

Marine Science Review - 180

Pollution

In this review:

- A. Recent articles – no abstract available
- B. Recent articles with abstracts

A. Recent articles – no abstract available

Garrison, A.W. **Probing the enantioselectivity of chiral pesticides.** *Environmental Science and Technology* 40(1): 16-23, 2006.

Garaventa, F., Faimali, M., and Terlizzi, A. **Imposex in pre-pollution times. Is TBT to blame?** *Marine Pollution Bulletin* 52(6): 701-702, 2006.

B. Recent articles with abstracts

Manzo, S., Buono, S., and Cremisini, C. **Toxic effects of Irgarol and Diuron on sea urchin *Paracentrotus lividus* early development, fertilization, and offspring quality.** *Archives of Environmental Contamination and Toxicology* 51(1): 61-68, 2006.

Notes: Irgarol and Diuron are the most representative "organic booster biocides" that replaced organotin compounds in antifouling paints. It cannot be assumed beforehand that their use will have no environmental impact: more ecotoxicological data and a significant environmental monitoring are required. Spermio and embryotoxicities of the biocides Irgarol and Diuron were investigated on *Paracentrotus lividus*, the dominant echinoid species of the Mediterranean Sea. Spermio toxicity was studied by assessing the effects of sperm exposure on fertilization rate as well as on the induction of transmissible damages to the offspring. Embryotoxicity was studied by assessing the developmental defects in the exposed larvae. The experimental results show a Diuron EC50 of 2.39 (+/- 0.21) mg/L with a NOEL of 0.25 mg/L for embryos, and of 5.09 (+/- 0.45) mg/L with a NOEL of 0.5 mg/L for sperms, respectively. Data obtained from the embryotoxicity test on Irgarol [EC50 0.99 (+/- 0.69) mg/L] are of the same order of magnitude as the literature data about Japanese urchins. Spermio toxicity tests show an Irgarol EC50 of 9.04 (+/- 0.45) mg/L with a NOEL of 0.1 mg/L. These data show the different sensitivities of the two tests: embryos are more sensitive than sperms for both the tested chemicals and Diuron seems to be the less toxic one. Moreover, as a major output of the experimental work, tested herbicides exert transmissible damage to spermatozoa evidenced by larval malformations in the offspring, mainly P1 type (skeletal alterations). The comparison of the endpoints results offers an interesting indication of a probable different mode of action (Irgarol seems to interact with calcium homeostasis) of the two biocides.

Fossi, M.C., Casini, S., and Marsili, L. **Endocrine disruptors in Mediterranean top marine predators.** *Environmental Science and Pollution Research* 13(3): 204-207, 2006.

Notes: *Background, Aims and Scope.* Man-made Endocrine Disruptors (EDs) range across all continents and oceans. Some geographic areas are potentially more threatened than others: one of these is the Mediterranean Sea. Levels of some xenobiotics are much higher here than in other seas and oceans. In this paper we review the final results of a project in which the hypothesis that Mediterranean top predator species (such as large pelagic fish and marine mammals) are potentially at risk due to EDs was investigated. *Methods.* In a four-year survey on the Mediterranean population of swordfish (*Xiphias gladius*), the potential toxicological effects of organochlorine compounds (OCs) on specimens of swordfish and tuna fish (*Thunnus thynnus thynnus*), caught in the spawning seasons from 1999 to 2002 in the Straits of Messina, Sicily (Italy), were investigated using

vitellogenin (Vtg), Zona radiata proteins (Zrp), and cytochrome P4501A (CYP1A) activities (EROD, BPMO). Tissues (skin and blubber) were obtained from *Stenella coeruleoalba*, *Tursiops truncatus*, *Delphinus delphis* and *Balaenoptera physalus* from the western Ligurian Sea, between Corsica and the French-Italian coast, and Ionic Sea using biopsy darts launched with a crossbow. Benzo(a)pyrene monooxygenase (BPMO) activity was measured in biopsies and chlorinated hydrocarbon levels were detected. *Results and Discussion.* We illustrate the need to develop and apply sensitive methodological tools, such as biomarkers (vitellogenin, Zona Radiata proteins and CYP1A activities) for evaluation of toxicological risk in *Xiphias gladius* and *Thunnus thynnus thynnus*, and nondestructive biomarkers (CYP1A activities and fibroblast cell culture in skin biopsy), for the hazard assessment of threatened marine mammals species (*Stenella coeruleoalba*, *Tursiops truncatus*, *Delphinus delphis* and *Balaenoptera physalus*) exposed to EDs. *Conclusion.* The present research shows that: a) Vtg and Zrp can be used as diagnostic tools for fish stocks hazard assessment in the Mediterranean Sea; b) that CYP1A1 (BPMO) induction in cetaceans skin biopsy may be an early sign of exposure to EDs such as OCs and a potential alert for transgenerational effects. *Recommendation and Outlook.* This research represents a warning signal of the potential reproductive alterations in marine top predators and suggest the need for continuous monitoring to avoid reductions in population and biodiversity in the Mediterranean Sea.

Rohr, J.R., Sager, T., Sesterhenn, T.M., and Palmer, B.D. **Exposure, postexposure, and density-mediated effects of atrazine on amphibians: Breaking down net effects into their parts.** *Environmental Health Perspectives* 114(1): 46-50, 2006.

Notes: Most toxicology studies focus on effects of contaminants during exposure. This is disconcerting because subsequent survival may be affected. For instance, contaminant-induced mortality can be later ameliorated by reduced competition among the survivors, a concept we refer to as "density-mediated compensation." Alternatively, it can be exacerbated by toxicant effects that persist or appear after exposure, a phenomenon we term "carryover effects." We developed a laboratory framework for testing the contribution of exposure, density-mediated, and carryover effects to net survival, by exposing embryos and larvae of the streamside salamander (*Ambystoma barbouri*) to atrazine (0, 4, 40, 400 ppb; 3 ppb is the U.S. drinking water maximum) and quantifying survival during and 14 months after exposure. Atrazine is the most commonly used herbicide in the United States and a documented endocrine disruptor. We show that atrazine-induced mortality during exposure was ameliorated by density-dependent survival after exposure, but complete density-mediated compensation was precluded by significant carryover effects of atrazine. Consequently, salamanders exposed to ≥ 4 ppb of atrazine had significantly lower survival than did control animals 14 months postexposure. The greatest change in survival occurred at low exposure concentrations. These nonlinear, long-term, postexposure effects of atrazine have similarities to effects of early development exposure to other endocrine disruptors. Together with evidence of low levels of atrazine impairing amphibian gonadal development, the results here raise concerns about the role of atrazine in amphibian declines and highlight the importance of considering persistent, postexposure effects when evaluating the impact of xenobiotics on environmental health.

