues of harbour porpoises (*Phocoenaphocoena*) from UK waters. *Mar. Poll. Bull.* 24(II):550-553.
- Martineau, D., Laglace, A., Masse, R., Morin, M. and Beland, P. 1985. Transitional cell carcinoma of the urinary bladder in a beluga whale (*Delphinapterus leucas*). *Can.Vet.* 5.26:297-302.
- Martineau, D., Laglace, A., Beland, P., Higgins, R., Armstrong, D. and Shugart L.R. 1988. Pathology of stranded beluga whales (*Delphinapterus leucas*) from St Lawrence estuary, Quebec, Canada. *J.Comp. Path.* 98: 287-311.
- Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C. and Kaminuma, T. 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environ. Sci. Technol.* 35:318-324.
- Neff, J.M. 1985. Polycyclic Aromatic Hydrocarbons. In: Rand, G.M. and Petrocelli, S.R. (eds). *Fundamentals of Aquatic Toxicology. Methods and Applications.* Hemisphere Publishing Corporation. NY, London.
- NRCC (National Research Council of Canada). 1984. Polycyclic aromatic hydrocarbons in the aquatic environment: formation, sources, fate and effects on Aquatic biota. *Ass. Comm. Sci. Crit. for Environ. Qual. Ottawa, Canada. No NRCC 18981.* 209 pages.
- OSPAR. 2000. OSPAR convention for the protection of the marine environment in the north-east atlantic: meeting of the OSPAR commission: Copenhagen: 26 - 30 June 2000. Annex 6: OSPAR List of Chemicals for Priority Action (Up-date 2000).
- Peterle, T.J. 1991. Wildlife toxicology. *Van Nostrand Reinhold, New York.*
- Ray, S., Dunn, B.P., Payne, J.F., Fancey, L., Helbig, R. and Beland, P. 1991. Aromatic DNA-carcinogen adducts in Beluga whales from the Canadian Arctic and the Gulf of St Lawrence. *Mar. Pollut. Bull.* 22:392-396.
- Ross, P.S., Ellis, G.M., Ikonomou, M.G., Barrett-Lennard, L.G. and Addison, R.F. 2000. High PCB concentrations in free-ranging Pacific killer whales, *Orcinus orca*: Effects of age, sex and dietary preference. *Mar. Poll. Bull.* 40(6): 504-515.
- Schwind, K.-H., Hosseinpour, J. and Thoma, H. 1988. Brominated/chlorinated dibenzo-p-dioxins and dibenzofurans part 1: Brominated/chlorinated and brominated dibenzo-p-dioxins and dibenzofurans in fly ash from a municipal incinerator. *Chemosphere* 17(9): 1875-1884.
- Simmonds, M.P. 1986. The case against tributyltin. *Oryx.* 20(4):217-220.

- Simmonds, M.P., Hanly, K. and Dolman, S.J. 2000. Toxic equivalency and cetaceans: a note on the threat posed by environmental pollutants. Paper submitted to the IWC Scientific Committee 52/E13. 17 pages.
- Stringer, R. and Johnston, P. 2001. Chlorine and the Environment: An Overview of the Chlorine Industry. *Kluwer Academic Publishers, Dordrecht, Netherlands*. 429 pages.
- Stringer, R., Labuska, I., Santillo, D., Johnston, P., Siddon, S., and Stephenson, A. 1999. Concentrations of Phthalate esters and identification of other additives in PVC children's toys. *ESPR – Environ. Sci. and Pollut. Res.* 6(4):1-10.
- Tanabe, S., Prudente, M., Mizuno, T., Hasegawa, J., Iwata, H., and Miyazaki, N. 1998. Butyltin contamination in marine mammals from North Pacific and Asian coastal waters. *Environ. Sci. Technol.* 32:193.
- Theriault, G., Tremblay, C., Cordier, S. and Gingras, S. 1984. Bladder cancer in the aluminium industry. *The Lancet*. April 28: 947-950.
- Troisi G., Haraguchi K., Simmonds M. and Mason, C. 1998. Methyl sulphone metabolites of polychlorinated biphenyls (PCBs) in cetaceans from the Irish & Aegean Seas. *Archives of Environmental Contamination & Toxicology*, 35 (1), 121-8.
- Weber, W.D.L. and Greim, H. 1997 The toxicity of brominated and mixed-halogenated dibenzo-p-dioxins and dibenzofurans: An overview. *Journal of Toxicology and Environmental Health* 50: 195-215.
- Van den Berg, M., Birnbaum, L., Bosveld, A.T.C., Brunström, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, S.W., Kubiak, T., Larsen, J.C., Van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Wærn, F. and Zacharewski, T. 1998 Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspectives* 106(12): 775-792.
- van Leeuwen, R.F.X., Feeley, M., Schrenk, D., Larsen, J.C., Farland, W. and Younes, M. 2000. Dioxins: WHO'S tolerable daily intake (TDI) revisited. *Chemosphere*. 40: 1095-101.
- Zelinski, V., Lorenz, W. and Bahadir, M. 1993. Brominated flame retardants and resulting PBDD/F in accidental fire residues from private residences. *Chemosphere* 27(8): 1519-1528
- Zelinski, V., Wichmann, H., Lorenz, W. and Bahadir, M. 1994. Chlorinated and brominated dioxins and furans in fire residues from private residences and vehicles- a comparison. *Fresenius Environmental Bulletin* 449-453.