Reynaud, S. and Deschaux, P. **The effects of polycyclic aromatic hydrocarbons on the immune system of fish: A review.** *Aquatic Toxicology* 77(2): 229-238, 2006.

Notes: Polycyclic aromatic hydrocarbons are an important class of environmental pollutants that are known to be carcinogenic and immunotoxic. This review summarizes the diverse literature on the effects of these pollutants on innate and acquired immunity in fish and the mechanism of PAH-induced immunotoxicity. Among innate immune parameters, many authors have focused on macrophage activities in fish exposed to polycyclic aromatic hydrocarbons. Macrophage respiratory burst appears especially sensitive to polycyclic aromatic hydrocarbons. Among acquired immune parameters, lymphocyte proliferation appears highly sensitive to polycyclic aromatic hydrocarbon exposure. However, the effects of polycyclic aromatic hydrocarbons on both specific and non-specific immunity are contradictory and depend on the mode of exposure, the dose used or the species studied. In contrast to mammals, fewer studies have been done in fish to determine the mechanism of polycyclic aromatic hydrocarbon-induced toxicity. This phenomenon seems to implicate different intracellular mechanisms such as metabolism by cytochrome P4501 A, binding to the Ah-receptor, or increased intracellular calcium. Advances in basic knowledge of fish immunity should lead to improvements in monitoring fish health and predicting the impact of polycyclic aromatic hydrocarbons on fish populations, which is a fundamental ecotoxicological goal.

Lohmann, R., Jurado, E., Pilson, M.E.Q., and Dachs, J. **Oceanic deep water formation as a sink of persistent organic pollutants.** *Geophysical Research Letters* 33(12): art. L12607, 2006.

Notes: The formation of deep oceanic waters occurs as part of the global thermohaline circulation due to gradients in salinity and temperature, and moves surface waters, including persistent organic pollutants (POPs), directly to the deep ocean. For the four main deep water formation regions, removal fluxes of polychlorinated biphenyl (PCB) congeners were calculated based on their surface water concentrations and deep water formation rates. PCB fluxes were higher in the Norwegian Sea (ca. 420 kg/yr) than in the Labrador, Ross and Weddell Seas (ca. 140 - 160 kg/yr each). In the four regions considered, more PCBs were removed due to deep water formation (ca. 870 kg/yr) than by the settling of PCBs associated to organic carbon (ca. 320 kg/yr), whereas the settling flux dominates on a basin scale. Several POPs could serve as tracers for oceanic deep water plumes, as they have only been produced for a few decades.

Finkelstein, M., Keitt, B.S., Croll, D.A., Tershy, B., Jarman, W.M., Rodriguez-Pastor, S., Anderson, D.J., Sievert, P.R., and Smith, D.R. **Albatross species demonstrate regional differences in North Pacific marine contamination.** *Ecological Applications* 16(2): 678-686, 2006.

Notes: Recent concern about negative effects on human health from elevated organochlorine and mercury concentrations in marine foods has highlighted the need to understand temporal and spatial patterns of marine pollution. Seabirds, long-lived pelagic predators with wide foraging ranges, can be used as indicators of regional contaminant patterns across large temporal and spatial scales. Here we evaluate contaminant levels, carbon and nitrogen stable isotope ratios, and satellite telemetry data from two sympatrically breeding North Pacific albatross species to demonstrate that (1) organochlorine and mercury contaminant levels are significantly higher in the California Current compared to levels in the high-latitude North Pacific and (2) levels of organochlorine contaminants in the North Pacific are increasing over time. Black-footed Albatrosses (*Phoebastria nigripes*) had 370-460% higher organochlorine (polychlorinated biphenyls [PCBs], dichlorodiphenyltrichloroethanes [DDTs]) and mercury body burdens than a closely related species, the Laysan Albatross (*P. immutabilis*), primarily due to regional segregation of their North Pacific foraging areas. PCBs (the sum of the individual PCB congeners analyzed) and DDE concentrations in both albatross species were 130- 360% higher than concentrations measured a decade ago. Our results demonstrate dramatically high and increasing contaminant concentrations in the eastern North Pacific Ocean, a finding relevant to other marine predators, including humans.

Valavanidis, A., Vlahogianni, T., Dassenakis, M., and Scoullou, M. **Molecular biomarkers of oxidative stress in aquatic organisms in relation to toxic environmental pollutants.** *Ecotoxicology and Environmental Safety* 64(2): 178-189, 2006.

Notes: The potential of oxygen free radicals and other reactive oxygen species (ROS) to damage tissues and cellular components, called oxidative stress, in biological systems has become a topic of significant interest for environmental toxicology studies. The balance between prooxidant endogenous and exogenous factors (i.e., environmental pollutants) and antioxidant defenses (enzymatic and nonenzymatic) in biological systems can be used to assess toxic effects under stressful environmental conditions, especially oxidative damage induced by different classes of chemical pollutants. The role of these antioxidant systems and their sensitivity can be of great importance in environmental toxicology studies. In the past decade, numerous studies on the effects of oxidative stress caused by some environmental pollutants in terrestrial and aquatic species were published. Increased numbers of agricultural and industrial chemicals are entering the aquatic environment and being taken up into tissues of aquatic organisms. Transition metals, polycyclic aromatic hydrocarbons, organochlorine and organophosphate pesticides, polychlorinated biphenyls, dioxins, and other xenobiotics play important roles in the mechanistic aspects of oxidative damage. Such a diverse array of pollutants stimulate a variety of toxicity mechanisms, such as oxidative damage to membrane lipids, DNA, and proteins and changes to antioxidant enzymes. Although there are considerable gaps in our knowledge of cellular damage, response mechanisms, repair processes, and disease etiology in biological systems, free radical reactions and the production of toxic ROS are known to be responsible for a variety of oxidative damages leading to adverse health effects and diseases. In the past decade, mammalian species were used as models for the study of molecular biomarkers of oxidative stress caused by environmental pollutants to elucidate the mechanisms underlying cellular oxidative damage and to study the adverse effects of some environmental pollutants with oxidative potential in chronic exposure and/or sublethal concentrations. This review summarizes current knowledge and advances in the understanding of such oxidative processes in biological systems. This knowledge is extended to specific applications in aquatic organisms because of their sensitivity to oxidative pollutants, their filtration capacity, and their potential for environmental toxicology studies.

Milnes, M.R., Bermudez, D.S., Bryan, T.A., Edwards, T.M., Gunderson, M.P., Larkin, I.L.V., Moore, B.C., and Guillette, L.J. **Contaminant-induced feminization and demasculinization of nonmammalian vertebrate males in aquatic environments.** *Environmental Research* 100(1): 3-17, 2006.

Notes: Many chemicals introduced into the environment by humans adversely affect embryonic development and the functioning of the male reproductive system. It has been hypothesized that these developmental alterations are due to the endocrine-disruptive effects of various environmental contaminants. The endocrine system exhibits an organizational effect on the developing embryo. Thus, a disruption of the normal hormonal signals can permanently modify the organization and future function of the male reproductive system. A wide range of studies examining wildlife either in laboratories or in natural settings have documented alterations in the development of males. These studies have begun to provide the causal relationships between embryonic contaminant exposure and reproductive abnormalities that have been lacking in pure field studies of wild populations. An understanding of the developmental consequences of endocrine disruption in wildlife can lead to new indicators of exposure and a better understanding of the most sensitive life stages as well as the consequences of exposure during theme periods.

Andersen, M., Gwynn, J.P., Dowdall, M., Kovacs, K.M., and Lydersen, C. **Radiocaesium (¹³⁷Cs) in marine mammals from Svalbard, the Barents Sea and the North Greenland sea.** *The Science of the Total Environment* 363(1-3): 87-94, 2006.

Notes: Specific activities of the anthropogenic radionuclide, ¹³⁷Cs, were determined in marine mammals from Svalbard and the Barents and North Greenland Seas. Muscle samples were collected from 12 polar bears, 15 ringed seals, 10 hooded seals, 7 bearded seals, 14 harp seals, one walrus, one white whale and one blue whale in the period 2000-2003. The mean concentrations (+/- SD) of ¹³⁷Cs were: 0.72 +/- 0.62 Bq/kg wet weight (w.w.) for polar bears; 0.49 +/- 0.07 Bq/kg w.w. for ringed seals; 0.25 +/- 0.10 Bq/kg w.w. for hooded seals; 0.22 +/- 0.11 Bq/kg w.w. for bearded seals; 0.36 +/- 0.13 Bq/kg w.w. for harp seals; 0.67 Bq/kg w.w. for the white whale sample; 0.24 Bq/kg w.w. for the blue whale; and below detection limit for the walrus. Significant differences in ¹³⁷Cs specific activities between some of the species were found. Ringed seals had higher specific activities than the other seal species in the study. Bearded seals and hooded seals had similar values, which were both significantly lower than the harp seal values. The results in the present study are consistent with previous reported results, indicating low specific activities of ¹³⁷Cs in Arctic marine mammals in the Barents Sea and Greenland Sea region during the last 20 years. The species specific differences found may be explained by varying diet or movement and distribution patterns between species. No age related patterns were found in specific activities for the two species (polar bears and hooded seals) for which sufficient data was available. Concentration factors (CF) of ¹³⁷Cs from seawater were determined for polar bears, ringed, bearded, harp and hooded seals. Mean CF values ranged from 79 +/- 32 (SD) for bearded seals sampled in 2002 to 244 +/- 36 (SD) for ringed seals sampled in 2003 these CF values are higher than those reported for fish and benthic organisms in the literature, suggesting bioaccumulation of ¹³⁷Cs in the marine ecosystem.

Garza-Gil, M.D., Prada-Blanco, A., and Vazquez-Rodriguez, M.X. **Estimating the short-term economic damages from the Prestige oil spill in the Galician fisheries and tourism.** *Ecological Economics* 58(4): 842-849, 2006.

Notes: The Prestige oil spill may be considered as one of the worst in the last years because of the amount of oil spilled (59,000 tons at the moment) and the wide zone affected: almost all the coastline in Galicia (Spanish region with a very important coast fishing and tourist activity) and some points in North Spain and in Southwest France. In this paper, we estimate the short-term economic damages from the Prestige oil spills in the Galician fishing and tourist activities. The economic losses arising from the Prestige oil spill exceed those items that can be indemnified under the IOPC system. Their magnitude could reach 5 times more than the applicable limit of compensations in the Prestige case. The consequence is net losses from repeated oil spills and internationally accepted incentives to risky strategies in the marine transport of hydrocarbons.

Porte, C., Janer, G., Lorusso, L.C., Ortiz-Zarragoitia, M., Cajaraville, M.P., Fossi, M.C., and Canesi, L. **Endocrine disruptors in marine organisms: Approaches and perspectives.** *Comparative Biochemistry and Physiology -- Part C* 143(3): 303-315, 2006.