Annex 1. OSPAR List of Chemicals for Priority Action (Up-date 2000)

Substance / group of substances	CAS No	IUPAC name	Identified at *	Lead country
4-tert-butyltoluene	98-51-1	benzene, 1-(1,1-dimethylethyl)-4-methyl-	OSPAR 2000	**
Brominated flame retardants			OSPAR/MMC 1998	Sweden
Cadmium			OSPAR/MMC 1998	**
Certain Phthalates – Dibutylphthalate and Diethylhexylphthalate			OSPAR/MMC 1998	Denmark & France
Dicofol	115-32-2	benzenemethanol, 4-chloro-.alpha.-(4-chlorophenyl)-.alpha.-(trichloromethyl)-	OSPAR 2000	**
Dodecylphenol	732-26-3	phenol, 2,4,6-tris(1,1-dimethylethyl)-	OSPAR 2000	**
Endosulphan	115-29-7	6,9-methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-,3-oxide	OSPAR 2000	Germany
	77-47-4	1,3-cyclopentadiene, 1,2,3,4,5,5-hexachloro-	OSPAR 2000	The Netherlands
Hexachlorocyclohexane isomers (HCH)			OSPAR/MMC 1998	Germany
HMDS	107-46-0	disiloxane, hexamethyl-	OSPAR 2000	France ¹
Lead and organic lead compounds			OSPAR/MMC 1998	Norway
Mercury and organic mercury compounds			OSPAR/MMC 1998	United Kingdom
Methoxychlor	72-43-5	benzene, 1,1'-(2,2,2-trichloroethylidene)bis(4-methoxy	OSPAR 2000	France ^{**1}
Musk xylene			OSPAR/MMC 1998	Switzerland
Nonylphenol/ethoxylates (NP/NPEs) and related substances			OSPAR/MMC 1998	Sweden
Octylphenol	140-66-9	phenol, 4-(1,1,3,3,tetramethylbutyl)-	OSPAR 2000	United Kingdom
Organic tin compounds			OSPAR/MMC 1998	The Netherlands
Pentachlorophenol (PCP)			OSPAR/MMC 1998	Finland
Polyaromatic hydrocarbons (PAHs)			OSPAR/MMC 1998	Norway
Polychlorinated biphenyls (PCBs)			OSPAR/MMC 1998	Germany & Belgium
Polychlorinated dibenzodioxins (PCDDs) Polychlorinated dibenzofurans (PCDFs)			OSPAR/MMC 1998	Denmark & Belgium
Short chained chlorinated paraffins (SCCP)			OSPAR/MMC 1998	Sweden
TBBA	79-94-7	phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-	OSPAR 2000	United Kingdom
Trichlorobenzene	87-61-6	benzene, 1,2,3-trichloro-	OSPAR 2000	Belgium (Flemish Region of Belgium) on the condition that another CP joins as co-lead country
1,2,4-trichlorobenzene	120-82-1	benzene, 1,2,4-trichloro-	OSPAR 2000	
1,3,5-trichlorobenzene	108-70-3	benzene, 1,3,5-trichloro-	OSPAR 2000	

- ¹ Secretariat note: In the Summary Record uploaded on the web-site on 12 July 2000, France was indicated as lead country for Methoxychlor instead of HMDS. This mistake was corrected on 19 July 2000.
- * OSPAR/MMC 1998: OSPAR Agreement reference number 1998-16 (Annex 2 to the OSPAR Strategy with regard to Hazardous Substances)
OSPAR 2000: OSPAR Agreement 2000-10
- ** These substances have currently no lead country to further the work within OSPAR and will have to be considered at a later date.