Notes: Organic pollutants exhibiting endocrine disrupting activity (Endocrine Disruptors-EDs) are prevalent over a wide range in the aquatic ecosystems; most EDs are resistant to environmental degradation and are considered ubiquitous contaminants. The actual potency of EDs is low compared to that of natural hormones, but environmental concentrations may still be sufficiently high to produce detrimental biological effects. Most information on the biological effects and mechanisms of action of EDs has been focused on vertebrates. Here we summarize recent progress in studies on selected aspects of endocrine disruption in marine organisms that are still poorly understood and that certainly deserve further research in the near future. This review, divided in four sections, focuses mainly on invertebrates (effects of EDs and mechanisms of action) and presents data on top predators (large pelagic fish and cetaceans), a group of vertebrates that are particularly at risk due to their position in the food chain. The first section deals with basic pathways of steroid biosynthesis and metabolism as a target for endocrine disruption in invertebrates. In the second section, data on the effects and alternative mechanisms of action of estrogenic compounds in mussel immunocytes are presented, addressing to the importance of investigating full range responses to estrogenic chemicals in ecologically relevant invertebrate species. In the third section we review the potential use of vitellogenin (Vtg)-like proteins as a biomarker of endocrine disruption in marine bivalve molluscs, used worldwide as sentinels in marine biomonitoring programmes. Finally, we summarize the results of a recent survey on ED accumulation and effects on marine fish and mammals, utilizing both classical biomarkers of endocrine disruption in vertebrates and non-lethal techniques, such as non-destructive biomarkers, indicating the toxicological risk for top predator species in the Mediterranean. Overall, the reviewed data underline the potential to identify specific types of responses to specific groups of chemicals such as EDs in order to develop suitable biomarkers that could be useful as diagnostic tools for endocrine disruption in marine invertebrates and vertebrates.

Jorundsdottir, H., Norstrom, A., Olsson, M., Pham Tuan, H., Huhnerfuss, H., Bignert, A., and Bergman, A. **Temporal trend of bis(4-chlorophenyl) sulfone, methylsulfonyl-DDE and -PCBs in Baltic guillemot (*Uria aalge*) egg 1971-2001 - A comparison to 4,4'-DDE and PCB trends.** *Environmental Pollution* 141(2): 226-237, 2006.

Notes: The dynamics of organohalogen contaminants and their metabolites are best studied over time by analysis of biota at high trophic levels. In this study, time trends, 1971-2001, of bis(4-chlorophenyl) sulfone (BCPS) and of methylsulfonyl-substituted metabolites of PCBs and 4,4'-DDE, were investigated in eggs of guillemot (*Uria aalge*) hatching in the Baltic Proper. Temporal trends of PCBs, trans-nonachlor, beta-HCH, 4,4'-DDT, and 4,4'-DDE were also assessed. Tris(4-chlorophenyl) methane (TCPMe), a 4,4'-DDT by-product, was detected in the eggs. The concentration of BCPS ranged between 2.6-0.76 mg/g on a lipid weight basis over the three decades and showed a significant 1.6% annual decrease. Three metabolites of PCBs, i.e. 3'-MeSO₂-CB101, 4'-MeSO₂-CB101 and 4-MCSO₂-CB149, were quantified in all samples over time and showed an annual decrease of approximately 3% compared to MeSO₂-DDE with a decrease of 8.9%. The methylsulfonyl-PCB and -DDE metabolites are eliminated more slowly than the persistent PCB congeners and 4,4'-DDE. Trans-nonachlor decreases by 16% compared to 19% and 9% for 4,4'-DDT and beta-HCH, respectively. The concentration of TCPMe in guillemot decreased by 8.2% per year. A linear relationship was found between TCPMe and 4,4'-DDE concentrations which supports the theory that TCPMe has an origin as a contaminant in commercial 4,4'-DDT products. The very slow decrease in BCPS concentrations is notable and remains to be explained. BCPS is still present at rather high concentrations in the guillemot eggs. The enantiomeric fraction varied between 0.27 and 0.67 which indicates less of a specific retention of the chiral MeSO₂-PCBs in guillemot eggs than in grey seal tissues, for example. Independent of meta- or para-substitution of the sulfone group, the most accumulative atropisomer of each of four MeSO₂-PCB pairs has been assigned an absolute R structure.

Sigler, J.M. and Lee, X. **Recent trends in anthropogenic mercury emission in the northeast United States.** *Journal of Geophysical Research* 111(14): art. D14316, 2006.

Notes: We combine wintertime measurements of total gaseous mercury (TGM) with a combustion tracer (carbon dioxide) at a background site in Connecticut to investigate changes in regional Hg emission from 1999/2000 through 2003/2004. This method allows timelier flux estimates than inventory approaches. We find a 20% decrease in emission between 1999/2000 and 2003/2004, although the rate has increased since 2001/2002. Air trajectory analysis reveals a source region of Hg influencing the site that encompasses most of the mid-Atlantic and New England states, and Maryland and Delaware, with small

interannual variation. The significant interannual changes in Hg emission therefore cannot be fully explained by climatological changes. Inventory calculations of Hg flux from the regional electric power sector show significant correlation with the emission trend derived from the atmospheric measurements, suggesting that the power sector strongly influences the regional Hg flux to the atmosphere. However, averaged over the five winters, the Hg flux from the power sector was 47-75% of the atmospheric flux, which is assumed to be >95% elemental Hg. If 50% or more of Hg emitted by power sources is speciated and deposits locally, the power sector can account for only 23-40% of the observed elemental Hg flux to the atmosphere. Possible explanations include conversion of some reactive Hg emitted by power plants to elemental Hg, underestimation of inventory emissions from sources outside the power sector, the possibility that emissions from municipal and medical waste combustion have not been curbed to the EPA targeted level, or that a combination of these factors exists.

Ghekiere, A., Verslycke, T., Fockedey, N., and Janssen, C. R. **Non-target effects of the insecticide methoprene on molting in the estuarine crustacean *Neomysis integer* (Crustacea: Mysidacea).** *Journal of Experimental Marine Biology and Ecology* 332(2): 226-234, 2006.

Notes: Ecdysteroids, the molting hormones in crustaceans and other arthropods, play a crucial role in the control of growth, reproduction and embryogenesis of these organisms. Insecticides are often designed to target specific endocrine-regulated functions such as molting and larval development such as methoprene, a juvenile hormone analogue. The aim of this study was to examine the effects of methoprene on molting in a non-target species, the estuarine mysid *Neomysis integer* (Crustacea: Mysidacea). Mysids have been proposed as standard test organisms for evaluating the endocrine disruptive effect of chemicals. Juveniles (< 24 h) were exposed for 3 weeks to the nominal concentrations 0.01, 1 and 100 µg methoprene/l. Daily, present molts were checked and stored in 4% formaldehyde for subsequent growth measurements. Methoprene significantly delayed molting at 100 µg/l by decreasing the growth rate and increasing the intermolt period. This resulted in a decreased wet weight of the organism. The anti-ecdysteroidal properties of methoprene on mysid molting were also evaluated by determining the ability of exogenously administered 20-hydroxyecdysone, the active ecdysteroid in crustaceans, to protect against the observed methoprene effects. Co-exposure to 20-hydroxyecdysone did not mitigate methoprene effects on mysid molting. This study demonstrates the need for incorporating invertebrate-specific hormone-regulated endpoints in regulatory screening and testing programs for the detection of endocrine disruption caused by man-made chemicals.

Hylland, K. **Polycyclic aromatic hydrocarbon (PAH) ecotoxicology in marine ecosystems.** *Journal of Toxicology and Environmental Health Part A* 69(1-2): 109-123, 2006.

Notes: Low levels of oil and hence polycyclic aromatic hydrocarbons (PAHs) are naturally present in the marine environment, although levels have increased significantly following human extraction and use of oil and gas. Other major anthropogenic sources of PAHs include smelters, the use of fossil fuels in general, and various methods of waste disposal, especially incineration. There are two major sources for PAHs to marine ecosystems in Norway: the inshore smelter industry, and offshore oil and gas production activities. A distinction is generally made between petrogenic (oil-derived) and pyrogenic (combustion-derived) PAHs. Although petrogenic PAHs appear to be bioavailable to a large extent, pyrogenic PAHs are often associated with soot particles and less available for uptake into organisms. There is extensive evidence linking sediment-associated PAHs to induction of phase-I enzymes, development of DNA adducts, and eventually neoplastic lesions in fish. Most studies have focused on high-molecular-weight, carcinogenic PAHs such as benzo[a] pyrene. It is less clear how two- and three-ring PAHs affect fish, and there is even experimental evidence to indicate that these chemicals may inhibit some components of the phase I system rather than produce induction. There is a need for increased research efforts to clarify biological effects of two- and three-ring PAHs, PAH mixtures, and adaptation processes in marine ecosystems.

Hylland, K., Beyer, J., Berntssen, M., Klungsoyr, J., Lang, T., and Balk, L. **May organic pollutants affect fish populations in the North Sea?** *Journal of Toxicology and Environmental Health Part A* 69(1-2): 125-138, 2006.

Notes: The North Sea is a highly productive area with large fish populations that have been extensively harvested over the past century. North Sea fisheries remain important to the surrounding countries despite declining fish stocks over the past decades. The main reason for declining fish stocks is nearly certainly overfishing, but other environmental pressures also affect fish populations, such as eutrophication, climate change, and exposure to metals and organic pollutants, including

polyaromatic hydrocarbons (PAHs), alkylphenols, and organochlorine compounds. There are three main sources of organic pollutants in the North Sea: atmospheric, land-based sources, and inputs from offshore gas and oil installations. All three sources contribute to elevated concentrations of organic pollutants in the North Sea compared to the Norwegian Sea. There is evidence that chlorinated organic contaminants were present in sufficiently high concentrations in the southern North Sea two decades ago, to alter embryonal development in fish. The results from extensive, long-term monitoring programs show that some diseases decreased whereas other increased in the southern North Sea and that, among other factors, contaminants may play a role in the temporal changes recorded in disease prevalence. Recent studies demonstrated that components in offshore effluents may affect fish reproduction and that tissues of fish near oil rigs are structurally different to tissues of fish from reference areas. Data on effluents from offshore activities have recently become available through an international workshop (BECPELAG) and follow-up studies.

Bejarano, A.C., Pennington, P.L., DeLorenzo, M.E., and Chandler, G.T. **Atrazine effects on meiobenthic assemblages of a modular estuarine mesocosm.** *Marine Pollution Bulletin* 50(11): 1398-1404, 2005.

Notes: Atrazine is a widely used herbicide in the US found at levels ranging from < 10 ng/L to 62.5 mg/L in estuaries throughout the southeast. Effects of atrazine on estuarine meiobenthic assemblages chronically exposed to environmentally relevant concentrations are unknown. The purpose of our research was to assess effects of atrazine on meiobenthos at concentrations near the proposed USEPA SWQC (26 mg/ L) using modular estuarine salt marsh mesocosms as a field surrogate. Indigenous copepod and nematode densities were assessed after 28 days of exposure in transplanted colonization chambers. Cluster analysis showed a group characterized by low copepod densities, mostly atrazine exposed chambers, and a group containing all but one control chamber. The later group included chambers with high densities of the copepods *Paronychocamptus wilsoni* and *Enhydrosoma baruchi*. Compared to controls, copepod densities was ~ 70% lower in atrazine chambers, with three of the most common copepod species (*E. baruchi*, *Onychocamptus* sp. and *P. wilsoni*) showing an average of 50-70% reduction in population densities ($p < 0.05$). Although nematode density did not differ between atrazine and control chambers, the nematode-to-copepod ratio was significantly higher in atrazine (9.95 ± 7.61 ; $p = 0.011$) than in control chambers (0.61 ± 0.35). Our findings suggest that chronic exposures over multiple generations to atrazine at concentrations near the proposed USEPA SWQC could have significant effects on the abundance and composition of estuarine meiobenthic copepod assemblages.

Stapleton, H.M., Dodder, N.G., Kucklick, J.R., Reddy, C.M., Schantz, M.M., Becker, P.R., Gulland, F., Porter, B.J., and Wise, S.A. **Determination of HBCD, PBDEs and MeO-BDEs in California sea lions (*Zalophus californianus*) stranded between 1993 and 2003.** *Marine Pollution Bulletin* 52(5): 522-531, 2006.

Notes: Blubber samples from male California sea lions (*Zalophus californianus*) stranded between 1993 and 2003 were analyzed for 27 polybrominated diphenyl ether (PBDE) congeners, three isomers of hexabromocyclododecane (HBCD) and 14 methoxylated polybrominated diphenyl ether (MeO-BDE) congeners. Total PBDEs ranged from 450 ng/g to 4740 ng/g wet mass and total HBCD ranged from < 0.3 ng/g to 12 ng/ g wet mass. The concentration of HBCD increased from 0.7 ng/g to 12.0 ng/g wet mass in sea lion blubber between 1993 and 2003. However, no significant temporal trend was observed for any of the other brominated compounds over this 10 year period. Only one of the 14 MeO-BDE congeners was detected in the blubber samples, 6-methoxy-2,2',4,4'-tetrabromodiphenyl ether (6-MeO-BDE 47), and concentrations ranged from < 0.2 ng/g to 12 ng/g wet mass. A bromo-, chloro- heterocyclic compound, 1,1'-dimethyl-tetrabromo-dichloro-2,2'-bipyrrole (DBP-Br4Cl2) previously reported in marine species along the Pacific coast, was also identified in the sea lion blubber. DBP-Br4Cl2 ranged from 44 ng/g wet mass to 660 ng/g wet mass and was present at concentrations rivaling the dominant PBDE congener, BDE 47 (2,2',4,4'-tetrabromodiphenyl ether). Concentrations of DBP-Br4Cl2 were positively correlated with 6-MeO-BDE 47 ($r = 0.71$; $p < 0.05$). Both of these compounds have been identified in marine algae and sponges, and studies suggest they are both produced from natural sources. This study demonstrates that brominated compounds from both anthropogenic and biogenic sources can accumulate to similar levels in marine mammals. In addition, HBCD concentrations appear to be increasing in California sea lion populations, whereas PBDE concentrations, between 1993 and 2003, were highly variable.

Carbery, K., Owen, R., Frickers, T., Otero, E., and Readman, J. **Contamination of Caribbean coastal waters by the antifouling herbicide Irgarol 1051.** *Marine Pollution Bulletin* 52(6): 635-644, 2006.

Notes: Irgarol 1051® is a s-triazine herbicide used in popular slime-resistant antifouling paints. It has been shown to be acutely toxic to corals, mangroves and sea grasses, inhibiting photosynthesis at low concentrations (> 50 ng l(-1)). We present the first data describing the occurrence of Irgarol 1051® in coastal waters of the Northeastern Caribbean (Puerto Rico (PR) and the US Virgin Islands (USVI)). Low level contamination of coastal waters by Irgarol 1051® is reported, the herbicide being present in 85% of the 31 sites sampled. It was not detected in water from two oceanic reference sites. In general, Irgarol 1051® was present at concentrations below 100 ng l(-1), although far higher concentrations were reported at three locations within Benner Bay, USVI (223-1300 ng l(-1)). The known toxicity of Irgarol 1051® to corals and sea grasses and our findings of significant contamination of the Northeastern Caribbean marine environment by this herbicide underscore the importance of understanding, more fully, local and regional exposure of reef and sea grass habitats to Irgarol 1051® and, where necessary, implementing actions to ensure adequate protection of these important ecosystems.

Isidori, M., Lavorgna, M., Nardelli, A., and Parrella, A. **Toxicity on crustaceans and endocrine disrupting activity on *Saccharomyces cerevisiae* of eight alkylphenols.** *Chemosphere* 64(1): 135-143, 2006.

Notes: In the last few years many concerns have been raised regarding the environmental safety of alkylphenol polyethoxylate surfactants (APnEOs). They are widely used in detergents, paints, herbicides and many other formulated products. It has been estimated that 60% of APnEOs end up in the aquatic environment; they are biodegradable and transformed into alkylphenols, such as nonylphenol and octylphenol that are hydrophobic and tend to accumulate. In the present study, acute and chronic aquatic toxicity and the estrogenic activity of the following eight alkylphenols were assessed: 4-nonylphenol, 4-octylphenol, 4-nonylphenol-10-ethoxylate, 4-tert-octylphenol, POE (1 to 2)-nonylphenol, POE (6)-nonylphenol, POE (3)-tert-octylphenol and POE (9 to 10)-tert-octylphenol. The toxic potential was measured on the crustaceans *Daphnia magna* and *Ceriodaphnia dubia*, while the estrogenic activity was determined by using the YES-test with the strain *Saccharomyces cerevisiae* RMY326. The results showed that the exposure of crustaceans to the eight xenoestrogens investigated caused both acute and chronic effects. The EC50 values found for *C. dubia* at 48 h were compared to *D. magna* at 24 h and, gave a first indication about the toxic activity of the compounds investigated, that is better expressed in the long-term. In fact, chronic data showed a strong increase in toxicity with EC50 values one or two orders of magnitude lower than the acute values. The results of the YES-test showed that nonylphenol, octylphenol and 4-tert-octylphenol were the most estrogenic and the bioassay was able to detect their estrogenicity at very low concentrations (ng-mg/l).

Law, R.J., Allchin, C.R., deBoer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S., Tronczynski, J., and deWit, C.A. **Levels and trends of brominated flame retardants in the European environment.** *Chemosphere* 64(2): 187-208, 2006.

Notes: In this paper, we review those data which have recently become available for brominated flame retardants (particularly the brominated diphenyl ethers (BDEs) and hexabromocyclodo-decane (HBCD)) in samples from the European environment. Environmental compartments studied comprise the atmosphere, sediments and soils, sewage sludges, and a variety of biological samples and food chains. This is currently a very active research area, and we cite over 70 studies reported in the literature during 2003-04. Findings include that the input of BDEs (especially BDE209) to the Baltic Sea by atmospheric deposition now exceeds that of PCBs by a factor of almost 40 times. Sewage sludge samples from both industrial and background locations show concentrations of BDEs, HBCD and tetrabromobisphenol-A (TBBP-A) that are of a similar order, indicating that the major source is from diffuse leaching from products into wastewater streams from users, households and industries generally. Point-sources from industries using BFRs (e.g. the textile industry) also generate local hot-spots. Sediment core studies identified the presence of two of the three PBDE formulations. The penta-mix formulation was clearly present from the beginning of the 1970s, but the deca-mix only appeared in the late 1970s. BDE183, BDE209 and HBCD were detected in peregrine falcons from Sweden and other birds feeding on terrestrial food chains. BDEs are found widely distributed in fish, including those from high mountain lakes in Europe, as a consequence of long-range atmospheric transport and deposition. A temporal trend study in archived freeze-dried mussels from the Seine estuary, France, indicated an exponential increase in BDE concentrations during the period 1982-1993, which levelled off in 1999 and 2001 and then began to decline after 2002. HBCD was detected in liver and blubber samples from harbour seals and harbour porpoises from the Wadden and North Seas. Though very few animals yielded positive values for TBBP-A, there are difficulties in comparing data

on SBDE from studies in which different suites of BDE congeners have been determined, and we suggest a common suite which will allow the study of all three commercial PBDE formulations.

deWit, C.A., Alae, M., and Muir, D.C.G. **Levels and trends of brominated flame retardants in the Arctic.** *Chemosphere* 64(2): 209-233, 2006.

Notes: Polybrominated diphenyl ethers (PBDEs) containing two to seven bromines are ubiquitous in Arctic biotic and abiotic samples (from zooplankton to polar bears (*Ursus maritimus*) and humans; air, soil, sediments). The fully brominated decabromodiphenyl ether (BDE-209), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA) and polybrominated biphenyls (PBBs) are also present in biotic and abiotic samples. Spatial trends of PBDEs and HBCD in top predators are similar to those seen for polychlorinated biphenyls (PCBs) and indicate western Europe and eastern North America as source regions. Concentrations of tetra- to heptaBDEs have increased significantly in North American and Greenlandic Arctic biota and in Greenland freshwater sediments paralleling trends seen further south. For BDE-209, increasing concentrations in Greenlandic peregrine falcons (*Falco peregrinus*) and in dated lake sediment cores in the Canadian Arctic have been seen during the 1990s. BDE-47, -99, -100 and -153 are observed to biomagnify in Arctic food webs. SPBDE concentrations in Arctic samples are lower than in similar sample types from more southerly regions and are one or more orders of magnitude lower than SPCB concentrations except for some levels for air. Air and harbor sediment results for PBDEs indicate that there are local sources near highly populated areas within the Arctic. Findings of PBBs on moss and TBBPA on an air filter, and that both are found in biota at high trophic levels indicates that these compounds may also reach the Arctic by long-range atmospheric transport. Based on the evidence of their presence in the Arctic and indications that most if not all are undergoing long-range transport, these brominated flame retardants (BFRs) have characteristics that qualify them as POPs according to the Stockholm Convention.

Kajiwara, N., Kamikawa, S., Ramu, K., Ueno, D., Yamada, T.K., Subramanian, A., Lam, P.K.S., Jefferson, T.A., Prudente, M., Chung, K.F., and Tanabe, S. **Geographical distribution of polybrominated diphenyl ethers (PBDEs) and organochlorines in small cetaceans from Asian waters.** *Chemosphere* 64(2): 287-295, 2006.

Notes: Polybrominated diphenyl ethers (PBDEs) are one of the flame retardants widely used in plastics, textiles, electronic appliances, and electrical household appliances. In this study, PBDEs and organochlorine compounds (OCs) were determined in the archived samples from the Environmental Specimen Bank for Global Monitoring (es-BANK) at Ehime University. The blubber of cetaceans found stranded along the coasts of Japan, Hong Kong, the Philippines and India during the period from 1990 to 2001 were employed for chemical analysis to understand the present status of contamination and the specific accumulation of PBDEs. PBDEs were detected in all the cetacean samples analyzed, and concentrations were one or two orders of magnitude lower than for PCBs and DDTs. Concentrations of PBDEs ranged from a low value of 6.0 ng/g lipid wt. in spinner dolphin (*Stenella longirostris*) from India to a high value of 6000 ng/g lipid wt. in Indo-Pacific humpback dolphin (*Sousa chinensis*) from Hong Kong. No difference in PBDE levels between coastal and offshore species from Japan was observed, implying the existence of pollution sources in this region other than Japan. Highest concentrations of PBDEs were found in animals from Hong Kong, followed by Japan, and much lower levels from the Philippines and India, suggesting that developing nations may also have pollution sources of PBDEs. Geographical distribution of PBDEs in Asian waters was different from PCBs but similar to DDTs.

Arukwe, A. **Modulation of brain steroidogenesis by affecting transcriptional changes of steroidogenic acute regulatory (StAR) protein and cholesterol side chain cleavage (P450scc) in juvenile Atlantic salmon (*Salmo salar*) is a novel aspect of nonylphenol toxicity.** *Environmental Science and Technology* 39(24): 9791-9798, 2005.

Notes: Gene expression patterns for key brain steroidogenic (StAR, P450scc, CYP11 beta) and xenobiotic- and steroid-metabolizing enzymes (CYP1A1 and CYP3A) have been investigated in waterborne nonylphenol (5, 15, and 50 mg/L) treated juvenile Atlantic salmon (*Salmo salar*), in addition to carrier vehicle (ethanol) exposed fish, sampled at different time intervals (0, 3, and 7 days) after exposure. Gene expression patterns were studied using the quantitative polymerase chain reaction (real-time PCR). Treatment of juvenile salmon with nonylphenol caused significant induction of steroidogenic acute regulatory (StAR) protein mRNA at day 7 postexposure in the group receiving 15 mg of nonylphenol/L. P450scc was first induced in the

group treated with 5 mg of nonylphenol/L at day 7; thereafter, an apparent nonylphenol-concentration-dependent decrease in P450_{1A1} mRNA was observed. CYP11 mRNA was significantly induced at day 3 after exposure to 5 mg of nonylphenol/L; thereafter, CYP11 mRNA levels were inhibited below control levels in the 15 and 50 mg of nonylphenol/L groups at day 3. At day 7, significant induction of CYP11 mRNA was observed only in the group exposed to 15 mg of nonylphenol/L. For CYP1A1 mRNA, apparent nonylphenol-concentration-dependent decreases were observed at day 7 postexposure. CYP3A mRNA was significantly induced by all nonylphenol exposure concentrations at day 7. When exposed groups were compared, CYP3A transcript was significantly induced between 5 and 15 mg of nonylphenol/L, and decreased between 15 and 50 mg of nonylphenol/L. The ethanol control showed a significant reduction of CYP3A mRNA at day 3 postexposure. The present study has demonstrated variations in three key steroidogenic proteins and xenobiotic- and steroid-metabolizing CYP isoenzyme gene transcripts in the brain of nonylphenol-exposed juvenile salmon. Therefore, the present study represents a novel aspect of neuroendocrine effects of nonylphenol in fish not previously demonstrated and should be studied in more detail.

Wania, F. **Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic.** *Environmental Science and Technology* 40(2): 569-577, 2006.

Notes: Model simulations of the fate of numerous hypothetical substances in the global environment can provide considerable insight into how an organic chemical's degradability and partitioning properties influence its absolute and relative Arctic enrichment behavior, as quantified by the Arctic Contamination Potential. For substances that degrade faster in water than in soil, but are quite persistent in the atmosphere, highest Arctic contamination is expected to occur if the substances have intermediate volatility and high hydrophobicity. Organic substances that are degradable in the atmosphere can still accumulate in the Arctic if they are soluble and highly persistent in water. These latter substances, which reach the Arctic in the ocean, also show the highest potential for relative enrichment in the Arctic, i.e., high amounts in northern high latitudes relative to the amounts in the total global environment. Beyond a threshold persistence in surface media of the order of several months to a year, chemical degradability leads to further relative enrichment. This is because only chemicals that are sufficiently long-lived get transferred to polar regions and once there can persist longer than at lower latitudes. The model simulations can inform the search for new potential Arctic contaminants, and can highlight combinations of properties which should be avoided in high production volume chemicals with the potential for environmental release. Three categories of organic substances are singled out for troublesome combinations of persistence, distribution, and potential bioaccumulation characteristics, only one of which contains "classical" Arctic POPs. Examples of potential Arctic contaminants within each of these categories are named.

Sonne, C., Dietz, R., Larsen, H. J. S., Loft, K. E., Kirkegaard, M., Letcher, R. J., Shahmiri, S., and Moller, P. **Impairment of cellular immunity in West Greenland sledge dogs (*Canis familiaris*) dietary exposed to polluted Minke whale (*Balaenoptera acutorostrata*) blubber.** *Environmental Science and Technology* 40(6): 2056-2062, 2006.

Notes: Minke whale (*Balaenoptera acutorostrata*) blubber is rich in organohalogen contaminants, mercury, and n-3 fatty acids. In the present study we show that a daily intake of 50-200 g of minke whale blubber causes an impairment of the nonspecific and specific cellular immune system in the West Greenland sledge dog (*Canis familiaris*). Immune reactions were measured by mitogen (PHA, Con A) and antigen (KLH) intradermal testing, and as the study used exposure levels similar to those of Inuits and polar bears (*Ursus maritimus*), it is reasonable to infer that Inuits and polar bears suffer from similar decreased resistance to diseases. It is speculated that food sources are depleted by thinning sea ice due to climate change and that more research should assess the forecasted rise in additive immunopathy effects in polar bears. Additionally, our study suggests that the fatty acid composition may be of importance when investigating combined immunotoxic effects of contaminated food resources in future Inuit and polar bear studies.

Houde, M., Martin, J.W., Letcher, R.J., Solomon, K.R., and Muir, D.C.G. **Biological monitoring of polyfluoroalkyl substances: A review.** *Environmental Science and Technology* 40(11): 3463-3473, 2006.

Notes: Polyfluoroalkyl substances (PFs) are used in industrial and commercial products and can degrade to persistent perfluorocarboxylates (PFCAs) and perfluoroalkyl sulfonates (PFsAs). Temporal trend studies using human, fish, bird, and

marine mammal samples indicate that exposure to PFSs has increased significantly over the past 15-25 years. This review summarizes the biological monitoring of PFCAs, PFSAs, and related PFSs in wildlife and humans, compares concentrations and contamination profiles among species and locations, evaluates the bioaccumulation/biomagnification in the environment, discusses possible sources, and identifies knowledge gaps. PFSs can reach elevated concentrations in humans and wildlife inhabiting industrialized areas of North America, Europe, and Asia (2-30000 ng/mL or ng/g of wet weight (ww)). PFSs have also been detected in organisms from the Arctic and mid-ocean islands (≤ 3000 ng/g ww). In humans, PFSAs and PFCAs have been shown to vary among ethnic groups and PFCA/PFSA profiles differ from those in wildlife with high proportions of perfluorooctanoic acid and perfluorooctane sulfonate. The pattern of contamination in wildlife varied among species and locations suggesting multiple emission sources. Food web analyses have shown that PFCAs and PFSAs can bioaccumulate and biomagnify in marine and freshwater ecosystems. Knowledge gaps with respect to the transport, accumulation, biodegradation, temporal/spatial trends and PFS precursors have been identified. Continuous monitoring with key sentinel species and standardization of analytical methods are recommended.

Houde, M., Bujas, T.A.D., Small, J., Wells, R.S., Fair, P.A., Bossart, G.D., Solomon, K.R., and Muir, D.C.G.

Biomagnification of perfluoroalkyl compounds in the bottlenose dolphin (*Tursiops truncatus*) food web.

Environmental Science and Technology 40(13): 4138-4144, 2006.

Notes: The environmental distribution and the biomagnification of a suite of perfluoroalkyl compounds (PFCs), including perfluorooctane sulfonate (PFOS) and C-8 to C-14 perfluorinated carboxylates (PFCAs), was investigated in the food web of the bottlenose dolphin (*Tursiops truncatus*). Surficial seawater and sediment samples, as well as zooplankton, fish, and bottlenose dolphin tissue samples, were collected at two U. S. locations: Sarasota Bay, FL and Charleston Harbor, SC. Wastewater treatment plant (WWTP) effluents were also collected from the Charleston area (n = 4). A solid-phase extraction was used for seawater and effluent samples and an ion-pairing method was used for sediment and biotic samples. PFCs were detected in seawater (range < 1-12 ng/L), sediment (range < 0.01-0.4 ng/g wet weight (ww)), and zooplankton (range 0.06-0.3 ng/g ww). The highest PFC concentrations were detected in WWTP effluents, whole fish, and dolphin plasma and tissue samples in which PFOS, C-8 and C-10-PFCAs predominated in most matrices. Contamination profiles varied with location suggesting different sources of PFC emissions. Biomagnification factors (BMFs) ranged from < 1 to 156 at Sarasota Bay and < 1 to 30 at Charleston. Trophic magnification factors (TMFs) for PFOS and C-8-C-11 PFCAs indicated biomagnification in this marine food web. The results indicate that using plasma and liver PFC concentrations as surrogate to whole body burden in a top marine predator overestimates the BMFs and TMFs.
